Adsorption – Filtration Hybrid System in Wastewater Treatment and Reuse

By

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CERTIFICATE

I certify that this thesis has not already been submitted for any degree and is not being submitted as part of candidature for any other degree.

I also certify that the thesis has been written by me and that any help that I have received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

Signature of Candidate

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Publications made from the study

NOMENCLATURE

a = Specific surface area (area per unit mass of adsorbent) (L^2M^{-1})

A = Surface area normal to the filter media (L^2)

a'_f = Specific surface area of the pellet with biomass (L^2M^{-1})

A_f = Biofilm surface area (L^2)

A_m = Membrane surface area perpendicular to the flow (L^2)

A_s = Surface area of the adsorbent (L^2)

b = Biofilm decay coefficient (T^{-1})

B_1 = Biologically attached bacterial biomass (ML^{-3})

B_2 = Reversibly adsorbed bacterial biomass (ML^{-3})

B_3 = Free bacterial biomass in the liquid phase (ML^{-3})

BIO = Biodegradation by the microbial community

b_{max} = Maximum uptake rate of S (T^{-1})

b_s = Biofilm shear loss coefficient (T^{-1})

b_{tot} = First order biofilm detachment coefficient for decay and shear (T^{-1}).

b_{tot} = First order biofilm detachment coefficient for decay and shear (T^{-1}).

b_{tot} = Overall loss rate of biomass due to both decay and fluid shear (T^{-1})

b_{tot} = Total shear and decay loss (T^{-1})

C = Concentration of the adsorbate in solution phase (ML^{-3})

C_0 = Initial Organic concentration in the feed tank (ML^{-3})

C_b = Organic concentration in the bulk phase in the reactor (ML^{-3})

C_e = Effluent concentration (ML^{-3})

C_i = Influent concentration (ML^{-3})

C_i = Liquid phase organic concentration of i^th species in the mixture (ML^{-3})

C_i^0 = Single solute liquid phase concentration in equilibrium (ML^{-3})

C_{io} = Initial liquid phase organic concentration of i^th component (ML^{-3})

C_p = Permeate organic concentration (ML^{-3})

C_r = Qβ concentration in the bulk phase (ML^{-3})

C_s = Concentration of the adsorbate in the liquid phase at the liquid-particle interface, (ML^{-3})

$\bar{c}$ = Concentration density function of the solution phase

C_r^{∞} = Equilibrium concentration of Qβ in the bulk phase (ML^{-3})

C_T = Total liquid phase concentration (ML^{-3})

C_{Tcal} = Calculated liquid phase concentration (ML^{-3})

C_{Texp} = Experimental liquid phase concentration (ML^{-3})

C_{to} = Initial total liquid phase concentration (ML^{-3})

d = Fixed bed depth (L)

= Sweeping diameter of the impeller (L)

D = Molecular diffusion coefficient for the substrate in the bulk liquid phase (L^2T^{-1})

D' = Dispersion coefficient (L^2T^{-1})

D_f = Substrate diffusion coefficient in the biofilm (L^2T^{-1})

D_m = Molecular diffusion coefficient (L^2T^{-1})

D_s = Effective surface diffusion coefficient of adsorbate (L^2T^{-1})

D_{si} = Surface diffusion coefficient (D_{si}) of the i^{th} component (L^2T^{-1})

$e_{i(max)}$ = Maximum rate of H_i hydrolysis (T^{-1})

F = Object function (%)

g_c = Gravity conversion coefficient (LT^{-2})

H = Adsorption constant (Henry's Law constant)

H_i = Macromolecular organic matter of utilization class i (ML^{-3})

J_0 = Initial flux rate ($L^3L^{-2}T^{-1}$)

J_f = Flux of substrate into the biofilm ($ML^{-2}T^{-1}$)

J_p = Permeate flux ($L^3L^{-2}T^{-1}$)

K = Reaction constant

k = Maximum specific rate of substrate utilization ($MM^{-1}T^{-1}$)

= First order reaction coefficient (T^{-1})

k''_d = Detachment rate coefficient (ML^{-3})

k'_d = Detachment rate coefficient ($ML^{-3}T^{-1}$)

k_a, = Coefficient for adsorption onto PAC
k_{ads} = Adsorption constant for bacteria ($M^{-1}L^3T$)
k_c = Cake formation filtration constant
k_{ct} = Complete blocking filtration constant
k_d = Coefficient for the bacterial decay (T^{-1})
k_{des} = Desorption constant for bacteria (T^{-1})
k_e = Coefficient for inactivation due to the desorption of Qβ from PAC
K_F = Freundlich adsorption coefficient
k_f = Liquid-film mass transfer coefficient, (LT^{-1})
K_{Hi} = Half saturation constant for H_i hydrolysis, (ML^{-3})
k_i = Freundlich constant for ith component
= Intermediate blocking filtration constant
k_m = Coefficient for attachment to the membrane
k_{max} = Maximum rate of substrate utilization, mg/mg/s
k_p = Particle phase mass transfer coefficient, (LT^{-1})
K_s = Monod half saturation coefficient (ML^{-3})
k_s = Solid phase mass transfer coefficient (LT^{-1})
= Standard blocking filtration constant
= Scale factor
L = Bed depth (L)
L_d = Diffusion layer thickness (L)
L_f = Biofilm thickness (L),
L_o = Initial bed depth (L)
M = Weight of the adsorbent (M)
M_b = Molecular weight of the solvent (M)
MCC = Membrane correlation coefficient,
M_p = Weight of the adsorbent (M)
n = Freundlich exponential coefficient
= Rotation speed (T^{-1})
N = Substrate uptake rate of the biofilm ($ML^{-2}T^{-1}$)
= Number of data points
N_p = Power number

P = Input power to the fluid (MLT^{-1})
P_C = Average concentrate pressure (Pa)
P_F = Average feed pressure (Pa)
P_p = Average permeate pressure (Pa)
$\overline{q}$ = Average adsorbed phase concentration (MM^{-1})
Q = Flow rate (L^3T^{-1})
q = Surface concentration of adsorbed substrate (MM^{-1})
q_i^0 = Adsorbed phase concentration in single solute state (MM^{-1})
q_m = Maximum specific rate of substrate utilization ($MM^{-1}T^{-1}$)
= Saturation amount of organic adsorbed (MM^{-1})
q_o = Initial adsorbed phase concentration (MM^{-1})
Q_p = Permeate flow (L^3T^{-1})
q_s = Equilibrium adsorbed phase organic concentration (MM^{-1})
q_t = Total solid phase organic concentration (MM^{-1})
q_w = Surface concentration at biofilm/activated carbon interface
r = Radial distance measured from the center of the pellet (L)
R = Radium of the carbon particle (L)
r_{diff} = Rate for substrate accumulation due to diffusion ($ML^{-3}T^{-1}$)
R_e = Total external resistance ($= R_p + R_f$)
REM = Fraction of biomass removed by backwashing
R_f = External fouling resistance formed by deposited cake layer
r_f = Radial coordinate in the biofilm (L)
r_{gr} = Rate of biomass growth within the biofilm (MT^{-1})
R_i = Internal resistance due to adsorbed substances into the pores
r_{loss} = Rate of loss of biomass (MT^{-1})
R_m = Intrinsic membrane resistance
R_p = Adsorbent particle radius (L)
= Polarization layer resistance caused by the concentration gradient
r_s = Radial coordinate in activated carbon (L)
R_T = Total resistance to the filtration,

r_{utl} = Rate of substrate utilization in the biofilm ($ML^{-3}T^{-1}$)

S = Substrate concentration (ML^{-3})

SB = Maximum adsorption capacity for bacteria (ML^{-3})

S_b = Substrate concentration in the bulk liquid (ML^{-3})

S_f = Substrate concentration in the biofilm (ML^{-3}),

S_{min} = Minimum substrate concentration (ML^{-3})

SP = Maximum capacity for biological bacterial fixation (ML^{-3})

S_s = Substrate concentration at liquid/biofilm interface (ML^{-3})

T = Temperature, °C

t = Time (T)

TOC = Total organic carbon (ML^{-3})

v = Fluid filtration velocity (LT^{-1})

V = Volume of the solute, fluid, or reactor (L^3)

V_M = Volume of the membrane (L^3)

W = Weight of adsorbent (M)

x = Distance along the biofilter length (L)

X_f = Cell density of biofilm (ML^{-3})

X_s = Suspended biomass concentration (ML^{-3})

X_{susp} = Suspended cell concentration (ML^{-3})

Y = Biomass growth yield factor

Z = Distance normal to the biofilm surface (L)

z_i = Mole fraction of the ith species in the adsorbed phase

ε = Bed porosity

ε' = Bed porosity with biofilm

ε_o = Initial bed porosity

σ = Biofilm shear loss coefficient (T^{-1})

ψ = Organic concentration spreading parameter

ξ = Void fraction

μ = Viscosity of the fluid ($ML^{-1}T^{-1}$)

μ_g = Specific biomass growth rate (T^{-1})

μ_{gave} = Average specific biomass growth rate (T^{-1})

ϕ = Association factor of the solvent

θ = Empty bed contact time (T)

β = Filtration efficiency

ΔP = Transmembrane pressure (Pa)

ρ_p = Particle density of adsorbent (ML^{-3})

ρ = Density of the fluid (ML^{-3})

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Figure 7.23 Permeate volume with time and its prediction (Membrane pore size = 0.11μ m, PAC dose = 150 mg/L, mixing intensity, G = 110.2 s^{-1}, mixing time = 6.6 min, TMP = 20 Kpa, $k_c = 8 \times 10^{-2}$ h/L^2, $k_s = 1 \times 10^{-1}$ L^{-1}, $J_0 = 2$ L/h)

Figure 7.24 Permeate volume with time and its prediction (Membrane pore size = 0.22 μ m, PAC dose = 150 mg/L, mixing intensity, G = 110.2 s^{-1}, mixing time = 6.6 min, TMP = 20 Kpa, $k_c = 8 \times 10^{-5}$ h/L^2, $k_s = 4 \times 10^{-2}$ L^{-1}, $J_0 = 5$ L/h)

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EXTENDED ABSTRACT

Wastewater contains a matrix of organic and inorganic substances both in dissolved form and in suspension. Most of the biodegradable substances are removed in primary and secondary treatment processes. However, the conventional wastewater treatment processes cannot remove a number of synthetic and refractive organic substances. These substances can cause tremendous problem in the sewage treatment processes and in the water body where the effluent from the sewage plant is discharged. These substances produce odour, colour, and require a large quantity of disinfectant dose before the wastewater can be discharged into a water body. They can also significantly deplete the dissolved oxygen level of the water receiving body thus putting all the aquatic life in danger. The effluent from the sewage treatment plant therefore, needs to be passed through further treatment process, which is called advanced sewage treatment process. The advanced treatment processes consist of many treatment options. Depending upon the characteristics of the sewage and the level of treatment required, one has to select an appropriate treatment technology. Physico-chemical processes such as coagulation-flocculation and filtration, adsorption, and membrane application are some of the most viable treatment processes that can remove the organic substances to the desirable level. In this study, adsorption, biosorption or biofiltration, and adsorption-membrane hybrid systems were investigated for the removal of organics (in terms of total organic carbon (TOC)) from a low strength synthetic wastewater and a biologically treated secondary effluent from a sewage treatment plant, Sydney.

Adsorption experiments were conducted on low strength synthetic wastewater and the biologically treated sewage effluent using granular activated carbon (GAC) and powder activated carbon (PAC). The synthetic wastewater was prepared using three organic substances (glucose, peptone and yeast extract) and seven inorganic chemicals ($MnSO_4$, $CaCl_2$, $NaHCO_3$, NaCl, $MgSO_4 \cdot 7H_2O$, KH_2PO_4, and $NH_2 \cdot NH_2 \cdot H_2SO_4$). The biologically treated sewage effluent was collected from the St. Marys sewage treatment plant, Sydney. Detailed experimental studies on adsorption equilibrium, batch kinetics and fixed bed were carried out, and the experimental results were predicted using suitable mathematical models.

The adsorption equilibrium was analysed with different initial organic concentration of the synthetic wastewater. The experimental results were then predicted using association theory (AT), characterization theory (CT), and the Freundlich isotherm. The experimental results showed unfavourable type of isotherm curve, and hence, the normal favourable isotherm equations such as Langmuir, Freundlich or Sipps isotherms were not very successful in describing the adsorption equilibrium results. The AT and the CT were better in predicting the adsorption equilibrium results than the commonly-used Freundlich isotherm. In this process, the adsorption equilibrium (isotherm) parameters were determined using a multivariable, non-linear regression, Nelder-Mead method by optimising an object function defined as the mean percent deviation between experimental and calculated equilibrium adsorption amounts. The isotherm parameters were found to be dependent on the initial organic concentration. Hence, it is important to estimate the isotherm parameters covering a wide range of organic concentration. Further, the adsorption equilibrium studies of the individual organic compounds indicated that the overall effects of the inorganic substances were unfavourable for the adsorption of organics in the wastewater. The organics of the synthetic wastewater were found to undergo biodegradation after 8 hours. Thus, the effect of the background substances in the wastewater, and the biodegradation effect are another important aspects that need to be considered while evaluating the effectiveness of the adsorption process for organic removal from the wastewater.

It is equally important to study the adsorption behaviour with time (i.e. adsorption kinetics). Adsorption kinetics of the organics in the wastewater was determined using linear driving force approximation (LDFA) model. Basically, the LDFA is a simplified expression of intraparticle diffusion of adsorbate into adsorbent particles. In this model, it is assumed that the uptake rate of adsorbate by an adsorbent particle is linearly proportional to the driving force developed due to the difference between the surface concentration and the average adsorbed phase concentration of the adsorbate. The main reason for using the LDFA method was the use of index (or lumped) parameter, total organic carbon (TOC), to express the total organic contents of the wastewater. The film mass transfer coefficient (k_f) was found to be dependent on the experimental conditions such as mixing intensity, the adsorbent dose and the initial organic concentrations. The film mass transfer coefficient (k_f) to the adsorbent increased when the mixing intensity and the adsorbent dose were increased. However, the k_f value decreased with the increase in the initial organic concentration of the solution.

The adsorption isotherm parameters obtained from the association theory (AT) and the characterization theory (CT), were utilized to fit the experimental results using LDFA model. The isotherm parameters obtained from both the theories were found equally effective in predicting the experimental results. The overall effect of the dissolved inorganic compounds in the synthetic wastewater solution was observed to enhance the mass transfer rate to the GAC particle. The average value of the overall mass transfer rate was in the order of 10^{-6} m/s.

The application of adsorption system in practice is usually carried out in the fixed bed adsorption mode. The adsorbent (usually GAC) is packed in a column and the target pollutants are passed through either end to be adsorbed by the adsorbent. In this study, the fixed bed adsorption study was carried out in acrylic columns in the laboratory. The GAC bed depth, organic concentration of the feed solution, and the filtration velocity through the GAC bed were varied to evaluate the effectiveness of the fixed bed adsorption system. The experiments were carried out with both the biologically treated sewage effluent and the synthetic wastewater. The experimental results were predicted using the dynamic adsorption model. The film mass transfer coefficient (k_f) was obtained by fitting the fixed bed experimental data. The k_f increased when filtration rate was increased, but it decreased with the increase in the organic concentration of the feed solution. As expected, the value of k_f remained constant with the increase in GAC bed depth. The effect of axial dispersion coefficient was negligible, as the GAC bed depth and the size of the GAC particles used in this study were shallow and small respectively. The average value of the overall mass transfer rate in the fixed bed study was also in the order of 10^{-6} m/s but slightly less than that obtained in batch kinetics study.

The fixed bed system with attached microorganisms on the surface of the adsorbent (fixed bed medium) is referred to as a biofilter, where the organics are adsorbed (biosorption) and biodegraded by the microorganisms. The fixed bed adsorption experimentations were conducted for a longer duration to investigate the biological activity on the granular activated carbon (GAC). The experimental results showed the growth of microorganisms on the surface of GAC particles. In other words, the adsorption system turned into biosorption or biofiltration system after few weeks of operation. The adsorption capacity of the GAC particles slowly exhausted with the growth of microorganisms with time. The overall organic removal efficiency of the system was however, not impaired by the growth of microorganisms. The organics were removed by the processes of biosorption and subsequent biodegradation. The biomass growth rate was found to fluctuate with time in sinusoidal pattern. Despite the fluctuation in the biomass, the TOC removal efficiency of the biofiltration system was consistent at 55 % for 77 days of continuous operation. Moreover, the daily backwashing provided at 30 % bed expansion to avoid filter clogging did not have adverse effect on the TOC removal efficiency of the biofilter. The organic removal efficiency of the biofilter changed when the filtration rate was altered from that in which the biofilter was acclimatized; however the organic removal pattern remained consistent with time. This result suggests that the biofilter should be operated in the same filtration velocity at which it is acclimatized to attain maximum efficiency of the filter.

A practical mathematical model was developed incorporating both adsorption and biodegradation of organics. The organic removal efficiency of the biofilter was successfully predicted using kinetics data obtained from the previous studies. The model was sensitive to the biofilm thickness and decay constant.

The adsorption-membrane hybrid system is emerging as a cost-effective membrane process for the organic removal. In this system, the organics are adsorbed on the adsorbent and the organic laden adsorbents are removed by the membrane separation process. In this study, the adsorption-membrane hybrid system was evaluated using submerged hollow fibre (pore size 0.1 μm), and the external loop crossflow microfiltration. Powdered activated carbon (PAC) was used to reduce the direct organic loading onto the membrane surface. The main function of membrane in these studies was to remove the organic laden PAC particles. The submerged PAC-Membrane hybrid system was found effective in removing dissolved organic substances both from the synthetic wastewater and the biologically treated effluent of a sewage treatment plant. The system has potential for its long-term application in the treatment of wastewater without the need of frequent membrane cleaning. This preliminary study showed that the PAC-membrane hybrid system could be used for a long time effectively (over 47 days). At the initial stage of operation, the organic removal was mainly due to adsorption by PAC, but during the long-term application of the system, the adsorption capacity of the PAC was exhausted gradually, and the microbial communities developed on the PAC, in the suspension of the reactor, and on the membrane surface actively participated in the biodegradation of the organics.

An empirical mathematical model was developed for the submerged hollow fibre membrane hybrid system. The model predicted the organic removal efficiency of the system satisfactorily. A new term, membrane correlation coefficient (MCC) was introduced in the model to account for the adsorption of organics onto membrane surface. The MCC and the filtration rate (flux) were found to be the main model parameters that controlled the quality of the effluent from the system. Greater the value of MCC, better was the organic removal efficiency of the system. The MCC value was found to increase with the increase in the PAC dose to the system. Since only the short-term experiments were conducted in this study, the biological degradation of the organics was not included in the model. It is necessary to incorporate the biological degradation part in the model to predict the long-term efficiency of the system.

The external loop cross-flow microfiltration system with prior PAC addition was also tested using the synthetic wastewater. This study showed that the use of PAC helped not only in the organic removal but also in the enhancement of the filtration flux. The use of PAC was instrumental in increasing the operational life the membrane hybrid system by reducing the organic fouling on the membrane. The conventional pressure filtration models, cake filtration model (CFM) and standard blocking model (SBM) were used to successfully predict the experimental results. Since CFM was more effective in predicting the volume of the permeate flux from the hybrid system, one could infer that the fouling mechanism of the membrane was mainly due to the formation of cake layer on the membrane surface. However, the experimental conditions used in the hybrid system were not so favourable for removing the organics from the synthetic wastewater. The organic removal efficiency of the PAC-membrane hybrid system was only 25% for the PAC dose of 150 mg/L. The organic removal efficiency of the system depends mainly on the characteristics of the adsorbent and the influent wastewater solution, and the adsorbent dose.

This study shows that activated carbon can effectively be used in different operational modes and in different treatment processes to remove organics from the wastewater, and to produce effluent of high quality that can be reused for many purposes.

Chapter 1

Introduction

1.1 Overview

Wastewater contains significant levels of organic contaminants. A number of organic substances of the wastewater are not removed by the conventional wastewater treatment processes. The conventionally used sewage treatment processes remove only biodegradable organics (in simple terms, those organics measured by biochemical oxygen demand (BOD_5) test). They are not as effective in removing the so-called refractive organic materials (or persisting organic pollutants) measured by the chemical oxygen demand (COD) test. Even well treated secondary sewage effluents may contain 50-120 mg/L of organics (Manka et al., 1974). The inherent problems associated with the remaining organics are the requirement of excessive amount of disinfectants, odor, unsightly color, foaming, corrosion of pipes, production of carcinogenic and harmful disinfectant-by-products (DBPs), and stimulation of microbial growth in the effluent-discharging watercourse. It has been observed that even the minimal level of organic substances (which is measured in terms of assimilable organic carbon (AOC)) present in the potable drinking water can stimulate microbial growth in the water distribution pipelines (Van der Kooij et. al., 1982; LeChevallier and Lowry, 1990; Bouwer and Crowe, 1988). Since wastewater contains significant amount of biodegradable and non-biodegradable (refractory and persistent organic substances), it can lead to the growth of massive amount of varieties of microorganisms in the watercourse where it is discharged, and threaten the aquatic life.

1.1.1 Organics in Wastewater: Sources and Problems

Wastewater contains heterogeneous matrix of a multitude of organic and inorganic substances, some of which are unknown. These substances include fats, carbohydrates, proteins, tannins, lignin, ethers, methylyne blue active substances (MBAS), herbicides, pesticides and trace metals. It would be misleading to generalize the composition of a wastewater. There have been few attempts to identify the organics in raw or treated municipal wastewater. Distribution of organics in biologically treated sewage effluent of a domestic wastewater is shown in Table 1.1 (Manka et al., 1974). The organic substances such as fats, carbohydrates, and proteins (which are biodegradable) are usually removed in the biological treatment processes. However, these processes do not remove refractory organics such as tannins and lignin. The treatment options to reduce the refractory organics are discussed in Section 1.1.2 of this chapter.

In practice, the pollution level in the wastewater is represented by index parameters such as biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total organic carbon (TOC) and similar collective parameters depending upon the characteristics of the wastewater.

Table 1.1 Composition of secondary effluent of domestic wastewater from activated sludge process (Manka et al., 1974)

Substance	% of Total COD
Proteins	23.1
Carbohydrates and polysaccharides	4.6
Tannins and lignin	1.0
Anionic detergents	16.0
Ether extracts	16.3
Fulvic acid	24.0
Humic acid	6.1
Hymathomelanic acid	4.8
Unidentified	4.1

The natural organic matter (NOM) in the surface water is broadly classified as humic (nonpolar) and nonhumic (polar) based on its absorption on XAD resins (Barrett et al. 2001)

1.1.2 Treatment Options for Organic Removal from Wastewater

As the global supplies of clean water diminish and demand for water rises, advanced wastewater treatment is becoming an international focus for the rational use of scarce water resources, and as means of safeguarding aquatic environments from the harm caused by wastewater disposal. Conventional sewage treatment includes primary treatment to remove the majority of suspended solids, secondary biological treatment to remove the biodegradable dissolved organics and nitrogen, and tertiary (advanced) treatment to remove most of the remaining organics, solids, and pathogenic microorganisms. Previously, the wastewater was usually discharged into the watercourse after the secondary biological treatment. This treatment was not sufficient to reduce the level of organic or inorganic pollutants to the desirable level. Now the trend is changing towards the total water recycle approach, which promotes ecological sustainability by managing the treated wastewater as a resource instead of a waste and at the same time, reducing the demand for water from the existing water resources. Water reuse from sewage treatment plants (STPs) in Australia in 2000 was 171 GL (i.e. 11% of STP effluent), and growing by 28 GL/year (Dillon, 2001). Some of the processes that are used in the advanced wastewater treatment to further reduce the organic and nutrient levels are: coagulation-flocculation-sedimentation, deep bed filtration, ion exchange, membrane processes such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and adsorption. The major advantageous impacts of these advanced wastewater treatment processes are: (a) production of high quality of effluent that can be reused for agricultural, industrial, and recreational purposes, (b) maintenance of ecologically healthy watercourse, and (c) conservation of water.

In this study, the application of adsorption, biosorption, and adsorption-membrane hybrid systems were evaluated in terms of organics removal from the synthetic wastewater and the biologically treated effluent from a sewage treatment plant.

1.1.2.1 Adsorption

Adsorption is a physical and surface phenomenon by which molecules of pollutants (adsorbates) are attracted to the surface of adsorbent by intermolecular forces of attraction. Physical adsorption is mainly caused by Van der Waals force and electrostatic force between adsorbate and adsorbent molecules. Since activated carbon has a strong affinity for binding dissolved organic substances even at low concentration; it is widely used as adsorbent for treating organic laden water and wastewater. The use of activated carbon in wastewater treatment facility can be either in granular or powdered form. The granular activated carbon (GAC) is packed inside a cylindrical column, and wastewater is passed downwards through the carbon bed where the dissolved contaminants are adsorbed onto the carbon surface. The powdered activated carbon (PAC) is usually added to the aeration tank where the wastewater is contained. It helps to produce sludge of high settlability. The primary advantages of using PAC are (a) low capital investment cost, and (b) possibility of changing the PAC dose as the water quality changes. The main disadvantages of use of PAC are: (a) high operating cost if high PAC dose is required, (b) low TOC removal, (c) inability to regenerate, and (d) difficulty of sludge disposal. However, the use of PAC can enhance the performance of the existing treatment system by removing dissolved substances, and forming settlable flocs (Cooney, 1999). Previous studies have shown that activated carbon adsorption can remove organics in significant quantities and produce high quality effluent (Summers and Roberts, 1988, Najm et al., 1991a, Yuasa et al., 1997, Cooney, 1999, Dabrowski, 2001).

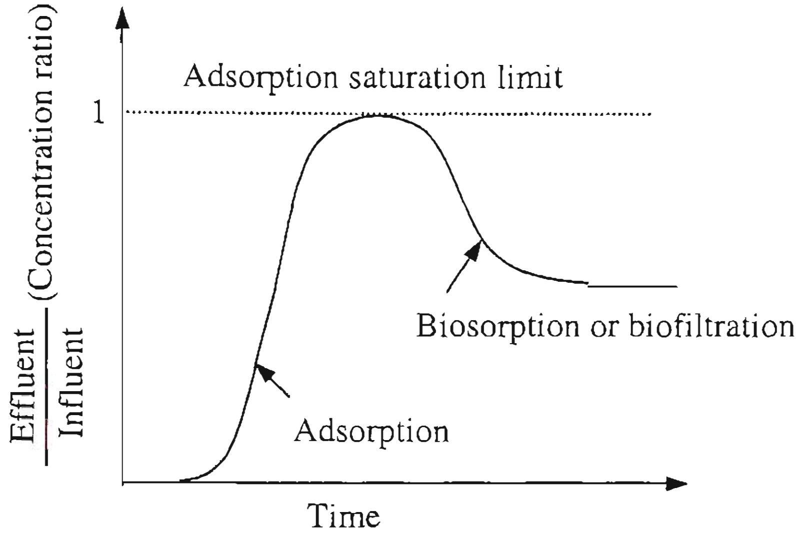
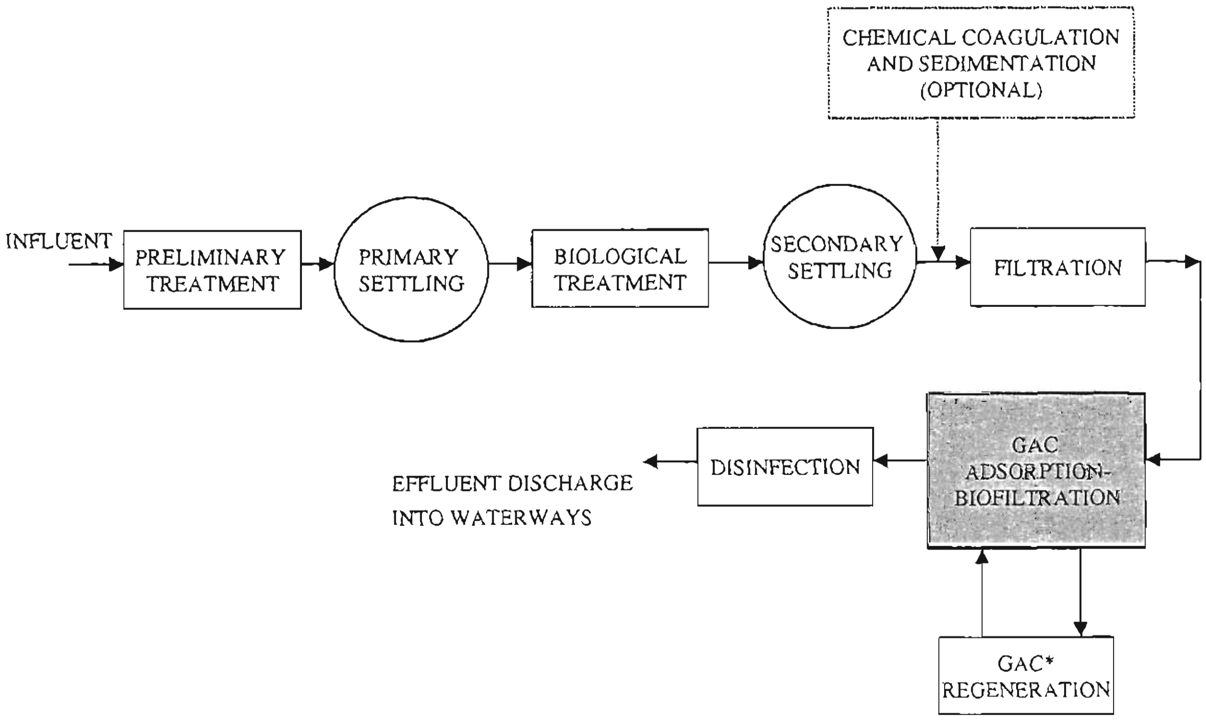


Figure 1.1 Schematic representation of GAC adsorption-biosorption or biofiltration process.

1.1.2.2 Biosorption or biofiltration

As shown in Figure 1.1, the adsorption capacity of the adsorbent gradually decreases with time, and hence the effluent quality deteriorates. Once the adsorption capacity is exhausted, the granular activated carbon (GAC) is regenerated to restore its adsorption capability. However, the regeneration process (normally thermal process) is expensive. It needs a huge capital investment to install the furnace for regeneration. Previous research has shown that GAC has great potential of developing biofilm (growth of microorganisms) on the surface of the GAC particle, which lead to the long-term operation of GAC adsorption column (Summers and Roberts, 1988). Initially, adsorption of the adsorbate (organics) takes place on the GAC surface, and as the biofilm growth progresses with time, the adsorption of organics occurs on the surface of the biofilm. The adsorption of organics on the biofilm coverage is termed here as the biosorption. The organics are first adsorbed on the surface of the biofilm, and then diffuse through the biomass, where it is biodegraded by the microorganisms. Since the GAC column is operated like a normal filtration unit, the process is also known as biofiltration. The biosorption or biofiltration process is very effective in removing organics from water and wastewater, and produces effluent of high quality (Alonso, 1998, Xie, 1996, Boon, 1997, Sakura, 1997, Bouwer and Crowe, 1988, Hozalski et. al., 1995, Ahmad et al., 1998, Carlson and Amy, 1998). Due to the lower concentration of dissolved organics or nutrients in the biologically treated sewage effluent, the biosorption or biofiltration system can become one of the most economical biological treatment options in the advanced wastewater treatment processes. The organic removal efficiency of the system depends on the amount of retained biomass on the media, and thus it is important to maintain the biomass especially during the backwash of the filter. A typical treatment scheme of the adsorption-biofiltration system is shown in Figure 1.2.



* Regeneration is not necessary for biofiltration

Figure 1.2 Typical treatment scheme of adsorption-biofiltration system.

1.1.2.3 Adsorption-membrane hybrid system

Membrane filtration is an emerging technology in water and wastewater treatment. Membrane filtration is basically, a pressure driven process in which membrane acts as selective barrier to restrict the passage of pollutants such as organics, nutrients, turbidity, microorganisms, inorganic metal ions and other oxygen depleting pollutants. With technological advances and the ever-increasing stringency of water quality criteria, membrane processes have become a more attractive solution to the challenge of water reuse. Although membrane processes such as reverse osmosis and nanofiltration could in theory remove all pollutants, including dissolved organics, their operational costs are high because of high-energy requirements and membrane fouling. Microfiltration and ultrafiltration are cost-effective options (due to the low pressure requirement), but they cannot remove dissolved organic matter due to their relatively larger pore sizes. In order to remove the persisting organic pollutants (POPs) in an economic manner and to reduce the membrane clogging (fouling) problem, the use of powdered activated carbon (PAC) to membrane filtration system (either microfiltration or ultrafiltration) have been investigated (Vigneswaran et al., 1991, Seo et al., 1996, 1997; Snoeyink et al., 2000; Kim et al., 2001; Matsui et al., 2001a). This process of coupling of adsorption and membrane filtration system is termed here as the adsorption-membrane hybrid system. In this process, the pollutants (particularly the dissolved organics) are first adsorbed onto PAC and thus the direct loading of the pollutants to the membrane surface is greatly reduced. The organic laden PAC is then removed by membrane separation process. The use of PAC in the membrane hybrid system not only increases the permeate flux (effluent filtration rate) through the membrane, it also prolongs the life of membrane application. The adsorption-membrane hybrid system can be of two types: (a) adsorption with external loop flat-plate membrane, and (b) submerged hollow fibre membrane hybrid systems. In the external loop membrane hybrid system, wastewater and PAC are first mixed in spiral tube outside then passed to the membrane set-up in crossflow mode, whereas in the submerged membrane hybrid system, the membrane is submerged in a PAC and wastewater mixed tank (Figure 1.3). The energy requirement for the operation of the external loop membrane hybrid system is usually much higher than that of submerged membrane hybrid system, and hence the submerged membrane hybrid system is emerging as one of the most promising methods of wastewater treatment. The submerged membrane system is simple to operate with less energy consumption, and it suffers minimum membrane clogging. Besides, in long-term use, it can be converted into membrane bioreactor where the organics are biodegraded by microorganism.

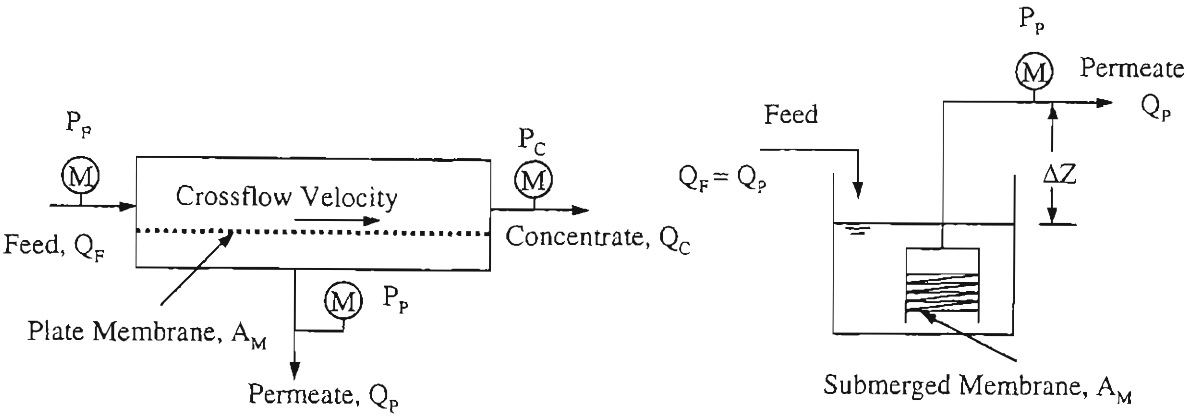


Figure 1.3 External loop flat-plate membrane and submerged hollow fibre membrane hybrid systems

It is being thought that the traditional biological treatment tank can be replaced by membrane bioreactor to reduce the pollutant level significantly down to the desirable level (Ben Aim and Semmens, 2001; Gunder, 2001). However, membrane fouling (clogging of membrane) is the major technical problem that is preventing the widespread use of the system at present. Since the adsorbent is used in the membrane hybrid system, the organics are adsorbed onto the adsorbent instead of the membrane surface, and the loading to the membrane surface is greatly reduced. This in turn, reduces the membrane clogging and prolongs the operation of the hybrid system (Vigneswaran et al., 1991, Seo et al., 1997, Snoeyink et al., 2000; Kim et al., 2001; Matsui et al., 2001a). A typical treatment layout of the submerged adsorption-membrane hybrid system is shown in Figure 1.4.

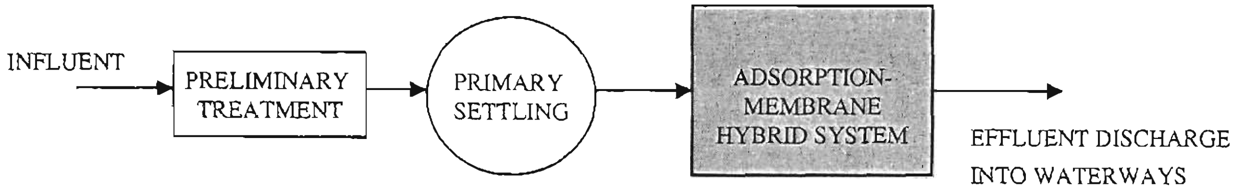


Figure 1.4 Typical treatment scheme of submerged adsorption-membrane hybrid system.

1.1.3 Imperatives of the Study

Most of the past studies on adsorption equilibrium and kinetics have been carried out on the single component where only one element or compound (such as phenol or herbicide) was targeted. Only few adsorption studies have been conducted with the mixtures of two or more organic compounds (Crittenden et al, 1985a, 1985b; Moon et al, 1991). However, there is limited research done on adsorption on wastewater system. Due to the complexity of the composition, and the concentration of different organics and inorganics present in a wastewater system, it is very difficult to develop a mathematical model that can be used to predict or design the adsorption system in the field. The model developed in one particular multicomponent system may not necessary be useful for another multicomponent system due to the competitive adsorption characteristics of different organics and inorganics and interactions among themselves. In this study, adsorption, biosorption or biofiltration (long-term adsorption), and adsorption-membrane hybrid systems were evaluated in terms of organics removal efficiency. The GAC and PAC were used as adsorbents, and the synthetic wastewater and the biologically treated effluent from a sewage treatment plant, Sydney were used as feed solutions to the systems. Adsorption characteristics were investigated through detailed adsorption equilibrium, batch kinetics, and fixed bed experiments. The biosorption or biofiltration system was evaluated through a long-term adsorption of a fixed bed GAC column, and the adsorption-membrane hybrid systems were studied using PAC as adsorbent in the external loop flat-plate membrane, and the submerged hollow fibre membrane systems.

1.2 Objectives of the Study

Most of the research on adsorption system has been done on single component and multi-solute system with known components. There has been hardly any systematic study on adsorption of organics from wastewater where the components and the concentrations of the organics are not completely known. The main objective of this study was to investigate the efficiency of the adsorption and biological degradation system of GAC and PAC in terms of organic removal from wastewater. The following aspects of the adsorption and biodegradation system were investigated in this study:

1.2.1 Adsorption Study

The performance of GAC and PAC in terms of organics removal from wastewater was investigated through a series of adsorption studies. Adsorption equilibrium, batch kinetics, and fixed bed column experimental studies were carried out to evaluate the GAC and PAC adsorption system. The following aspects of the adsorption system were investigated:

- Overall adsorption equilibrium of organics in the synthetic wastewater and biologically treated sewage effluent with GAC and PAC,
- Selection of a suitable adsorption isotherm to describe the unfavorable adsorption nature of the wastewater,

- Adsorption batch kinetics of the synthetic wastewater and the biologically treated sewage effluent with GAC and PAC
- Mathematical modelling of adsorption kinetics representing the heterogeneity of the wastewater as a lumped (index) parameter.
- Fixed bed adsorption system of the synthetic wastewater and the biologically treated sewage effluent with GAC
- Mathematical modelling of the fixed bed adsorption using the fixed bed dynamics.

1.2.2 Biosorption or Biofiltration Study

In the biosorption or biofiltration system, organics are removed by the adsorption and the biodegradation of the adsorbed organics. In view of designing and optimizing the GAC biofilter, following objectives were fulfilled:

- Investigation of biological degradation of organics in GAC biofiltration system using synthetic wastewater
- Estimation of the retained biomass on the GAC particles, and its effect on the efficiency of biofiltration system.
- Development of a mathematical model to predict the organic removal efficiency of the GAC biofiltration system.

1.2.3 Adsorption-membrane Hybrid System

The adsorption-membrane hybrid system is becoming a highly promising wastewater treatment system. In this study, an external loop and a submerged membrane filtration system with powdered activated carbon (PAC) adsorption were investigated to achieve the following objectives:

- Evaluation of the adsorption-membrane hybrid (microfiltration) system using the synthetic wastewater and the biologically treated effluent from sewage treatment plant with PAC. Submerged hollow fibre membrane, and external loop flat-plate membrane were employed to evaluate the organic removal efficiency of the systems, and

- Development of a conceptual mathematical model to predict the organic removal efficiency of the adsorption-membrane hybrid system.

1.3 Scope of the Study

1.3.1 Experimental

Detailed adsorption equilibrium, batch kinetics, and the fixed bed column experiments were carried out using synthetic wastewater in the laboratory and biologically treated sewage effluent in the field (St Marys Sewage Treatment Plant, Sydney). Equilibrium experiments were performed with different initial organic concentration to estimate the adsorption equilibrium constants of the multicomponent system in a wide range of organic concentration. The association theory was employed to describe the equilibrium characteristics of the system. The association theory was compared with the most commonly used characterization theory to decide which one represents the adsorption equilibrium better. Batch adsorption kinetics of the system was studied at different organic concentrations, GAC and PAC loading and different mixing speeds. Fixed bed column experiments were carried out at different organic concentrations, flow rate and bed depth. Fixed bed column experiments were prolonged to evaluate the biodegradation of organics and growth of biomass in the multicomponent adsorption system.

In addition, adsorption-membrane hybrid systems (PAC-plate membrane external loop, and submerged hollow fibre membrane) were evaluated in terms of TOC removal efficiency from the synthetic wastewater and the biologically treated sewage effluent. The effect of PAC dose and the filtration rate were investigated.

1.3.2 Mathematical Modelling

A suitable model was developed to describe the adsorption equilibrium of the wastewater adsorption system. The isotherm constants determined from the association theory were subsequently used to predict the experimental results of the batch and fixed bed adsorption systems. The batch and fixed bed experimental results were predicted using linear driving force approximation (LDFA) model, and the adsorption dynamic model respectively. The LDFA is a simplified model based on the assumption that the mass transfer is proportional to the concentration gradient developed between bulk phase and liquid phase, and the fixed bed dynamic model is based on the conventional convection equation. A new conceptual model for both the GAC biofiltration systems was developed and tested with the experimental results. Both adsorption and biodegradation processes were incorporated in the model. Similarly, a semi-empirical model was developed to predict the results of the submerged membrane hybrid system. An empirical term, membrane correlation coefficient (MCC) was introduced in the model to incorporate both adsorption of organics on membrane surface and retention of PAC (associated with organics adsorbed on it) on membrane. The scope of the research work is summarized in Table 1.2.

Table 1.2 Framework of the scope of the work of the research

Experimental system	Synthetic wastewater	Biologically treated sewage effluent	Remarks
1. Isotherm (GAC+PAC)	• Individual component • Three different initial TOC concentration	• Sewage effluent as a whole	Isotherm equation development
2. Batch kinetics (GAC+PAC)	• Different adsorbent dose • Different stirring speed • Different initial TOC concentration	• Different adsorbent dose • Different stirring speed • Sewage effluent as a whole	Experiments and mathematical modeling
3. Fixed bed (GAC)	Different bed depth • Different filtration rate • Different initial TOC concentration	• Different bed depth • Different filtration rate • Sewage effluent as a whole	Experiments and mathematical modeling
4. Biofiltration (GAC)	• Long-term experimental run • Biomass measurement • Effect of different parameters	• Long-term experimental run	New conceptual model development
5. Submerged-Membrane hybrid system	• Different filtration rate • Different PAC dose	• Different filtration rate • Different PAC dose	Simple semi-empirical model development
6. External loop membrane hybrid system	• Different filtration rate • Different PAC dose	• Different filtration rate • Different PAC dose	Fouling mechanism study

1.4 Organization of the Report

This report contains 8 Chapters. Chapter 1 described the general background, the objective, and the scope of the study. Theoretical background on the application of adsorbent and the related past studies are summarized in Chapter 2. The details of the adsorption equilibria and the models; and the adsorption kinetics in batch stirring conditions and the description of the models are presented in Chapters 3 and 4 respectively. Chapter 5 explains the details of the fixed bed adsorption study and the mass transfer in adsorption dynamics mode. Investigation of the long-term performance of the fixed bed system with GAC is included in Chapter 6. Application of PAC in adsorption-membrane hybrid system (external loop and submerged) is discussed in Chapter 7. Chapters 3 to 7, which cover the main body of the study, present also the individual specific conclusions. Chapter 8 summarizes the overall conclusion of the study, and the recommendation for future study.

Effects of coagulation-flocculation on adsorption, and the relationship between different index parameters of the wastewater used in the study are discussed and presented in the appendices.

Chapter 2

Literature Review

2.1 Introduction

Water is indispensable part of life. Due to uncontrolled population growth, industrial and agricultural development, deforestation, water pollution, climatic changes, and excessive use or misuse of water, the fresh water resources from the earth are diminishing. Sustainable management of the existing natural water resources are therefore, necessary to preserve the environment and maintain the ecological balance. The wastewater treatment and reuse is one of the most important aspects of the sustainable management of the natural water resources. In Australia, water reuse from sewage treatment plants (STP) was 171 GL (i.e. 11% of STP effluent) in 2000, and it is growing by 28 GL/year (Dillon, 2001). The water reuse from STPs in different regions of Australia is shown in Table 2.1. According to the Australian Bureau of Statistics (2000) the reuse of effluent in Australia by different economic sectors are as follows: mining 32%, agriculture 28%, recreation 24%, electrical and gas 5%, metals 3%, water supply 3%, forestry 2% and other 3%. The various categories of wastewater reuse are presented in Table 2.2. In general, the conventional wastewater treatment processes are not so effective in removing all the organics effectively from the wastewater. Hence, further treatment (known as advanced wastewater treatment) is required to produce the effluent of reusable quality. The advanced wastewater treatment not only plays a critical role in the effective treatment of the wastewater to meet water quality objectives for water reuse but also it helps to protect the public health. The conventional wastewater treatment consists of a combination of physical, chemical, and biological processes that remove settable, suspended, and dissolved solids, organic substances, metals, nutrients, and pathogens from the wastewater. Similarly, the advanced wastewater treatment is not a single treatment process. A series of treatment processes need to be considered to remove the organics, inorganics, nutrients, ions and salts, bacteria and viruses that are not removed in the conventional treatment processes.

Some of the processes that can be used in the advanced wastewater treatment are coagulation-flocculation-sedimentation, filtration, adsorption, biofiltration, membrane filtration, and reverse osmosis.

This chapter presents only a general literature review on adsorption, biofiltration, and adsorption-membrane hybrid system. The purpose of this chapter is to configure the framework of this study. It also incorporates past studies with activated carbon (GAC and PAC) used to remove organic substances from water and wastewater. The specific review related to the objectives of this study is presented in the individual chapters.

Table 2.1 Water reuse from STPs in Australia in 2000 (Dillon, 2001)

Region	Effluent (GL)	Reuse (GL)	Reuse (%)	Rate of increase in Effluent (GL/yr/yr)	Rate of increase in Reuse (GL/yr/yr)
Queensland	342	54	16	7.2	8.0
New South Wales	560	65	12	3.1	6.3
Australian Capital Territory	30	0.7	2	-0.3	0.2
Victoria	370	25	7	3.2	8.5
Tasmania	43	1.3	3	0.3	0.3
South Australia	91	15	16	0	2.8
Western Australia	115	7.8	7	5.5	1.2
Northern Territory	21	2.4	11	0	0.7
Australia	1573	171	11	19	28

Table 2.2 Categories of municipal wastewater reuse (after US EPA, 1992)

Category of wastewater reuse	**Treatment goals**	**Example applications**
Urban use **Unrestricted**	Secondary, filtration, disinfection BOD$_5$: <10 mg/L, Fecal coliform: ND/100 mL, Turbidity: <2 NTU, Cl$_2$ residual: 1 mg/L, pH: 6 to 9	Landscape irrigation: parks, playgrounds, school yards, fire protection, construction, ornamental foundations, aesthetic impoundment, In-building uses: toilet flushing, air conditioning
Restricted access irrigation	Secondary and disinfection BOD$_5$: <30 mg/L, TSS: <30 mg/L, Fecal coliform: 200/100 mL, Cl$_2$ residual: 1 mg/L, pH: 6 to 9	Irrigation of areas where public access is infrequent and controlled: freeway medians, golf courses, cemeteries, residential areas, greenbelts
Agricultural irrigation **Food crops**	Secondary, filtration, disinfection BOD$_5$: <10 mg/L, Turbidity: <2 NTU, Fecal coliform: ND/100 mL, Cl$_2$ residual: 1 mg/L, pH: 6 to 9	Crops grown for human consumption and consumed uncooked
Non-food crops and food crops consumed after processing	Secondary, disinfection BOD$_5$: <30 mg/L, TSS: <30 mg/L, Fecal coliform: 200/100 mL, Cl$_2$ residual: 1 mg/L, pH: 6 to 9	Fodder, fiber, seed crops, pastures, commercial nurseries, sod farms, Commercial aquaculture
Recreational use **Unrestricted**	Secondary, filtration, disinfection BOD$_5$: <10 mg/L, Turbidity: <2 NTU, Fecal coliform: ND/100 mL, Cl$_2$ residual: 1 mg/L, pH: 6 to 9	No limitations on body-contact: lakes and ponds used for swimming, snowmaking
Restricted	Secondary, disinfection BOD$_5$: <30 mg/L, TSS: <30 mg/L, Fecal coliform: 200/100 mL, Cl$_2$ residual: 1 mg/L, pH: 6 to 9	Fishing, boating, and other non-contact recreational activities
Environmental reuse	Site specific treatment levels, pH, dissolved oxygen, coliforms, nutrients	Use of reclaimed wastewater to create artificial wetlands, enhance natural wetlands and sustain stream flows
Groundwater recharge	Secondary and disinfection BOD$_5$: <30 mg/L, TSS: <30 mg/L, Fecal coliform: 200/100 mL,	Cooling-system make-up water, process waters, boiler feed water, construction activities and washdown waters
Potable reuse	Safe drinking water requirements	Blending in municipal water supply reservoir, pipe to pipe supply

2.2 Activated Carbon Adsorption in the Advanced Wastewater Treatment

In principle, any porous solid can be an adsorbent, however for an efficient and economical adsorption process, the adsorbent must have a large surface are and a well-defined microcrystalline structure to possess high adsorption selectivity and capacity, and long life. Common natural adsorbents are fly ash, bone char, sawdust, fuller's earth, bauxite (aluminium oxide), charcoal, woodmeal, bagasse pith, peat, and lignite. Silica gel, activated alumina, activated carbon, and carbon molecular sieves are natural adsorbent but they are passed through a special treatment to develop their inframicrocrystalline structure. There are a number of synthetic adsorbents such as Aluminosilicate or zeolite. Activated carbons, both granular activated carbon (GAC) and powdered activated carbon (PAC) are one of the oldest and most widely used adsorbents commercially as well as in the laboratory. It can be used for wastewater effluent treatment, potable water treatment, solvent recovery, air treatment, decolorizing, and many more other applications. Most of the carbonaceous materials are porous and have internal surface area of approximately 10 m^2/g. When they are passed through the activation process, their internal areas are greatly expanded and subsequently they acquire an internal surface area of around 1000-1500 m^2/g. It is this huge surface area on which adsorption of organics (or any other pollutants) can occur. Both GAC and PAC can be used in a wastewater treatment process. The GAC is used as a fixed filter bed where as the PAC is used directly in the aeration tank. The use of activated carbon greatly reduces the pollutant load in the subsequent treatment processes. Basic types of industrial adsorbents are listed in Table 2.3.

Table 2.3 Basic types of industrial adsorbents (Dabrowski, 2001)

Carbon adsorbents	Mineral adsorbents	Other adsorbents
• Active carbons • Activated carbon fibres • Molecular carbon sieves • Mesocarbon microbeads • Fullerenes • Heterofullerenes • Carbonaceous nanomaterials	• Silica gels • Activated alumina • Oxides of metals • Hydroxides of metals • Zeolites • Clay minerals • Pillared clays • Porous clay hetero-structures (PCHs) • Inorganic nanomaterials	• Synthetic polymers • Composite adsorbents such as complex mineral-carbons, Zn-elutrilithe, Ca-elutrilithe • Mixed sorbents

The use of activated carbon is a very effective method of removing organic substances from wastewater as it has a strong affinity for binding organics even at lower concentration. The activated carbon is used either in the granular form (GAC) or in powdered form (PAC). The granular activated carbon is placed inside a cylindrical vessel with screens at the bottom and top to confine the carbon in the form of a packed bed. More than one vessel either in parallel or in series can be used. The wastewater is passed downwards through the packed bed by gravity. Alternately, it can be operated in upflow mode with a pump. Most of the suspended solids of the wastewater are filtered out, and the organic substances are adsorbed onto GAC surface. The GAC bed can be periodically backwashed to flush out the suspended solids. However, the adsorption capacity of the GAC particles is gradually exhausted with the adsorption of contaminants (organics and inorganics) onto GAC. The exhausted carbon particles are either discarded into the secured landfill or regenerated for further use depending upon the facility available in the proximity. It has been observed that the prolonged use of GAC bed can develop the growth of microorganisms on the GAC surface, and the adsorption bed is turned into a biofilter, where organics are removed by the microbial biodegradation. In this way, the GAC can be used for longer period of time without regeneration.

The powdered activated carbon (PAC) is usually added to the tank (activated sludge tank) where the main biological treatment of the wastewater takes place. It helps in reducing the problems of bulking of sludge or foaming associated with activated sludge process. The PAC particles enhance the biological assimilation of organics. During the process, the adsorption capacity of the PAC is also partially renewed by concurrent microbial degradation of adsorbed organic substances (McKay, 1996).

The use of PAC with membrane (adsorption-membrane) hybrid system is currently being emerged as a cost-effective wastewater treatment technology. It helps in removing refractory organics. The use of PAC in a membrane system not only reduces the clogging of membrane but also helps produce consistent permeate flux from the hybrid system. The PAC can be used in both submerged membrane and external loop membrane. In the submerged membrane hybrid system, the membrane unit is submerged in a tank containing wastewater and PAC in suspension. The submerged membrane hybrid system requires only minimum power for its operation. In external loop membrane hybrid system, membrane is fed with wastewater mixed with PAC in crossflow mode. Hence the power requirement to operate the system is higher in comparison to the submerged membrane system.

2.2.1 Adsorption Mechanism

The adsorption process is a complex phenomenon. It takes place when atoms of surface functional group of adsorbent (activated carbon) donate electrons to the adsorbate molecules (organics). The position of the functional groups (which are generated during activation process) of the adsorbent determines the type of adsorbent-adsorbate bond, and the thus the type of adsorption. The physical adsorption is mainly caused by van der Waals and electrostatic bonds between the adsorbate molecules and the atoms of the functional groups. The process is reversible, and thus desorption of the adsorbed solute can occur. The process is exothermic and the heat of adsorption is very low. The physical adsorption takes place at lower temperature (in the neighbourhood of room temperature), and it is not site-specific. The adsorption can occur over the entire surface of the adsorbent at multilayers. On the other hand, the chemical adsorption involves ionic or covalent bond formation between the adsorbate molecules and the atoms of the functional groups of the adsorbent. The chemical adsorption is irreversible, and the heat of adsorption is typically high. The chemical adsorption process is site-specific and it occurs only at certain sites of the adsorbent at only one layer (monolayer).

Since the wastewater contains a large amount of organic and inorganic substances, it is possible that both physical and chemical adsorption takes place when it comes into contact with activated carbon. However, for simplicity reasons, only physical adsorption process is considered in this study, as most of the adsorption-separation processes depend on physical adsorption. The adsorption process with wastewater is competitive in nature. The extent of competition depends upon the strength of adsorption of the competing molecules, the concentrations of these molecules, and the characteristics of the adsorbent (activated carbon). In a competitive adsorption environment, the desorption of a compound may take place by displacement by other compounds, as the adsorption process is reversible in nature. It sometimes results in an effluent concentration of an adsorbate greater than the influent concentration (Snoeyink, 1990). The desorption of a compound may take place when its influent concentration is decreased. Thacker et al. (1983) showed that the quantity of adsorbate that can desorb in response to a decrease in influent concentration increased as (i) the diffusion coefficient of the adsorbate was increased, (ii) the amount of compound adsorbed was increased, (iii) the strength of adsorption was decreased, and (iv) the particles size of the activated carbon was decreased.

It has been observed that the adsorbed organics on the surface of activated carbon lead to the growth of microorganisms on the surface of the adsorbent, which can assimilate and degradate the organic matters. Seo et al. (1997) found that the apparent adsorptive capacity of biological powder activated carbon (BPAC) i.e. biosorption was almost four times higher than the capacity calculated from the PAC adsorption isotherm.

2.2.2 Adsorption Kinetics and Equilibrium

The adsorption process is characterized by mainly two phenomena: (i) adsorption equilibrium, and (ii) adsorption kinetics. The constant-temperature equilibrium relationship between the quantity of adsorbate per unit of adsorbent and the equilibrium concentration of adsorbate in solution is called the adsorption isotherm. It determines the quantity of adsorbate that an adsorbent can adsorb. There are a number of isotherm equations proposed by different researchers. Langmuir and Freundlich equations are the most widely used isotherms to describe the single component adsorption whereas the ideal adsorbed solution theory (IAST) has been extensively used to describe the multicomponent adsorption (Crittenden et al., 1985b; Matsui et al., 1998). The multicomponent system can be either a mixture of known organics and inorganics (synthetic wastewater) or unknown organics and inorganics (sewage, peat water etc).

Langmuir isotherm:

$$q = \frac{aC}{1+bC} \tag{2.1}$$

where,

q = the adsorbed phase concentration (mg of adsorbate/mg of adsorbent),

C = bulk phase concentration (mg/L), and

a and b = Langmuir constants

Freundlich equation:

$$q = K_F C^{\frac{1}{n}} \tag{2.2}$$

Here, K_f and n are Freundlich constants

The IAST theory consists of five main equations (Equation 2.3 - 2.7). It considers the interactions among the different adsorbing component with known or unknown background.

$$C_i = C_i^0 z_i \tag{2.3}$$

$$q_i = q_T z_i \tag{2.4}$$

$$q_T = \left[\sum_{i=1}^{N} \frac{z_i}{q_i^0} \right]^{-1} \tag{2.5}$$

$$\sum_{i=1}^{N} z_i = 1 \tag{2.6}$$

$$\pi = \left(\frac{RT}{A} \right) \int_0^{C_i^0} \frac{q_i^0}{C_i^0} dC_i^0 \ , \qquad \pi = \pi_1 = \pi_2 = \cdots = \pi_N \qquad \text{at equilibrium} \tag{2.7}$$

Here, z_i is the mole fraction of the i^th^ species in the adsorbed phase corresponding to adsorbate concentration C_i, q_i^0 is the equilibrium concentration with respect to C_i^0 in its single species state. Here the superscript ^{0} represents single species state and is the total adsorption amount, π the concentration spreading factor, and RT/A the gas constants. The adsorption equilibrium is discussed in detail in Chapter 3.

The adsorption kinetics is the measure of rate of adsorption, and it describes the adsorbate transport mechanism from bulk solution to the adsorption site on adsorbent surface. There are basically four steps an adsorbate passes through to get adsorbed onto the porous adsorbent. First, the adsorbate must be transported from bulk solution to the boundary layer (bulk solution transport) of the wastewater surrounding the adsorbent. The transport occurs by diffusion if the adsorbent is in quiescent state. In the fixed bed or in the turbulent mixing batch reactors, the bulk solution transport occurs by turbulent mixing. Second, the adsorbate must be transported by molecular diffusion through the boundary layer (film diffusion transport) surrounding the adsorbent particles. Third, after passing through the boundary layer, the adsorbate must be transported through the pores of the adsorbent to the available adsorption sites (pore transport). The intraparticle transport may occur by molecular diffusion through the wastewater solution in the pores (pore diffusion) of by diffusion along the surface of the adsorbent (surface diffusion). Finally, when the adsorbate reaches the adsorption site, the adsorption bond is formed between the adsorbate and the adsorbent. This step is very rapid for physical adsorption (Tien, 1994). Thus, it is either the bulk solution transport or film diffusion transport or pore transport that controls the rate of organic removal from the wastewater. In turbulent mixing condition (in fixed bed or in batch reactor), it is most likely that a combination of film diffusion and pore diffusion controls the rate of adsorption of organics. At the initial stage, the film diffusion may control the adsorption rate but after the accumulation of adsorbates within the pore of the adsorbent, it is possible that the adsorption rate is controlled by the pore transport. The mass transfer mechanisms of the models are shown in Figure 2.1.

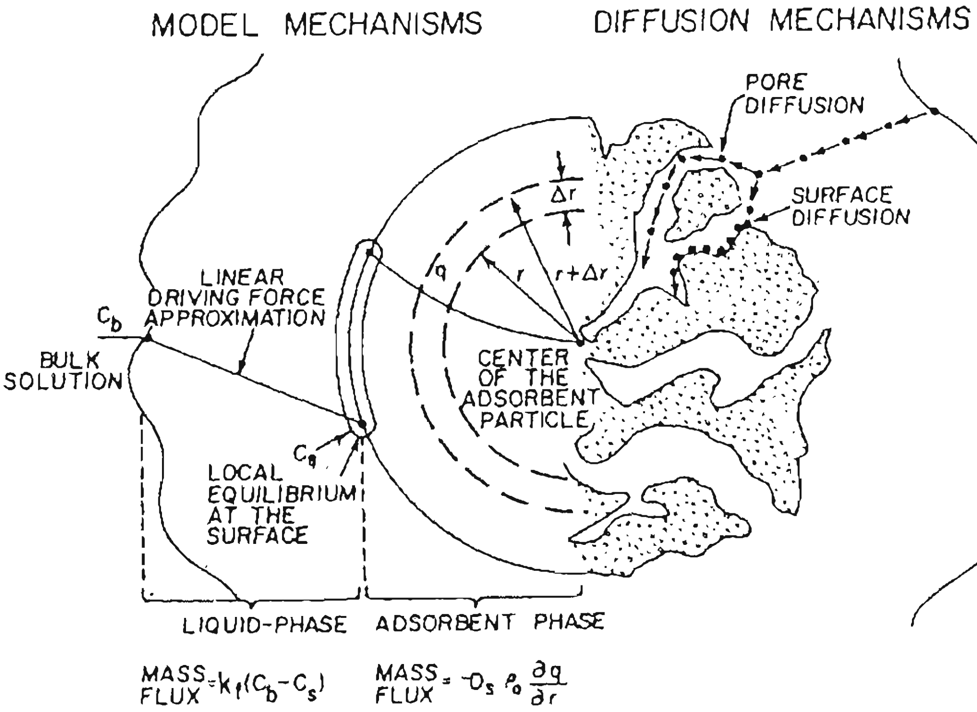


Figure 2.1 The mass transfer mechanisms in GAC (Hand et al., 1983)

Since the wastewater contains a complex mixture of organic and inorganic substances, it is possible that the adsorption is not completely physical. If the adsorption is accompanied by a chemical reaction that changes the nature of the molecules of the adsorbates, the chemical reaction could be slower than the diffusion step and thus controls the rate of adsorption. The characteristics of the solution (wastewater) and the adsorbent particles (GAC) control the rate of adsorption significantly. Usually, the adsorption of the larger molecular weight substances (humic substances) takes longer than the adsorption of lower molecular weight substances (phenol). It is because the intraparticle diffusion coefficient is reduced as the molecular size of the substance increases. The adsorption kinetics has been described by different types of models. The surface diffusion model (SDM) and pore diffusion model (PDM) are extensively used adsorption models. Both the SDM and the PDM result in very complex differential equations while describing the multicomponent adsorption phenomenon, and hence a more simplified kinetic model known as linear driving force approximation model (LDFA) is often used to describe the adsorption behaviour of organics in wastewater (which is a multicomponent system). The LDFA model states that the mass transfer is directly proportional to the driving force developed due to the difference between the surface concentration and the average adsorbed phase concentration of the adsorbate. The SDM, PDM and LDFA are discussed in detail in Chapter 4.

2.2.3 Factors Affecting Adsorption of Organics

The main factors that affect the adsorption of organics from wastewater are: (a) the characteristics of adsorbent: surface area, particle size, pore structure, (b) the characteristics of adsorbate: solubility, molecular structure, ionic or neutral nature, and (c) the characteristics of the solution: pH, temperature, presence of competing organic and inorganic substances. The maximum amount of adsorption is proportional to the amount of surface area within the pores of the adsorbents that is accessible to the adsorbate. Smaller the pore size (< 2 nm in diameter, d), larger the volumes of the pores and larger the adsorption capacity (for smaller molecules). However, the adsorption capacity of the adsorbent with smaller pore size is relatively low for the larger molecules such as fulvic acid molecules. The effect of carbon particle size on the adsorption isotherm of humic acid is shown in Figure 2.2. It shows that adsorption of organic increases with the increase in the adsorbent size. The surface chemistry of adsorbent and adsorbate can have significant effect on adsorption process. Highly soluble organics are less adsorbable. The organic substances, which are non-polar and hydrophobic in nature, are more adsorbable. The aromatic and the branched-chain molecules are usually more adsorbable than aliphatic and straight chain molecules. The effect of pH of the solution is crucial when the adsorbing solutes are capable of ionization. When the pH of solution is such that the adsorbates exist in ionized form, the adjacent molecules of the adsorbed solutes on the adsorbent surface repel each other to a significant degree, as they carry the same electrical charge. As a result, the adsorbing solutes can not pack together on the adsorbent surface, and the equilibrium amount of the adsorbed solutes is less. The effect of pH on the adsorption isotherm of humic acid is shown in Figure 2.3. In general, the adsorption capacity of an adsorbent decreases at higher temperature. At higher temperature, the adsorbed molecules are more energetic and get desorbed from the adsorbent surface. Similarly, the background compounds and their concentrations can have a very significant effect on adsorption of a particular solute. If the background compounds are adsorbable in nature, then there exists a competitive adsorption, and hence the available adsorption site for that particular solute is significantly reduced. Effects of background substance and initial organic concentration on adsorption isotherm of humic acid are shown in Figures 2.4 and 2.5 respectively.

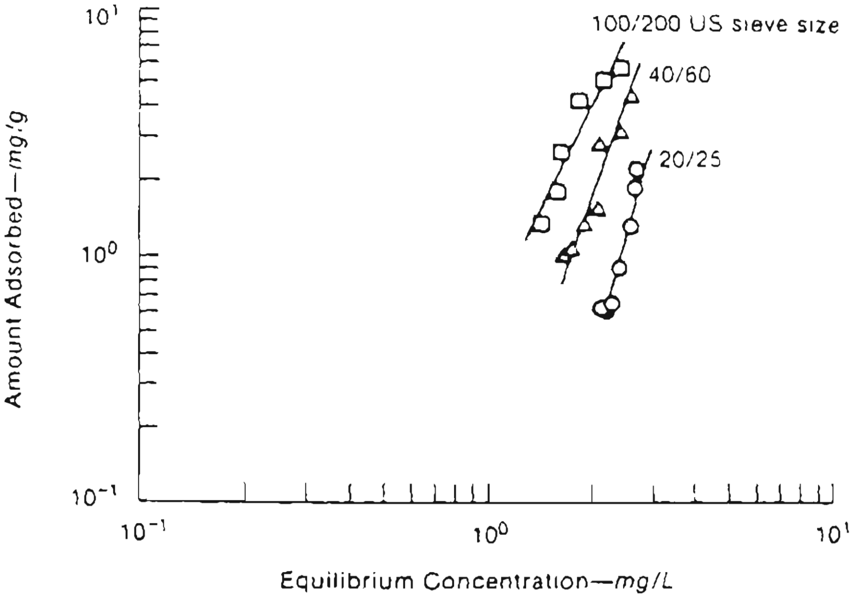


Figure 2.2 Effect of carbon particle size on the adsorption isotherm of humic acid (Weber et al., 1983)

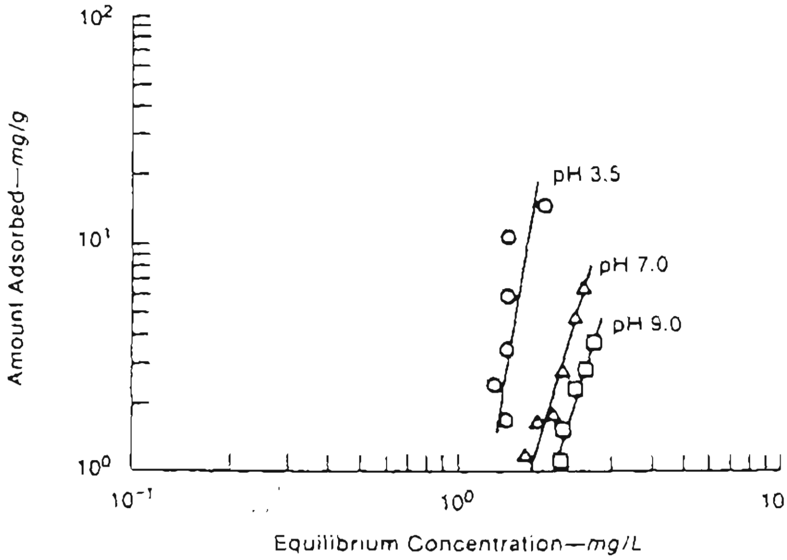


Figure 2.3 Effect of pH on the adsorption isotherm of humic acid (Weber et al., 1983)

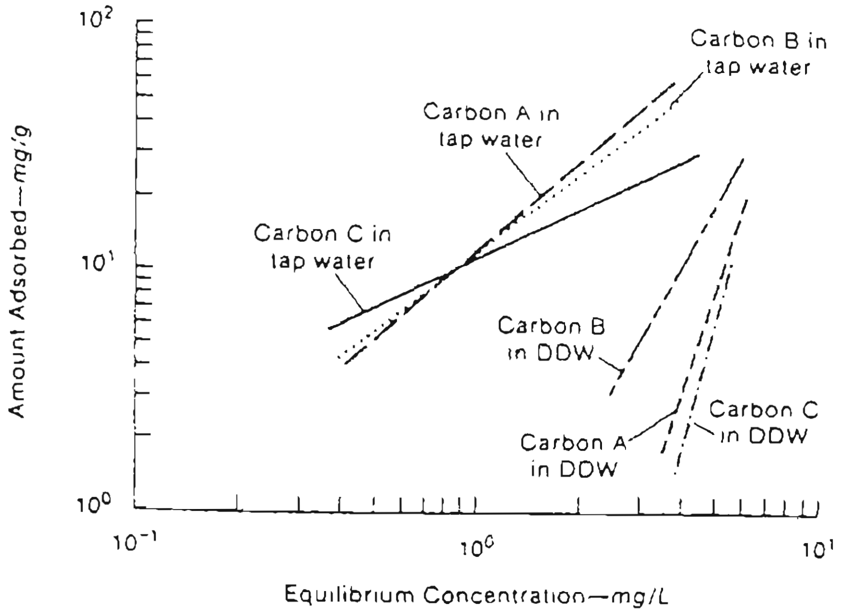


Figure 2.4 Effect of background solution on the adsorption of humic acid (Weber et al., 1983)

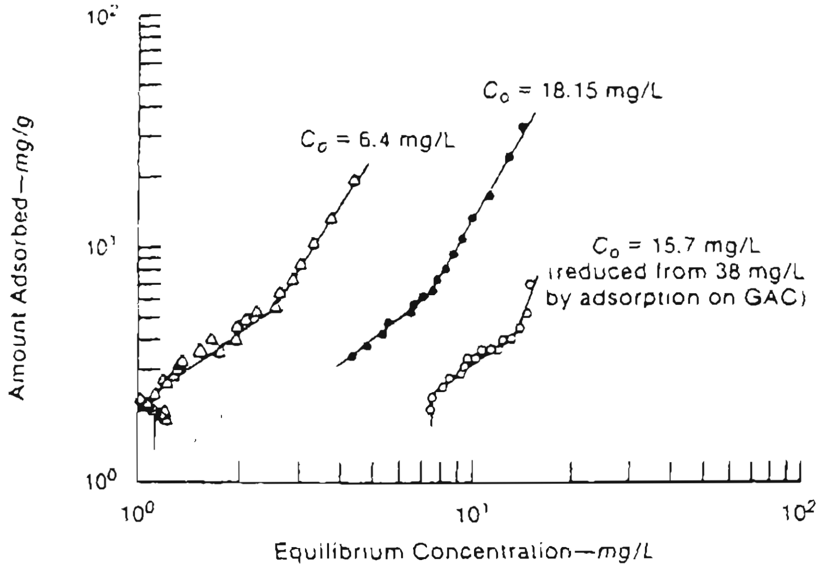


Figure 2.5 Effects of initial organic concentration on the adsorption isotherm of humic acid (Weber et al., 1983)

2.2 Past Studies on Adsorption

Most of the past studies on adsorption have been carried out on the single component where only one element or compound (such as phenol or herbicide) was targeted. Only few adsorption studies have been conducted with the mixtures of two or more organic compounds (Crittenden et al, 1985a, Moon et al, 1991). However, there are very limited numbers of adsorption research on wastewater system (Matsui et al., 1998). Due to the complexity of the composition, and the concentration of different organics and inorganics present in a wastewater system, it is very difficult to develop a mathematical model that can be used to predict or design the adsorption system in the field. The model developed in one particular multicomponent system may not necessary be useful for another multicomponent system due to the competitive adsorption characteristics of different organics and inorganics and interactions among themselves. There are two approaches to describe the adsorption characteristics of a multicomponent system: (a) single component approach, and (b) multicomponent approach. In single component approach, the overall adsorbate content is represented by an index (or lumped) parameter such as BOD_5, COD, TOC, AOC, DOC, and the adsorption phenomenon is described by a single component adsorption equilibrium model such as Langmuir or Freundlich isotherm. The single component approach does not account for the interactions among the components (organic substances) present in the system (Summers and Roberts, 1984, Lee et al., 1983). In the multicomponent approach, the adsorption characteristics of each individual component (if known) are determined, and then the total adsorption capacity is calculated using IAST theory (Crittenden et al., 1985b). If the adsorption characteristics of individual component are not known then the overall component is represented by several hypothetical components with different adsorption characteristics (Smith, 1994, Matsui et al., 1998). In both these approaches, the intraparticle mass transfer of organics is described either by the homogeneous surface diffusion model or by the pore diffusion model (Li et al., 1998).

Since wastewater contains a matrix of organic and inorganic compounds, it is not possible to identify all these compounds and their individual adsorption extent. It is also not possible to incorporate the effects of all the interactions among different organic and inorganic substances present in the wastewater. Therefore, attempts have been made by the previous researchers to combine the single component approach into multicomponent theory. Radke and Prausnitz (1972), Okazaki et al. (1980), and Fritz and Schlunder (1981) demonstrated that when all the compounds of a mixture were identified, ideal adsorbed solution theory (IAST) could be used to predict the multicomponent equilibrium of individual component using single solute isotherm parameters.

Crittenden et al. (1985b) assumed theoretical components (TCs) and used ideal adsorbed solution theory (IAST) to describe the competitive interactions between known adsorbates (chloroform, bromoform, trichloroethene, tetrachloroethene, 1, 2-dibromoethane, and chlorodibromomethane) and unknown mixture background. They applied the TC procedure to three synthetic mixtures made up of 2, 3, and 6 components. One component was singled out as the tracer component and the reduction in its capacity as compared to its single solute capacity was used to determine the TC properties. The TC properties were used to predict the competitive interactions between the synthetic mixture and an individual component

Calligaris and Tien (1982) suggested that multi-component mixtures of volatile organic chemicals could be grouped into fewer pseudo-species to describe the overall multicomponent adsorption phenomenon. The concept was later developed by Jayaraj and Tien (1984), and Kage and Tien (1987). The multicomponent adsorption calculations were significantly simplified by grouping the similar adsorbates into pseudospecies. As shown in Figure 2.6, one may combine the adsorbates represented by the various points in A-n network to form a pseudospecies corresponding to grid point, and the solution then can be characterized by assigning concentration values to the pseudospecies.

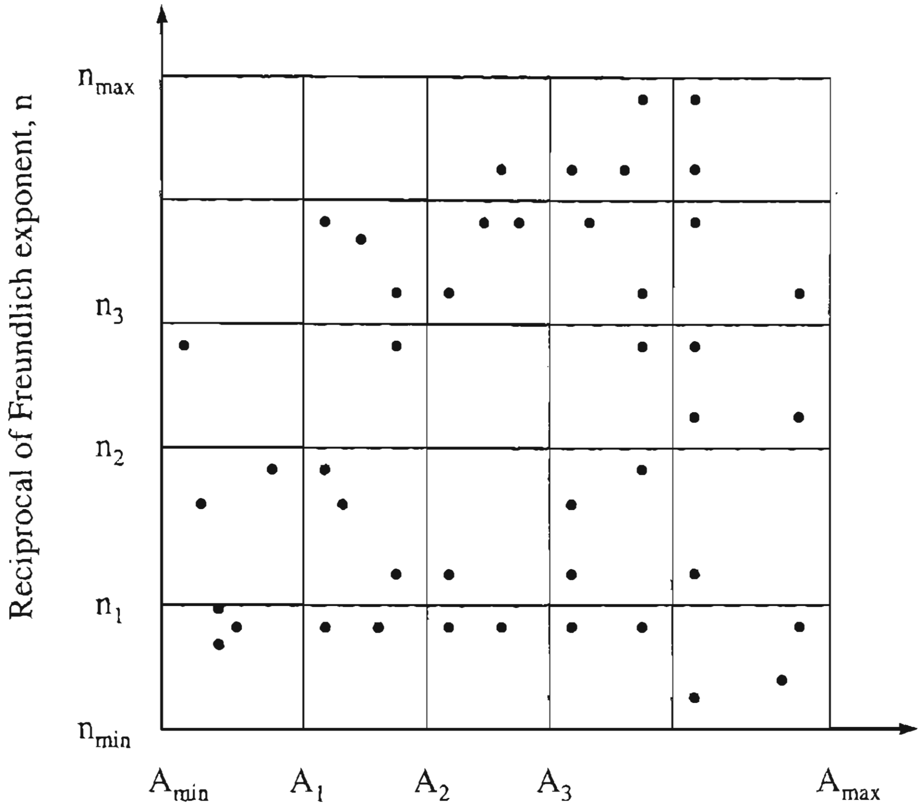


Figure 2.6 An A-n network used to represent a solution with multiple solutes (Kage and Tien, 1987)

Frick and Sontheimer (1983) also used theoretical components method to predict adsorption isotherms of total organic carbon (TOC) where each theoretical component represented a portion of the total TOC and sum of the TC concentrations equalled to the total TOC concentration. They developed the concept of classifying the background substances into 3 major groups: (a) non-adsorbable, (b) weakly adsorbable, and (c) strongly adsorbable as shown in Figure 2.7, and applied this concept in describing the adsorption equilibrium results in the A-n network with humic acid using Norit ROW carbon (Figure 2.8).

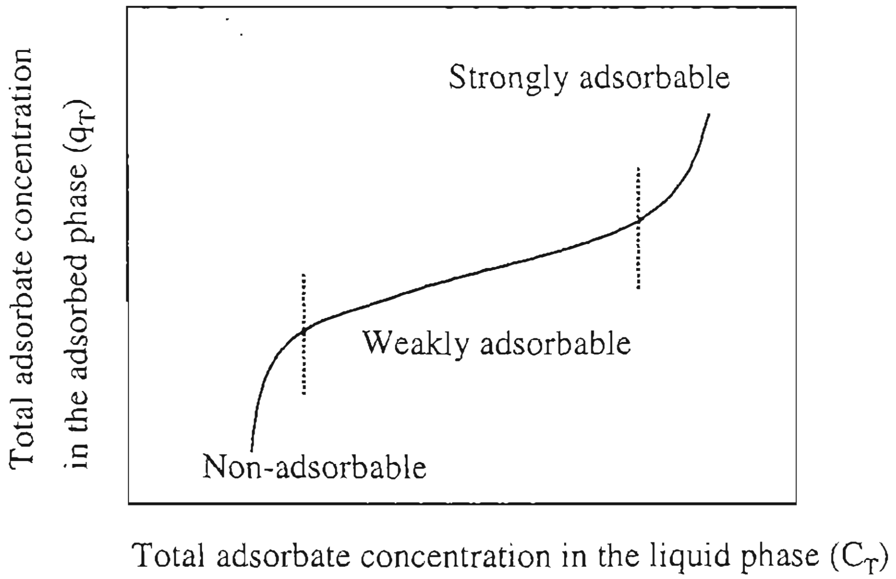
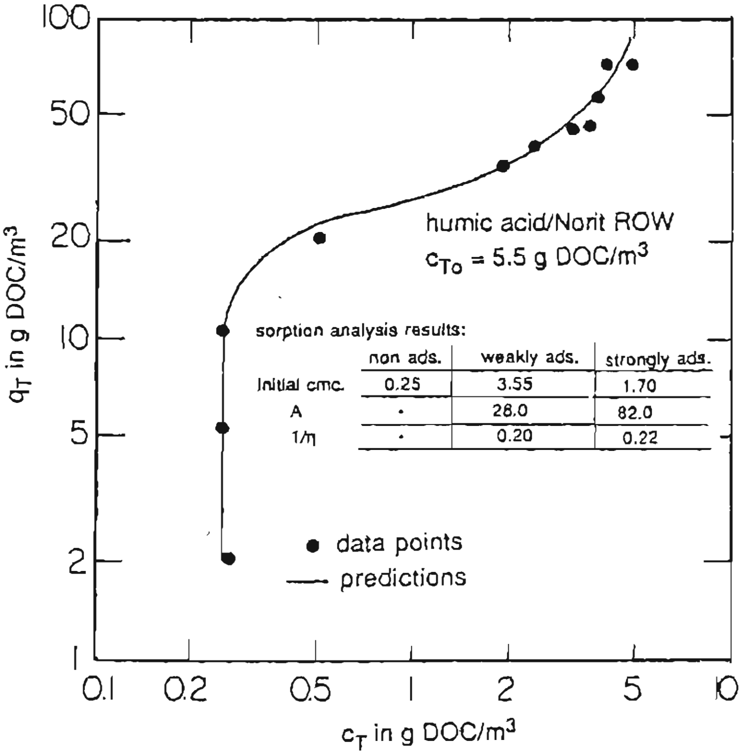


Figure 2.7 Extent of adsorption for a solution containing several adsorbates of equal amount but with different adsorption affinity (Frick and Sontheimer, 1983)



sorption analysis results:

	non ads.	weakly ads.	strongly ads.
Initial cmc.	0.25	3.55	1.70
A	•	28.0	82.0
1/n	•	0.20	0.22

Figure 2.8 Integral batch adsorption of humic acid (Frick and Sontheimer, 1983)

Yuasa et al. (1996a) fractionated the background organics of a biological process effluent and peat water in terms of their adsorptive strength described by the constants K_F and n of the Freundlich isotherm. They described the overall isotherm on the basis of TOC and UV-260 absorbance using IAST and Freundlich isotherm. They assumed that the overall background organics consisted of the organic components of different values of the Freundlich constant (K_F) but the same value of Freundlich exponent (n^{-1}), and the constant (K_F) could be represented by the logarithmic normal distribution (Equation 2.8, Figure 2.9).

$$f(\log_{10} k) = \frac{1}{\sqrt{2\pi}\sigma} e^{-(\log_{10} k-\mu)^2 / 2\sigma^2} \tag{2.8}$$

where,

μ and σ are the mean and standard deviations of $\log_{10}$ (k) respectively.

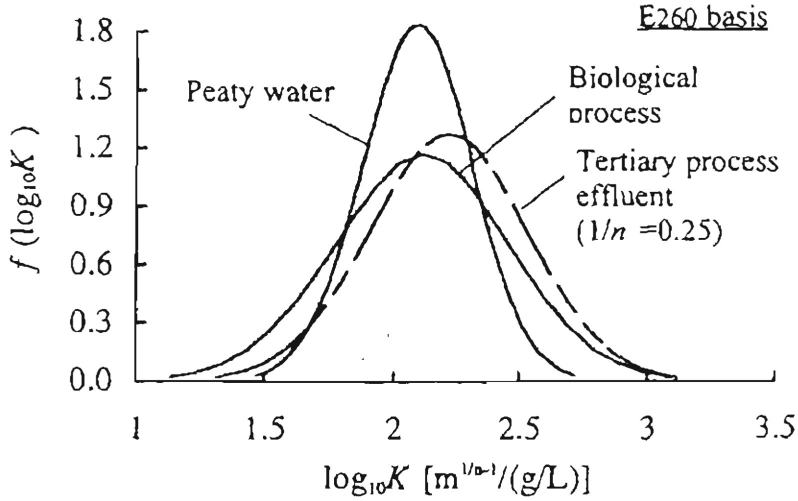


Figure 2.9 Freundlich constant (K) distribution of organics (Yuasa et al., 1996a)

They observed the position of the isotherms shifted in a direction from the right to the left as the initial concentration was decreased, exhibiting a strong dependence on the overall initial concentration. The adsorptive capacities for the solution of a lower initial concentration were generally higher than that for the solution of a higher initial concentration (Figure 2.10). Using IAST-Freundlich equations and basic mass balance equations, they derived Equation 2.9 assuming different value of Freundlich constant (K_F) but same value of Freundlich exponent (n^{-1}) for all components.

$$\sum_{i=1}^{N} \frac{\dfrac{C_{i0}}{C_{t0}}}{\left(\dfrac{q_t}{k_i}\right)^{n} \cdot \left(\dfrac{1}{C_{t0}}\right) + 1 - \left(\dfrac{C_t}{C_{t0}}\right)} = 1 \tag{2.9}$$

where,

C_{io} = initial liquid phase organic concentration of ith component

C_{to} = initial total liquid phase concentration

C_t = total liquid phase organic concentration

q_t = total solid phase organic concentration

k_i = Freundlich constant for ith component

The Equation 2.9 indicates that the overall adsorption isotherm represented by the relationship between q_t and Ct depends not only the composition of the multicomponent solution (C_{io}/C_{to}) but also on the initial overall concentration (C_{to}).

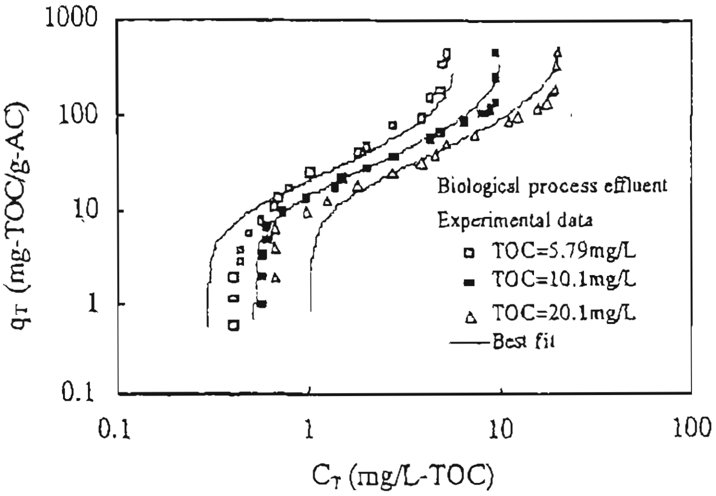


Figure 2.10 The overall adsorption isotherm of the biological process effluent (Yuasa et al. 1996a)

Li et al. (1998) found the combined plug flow-pore and surface diffusion model (PFPSDM) more precise than plug flow-surface diffusion model (PFSDM) or plug flow-pore diffusion model (PFPDM) alone in describing the multi-component adsorption when incorporated with the IAST-Freundlich isotherm. They also generalized the surface diffusion coefficient of the hypothetical components for the PFPSDM as a power function of Freundlich constant (K_F) and molecular weight fraction of the component (M):

$$D_{si} = \alpha \cdot (K_{Fi})^{\beta} \cdot (M_{mi})^{\gamma} \tag{2.10}$$

Where,

$\alpha = 3.09 \times 10^{-10}$, $\beta = 2.4$ and $\gamma = 0.15$ for peat water

$\alpha = 5.10 \times 10^{-10}$, $\beta = 2.4$ and $\gamma = 0.15$ for biological process effluent from STP

$\alpha = 1.08 \times 10^{-10}$, $\beta = 2.4$ and $\gamma = 0.15$ for tertiary process effluent (coagulation/sedimentation and filtration)

Matsui et al. (1999) studied the effects of pretreatment such as coagulation, ozonation and chlorination on adsorption of TOC using biological effluent from STP (Kakamigahara, Gifu, Japan) and peat water (Kitamura, Hokkaido, Japan). The effects of these pretreatment on adsorption characteristics were evaluated in terms of changes in distributed fictive component (DFC) parameters such as Freundlich K_F (average adsorption affinity), standard deviation of K_F (heterogeneity of adsorbed compounds), Freundlich 1/n (concentration dependence of adsorption capacity), and the fraction of non-adsorbable organics. Coagulation treatment was found remove larger molecular weight and more hydrophilic fractions and increased adsorption capability of organics (TOC 0.1-20 mg/L) on GAC but Freundlich exponent (1/n) remained unchanged. Ozonation and Chlorination were found to decrease the adsorption capacity but the heterogeneity (standard deviation of K_F) and concentration dependency of adsorption (1/n) was increased. Non-adsorbable fraction was found to increase after all these pretreatment processes.

Talu and Meunier (1996) developed a general theory, the theory of association, for the adsorption of self-associating molecules in micropores (that exhibit S-shaped isotherm classified as Type 5) and applied it to water adsorption data on several activated carbons at different temperatures successfully. The theory was capable of explaining Isotherm Types 1 to 5 transitions (as given in Figure 3.1, Chapter 3) as well. The clusters of the solutes around the adsorption site by the association theory are shown in Figure 2.11. The theory of association of the molecules was described by chemical equilibria, equation of state and phase equilibrium. The chemical equilibria and the equation of state were used to describe the behaviour of the surface phase whereas the phase equilibrium to link the surface phase properties to bulk phase properties. The isotherm equation derived from these 3 theoretical considerations consists of 3 parameters, H, K and q_m that describe the overall isotherm. These isotherm parameters are interrelated as follows:

$$C_e = \frac{H\Psi \cdot \exp\left(\dfrac{\Psi}{q_m}\right)}{(1+K\Psi)} \tag{2.11}$$

$$\Psi = \left(\frac{-1 + (1 + 4K\zeta)^{0.5}}{2K} \right) \tag{2.12}$$

$$\zeta = \frac{q_m q}{q_m - q} \tag{2.13}$$

where,

C_e = Equilibrium organic concentration, mg/L

H = Adsorption constant (Henry's Law constant)

K = Reaction constant

q_m = Saturation amount of organic adsorbed, mg/g

ψ = Organic concentration spreading parameter, and

q = measured amount organic adsorbed, mg/g

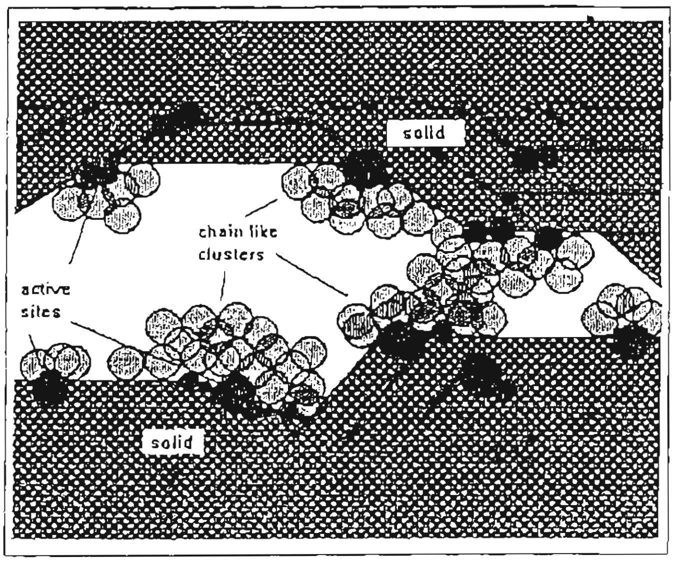
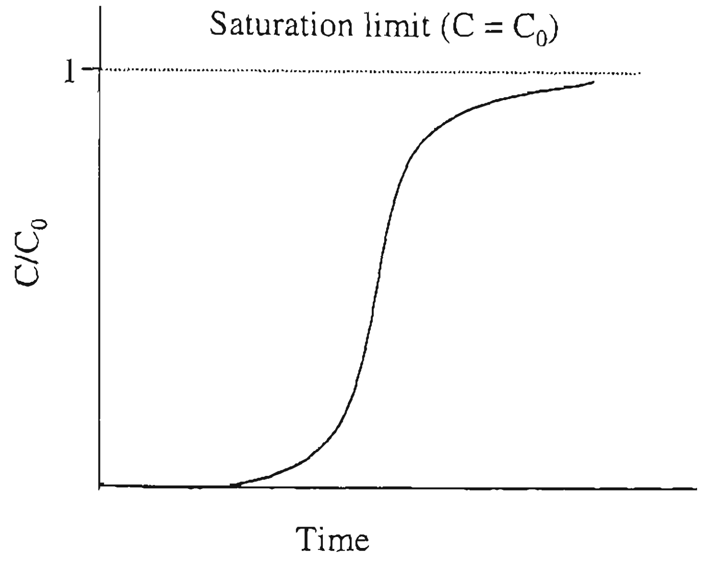


Figure 2.11 Clusters of the solutes around adsorption site in the association theory (Talu and Meunier, 1996).

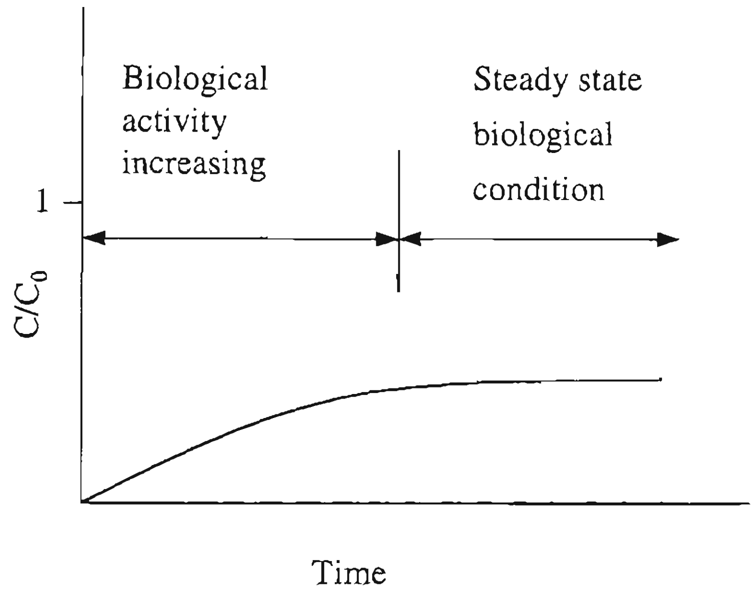
2.3 Biosorption and Biodegradation of Organics

2.3.1 Biosorption Process

The adsorption capacity of GAC is gradually reduced with its operational time depending on the organic and hydraulic loading rates of the wastewater through the column. However, the adsorbed organics on the surface of the GAC leads to the growth of microorganisms on the surface of the adsorbent, which can further assimilate and degradate the organic matters. The fixed bed system with attached microorganisms on the surface of the adsorbent is referred to as biofilter. Thus, biofilter is a conventional filter with biomass attached onto the filter media as a biofilm, where the organics are adsorbed and biodegraded by the microorganisms. Typical idealized performance of activated carbon fixed bed with and without biological activity is shown in Figure 2.12. The shape of this curve can take a number of patterns depending on fixed bed depth, filtration velocity, wastewater characteristics, and reactor volume. In the initial stage, adsorption alone, then adsorption and biological degradation occur simultaneously. Initially, adsorption controls the effluent organic concentration. As the adsorption capacity of the GAC is exhausted gradually with time, at some stage of continuous operation, biological reactions control the overall organic removal process and a constant effluent organic concentration is achieved. Three main biological processes that can be assumed to occur in a biofilter are: (i) attachment of microorganisms, (ii) growth of microorganism and (iii) decay and detachment of microorganisms. The fundamental biofilm kinetics that control the performance of the biofilter are: (a) substrate utilization and diffusion inside the biofilm, (b) mass transport between the bulk liquid and the biofilm, and (c) biofilm growth and loss. The details of these processes are described in Chapter 6.



(a) Non-biological GAC



(b) Biological GAC

Figure 2.12 Typical idealized performance of activated carbon fixed bed with and without biological activity (C = effluent organic concentration, C_0 = influent organic concentration)

2.3.2 Biomass and its Measurement Techniques

Careful control and maintenance of biomass on the filter media is important for the successful operation of a biofilter. The organics are first adsorbed onto the biomass, and then diffuse into the biomass where they are biodegraded by the microbial activities. The amount of biomass accumulation depends on the filtration velocity, the organic concentration, and the type of filter medium. Hence, it is important to maintain an optimum biomass based on the operating condition of the biofilter. Several methods are adopted in practice to measure the biomass depending on the availability of the analytical facilities. Some of the widely-used methods are discussed in this section.

2.3.2.1 Van der Kooij Method

The Van der Kooij method was originally proposed to determine AOC in a water sample by measuring the growth of Pseudomonas fluorescence strain (P17 strain). The Pseudomonas strain can utilize most of the easily biodegradable compounds such as amino acids, carboxylic acids, hydrocarboxylic acids, alcohols, and carbohydrates, but the organic compounds such as oxalic acid, glycerol, and a number of oligosaccharides, and polysaccharides are not accounted for by Pseudomonas alone. So other species such as Spirillum strain (NOX) and flavobacterium species are also utilized in this method (Van der Kooij, 1990).

Since, there is a good correlation between the maximum number of P17 cfu/ml and the concentration of sodium acetate added to a tap water (Van de Kooij et al., 1982), the result of this method is often expressed as μg acetate C eq/L. The results of the strain NOX are usually expressed as μg oxalate C eq/L. This makes it difficult to express the total AOC (AOC-P17+AOC-NOX) meaningfully. In such case, an yield factor for NOX on acetate is used to express the total AOC as μg acetate C eq/L.

2.3.2.2 Kemmy et al. Method

This method (Kemmy et al., 1989) is similar to that of Van der Kooij. In this method, the filtered sample is inoculated with a defined mixed bacterial species (P. flouorescens, curtobacterium sp., corynebacterium sp. and coryneform), and then incubated at 20°C. After six days of incubation, colony forming units (cfc/ml) are determined with a drop-counting method using a nutrient agar. It is later converted into AOC μg/L based on a calibration curve obtained with a standard mixed solution of organic compounds (peptones and yeast extract supplemented with acetate and glucose).

2.3.2.3 US-EPA Method

This method is also similar to Van der Kooij method. In this method, coliform growth response is measured (Rice et al., 1989). An inoculum of one or more coliform organisms (E. coli, enterobacter cloacae, klebsiella oxytoca) is added to the sample after filter sterilization, which is first done to remove the indigenous bacteria from the sample. The colony forming units (cfc/ml) of the sample are analysed at the beginning (N_0) and after five days of incubation at 20°C (N_5). The coliform growth response (CGR) is determined in logarithmic form as log (N_5/N_0).

2.3.2.4 Werner Method

In this method, the total bacterial cell is measured in terms of turbidity (Werner and Hambsch, 1986). The sample is first filter-sterilized, placed into a cuvette, and a sterile nutrient salt solution containing no carbon is added. The sample is then inoculated with a specific volume of a suspension of bacteria (usually washed from the sterilizing filter, and the cuvette is incubated in a specially modified turbidimeter at 20° C. The turbidity is normally measured every 30 minutes over a period of 30-150 h. Here, the slope of the logarithmic plot between the turbidity (biomass) and the incubation time indicates the biodegradability quality of the substrate.

2.3.2.5 Jago-Stanfield Method

In this method, the bacterial growth is measured by means of adenosine triphosphate (ATP) concentration (Stanfield and Jago, 1987). A luminometer is required for the ATP measurement. The microbial population is first is first removed from the sample by filtration, and then a known volume of inoculum is added. Each day a sample is taken from the inoculated flask for ATP analysis, until a maximum ATP concentration is reached. The ATP concentration is then converted into AOC values by means of a standard conversion factor.

2.3.2.6 Billen-Servais Method

In this method, the biomass is determined as function of time (Servais et al., 1987). The sample is first filtered through 0.2 μm filter, and then it is inoculated with 1 % by volume of water (influent water after passing through 0.2 μm). The inoculated sample is then incubated at room temperature for at least 300 hour. Each day, a sample is taken from the incubation flask for the analyses of bacterial numbers and total bacterial volume (based on cell size) until total bacterial mortality is achieved (total bacterial mortality is the total biomass), and finally the data are converted into biomass by means of conversion factor. This method requires epifluorescence microscope for the analyses of bacterial numbers and bacterial volume. The results are often expressed in terms of BDOC, which is the determined from the plot of the biomass as a function of time. The BDOC is the total biomass divided by the biomass growth rate (the slope of the plot between biomass and time).

2.3.3 Past Studies on Biofiltration

Many studies have been carried out on biofiltration during last decade especially with GAC as filter media. However, theoretically, it is still difficult to explain the behaviour of a biofilter. The growth of different types of microorganisms in different working conditions makes it impossible to generalize the microbial activities in a biofilter. It is thus, important to evaluate the biofilter in terms of its operating conditions and the characteristics of the influent feed. The efficiency of a biofilter operated at different filtration rates and influent characteristics can vary significantly for different target pollutants. Besides, some of the operational drawbacks of the biofilter such as performance fluctuation, maintenance of biomass, release of microorganisms, have made the research on it more imperative.

Previous studies with tertiary wastewater and surface water have shown that the GAC (an adsorptive media) is better than anthracite or sand (non-adsorptive media) in removing organic substances from tertiary wastewater and surface water (LeChevallier et. al., 1992; Wang et al., 1995a). The microporous structure and irregular surface of the GAC offer more sites appropriate for biomass attachment. It also provides protection from shear loss of biomass. The GAC adsorbs and retains slowly biodegradable organic substances that are biodegraded by the attached microbial mass leading to continuous bioregeneration of the GAC (AWWA research and technical committee report, 1981). Biofilters have been found to remove organics and nutrients in significant quantities and produce high quality effluent (Yang et al., 2001, Boon, 1997, and Sakuma et. al., 1997, Hozalski et al., 1995, Ahmad et al., 1998).

The past studies on biofilter are summarized in Table 2.4.

Table 2.4 Summary of the past studies on biofilter

Researcher, Source	Filter Medium	Experimental parameter		Major Observation
		Organic	Biomass	
Ahmad et al. (1998), water	Anthracite + sand,	AOC-P17, AOC-NOX, NPOC, turbidity	HPC	Backwashing technique and hydraulic transient can affect the performance of a biofilter.
Boon et al. (1997), Wastewater	Granite, blast-furnace slag	BOD, ammonia, SS	None	Performance a biofilter depends on organic loading rate, temperature, filter design configuration.
Carlson and Amy (1998), water	Anthracite	DOC, BDOC	Phospholipid analysis	DOC removal is controlled by biomass. The filter acclimatized at higher HLR had a substantially higher cumulative biomass.
Hozalski et al. (1995), synthetic water, NOM.	Sand	TOC	None	No effect of EBCT (range 4 - 20 mins) on TOC removal.
Hozalski and Bouwer (1998), synthetic water, NOM	Glass beads + sand	TOC	HPC bacterial count	Biomass accumulation is not impaired by backwash with water
LeChevallier et al. (1992), river water	Anthracite + sand + garnet, GAC+ Sand	TOC, AOC-P17, NOX, THMFP, DBPs	HPC and coliforms	AOC and TOC removal better in GAC-sand filter.

Researcher, Source	Filter Medium	Experimental parameter		Major Observation
		Organic	Biomass	
Miltner et al. (1995), water	Anthracite +sand	Aldehydes, AOC-NOX, TOC, DBP products	Phospholipid analysis	Efficiency of the biofilter is not impaired by backwash with non-chlorinated water.
Niquette et al. (1998), water	GAC	DOC, DO, NH_3, NO_2	Bacterial count	Shut down of biofilter promotes anaerobic conditions reducing the quality of the effluent. The biofilter should be backwashed when anaerobic condition occurs.
Prevost et al. (1992), river water	Anthracite + sand, GAC+ sand	Aldehydes, DOC, BDOC, oxalate	^{14}C- Glucose respiration	Aldehyde removal better in GAC-sand filter.
Servais et al. (1994), water	GAC	DOC, BDOC, NBDOC	^{14}C- Glucose respiration	3 month acclimatization period is required for a biofilter to function properly. Removal efficiency of a biofilter depends on EBCT, not on filtration rate
Wang et al. (1995b)	Anthracite + sand, GAC+ sand, sand	TOC, BDOC, aldehydes, AOC-NOX, THM and TOX formation potential	Phospholipid analysis	GAC contained 3-8 times more biomass than anthracite or sand

2.4 Adsorption-membrane Hybrid System for Wastewater Treatment

The use of membrane separation technologies in wastewater treatment and reuse is gaining popularity due to the increasing environmental regulations being placed on effluent discharge. The membrane technologies can be used in secondary or tertiary wastewater treatment systems. The primary advantages of submerged membrane technologies over existing separation processes such as activated sludge process or filtration are: (a) lower energy costs, (b) low-cost modular construction, and (c) effective in removing wide range of organics and other pollutants even at lower concentration. The limitation of using membrane separation process are: (i) membrane fouling and hence the feed solution should have low solid contents, and it should be operated at low flow rate to minimize the fouling, and (ii) high capital cost. The capital cost will reduce when the application of the membrane technology increases. However, it would be very costly to operate the membrane separation system at reduced flow rate to minimize the membrane fouling, and hence it needs to be coupled with another separation system such as adsorption. Further, the micro- and ultrafiltration processes alone cannot remove dissolved organics matters. Previous studies have shown that in adsorption-membrane hybrid system, the rate of membrane fouling is significantly reduced and thus the operational life of the membrane is increased (Adham et al., 1993, Pirbazari et al., 1992, Clark et al., 1996, Matsui, et al., 2001a). Most of the dissolved organics/ pollutants are adsorbed onto the adsorbents reducing the direct loading to the membrane surface. The organic laden adsorbent is then separated by the membrane separation processes.

In this section, fundamentals of membrane processes, problems and past studies on membrane are summarised. Detailed literature review is presented in Chapter 7.

2.4.1 Membrane Fundamentals

2.4.1.1 Membrane Definition

A membrane can be defined as a material through which one type of substance can pass more readily than others, thus presenting the basis of a separation process (Stephenson et al., 2000). The membrane thus can be used as a barrier to separate pollutants from water or wastewater. The membrane rejects the pollutants and allows the water to pass through it. The schematic of the membrane process is shown in Figure 2.13.

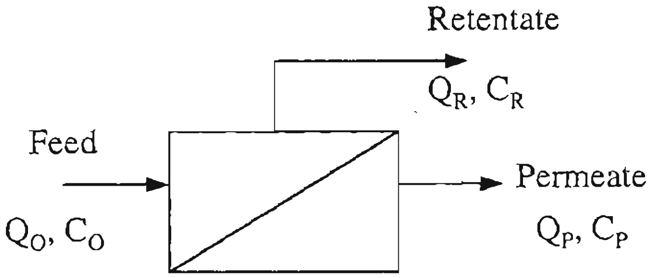


Figure 2.13 Schematic of the membrane process
(Q = flow m3/s, C = concentration of the pollutants to be removed, mg/L, subscripts O, P, and R refer to influent, permeate and retentate respectively)

2.4.1.2 Process Definition

The fundamental processes involved in the membrane separation systems are defined in this section. Additional information on membrane hybrid system is presented in Chapter 7.

2.4.1.2.1 Permeate Flux

The flux is the quantity of material passing through a unit area per unit time. Thus, the permeate flux of a membrane filtration system can be defined as the permeate volume flow per unit time per unit membrane surface area. It can also be referred to as the permeate velocity. It is the most critical parameter and is widely used in the characterization of the membranes.

2.4.1.2.2 Conversion or Recovery

The product of the flux and the membrane area is known as conversion or recovery of the membrane process. The conversion or recovery is defined as the percentage of the feed, which is recovered as permeate

$$\theta = \frac{Q_P}{Q} \times 100 \tag{2.14}$$

where, Q_p and Q are the permeate and feed flows respectively.

2.4.1.2.3 Rejection

Rejection of a membrane process is the percentage of pollutants rejected by the membrane.

$$R(\%) = \left(1 - \frac{C_P}{C}\right) \times 100 \tag{2.15}$$

where, C_p and C are the concentration of the pollutants in the permeate and the feed solutions respectively.

2.4.2 Membrane Separation Process

There are four major pressure-driven membrane processes: (i) microfiltration, (ii) ultrafiltration, (iii) nanofiltration, and (iv) reverse osmosis. The main difference between these four membrane processes is the size of the particles that the membrane rejects, which is determined partially by the pore size of the membrane. The particle size range of the membrane separation processes is presented in Table 2.5.

Table 2.5 Particle size range of membrane separation process (after Johns, 2000).

Membrane Process	Reverse Osmosis	Nanofiltration	Ultrafiltration	Microfiltration	Particle Filtration
Size (Microns)	0.0001	0.001	0.01	0.1	10
Molecular Weight Cutoff (Daltons)	<100	200	20,000	500,000	
Detection Method of pore size	Scanning Tunnelling Electron Microscope		Scanning Electron Microscope		Naked Eyes

2.4.2.1 Microfiltration (MF)

Microfiltration (MF) refers to membranes that have pore diameters from 0.1 to 10 microns (Cheryan, 1998). It is the membrane process with the largest pores. It can be used to filter suspended particulates, large colloids, bacteria, and organics. The MF is also used as a pretreatment for nanofiltration and reverse osmosis processes. Since the pore size of the MF is relatively large, air backflush or permeate backwash can be used to clean the deposits from the pores and surface of the membrane. Physical sieving is the major rejection mechanism in MF. The deposit or cake on the membrane also act as a self-rejecting layer, and thus MF can retain even smaller particles or solutes than it pore size.

The microfiltration system is discussed in detail in Chapter 7.

2.4.2.2 Ultrafiltration (UF)

Ultrafiltration (UF) refers to membranes that have pore diameters from 0.001 to 0.02 microns. UF is generally used for the separation of colloids up to a range of 0.001 to 0.1 microns. It enables the concentration, purification and fractionation of macromolecules such as proteins, dyes, and other polymeric materials. It is widely used in the industrial wastewater treatment where recycling of raw materials, products, and by-products are of primary concern. For example, it can be used to recover paints in the electrophoretic painting industries, and lignin and lignosulforates from black liquor in the pulp and paper industry. UF is also used as a pretreatment to Nanofiltration and Reverse Osmosis processes (Schafer, 2001).

2.4.2.3 Nanofiltration (NF)

The nanofiltration (NF) is a membrane process located between ultrafiltration (UF) and reverse osmosis (RO). Simpson et al. (1987) has defined NF as charged UF. Sometimes it is referred to as a low pressure RO. The NF can remove 60-80% of hardness, more than 90% of colour causing substance and almost all turbidity. The NF has the advantage of low operating pressure compared to RO, and has a high rejection of organics compared to UF. Both charge and size are important in NF rejection. At a neutral pH, most NF membranes are negatively charged. At lower pH, it is positively charged (Zhu and Elimelech., 1997). Physical sieving is the dominant rejection mechanism for the colloids and large molecules. However, for the ions and lower molecular weight organics, chemical interactions between the solutes and membrane can play an important role in rejection mechanisms.

2.4.2.4 Reverse Osmosis (RO)

Reverse osmosis was the first membrane process to be widely commercialized. Reverse osmosis is a reversal of the natural process of osmosis in which water from a dilute solution passes through a semipermeable membrane into a more concentrated solution due to osmotic pressure. In reverse osmosis, an external pressure greater than osmotic pressure is applied so that the water from concentrated solution passes into the diluted solution. Thus it can be used to separate salts and low molecular weight pollutants from water and wastewater (Vigneswaran et al, 1991).

Other membrane technologies include: (i) dialysis, (ii) electrodialysis, and (iii) pervaporation. These membrane processes are very specific in nature and hence are not discussed here.

2.4.3 Membrane Fouling

As the filtration through the membrane proceeds, the pore of the membrane is blocked by organic and inorganic substances reducing the effluent flux through the membrane. The blockage of the pore of the membrane is known as membrane fouling. Normally, membranes with larger pores exhibit a greater flux decline. It should be noted that the flux decline is not necessarily due to the membrane fouling only. Concentration polarization, or osmotic pressure or membrane compaction can appear as fouling. Therefore careful experimental study is necessary to distinguish membrane fouling from other effects. Membrane fouling is an important and a vast area in membrane research. In this review only related aspects to this study is presented in brief.

2.4.3.1 Organic Fouling

The membrane fouling due to organic substances depends on the characteristics of the organics. Membrane characteristics and operating conditions also affect membrane fouling. DiGiano et al. (1994) found that organics of molecular weight greater than 30 kDa (kilo Daltons) was responsible for NF fouling. They also observed a change in the fouling pattern after 20 h of operation of the membrane. This is possibly due to the interaction of hydrophilic and hydrophobic fractions of organics. Wiesner et al. (1992) identified that proteins, aminosugars, polysaccharides, and polyhydroxyaromatics were strong foulants. Kaiya et al. (1996) observed that the organic compounds with molecular weight larger than 100 kDa are major foulants in MF. Braghetta and DiGiano (1994) reported higher flux decline due to natural organic matter (NOM) at lower pH. Clark and Heneghan (1991) found hydrophobic membrane suffers more fouling than hydrophilic membrane. The organic fouling can occur due to adsorption, precipitation, and the interactions with cations. Therefore, depending on the characteristics of the organics, the membrane type and its operating condition need to be selected. Organic fouling is normally irreversible and needs careful chemical treatment.

2.4.3.2 Inorganic Fouling or Scaling

Inorganic solutes can cause fouling when precipitation occurs on the membrane due to hydrolysis and oxidation during filtration (Mallevialle et al., 1996). The precipitation occurs when salt rejected by the membrane passes the solubility limit in the boundary layer. The precipitation occurs mainly in NF and RO processes. The scaling is severe in RO due to higher rejection of ions which increases the osmotic pressure gradient across the membrane. Calcium, magnesium, carbonate, sulphate, silica, and iron are the main inorganic substances that cause scaling of the membrane (Potts et. al., 1981). The membrane scaling can be reduced by adding anti-scalants to the system or reducing the pH of the solution to lower value.

2.4.4 Membrane Fouling Control Measures

Membrane fouling can be controlled by altering the operating conditions (i.e. operating under critical flux and pressure), adding anti-foulant chemicals (especially for membrane scaling) and by pretreatment. A brief summary on the pretreatment is presented in this section.

2.4.4.1 Pretreatment for Fouling Prevention

Gusses et al. (1997) reported that the conventional treatment processes could not provide sufficient pretreatment to the membrane process. Thus a combination of biological and physico-chemical processes such as coagulation-flocculation, sedimentation, conventional filtration, and adsorption processes is necessary to control the membrane fouling. In coagulation-flocculation process, ferric chloride, alum or polyelectrolyte is normally used as coagulant. These chemicals form flocs with organics, which are removed, in sedimentation and/or in conventional filtration process. Ben Aim et al. (1988) investigated in-line flocculation with crossflow microfiltration (CFMF). They used poly aluminium chloride (WAC) and alum as flocculant to the bentonite and kaolin clay suspensions respectively, and found that optimum dose of flocculant and cross-flow velocity was essential for optimum performance of the in-line flocculation-microfiltration system. Wiesner et al. (1989) used polyaluminium chloride coagulation prior to MF. They observed that formation of larger particles prior to MF reduced penetration into pore and the organic rejection was more than 95%. A detailed experimental study conducted with sewage indicated that the flocculation with alum helped to increase the permeate flux by almost 100 % (Vigneswaran and Chen, 1988). Ravindran and Badriyha (1993) used alum coagulation with MF and observed that the coagulation increased both flux and organic rejection. Tang et al. (1994) found the coagulation with MF process very effective in removing organic from secondary treated effluent. Activated carbon adsorption is being emerged as a promising and cost-effective pretreatment method to the membrane processes. Activated carbon adsorption as a pretreatment to the membrane processes is discussed in the next section (Section 2.11) of the Chapter. Iron Oxide adsorption has also been used as pretreatment to the membrane processes. Chang and Benjamin (1996) found that when iron oxide particles were added, the UF rejection of natural organics was increased from 10-20% to 50-85%.

2.4.4.2 Backwashing, Backflushing, and Operation Mode

Air backflush and/or permeate backwash can be used to remove the cake deposits from the MF and UF membrane surfaces. Nakatsuka and Ase (1995) reported that the backwash was more effective when the backwash pressure was more than double the operating pressure. Hagmeyer et al. (1996) optimized the backwash interval to 30 sec every 30 minutes of operation. It was observed by Van Duijn (1996) that a short backwash with high pressure gave better cleaning than long backwash with low pressure. Similarly, more the frequency of backwash, higher was the production time of the membrane. The backflush (1 min every 30 min) and flux pulsation technique (1sec every 3 min) was found to effectively clean the membrane surface in waster and wastewater treatment application (Vigneswaran et al., 1991).

In submerged membrane filtration, air, which is supplied to agitate the membrane also helps to reduce the concentration polarization and thus the fouling rate.

2.4.4.3 Membrane Cleaning

Chemical cleaning is the last option. Pure water can be used to remove the loosely associated solutes from the membrane surface. For irreversible fouling, chemicals are required. The selection of chemicals depends on the type of foulant and the membrane characteristics. The fouling mechanism need to be understood to optimize the cleaning procedure. Speth et al. (1996) found acid cleaning very effective in removing inorganic foulants. Alborzfar et al. (1998) used alkaline cleaning to remove NOM deposits, and both acidic and alkaline cleaning to remove inorganic deposits. One need to make sure beforehand that the cleaning chemicals will not damage the membrane surface.

The chemical cleaning procedure used in this study is described in Section 7.4.3.1, Chapter 7.

2.4.5 Past Studies on Adsorption-membrane Hybrid System

Most of the past studies on adsorption-membrane hybrid system have been conducted using activated carbon (Seo et al., 1996; Matsui et al., 2001a). The use of powdered activated carbon (PAC) to membrane filtration system, either microfiltration or ultrafiltration improves the permeate flux and removes significant level of organic substances (Vigneswaran et al., 1991; Seo et al., 1997; Snoeyink et al., 2000; Kim et al., 2001). In this process, the pollutants (particularly the dissolved organics) are first adsorbed onto PAC and thus the direct loading of the pollutants to the membrane is greatly reduced. The use of PAC in the system not only increases the permeate flux (effluent filtration rate) through the membrane, it also prolongs the life of membrane application.

Activated carbon adsorption is very effective pretreatment to membrane processes. Laine et al. (1990) studied a hydrophobic and a hydrophilic UF membrane with coagulation and PAC-adsorption to remove organics from lake water. They achieved 30% rejection with coagulation, and 85% with PAC pretreatment. No removal was achieved when UF was used alone. Crozes et. al. (1993) reported reduction in fouling of a hydrophilic UF membrane after PAC pretreatment. PAC adsorbed the fraction of organics that were responsible for fouling. They further observed that the fouling remained severe in the hydrophobic membrane despite pretreatment. DiGiano et al. (1994) found that PAC only adsorbed the middle MW fractions of organics and fouling increased with PAC contact time, and hence the PAC slurry need to be agitated to reduce the PAC contact with membrane surface. Meier et al. (2002) studied the application of PAC with Nanofiltration in treating wastewater. The results from the semi-continuous pilot plant indicated that the use of PAC reduced the membrane fouling, increased the volume of the permeate flux, and the cake deposition on the membrane surface could be controlled by the simple air flushing and permeate backflushing arrangement.

Chapter 3

Adsorption Equilibria

3.1 Introduction

When an amount of adsorbent come into contact with a given volume of a solution containing an adsorbable solute (adsorbate), adsorption of adsorbate on the adsorbent occurs until equilibrium is reached. The state of equilibrium is characterized by an adsorbed solute concentration in the adsorbent and the resulting equilibrium solute concentration in the liquid phase. The amount of adsorbate adsorbed onto an adsorbent at equilibrium is a function of temperature and adsorbate concentration.

$$q = f(C,T) \tag{3.1}$$

where, q = amount adsorbed per unit mass of adsorbent

C = concentration of the adsorbate in the solution

T = temperature

When the adsorption equilibrium is reached at constant temperature,

$$q = f(C),\ T = \text{constant} \tag{3.2}$$

Equation (3.2) is most fundamental representation of an adsorption isotherm. The relationship between equilibrium adsorbate concentrations in suspension and adsorbent at constant temperature is called adsorption isotherm. Description of adsorption equilibrium by an appropriate isotherm equation is the first step in the design of an adsorption system as it reflects the capacity or affinity of an adsorbent for a particular adsorbate. The existing isotherm equations for single component (one solute, adsorbate only) and multicomponent (many solutes) system are discussed later in this chapter.

3.2 Adsorption Isotherm

According to the classification of Brunauer, Emmett and Teller (BET classification) (Brunauer et al., 1940), five types of isotherm curves (Figure 3.1) are possible when a physical adsorption takes place. Type I isotherm is characterized by a unimolecular adsorption onto microporous adsorbent such as activated carbon. Type II and III isotherms represent a wide range of pore sizes and are due to unrestricted monolayer to multiplayer adsorption, for example adsorption of nitrogen in silica gel. Type IV isotherm is resulted when adsorption occurs in two surface layers, and the type V isotherm is usually exhibited in the adsorption of water vapour on activated carbon (Tien, 1994).

Types I and III are referred to as favourable isotherm and unfavourable isotherm respectively while types II, IV, and V are mixed type of isotherms. In case of multicomponent adsorption system, usually one experiences a mixed type of isotherm curve.

Some of the commonly used isotherms for single component adsorption system are summarized in Table 3.1. The Langmuir equation (Langmuir, 1918) is the simplest isotherm, and it can describe most of the single component isotherms satisfactorily. However, it is based on the assumptions that (i) the adsorption is confined to a monolayer, (ii) the adsorbent surface is homogenous, (iii) there is no lateral interaction between adsorbate molecules, and (iv) the adsorbate molecules, once adsorbed, remain attached on the adsorbent surface. Due to these assumptions, the Langmuir isotherm is not capable of describing the isotherm resulting from a heterogeneous system.

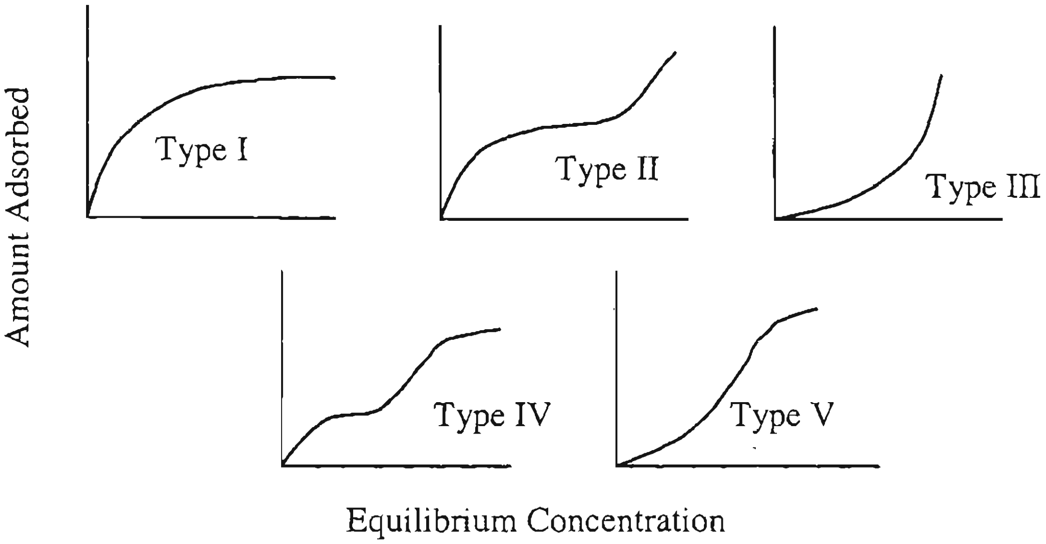


Figure 3.1 Types of pure component gas adsorption isotherms in the classification of Brunauer, Emmett and Teller (BET classification, Brunauer et al., 1940).

Table 3.1. Isotherms for single component adsorption system

Type	Equation	Parameters	Characteristics
Langmuir	$q = \frac{aC}{1+bC}$	a , b	Homogeneous monolayer
Freundlich	$q = K_F C^{\frac{1}{n}}$	K_F, n	Heterogeneous not reduce to Henry's law
Redlich and Peterson	$q = \frac{a'C}{1+b'C^m}$	a′, b′, m	Combined Langmuir and Freundlich
Langmuir – Freundlich (Sips)	$q = \frac{q_m C^{\frac{1}{n}}}{1+K_S C^{\frac{1}{n}}}$	q_m, K_S, n	Hybrid Langmuir and Freundlich
Generalized Toth	$q = \frac{a'(C/b')^m}{1+(C/b')^m-(C/b')^n}$	a′, b′ m, n	Heterogeneous multiplayer
Two – site Langmuir model	$q = \frac{a_1'C}{1+b_1'C} + \frac{a_2'C}{1+b_2'C}$ $q = \frac{a_1'C}{1+b_1'C}\left(1+\frac{a_2'C}{1+b_2'C}\right)$	a'_1, b'_1 a'_2, b'_2	Independent two-site Superimposed two site
Statistical model	$q = \frac{kC+(kC)^2\Gamma}{1+kC+(kC)^2\Gamma/2}$	k, Γ	Two adsorbate molecules

Where C is the bulk phase concentration (mg/L), q the adsorbed phase concentration (mg/g), and all other parameters are the respective isotherm constants.

The Freundlich isotherm has been widely used as an empirical equation for qualitative purposes in both single component and multicomponent adsorption systems. The Freundlich isotherm is based on the assumption that there is no association or dissociation of the molecules after they are adsorbed on the surface and chemisorption is completely absent (Freundlich, 1926). As can be seen from the Freundlich equation, the adsorbed amount increases infinitely with the increase in concentration, which is unrealistic and therefore, the Freundlich isotherm is not very successful in describing the isotherm results over a wide range of concentrations. Other isotherm equations shown in Table 3.1 are derived equations and they have limited use in practice.

In a multicomponent adsorption system, isotherm equation becomes very complex due to the interactions between several adsorbate components and competitive adsorption phenomena. Several isotherm models have been developed by the previous researchers to describe multicomponent systems of different characteristics. Some of the commonly used multicomponent isotherms are presented in Table 3.2. The extended-Langmuir (Markham and Benton, 1931) is the simplest isotherm for the multicomponent adsorption system, which is based on the assumption that there is no interaction between the adsorbing molecules. Out of these models, the IAST (Ideal Adsorbed Solution Theory) model developed by Myers and Prausnitz (1965) for gas mixtures is the most commonly used to describe the multicomponent adsorption system. It is based on the theory of adsorption thermodynamics, and since the extension of the theory to multicomponent liquid phase adsorption by Radke and Prausnitz (1972), most of the researchers have used this theory along with Freundlich isotherm to describe the multicomponent isotherm results (Crittenden et al., 1985b, Matsui et al., 1998). The IAST theory is based on the assumption that adsorption takes place at constant temperature and that the same adsorbent site is available for all adsorbates. Basically all these isotherm models are based on three main theoretical backgrounds namely (i) Langmuir theory, (ii) potential theory and (iii) adsorption thermodynamics.

Table 3.2. Isotherms for multicomponent adsorption system

Isotherm Model	Model Equation and Multispecies Extension	
Extended Langmuir	$q_i = \frac{a_i C_i}{1 + b_i C_i}$	$q_i = \frac{a_i C_i}{1 + \sum_{j=1}^{N} b_j C_j}$
Extended Langmuir-Freundlich	$q_i = \frac{a_i C^{1/n}}{1 + b_i C^{1/n}}$	$q_i = \frac{a_i C_i^{1/n_i}}{1 + \sum_{j=1}^{N} b_j C_j^{1/n_i}}$
Ideal Adsorbed Solution Theory (IAST)	$C_i = C_i^0 z_i$	$q_T = \left[\sum_{i=1}^{N} \frac{z_i}{q_i^0} \right]^{-1}$
	$q_i = q_T z_i$	
	$\pi = \left(\frac{RT}{A} \right) \int_0^{C_i^0} \frac{q_i^0}{C_i^0} dC_i^0$	$\sum_{i=1}^{N} z_i = 1$
	$\pi = \pi_1 = \pi_2 = \cdots = \pi_N$	at equilibrium

Where a_i, b_i and n_j are the isotherm constants of the respective models, z_i is the mole fraction of the i^{th} species in the adsorbed phase corresponding to adsorbate concentration C_i, q_i^0 is the equilibrium concentration with respect to C_i^0 in its single species state. Here the superscript ^{0} represents single species state and is the total adsorption amount, π the concentration spreading factor, and RT/A the gas constants.

3.3 Association Theory

The association theory was first proposed by Talu and Meunier (1996) for better understanding of water vapour adsorption on hydrophobic surfaces especially on activated carbon. The association theory basically, takes into account of three main characteristics of the adsorption system, chemical equilibria, equation of state (EOS) and phase equilibrium. Here, chemical equilibria and equation of state describe the behaviour of the surface phase, and the phase equilibrium links the surface phase properties to bulk phase properties. It has been assumed in this theory that: (i) primarily organic adsorption takes place on the active sites of the GAC surface, (ii) the dissolved organic molecules form clusters around these sites by association, and (iii) the adsorption site is limited by micropore volume irrespective of the shape and size of the micropores. It was further stipulated that at low organic concentration, the adsorption behaviour is solely controlled by molecule to surface and vertical interactions whereas at higher concentration, the adsorbate molecules are crowded to the limited adsorption volume/sites available and the plateau level (saturation capacity) is stabilized. The saturation capacity and the micropore volume were found to be highly correlated by Tsunoda (1990). The governing adsorption mechanism in the intermediate organic loading range is difficult to assess as it contains inflection point of the isotherm curve. Nevertheless, it was stipulated that the adsorbed organic molecules form large clusters by association through cooperative molecule-to-molecule lateral interaction. After combining the equation of chemical equilibria, EOS and phase equilibria, Talu and Meunier (1996) derived the following isotherm equations. The terms used in these equations here have been redefined to best describe the adsorption isotherm characteristics of the wastewater.

$$C_e = \frac{H\Psi \cdot \exp\left(\dfrac{\Psi}{q_m}\right)}{(1 + K\Psi)} \qquad (3.1)$$

$$\Psi = \left(\frac{-1 + (1 + 4K\zeta)^{0.5}}{2K} \right) \tag{3.2}$$

$$\zeta = \frac{q_m q}{q_m - q} = \Psi(1 + K\Psi) \tag{3.3}$$

where,

C_e = Equilibrium organic concentration, mg/L

H = Adsorption constant (Henry's Law constant)

K = Reaction constant

q_m= Saturation amount of organic adsorbed, mg/g

ψ = Organic concentration spreading parameter, and

q = measured amount organic adsorbed, mg/g

Thus, the isotherm expression contains only three parameters, H, K and q_m. Here, the adsorption constant, H, increases the value of equilibrium concentration. However, as can be seen from Equation 3.3, the shape of the isotherm curve is mainly determined by the saturation capacity of the adsorbent (q_m). The association theory is based on adsorption thermodynamics. The chemical equilibrium, phase equilibrium, and the state dynamics have been considered in the derivation of the isotherm equations.

In this study, the association theory was utilized to describe the isotherm equilibrium of the wastewater multicomponent system. The main reason of utilizing this theory was due to the unfavourable nature of the isotherm curves in a wide range of initial organic concentration of the wastewater. The theory is very simple and the parameters (C_e and q) required to describe the equilibrium state by the theory can be obtained from simple integral adsorption equilibrium test in the laboratory.

3.4 Characterization Theory

Surface water and wastewater contain a matrix of dissolved inorganic and organic substances of unknown characteristics. It is not practical to identify each of the constituents just for adsorption study. It is therefore, a common practice to use a surrogate parameter such as BOD, COD, TOC or DOC or UV-absorbance to characterize them together. These surrogate parameters are not specific representation of the dissolved inorganic or organic substances. The BOD represents only biodegradable substances whereas the TOC covers all organic substances but does not characterize the adsorption affinity of the various dissolved substances. In order to evaluate and predict the dynamics of an adsorption system correctly, the competitive interactions of all the dissolved substances should be considered. The characterization method is one of the most widely used techniques to describe the interactions among various dissolved substance on adsorption.

Kage (1980) suggested that adsorptive characteristics of a solution containing a large number of adsorbates could be described by the concentration density function (CDF) as a continuous spectrum with the following assumptions: (i) the extended Langmuir equation can describe the adsorption equilibria of the multicomponent system, (ii) Langmuir coefficients can describe the adsorptive characteristics, and (iii) the number of components (adsorbates) in the solution is infinite.

$$c_T = \int_0^\infty \int_0^\infty \bar{c}(q_{\max}, b)\, dq_{\max}\, db \qquad (3.4)$$

where c_T = total adsorbate concentration in the solution

$\bar{c}$ = concentration density function of the solution phase

q_{max} = maximum adsorption = ratio of Langmuir constants (a/b)

Kage (1980) used incremental batch adsorption data to determine CDF and validated it by applying integral batch adsorption data. However, in this CDF method, a number of coefficients need to be determined to define the concentration density function (CDF) of the solutions.

Based on a number of experimental observations, Frick and Sontheimer (1983) demonstrated that the relative adsorption affinity of the various adsorbates in a multicomponent aqueous system could be quantified from the integral batch adsorption data. They proposed the following methods to characterize the multicomponent solution: (i) the total adsorbable substances can be classified into three groups of non-adsorbable, weakly adsorbable, and strongly adsorbable substances, (ii) the single species isotherms of the weakly adsorbable and strongly adsorbable species obey the Freundlich equation, and (iii) the adsorption phenomenon in a multicomponent aqueous system can be described by a multicomponent adsorption theory such as ideal adsorption solution theory (IAST). Since the total surrogate parameter such as TOC or DOC can be measured experimentally, a multicomponent solution can be characterized by only six parameters, namely, the two initial concentrations and the two sets of Freundlich constants for weakly adsorbable and strongly adsorbable species. They further suggested to use search-optimisation technique to determine these six parameters by minimizing the objective function (*f*) defined as

$$f = \sum_{j} \left[\left(C_{T\infty} \right)^{j}_{\exp} - \left(C_{T\infty} \right)^{j}_{cal} \right]^{2} \qquad (3.5)$$

Jayaraj and Tien (1984, 1985) proposed a pseudospecies representation method to characterize a multisolutes solution with a finite number of pseudospecies. The method of representation of the pseudospecies was based on the principle of species grouping reported by Calligaris and Tien (1982). In this species grouping principle, they proposed to combine the various adsorbates into an A-n network grid point. The A-n network was used to represent a solution with multiple solutes. By this concept, a large number of adsorbates can be approximated by a few numbers of pseudospecies, and the solution can then be characterized by assigning concentration values to the pseudospecies. They also assumed that all the pseudospecies obey Freundlich equation and that the adsorption equilibria can be described by ideal adsorption solution theory (IAST). The advantage of this method over the method proposed by Frick and Sontheimer (1983) is that, it requires less number of unknowns to be determined, and the accuracy of the representation can be increased by increasing the number of pseudospecies.

Moon et al. (1990) used binomial distribution function (instead of species grouping method) to characterize a multisolutes solution. In this development, they assumed that a simple discrete distribution function could be used to represent the pseudospecies concentration with the same Freundlich exponents. The initial concentration of each pseudospecies was assigned by a binomial function in terms of Freundlich constant, and the competitive adsorption between species was estimated by the conventional equilibrium theory, IAST. The characterization method as developed by Moon et al. (1991) has been used in this study and hence it is discussed in detail. Since all the pseudospecies are assumed to obey the Freundlich equation with the same Freundlich exponent,

$$q_i^0 = k_i C_i^{0^{\frac{1}{n}}} \tag{3.6}$$

The multicomponent equilibria of species are described by the following IAST equations,

$$C_i = C_i^0 z_i \tag{3.7}$$

$$C_T = \sum_{i=1}^{N} C_i^0 z_i \tag{3.8}$$

$$q_i = q_T z_i \qquad (3.9)$$

$$q_T = \left[\sum_{i=1}^{N} \frac{z_i}{q_i^0} \right]^{-1} \qquad (3.10)$$

$$\pi = \frac{RT}{A} \int_0^{C_i^0} \frac{q_i^0}{C_i^0} dC_i^0 = \frac{RT}{A} n k_i C_i^{0\frac{1}{n}} \qquad (3.11)$$

$$\sum_{i=1}^{N} z_i = 1 \qquad (3.12)$$

$$\pi = \pi_i = \pi_2 = \cdots\cdots = \pi_N \text{ at equilibrium} \qquad (3.13)$$

Here, the superscript ^{0} represents single solute/species state and is the total adsorption amount in the mixture, z_i is the mole fraction of the i^{th} species in the adsorbed phase corresponding to the liquid phase concentration of the i^{th} species in the mixture (C_i). Equation 3.7 is analogous to Raoult's law where C_i^0 is the single solute liquid phase concentration in equilibrium with adsorbed phase concentration (q_i^0) in single solute state. Equations 3.8 and 3.9 define the total liquid phase concentration (C_T) and adsorbed phase concentration of the mixture. Equation 3.10 is the expression for no area change per mole from the single solute isotherms at the spreading pressure/concentration when the solutes are mixed together, and Equation 3.11 equates the spreading concentrations of the pure components to the spreading concentration of the mixture.

The spreading pressure or spreading concentration (π) can be determined by Newton's method and only the Freundlich coefficient can be used to identify the adsorption affinity of the pseudospecies for convenience. The Freundlich exponential constant can be obtained by an search-search procedure. Using the binomial distribution function, the organic fraction of the j^{th} species can be represented by:

$$x_j = \sum_{j=1}^{N} s^j (1-s)^{N-j} \quad , j = 0, 1, 2, \ldots, N \tag{3.14}$$

Here s is the binomial distribution skewness factor and each species, *j* is specified by a Freundlich coefficient, k_j.

$$k_j = k_s j^2 \tag{3.15}$$

where k_s is the scale factor.

In order to characterize a given solution, an appropriate object function, *F* is necessary to be optimised. The following objective function can be used for the characterization procedure.

$$F(\%) = \frac{100}{N} \sum_{m=1}^{N} \left[\left(\frac{C_{T\exp} - C_{Tcal}}{C_{T\exp}} \right) \right]_m \tag{3.16}$$

where,

N = number of data points

C_{Texp} = experimental liquid phase concentration

C_{Tcal} = calculated liquid phase concentration

In this study, the isotherm data were obtained for different initial organic concentration, and then the Nelder-Mead method (Riggs, 1988) was used to determine the characterization results of the wastewater solution by minimizing the object function.

3.5 Experimental Investigation

Isotherm experiments were conducted using 250 ml of synthetic wastewater and real wastewater solutions in flasks. The amount of GAC and PAC used for the study varied from 0.003 g to 3 g and 0.1 g to 1.7 g respectively. The flasks were kept shaking continuously for 7 days at 130 rpm at 25°C. Three different initial organic concentrations (of TOC) of the synthetic wastewater were used to evaluate the effect of initial organic concentration on isotherm parameters. Isotherm experiments of individual organic component and binary organic component system with and without inorganic substances of the synthetic wastewater were also carried out to evaluate the effect of inorganic and competitive organic substances in the multicomponent adsorption system.

Total organic carbon (TOC) was measured using the UV-persulphate TOC analyser (Dohrmann, Phoenix 8000). GAC used in the experiments was washed 3 times with distilled water and dried in the oven at 103.5° C for 24 hours. It was kept in a desiccator before using in the experiments.

The chemical composition of the synthetic wastewater used is shown in Table 3.3. The TOC contribution of glucose, peptone and yeast extract with inorganics are 79%, 11% and 10% respectively. This represents diluted domestic wastewater (TOC = 3.5 mg/L and COD = 30 mg/L) (Matsui, et al., 1998).

Biodegradation of the individual organic compound and the overall synthetic wastewater was studies in both static and dynamic conditions. In static condition, the synthetic solutions were allowed to degradate with time in a beaker whereas, in dynamic condition, the synthetic solutions were stirred at 100 rpm speed, and the TOC was measured at different time intervals. The biodegradation rate of the synthetic solutions was observed to be the same in both static and dynamic conditions.

Table 3.3 Constituents of the synthetic wastewater used

Compounds	Weight (mg/L)	Compounds	Weight (mg/L)
$MnSO_4$	0.125	KH_2PO_4	1.250
$CaCl_2$	0.925	$NH_2.NH_2.H_2SO_4$	3.500
$NaHCO_3$	0.875	Glucose	16.500
NaCl	2.500	Yeast Extract	1.750
$MgSO_4.7H_2O$	3.750	Peptone	1.750

Table 3.4 Physical properties of the GAC and PAC used in the study

Specification	Estimated Value	
	GAC	PAC
Iodine number, mg/g.min	800	900
Maximum Ash content	5 %	6 % max
Maximum Moisture content	5 %	5 % max
Bulk density, kg/m^3	748	290 – 390
BET surface area, m^2/g	1112	900
Nominal size, m	3×10^{-4}	80 % min finer than 75 μm
Average pore diameter, Å	26.14	25.3

3.6 Results and Discussion

Description of adsorption equilibrium by an appropriate isotherm is the most initial step in designing an adsorption system as it reflects the capacity or affinity of an adsorbent for a particular adsorbate. The results of the equilibrium adsorption studies of GAC with both the synthetic wastewater and the biologically treated sewage effluent are presented and discussed in this section. Biodegradation rate of the organics in the wastewater was also estimated and incorporated in the model simulation. The experimental results of the biodegradation study are presented in section 3.6.1 of this Chapter. The results of characterization of wastewater are also discussed in section

3.6.6 of the Chapter. The details of the adsorption study with PAC are discussed in Chapter 7, where adsorption-membrane hybrid system has been investigated.

Although peptone and yeast extract are complex compounds, they have been referred to as individual component (and not as single component) in this study.

3.6.1 Biodegradation of Organics

Biodegradation of organics in the synthetic wastewater or in the real wastewater needs to be analysed first for precise description or prediction of adsorption phenomenon in the wastewater system, which contains a matrix of organic and inorganic substances. It is necessary to differentiate the biodegradable and adsorbable portions of organics of the wastewater for modelling the adsorption phenomenon of organic compounds. Experiments were conducted to determine the biodegradation rate of the organic compounds in the synthetic wastewater and the biologically treated effluent from a sewage treatment plant. Biodegradation of organics in the biologically treated sewage effluent was not significant. It might be due to the fact that after biological treatment, the remaining biodegradable portion of organics was almost negligible. However, significant change of total organic carbon level was observed in the synthetic wastewater used in this study when the wastewater was allowed for biodegradation. Biodegradation of the organics used to prepare the synthetic wastewater was investigated to evaluate the net adsorption of the organics by GAC.

Biodegradation of individual organic such as glucose, peptone and yeast extract with and without the inorganics was not substantial for 24 hours (Figures 3.2 and 3.3, minor scattering in the experimental data may be due to the variation in the accuracy of TOC analyser). Biodegradation in the binary system of these organics (i.e. two of the organics were mixed together) in presence of the inorganics was also not significant (Figure 3.4). Slight rise and fall in the TOC values are due to the minor error in TOC measurement. However, the synthetic wastewater prepared by mixing these organics with and without inorganics had significant biodegradation after 10 hrs (Figure 3.5). It was further observed that biodegradation of the mixture of these organics was higher in the presence of inorganic compounds. It may be due to the abundant supply of nutrients from these inorganic substances.

Assuming a first order biodegradation reaction, the average biodegradable reaction rate of the synthetic wastewater was calculated to be 0.0178 h^{-1} and 0.0072 h^{-1} with and without inorganics respectively. The biodegradation of the organics was further investigated for different initial organic concentrations of the synthetic wastewater under dynamic condition using simple mechanical stirrer. The biodegradation rate was found to decrease with the increase in initial organic concentration of the solution.

Table 3.5. Biodegradation of the synthetic wastewater at different organic concentrations

Initial organic concentration (mg/L)	Biodegradation rate (h^{-1})
2.89	0.08
4.09	0.0164
8.20	0.015
11.35	0.0071
18.56	0.0063

The biodegradation of the organics in the synthetic wastewater was not affected by its static and dynamic mixing conditions. The small dose (1 mg/L) of silver sulphate ($AgSO_4$) retarded the biodegradation rate for few hours. However, the silver sulphate solution was not used to avoid the possible interference of the solution on adsorption process.

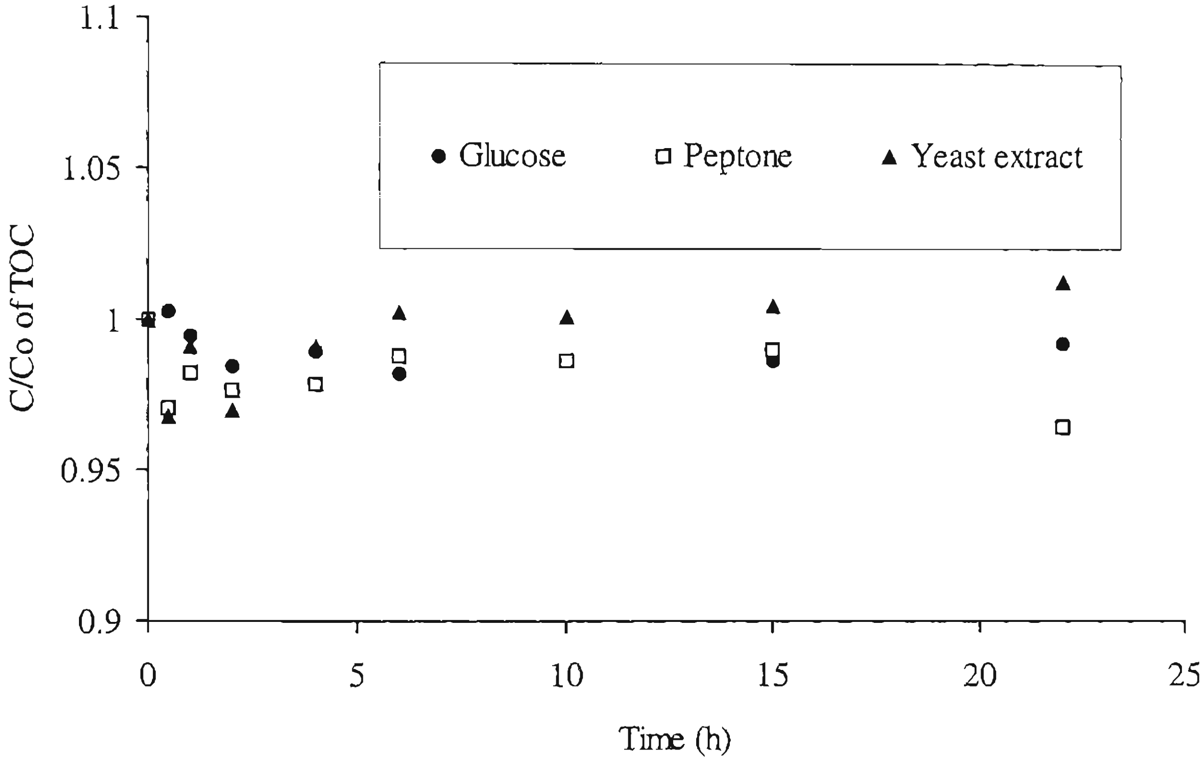


Figure 3.2. Biodegradation of the individual component without inorganics

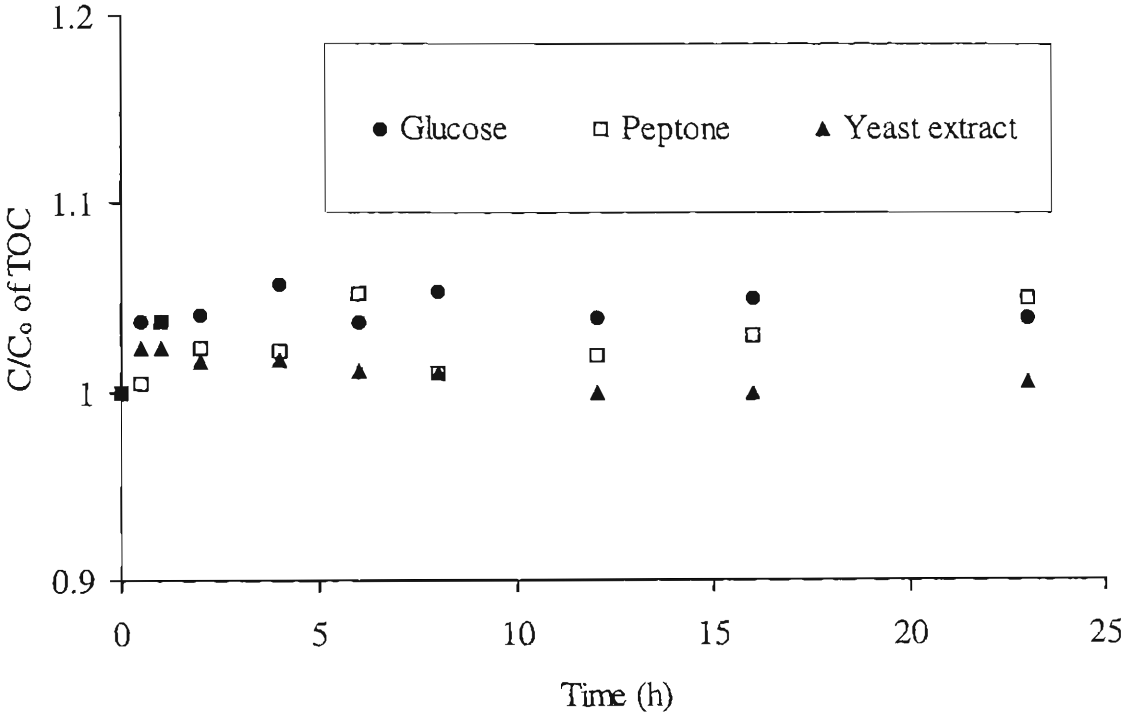


Figure 3.3. Biodegradation of the individual component with inorganics

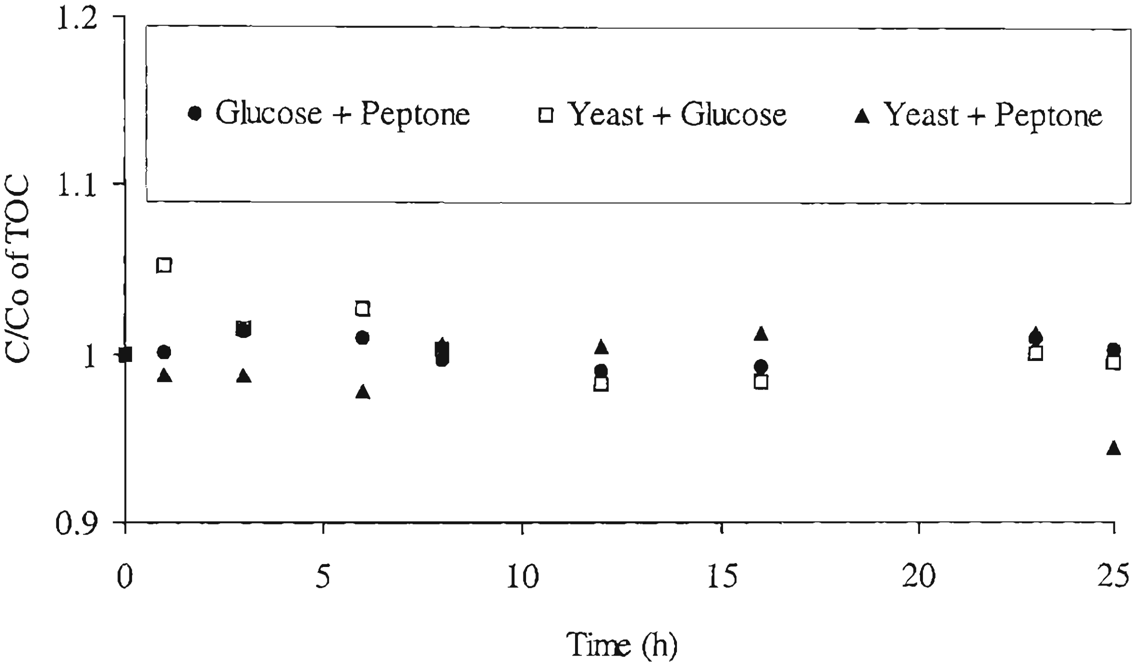


Figure 3.4. Biodegradation of the binary mixture of the organics with inorganics

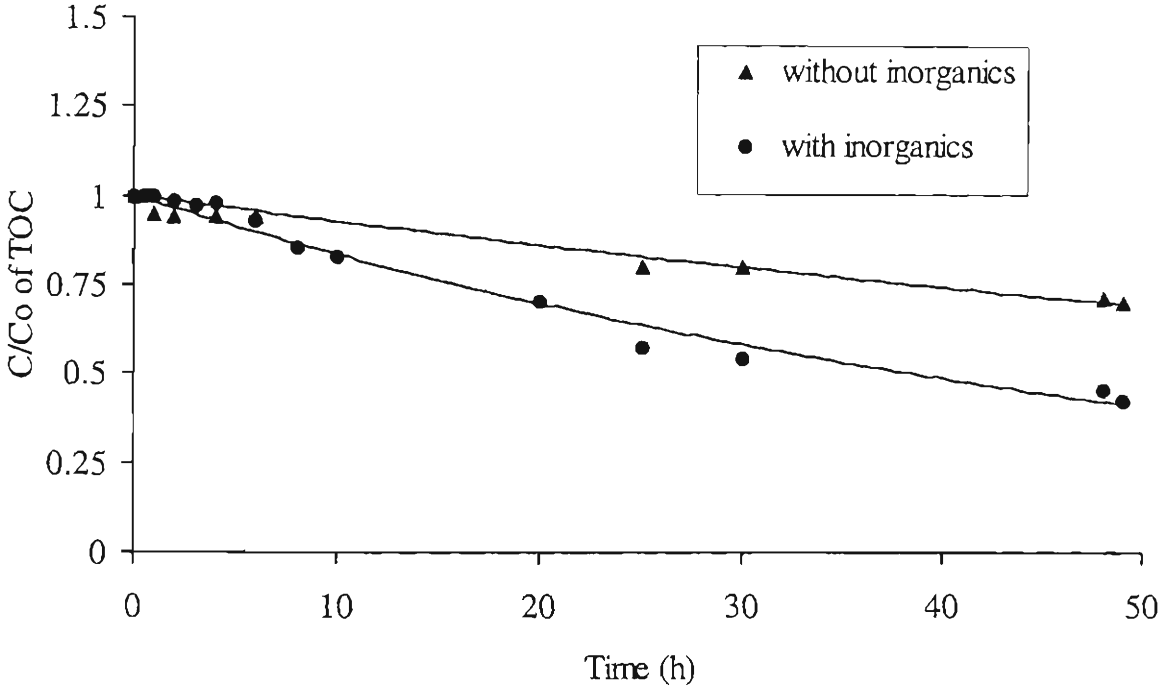


Figure 3.5. Biodegradation of the synthetic wastewater with and without inorganics

3.6.2 Effect of Inorganic Substances on the Overall Adsorption Isotherm

The equilibrium isotherm of a multicomponent adsorption system is influenced by many factors such as pH, temperature, organic or inorganic contents (Cooney, 1999). Inorganic compounds display a wide range of adsorbability (Randtke and Jepsen, 1982). Strongly dissociated inorganic compounds such as sodium chloride are essentially not adsorbed by activated carbon whereas nondissociating inorganic compounds such as iodine chloride are readily adsorbed onto activated carbon. Similarly, hydroxyl, amino and sulphonic substituent groups were found to decrease the adsorbability of the solution whereas nitro groups often enhanced adsorption activity (Cooney, 1999). Snoeyink et al. (1969) reported significant increase in adsorption of p-nitrophenol to activated carbon when NaCl was added at pH 10 (at which p-nitrophenol is fully ionised) but there was no effect at pH 2 (at which the p-nitrophenol is not ionised at all). Similarly, $CaCl_2$ was also found to improve the adsorption of sodium benzene sulphonate (Coughlin and Tan, 1968).

Since the synthetic wastewater contained seven inorganic and three organic compounds, it would be worthwhile to discuss the effect of inorganic compounds on the isotherm pattern of the multicomponent adsorption system. The effect of individual organic compounds on the isotherm is not discussed here as the adsorption of the multicomponent system is represented in this study by the total organic carbon (TOC).

The isotherm experimental results of the synthetic wastewater and the individual organic compound with presence and absence of inorganic substances revealed that the overall effect of the inorganic compounds used in the preparation of the synthetic wastewater had unfavourable effect on the adsorption of the organics (Figures 3.6 – 3.8). It is due to the fact that these inorganic substances are also adsorbed onto the GAC surface thus limiting the adsorption sites for the organics. Due to the presence of inorganic compounds, the isotherm curve was found to shift towards right increasing the value of equilibrium concentration. It clearly indicated that the presence of

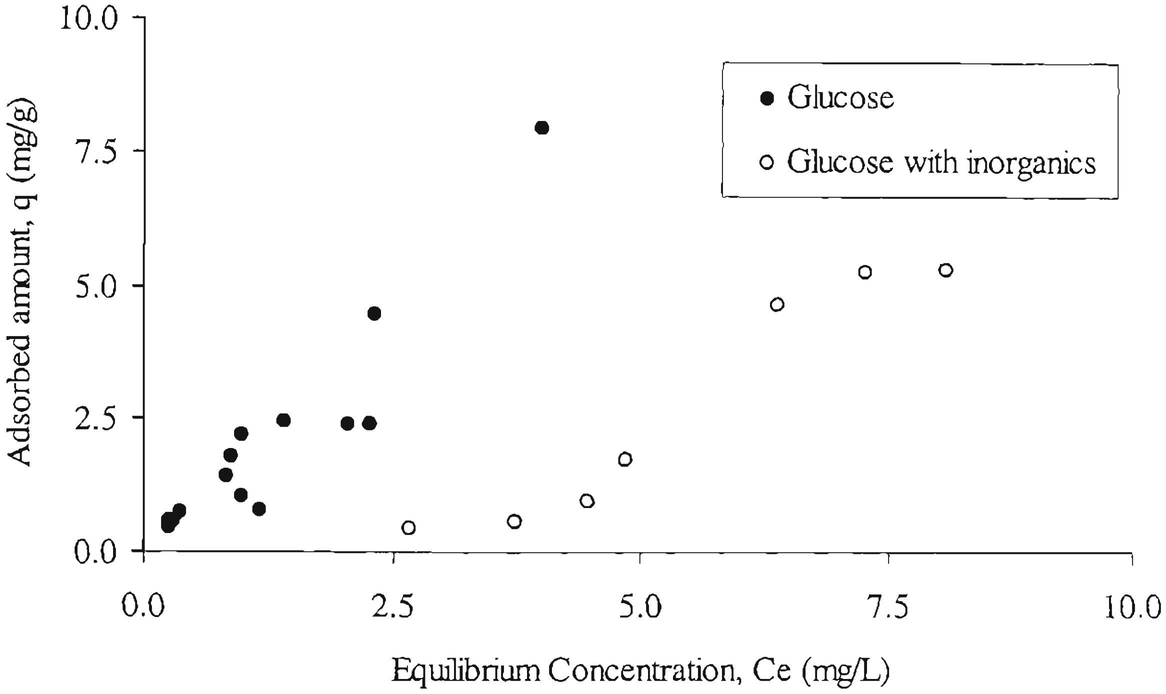


Figure 3.6. Equilibrium isotherm of glucose with and without inorganic compounds (contact time 7 days at 130 rpm shaking at lab temperature)

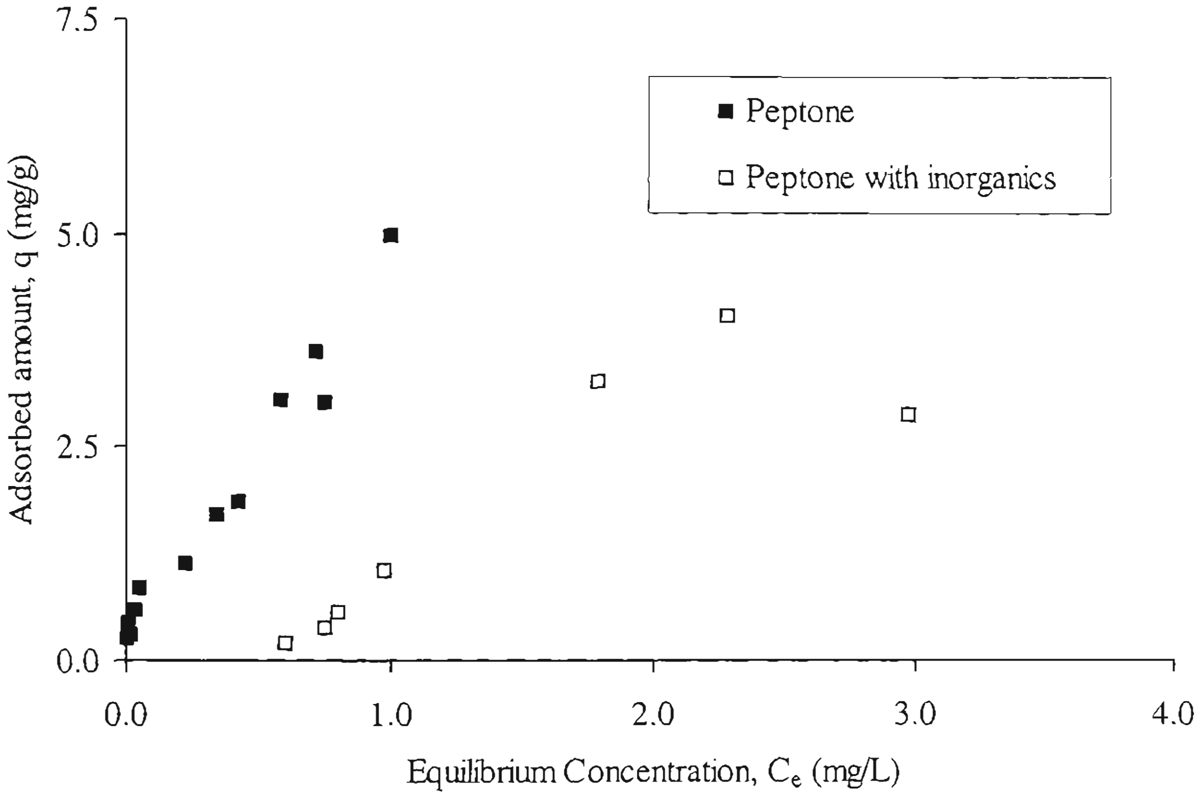


Figure 3.7. Equilibrium isotherm of peptone with and without inorganic compounds (contact time 7 days at 130 rpm shaking at lab temperature)

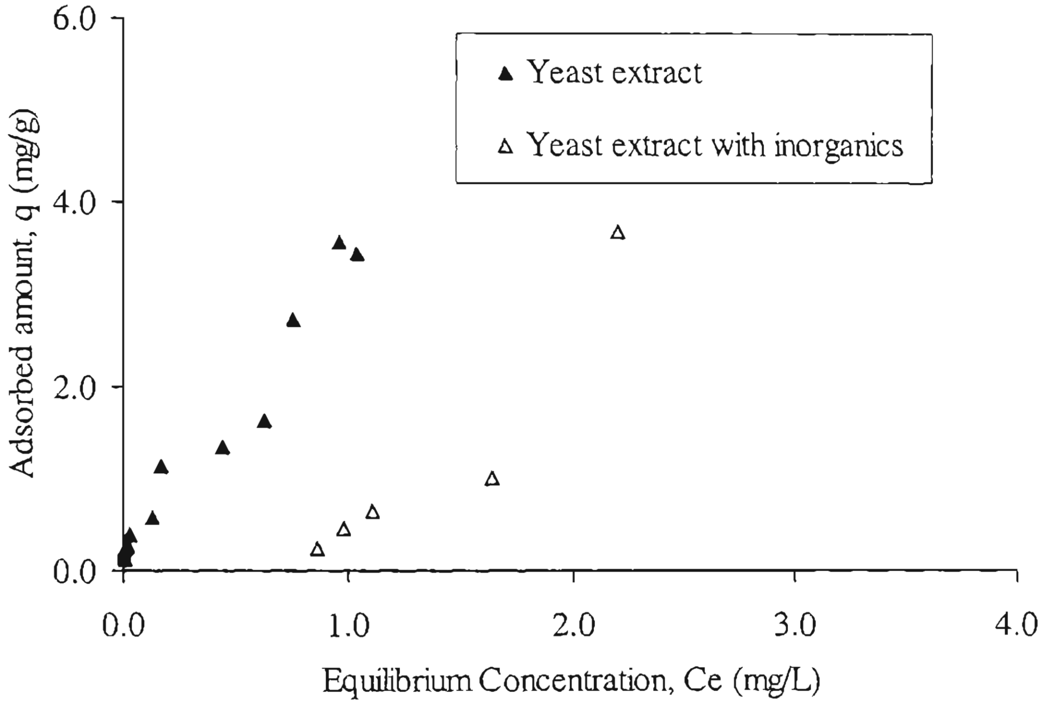


Figure 3.8. Equilibrium isotherm of yeast extract with and without inorganic compounds (contact time 7 days at 130 rpm shaking at lab temperature)

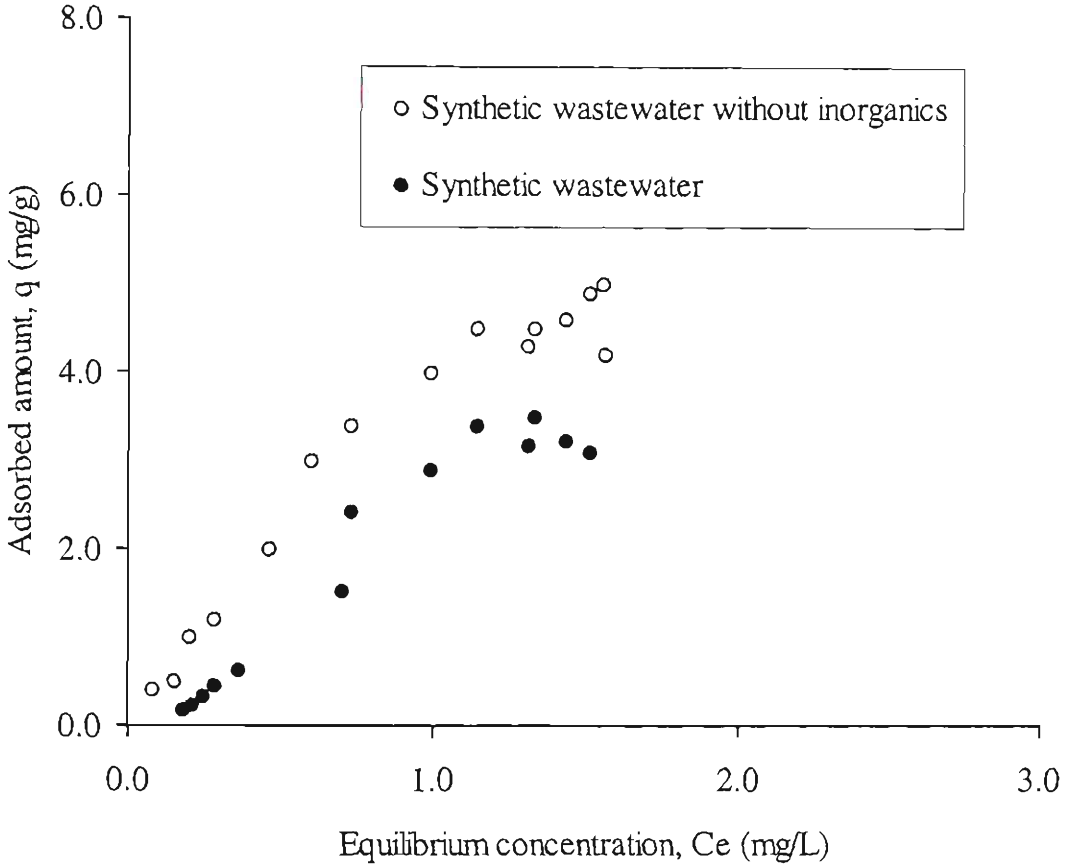


Figure 3.9. Overall adsorption isotherm with and without inorganic compounds (Average initial TOC concentration = 3.3 mg/L) (contact time 7 days at 130 rpm shaking at lab temperature)

inorganic compounds had unfavourable effect on the adsorption characteristics of the organics. It might be due to the fact that some of the inorganic compounds in the solution got adsorbed thus reducing the available adsorption site for organic compound. As a result, the equilibrium TOC concentration in the bulk phase was higher in case when inorganic substances were used in the solution.

3.6.3 Adsorption Equilibrium of Individual Organic Component

As mentioned earlier, the equilibrium isotherm of a multicomponent adsorption system is influenced by many factors such as pH, temperature, and organic or inorganic contents. The equilibrium experimental results of the individual organic compound with and without inorganic substances revealed that the overall effect of the seven inorganic compounds used in the preparation of the synthetic wastewater had unfavourable effect on the adsorption of the organics. The equilibrium adsorption results in this study are predicted using association theory, characterization theory and Freundlich isotherm.

The association theory and Freundlich model was found to predict the equilibrium adsorption results of the individual organic component efficiently whereas the characterization theory was unable to predict the isotherm results for individual organic component (Figures 3.10-3.12, minor scattering in the experimental data could be due to the variation in the accuracy of TOC analyser). The later was due to the fact that the solutions of the individual component did not contain sufficient pseudospecies to be characterized. However, when the individual component was mixed with the inorganic compounds, the characterization theory was found to be equally effective in describing the equilibrium adsorption results along with Freundlich and association theory (Figure 3.13-3.15). This conclusion can be drawn based on the visual observation on the Figures 3.10 – 3.15.

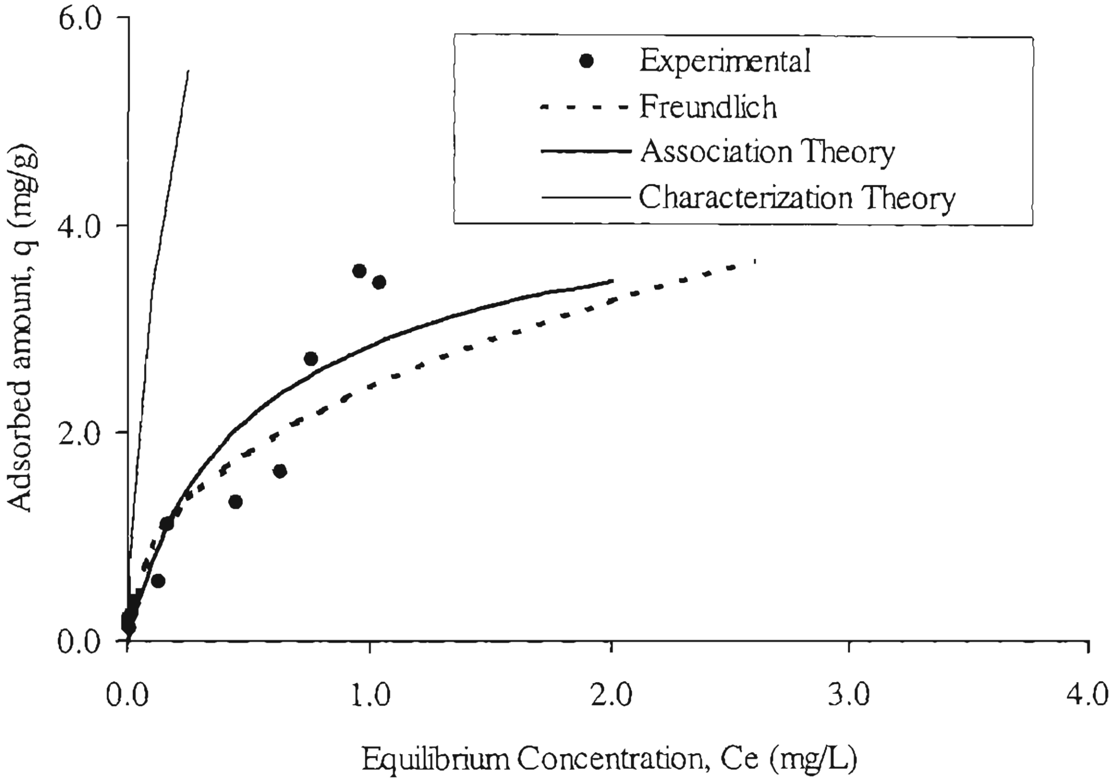


Figure 3.10. Equilibrium isotherm of yeast extract (contact time 7 days at 130 rpm shaking at lab temperature)

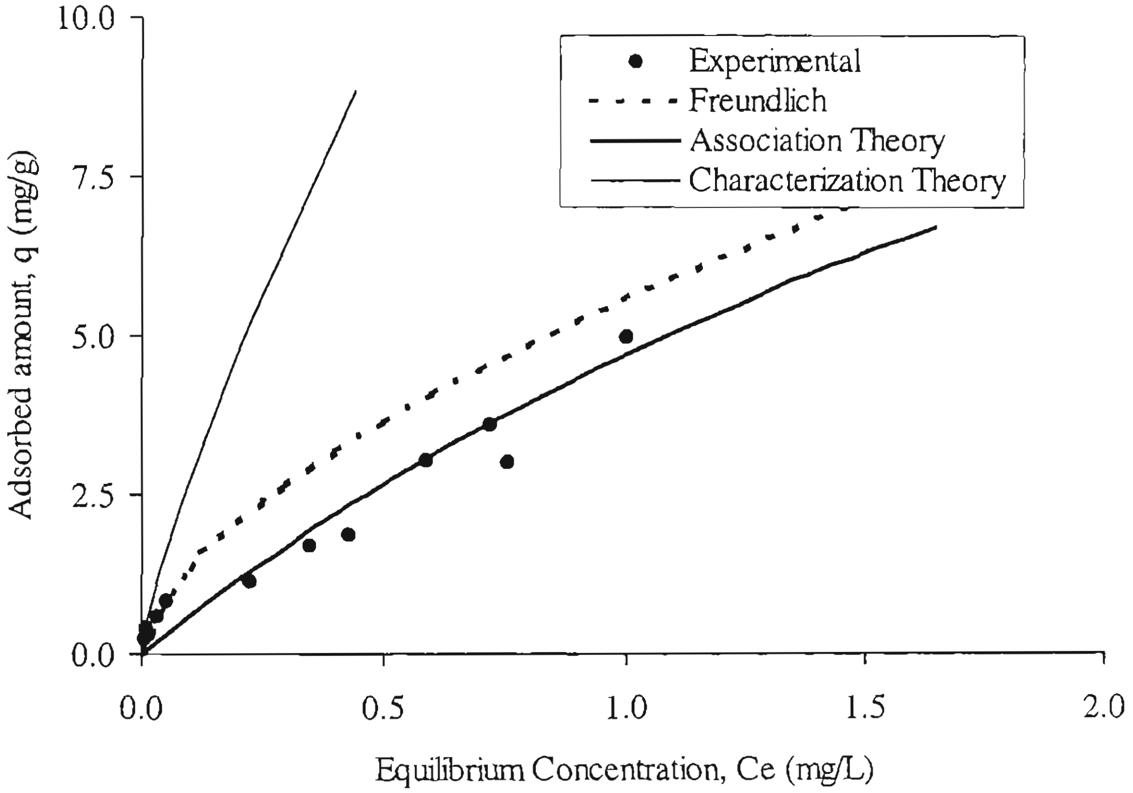


Figure 3.11. Equilibrium isotherm of peptone (contact time 7 days at 130 rpm shaking at lab temperature)

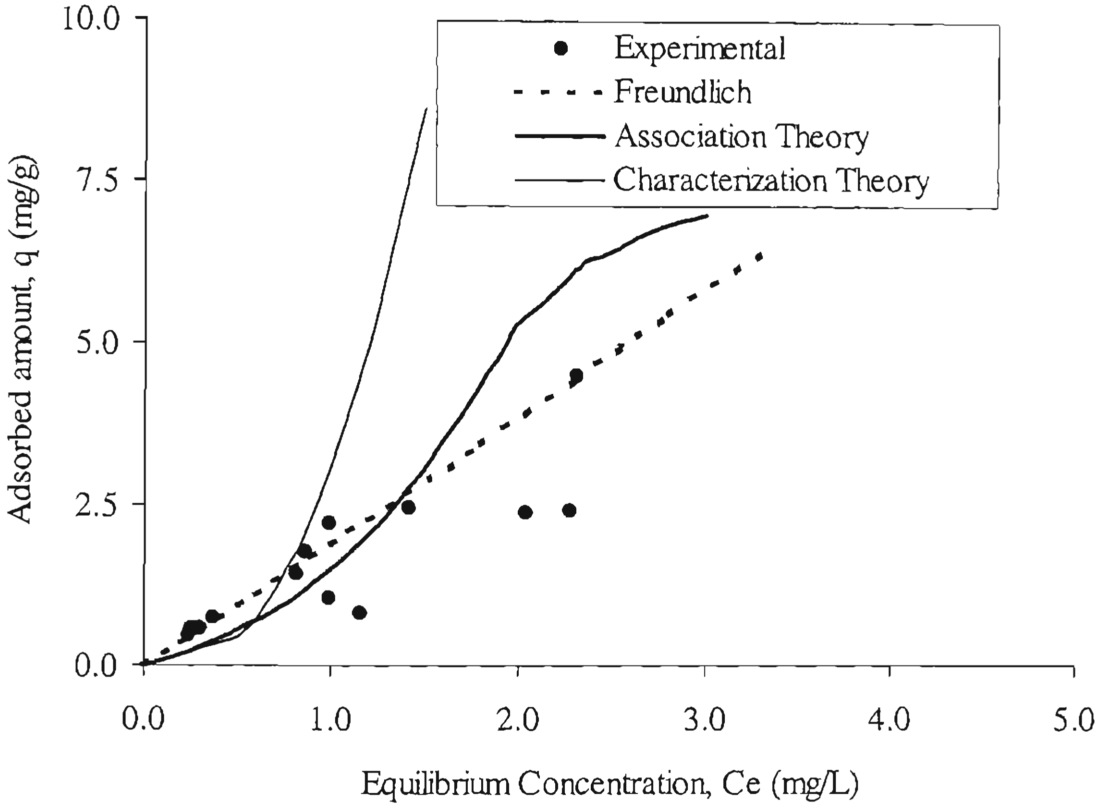


Figure 3.12. Equilibrium isotherm of glucose (contact time 7 days at 130 rpm shaking at lab temperature)

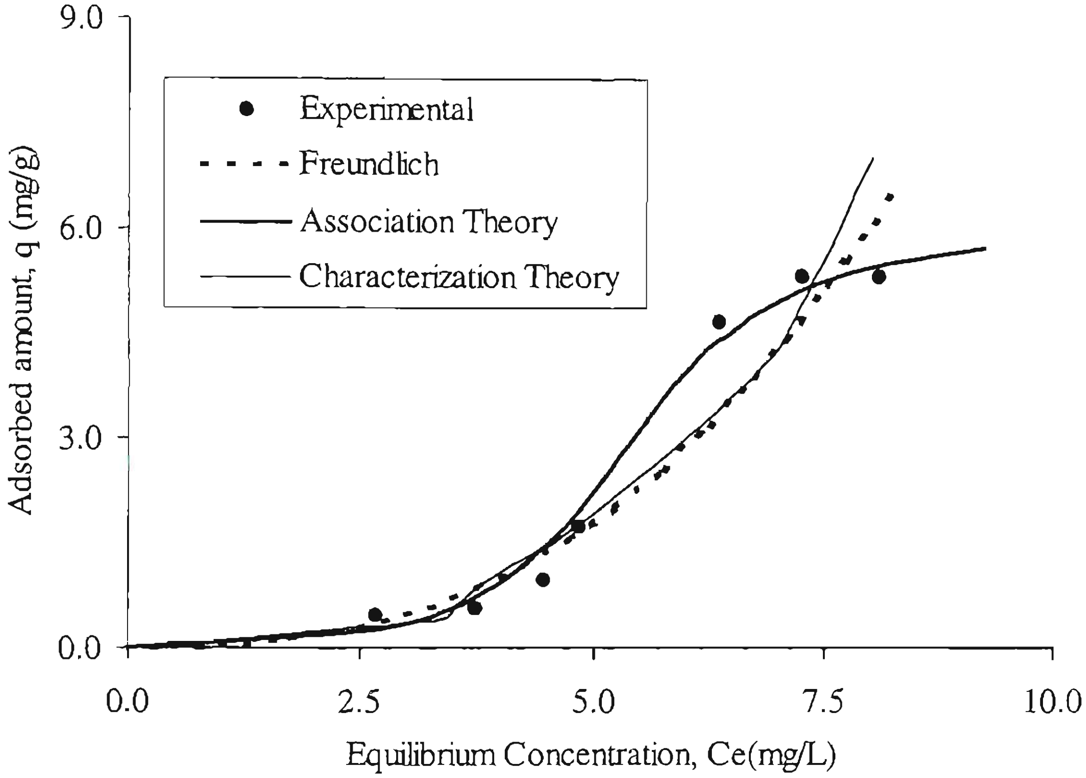


Figure 3.13. Equilibrium isotherm of glucose with inorganic compounds (contact time 7 days at 130 rpm shaking at lab temperature)

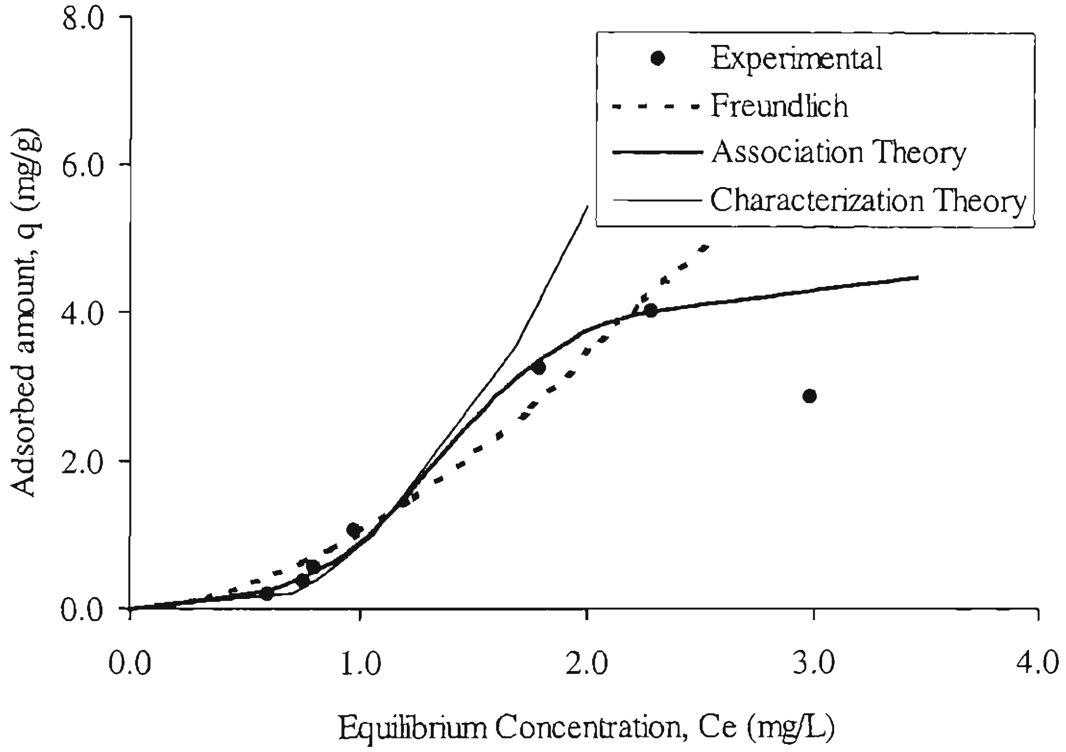


Figure 3.14. Equilibrium isotherm of peptone with inorganic compounds (contact time 7 days at 130 rpm shaking at lab temperature)

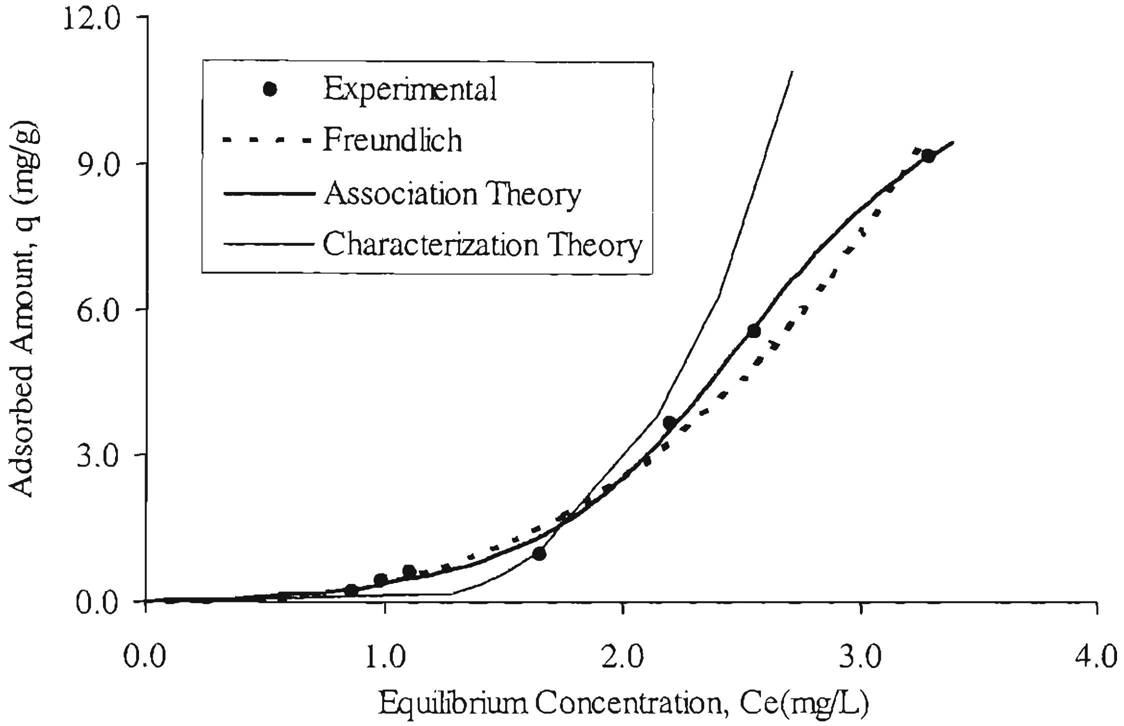


Figure 3.15. Equilibrium isotherm of yeast extract with inorganic compounds (contact time 7 days at 130 rpm shaking at lab temperature)

The isotherm parameters of the individual component with and without inorganic compounds of the synthetic wastewater are presented in Table 3.6.

Table 3.6. Isotherm results of individual component with and without inorganics

Individual component	Association theory			Characterization theory		Freundlich isotherm	
	q_m	K	H	n	S	k	1/n
Glucose	20.2	0.41	1.24	0.50	0.30	1.87	1.04
Peptone	33.6	0.003	0.16	2.00	0.53	5.59	0.61
Yeast extract	6.49	0.01	0.10	2.10	0.53	2.24	0.43
Glucose + inorganics	6.22	6.20	34.5	1.90	0.11	0.03	2.60
Peptone + inorganics	4.79	3.76	5.58	0.68	0.20	1.02	1.73
Yeast extract + inorganics	12.1	2.30	6.10	0.41	0.16	0.40	2.67

It is very difficult to express the effects of inorganics on the isotherm mathematically as the isotherm parameters of the individual component do not follow any fixed pattern. It may be due to the fact that in association theory, the isotherm parameters q_m, K and H are inter-related and have great influence on one another, whereas the isotherm parameters of characterization theory just show how closely the experimental equilibrium results can be predicted only. The parameters n and S used in characterization theory are Freundlich exponential constant and the skewness factor of the binomial distribution function (sections 3.4 and 3.6.6). These parameters do not show the actual adsorption capacity. The effect of inorganics on adsorption, however can be seen from the values of Freundlich isotherm parameter, k. The adsorption capacity coefficient, k decreased substantially when inorganics were added to the solution suggesting that the overall effect of the inorganics was unfavourable to the adsorption of these organic compounds (Table 3.6).

3.6.4 Overall Adsorption Equilibrium of the Synthetic Wastewater

As can be seen from Figures 3.16 – 3.18, the association theory as proposed by Talu and Meunier (1996) was found to fit better with the adsorption equilibrium results than most commonly used Freundlich isotherm. Yuasa et al. (1996) also found that the overall adsorption equilibrium of a multicomponent system could not be described well by Freundlich equation alone. Figure 3.19 shows the effect of initial organic concentration on the isotherm parameters. This study indicates that the isotherm parameters are highly dependent on the initial concentration of the organics in the wastewater. Thus, it is important to obtain isotherm parameters covering a wide range of initial organic concentrations for more precise evaluation of the adsorption equilibrium parameters. The dependency of isotherm parameters on initial adsorbate concentration has not been discussed by the previous researchers. Matsui et al. (1998) had indicated that the initial organic concentration could have significant effect on the isotherm curve. However, none of the earlier studies took into account (i) the biodegradation effect on the adsorption isotherm constants or (ii) the use of different isotherm parameters based on the initial organic concentration) during the prediction of batch and fixed bed experimental results. The isotherm parameters calculated for the synthetic wastewater system are presented in Table 3.7.

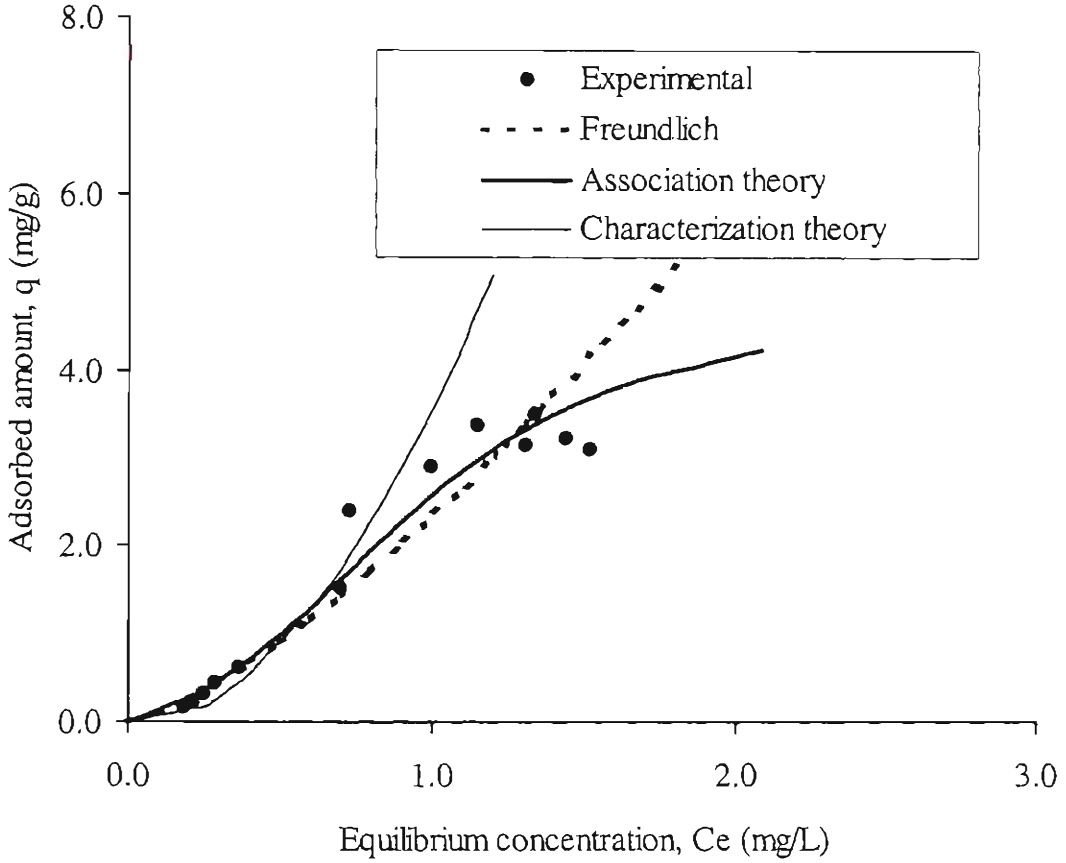


Figure 3.16. Overall adsorption isotherm at initial TOC concentration of 3.5 mg/L (contact time 7 days at 130 rpm shaking at lab temperature)

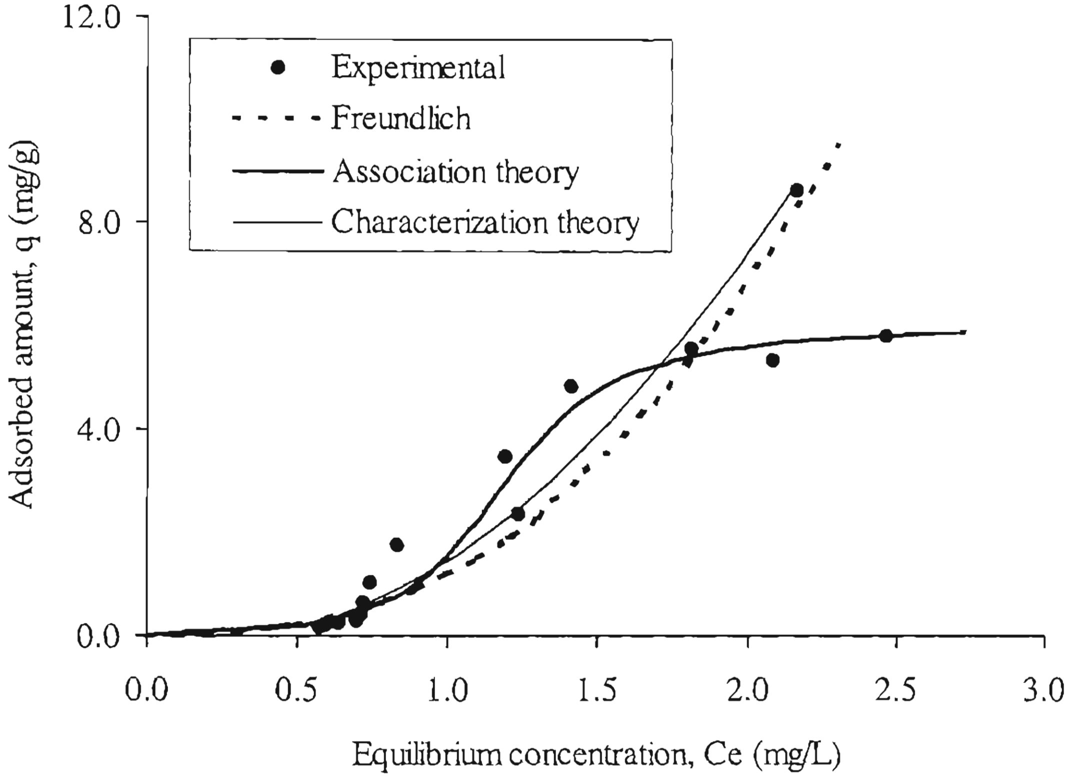


Figure 3.17. Overall adsorption isotherm at initial TOC concentration of 6.4 mg/L (contact time 7 days at 130 rpm shaking at lab temperature)

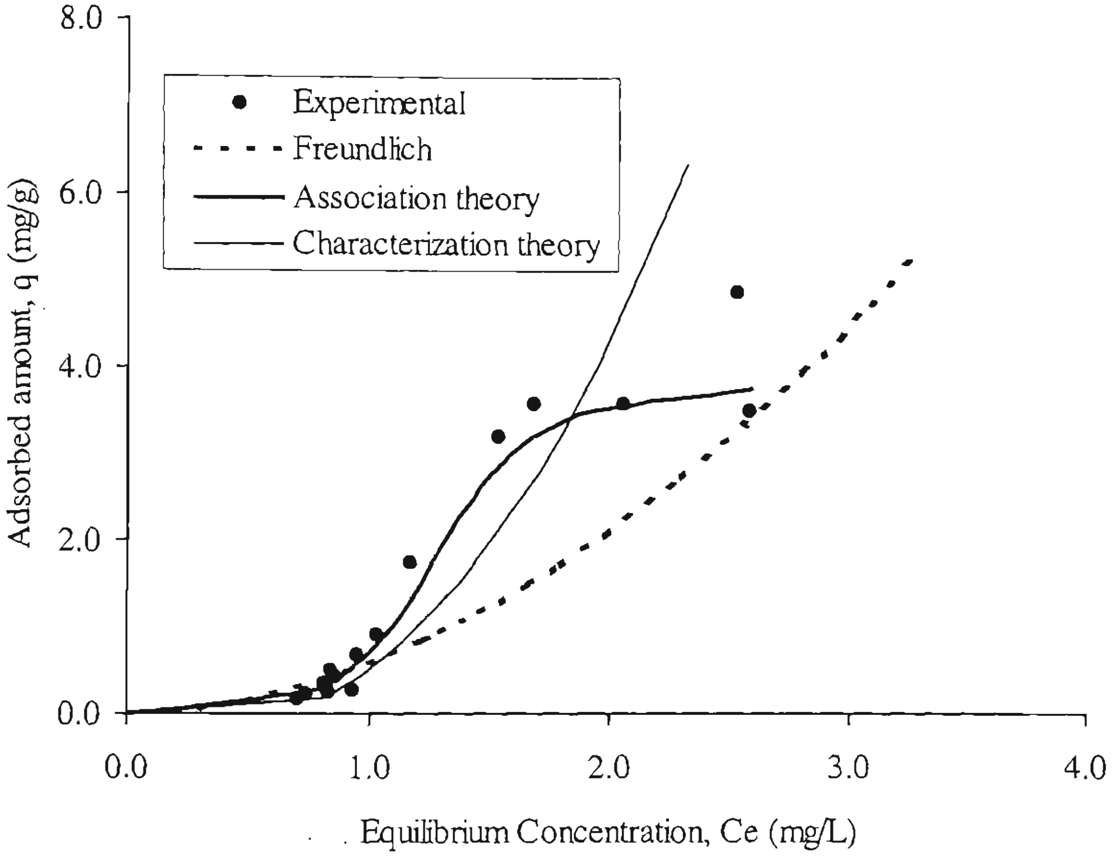


Figure 3.18. Overall adsorption isotherm at initial TOC concentration of 11.2 mg/L (contact time 7 days at 130 rpm shaking at lab temperature)

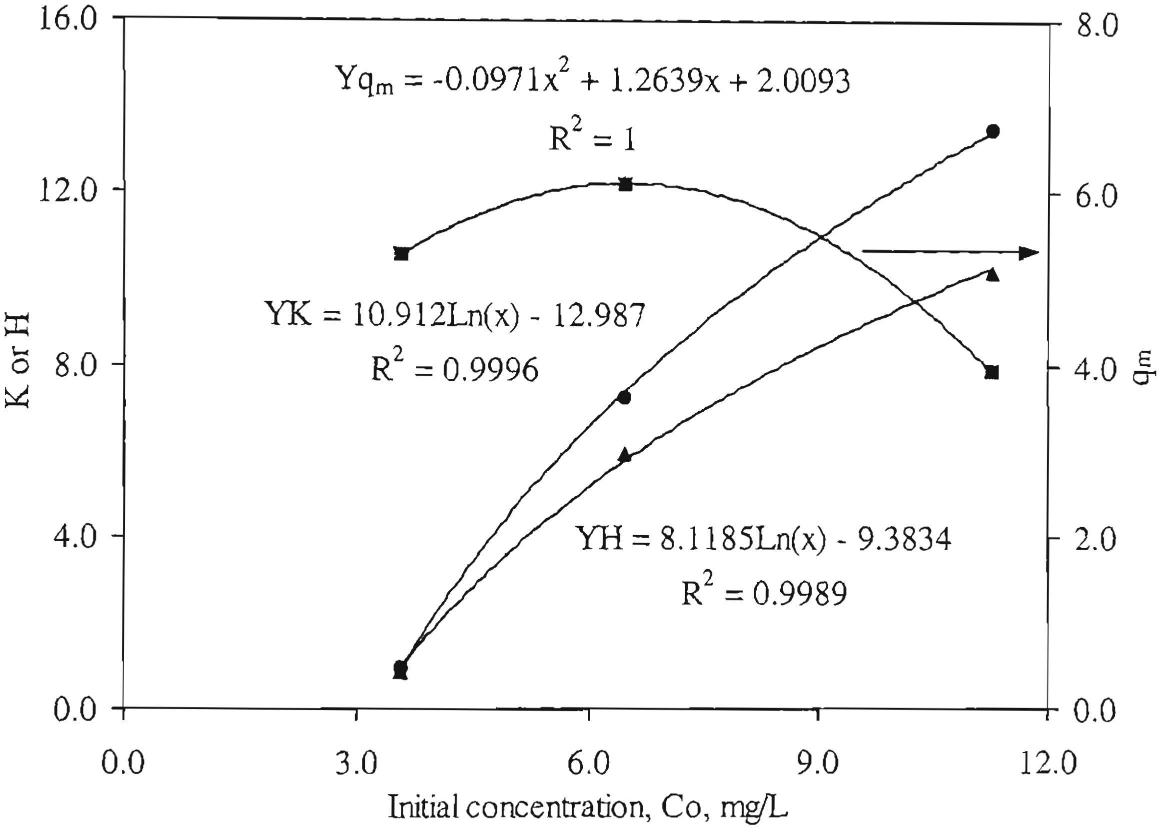


Figure 3.19. Effect of initial TOC concentration on isotherm parameters of the association theory

Table 3.7. Isotherm parameters of the synthetic wastewater

Initial TOC of Synthetic Wastewater	Association theory			Characterization theory		Freundlich isotherm	
(mg/L)	q_m	K	H	n	s	k	1/n
3.5	5.28	0.85	0.95	0.78	0.26	2.36	1.38
6.4	6.12	5.95	7.24	0.68	0.22	1.19	2.54
11.2	3.93	10.20	13.50	0.68	0.17	0.57	1.87

The number of pseudo-components assumed in the characterization theory was eight. The characterization results showed that four pseudospecies was the optimum number of pseudo-components in the case of the synthetic wastewater and eight in the case of biologically treated sewage effluent. The characterization of the wastewaters is discussed in Section 3.6.6.

3.6.5 Overall Adsorption Equilibrium of the Biologically Treated Sewage Effluent

The isotherm models were also tested for biologically treated sewage effluent (TOC = 3.7 mg/L, COD = 22 mg/L) (Figure 3.20). The results indicated that the association theory and characterization theory were both capable of describing the overall isotherm of the multicomponent organic system in the wastewater in an adequate manner. The isotherm parameters of the models are presented in Table 3.8. As mentioned earlier, assigning higher number of pseudospecies did not improve the object function of the characterization theory. Here, the optimum number of psedospecies was eight (Table 3.9).

Table 3.8. Isotherm parameters of the biologically treated sewage effluent

Initial TOC of the sewage effluent (mg/L)	Association theory			Characterization theory		Freundlich isotherm	
	q_m	K	H	N	s	k	1/n
3.7	6.68	1.55	0.95	0.68	0.42	7.13	0.58

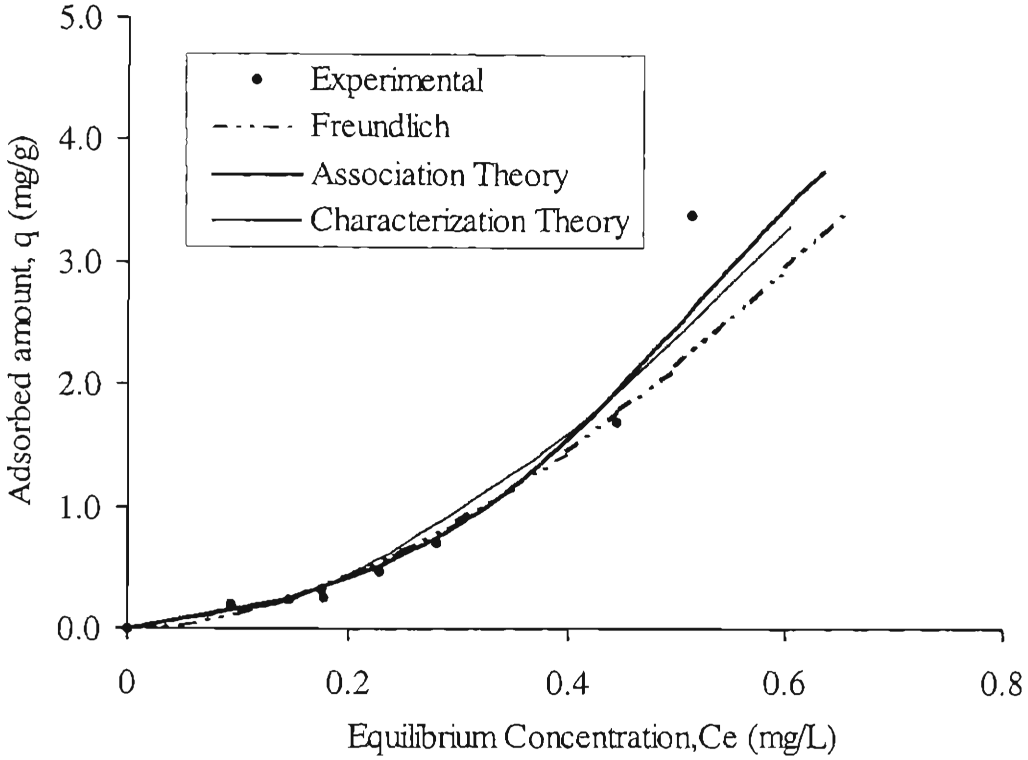


Figure 3.20. Overall adsorption isotherm of the biologically treated sewage effluent (initial TOC = 3.7 mg/L) (contact time 7 days at 130 rpm shaking at lab temperature)

3.6.6 Characterization of the Wastewater

The characterization of the wastewater was performed by two well-known methods namely, dilution method, and average method (Figure 3.21). In the dilution method, the concentration density function of higher concentration (TOC = 16.5 mg/L) was first determined, and the integral adsorption results with lower concentration were then predicted using these functional values. In the average method, the average values of the characterization results of the wastewater with all three concentrations (TOC = 16.5, 11.3 and 4.6 mg/L) were used to predict the experimental results. This shows that the characterization method is flexible and can be used efficiently to predict the isotherm results of wide range of initial organic concentration of a multicomponent system. The characterization results of the synthetic wastewater showed that number of pseudospecies assigned by k values hardly increases beyond four, whereas in case of biologically treated sewage effluent (TOC = 3.7 mg/L), the concentration distribution is log normal distribution with k value increasing to eight (Figure 3.22). Matsui et al. (1998) also obtained log normal distribution behaviour with peat water and biologically treated sewage effluent. As can be seen from Figure 3.22, a non-adsorbable species exists with about 40-50% fraction of TOC in the synthetic wastewater, while the non-adsorbable fraction is negligible in the biologically treated sewage effluent.

The characterization results of the synthetic and real wastewater with GAC are presented in Table 3.9.

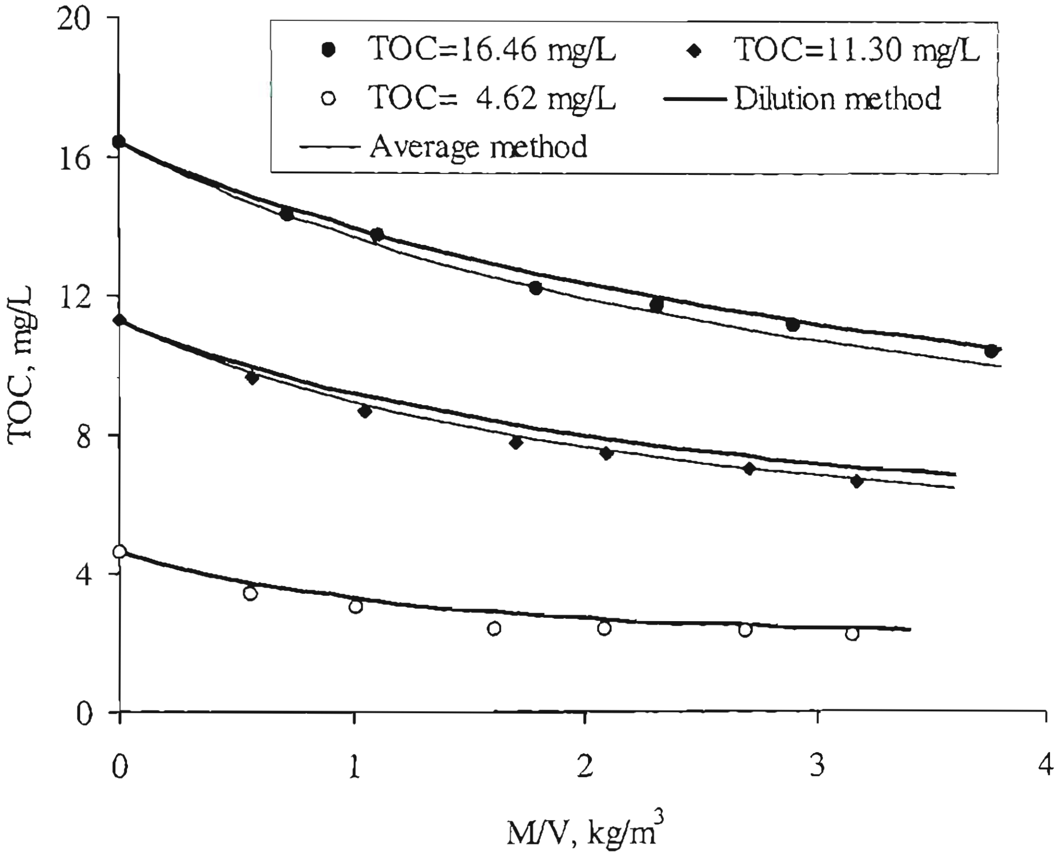


Figure 3.21. Prediction of integral adsorption equilibrium by characterization technique

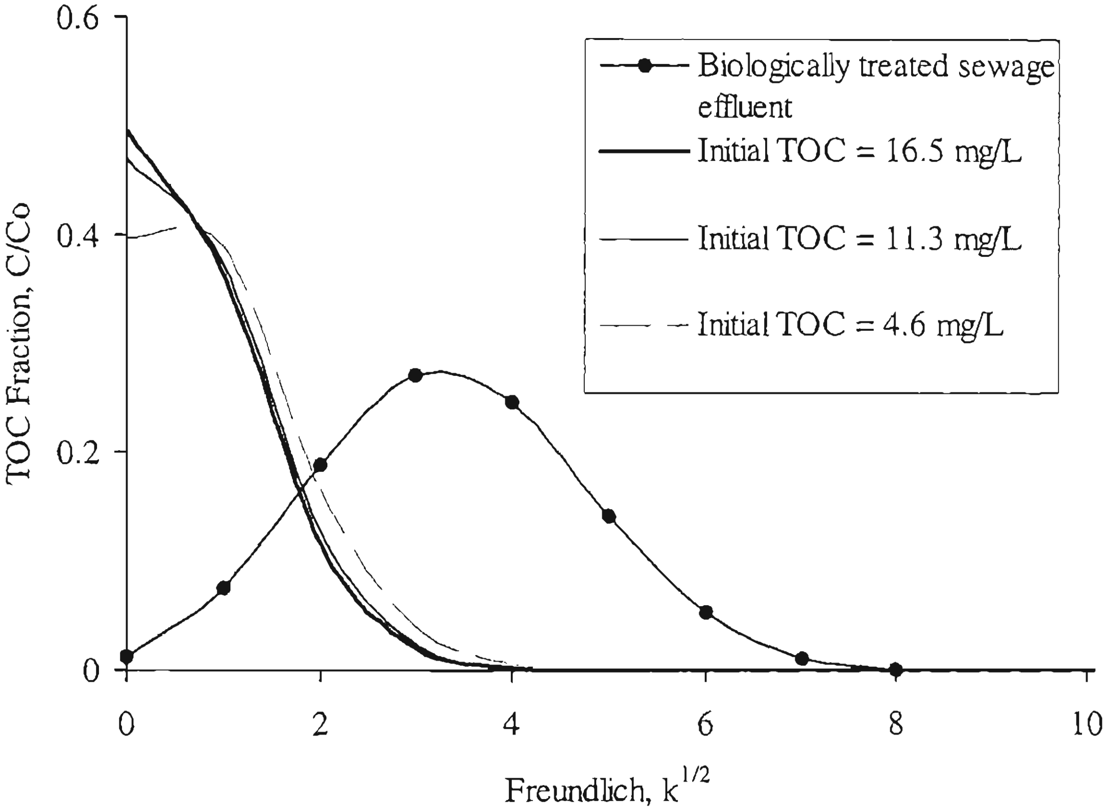


Figure 3.22 Concentration distribution fractions for the synthetic and the biologically treated sewage effluent

Table 3.9 Characterization results of the wastewater with GAC

k_s	N	n	S	F%	C_{TO} (mg/L)
1.0	6	2.0	0.15	3.70	4.6
	8	2.3	0.11	3.10	(Synthetic wastewater)
	10	2.0	0.09	3.26	
1.0	6	2.2	0.12	0.92	11.3
	8	2.3	0.09	0.86	(Synthetic wastewater)
	10	2.3	0.07	1.11	
1.0	6	2.2	0.10	1.23	16.5
	8	2.2	0.08	1.90	(Synthetic wastewater)
	10	2.2	0.06	1.34	
1.0	6	0.66	0.45	13.5	3.7
	8	0.68	0.42	13.1	(Biologically treated
	10	0.68	0.40	13.3	sewage effluent)

The isotherm parameters shown in Tables 3.2 and 3.3 were employed to predict the adsorption kinetics of organics of the multicomponent system in batch and fixed bed experiments in Chapters 4 and 5 respectively. The characterization results of the wastewater indicated that the number of active pseudospecies governing the adsorption phenomenon was four and eight in the synthetic wastewater and the biologically treated sewage effluent respectively.

The overall adsorption equilibrium results using PAC as adsorbent are discussed in Chapter 7.

3.7 Conclusions

The association and the characterization theories were found to describe the adsorption equilibrium results of the multicomponent organics in the wastewater more efficiently than the more commonly-used Freundlich isotherm. The adsorption equilibrium depended on the initial adsorbate concentration. Therefore, the isotherm parameters should be determined covering a wide range of initial adsorbate (organic) concentrations. In a multicomponent organics adsorption system, where biodegradation of the organics is also likely to occur, the biodegradable and adsorbable organic fractions should be differentiated while determining the adsorption equilibrium parameters. Background inorganic substances can influence the adsorption behaviour of organics present in wastewater. In this study, the overall effect of the inorganics present in the synthetic wastewater was unfavourable for the adsorption of organics. The characterization results indicated that the number of active and optimum components controlling the adsorption phenomenon was four and eight in the synthetic wastewater and the biologically treated sewage effluent respectively, and increasing the number of component beyond these numbers could not improve the object function minimization. The synthetic wastewater contained 40-50% non-adsorbable fractions of total organic carbon whereas the biologically treated sewage had negligible fraction of non-adsorbable organics.

Chapter 4

Adsorption Kinetics

4.1 Introduction

Adsorption kinetics is the measure of rate of adsorption, and it describes the adsorbate transport mechanism from bulk solution to the adsorption site on adsorbent surface. The study of batch adsorption kinetics is important in designing the adsorption system. It provides both equilibrium and kinetic data required for modelling an adsorption system. There are several steps involved in the uptake of adsorbate by an adsorbent particle. Basically, the adsorption mechanism can be described by three consecutive steps (Zogorski et al, 1976), namely, (i) adsorbate mass transfer from bulk liquid phase to the adsorbent surface piercing through the stagnant boundary layer surrounding the particle, succeeded by (ii) diffusion of the adsorbate within the internal structure (pores) of the adsorbent particle to the sorption site where (iii) actual adsorption occurs. The mass transfer of the adsorbate from the bulk liquid phase to the external surface of the adsorbent particle is characterized by external (film) mass transfer coefficient (k_f), whereas the mass transfer from the external adsorbent surface to the interior, pores surfaces within the adsorbent particle is governed by intraparticle diffusion coefficient (D_s). The step 3 is immeasurably fast and therefore contributes no resistance to the adsorption process. So the film mass transfer and the intraparticle diffusion are the adsorption rate determining coefficients. While the film mass transfer takes only first few minutes of the process, intraparticle diffusion occurs over several hours constituting the main course of adsorption. Several mathematical models have been developed to describe the adsorption process and predict the process rate using different modes of intraparticle diffusion.

In this Chapter, some of the most widely used models are discussed in the context of adsorption of organics from wastewater.

4.2 Mass Transfer Mechanism

As shown in Figure 4.1, external and internal diffusion are the two rate determining processes that control the adsorption phenomenon within the batch system. These two processes are discussed in detail in the following sections.

4.2.1 External Diffusion

As mentioned earlier, the first step of the adsorption process is the transfer of adsorbate from bulk liquid phase to the adsorbent surface penetrating through the stagnant boundary layer thickness (δ) surrounding the adsorbent particle by molecular diffusion. The boundary layer often offers resistance to the molecular diffusion, which is proportional to the ratio of film thickness and molecular diffusivity of the adsorbate (δ/D_m). The film thickness of the boundary layer and hence the resistance to the mass transfer can be decreased substantially by increasing the mixing intensity in the batch adsorption system. The rate of transfer of adsorbate across the film is proportional to surface area of the adsorbent particle (A_s) and the concentration driving force (C_b-C_s). Further, the rate of accumulation of adsorbate in the solid phase must be equal to the rate of transfer of adsorbate across the liquid film. Therefore,

$$M_p\left(\frac{\partial \bar{q}}{\partial t}\right) = k_f A_s (C_b - C_s) \qquad (4.1)$$

where, M_p = the weight of the adsorbent, g

$\bar{q}$ = the average adsorbed phase concentration (on a mass basis), mg/g

k_f = the external or interphase mass transfer coefficient, m/s

A_s = the surface area of the adsorbent, m^2

C_b = the uniform concentration of the adsorbate in the bulk of liquid (far from the adsorbent surface, mg/L

C_s = the concentration of the adsorbate in the liquid phase at the liquid-particle interface, mg/L

The Equation (4.1) can be rearranged as shown in Equation 4.2 (Ruthven, 1984).

$$\frac{\partial \bar{q}}{\partial t} = k_f a(C_b - C_s) = \frac{3k_f}{R_p \rho_p}(C_b - C_s) \tag{4.2}$$

where, a = specific surface area (area per unit mass of adsorbent), m^2/g

$= \frac{3}{R_p \rho_p}$ (for spherical particles)

R_p = radius of the adsorbent particle, m

ρ_p = density of the adsorbent particle, g/m^3

D_s = Effective surface diffusion coefficient of adsorbate, m^2/s

q_s = Adsorbed phase concentration at the external surface of adsorbent particle, mg/g

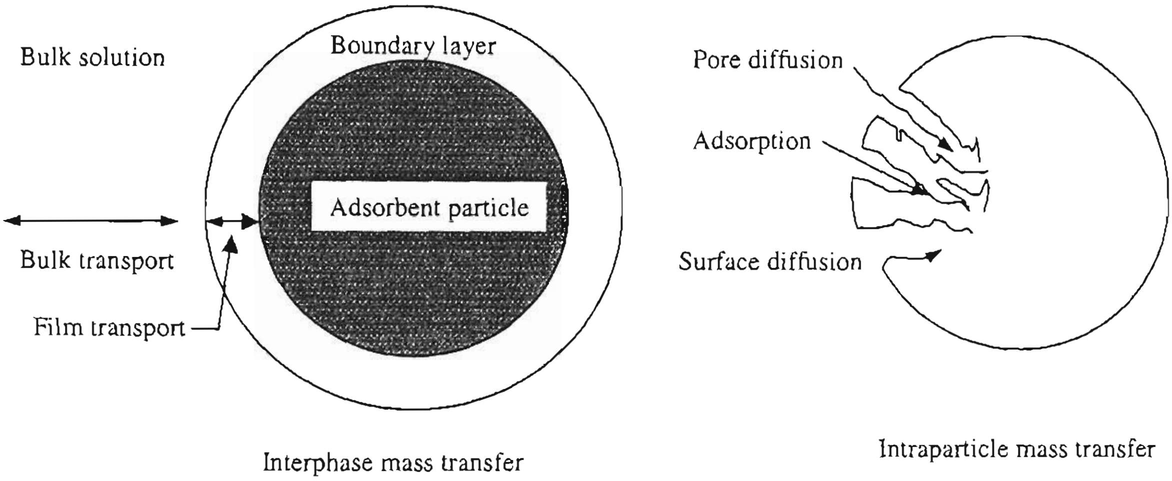


Figure 4.1 Mass transfer steps in adsorption process

4.2.2 Internal Diffusion

The internal diffusion of the adsorbate into the micropores of the adsorbent generally constitutes the major part of adsorption process. Surface diffusion (Crittenden et al, 1980), pore diffusion (Berninger et al., 1991), and combined surface and pore diffusion (Hu and Do, 1994, Li et. al., 1998) are the widely used mathematical models to describe and predict the adsorption process.

4.2.2.1 Surface Diffusion Model

In this model, it is assumed that the intraparticle mass transfer of the adsorbate takes place along the surface walls of the micropore inside the adsorbent particle. The surface diffusivity occurs due to the concentration gradient of the adsorbed adsorbate along the pore walls. Assuming the diffusion follows Fick's law, the intraparticle mass transfer can be described by the following equation:

$$\left(\frac{\varepsilon_p}{\rho_p}\right)\frac{\partial C}{\partial t}+\frac{\partial q}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(D_s r^2\frac{\partial q}{\partial r}\right) \qquad (4.3)$$

The initial and boundary conditions are given by the Equations 4.4 and 4.5.

$$k_f\left(C_b-C_s\right)=D_s\rho_p\frac{\partial q}{\partial r} \qquad at\ r=R_p \qquad \text{and} \qquad (4.4)$$

$$\frac{\partial q}{\partial r}=0 \qquad at\ r=0 \qquad (4.5)$$

The term $(\varepsilon_p/\rho_p)(\partial C/\partial t)$ in equation (4.3) is very much smaller in comparison to $(\partial q/\partial t)$ and is often neglected in its solution.

Here,

ε_p = Pellet porosity

C = Concentration of the adsorbate in solution phase

q = Adsorbed-phase concentration

r = radial distance measured from the centre of the pellet.

4.2.2.2 Pore Diffusion Model

In this model, the adsorbate molecules are assumed to diffuse through the pore fluid only. The macroscopic conservation equation is given below.

$$\varepsilon_p \frac{\partial C}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{\varepsilon_p}{r^2} \frac{\partial}{\partial r}\left(r^2 D_p \frac{\partial C}{\partial r} \right) \tag{4.6}$$

The initial and boundary conditions of the model are given by Equations 4.7 to 4.9.

$$k_f \left(C_b - C_s \right) = D_p \varepsilon_p \frac{\partial C}{\partial r} \qquad at\ \ r = R_p \tag{4.7}$$

$$\frac{\partial C}{\partial r} = 0 \qquad at\ \ r = 0 \qquad \text{and} \tag{4.8}$$

$$C = C_{b,} \qquad q = q_o \qquad at\ \ t = 0 \tag{4.9}$$

Here, C and q are the adsorbate concentration in the pore fluid and of the adsorbed phase corresponding to any point within the adsorbent particle respectively, and q_o is the initial adsorbed phase concentration.

4.2.2.3 Combined diffusion Model

In practice, the intraparticle diffusion in an adsorption system cannot be controlled by surface or pore diffusion alone. Therefore, for a more general description of the intraparticle diffusion mechanism, both the surface and pore diffusion model are combined together. Thus the diffusion of the adsorbate is described by the following macroscopic conservation equation (Fritz et al, 1981).

$$\varepsilon_p \frac{\partial C}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 \left(\varepsilon_p D_p \frac{\partial C}{\partial r} + D_s \rho_p \frac{\partial q}{\partial r} \right) \right] \qquad (4.10)$$

The initial and boundary condition are given by the Equations 4.11 - 4.13.

$$k_f (C_b - C_s) = D_p \varepsilon_p \frac{\partial C}{\partial r} + D_s \rho_p \frac{\partial q}{\partial r} \qquad at\ \ r = R_p \qquad (4.11)$$

$$\frac{\partial C}{\partial r} = 0 \qquad at\ \ r = 0 \qquad \text{and} \qquad (4.12)$$

$$C = C_b, \qquad q = q_o \qquad at\ \ t = 0 \qquad (4.13)$$

In a low strength adsorbate solution, if the adsorption is favourable in nature, then the first term in the left hand side of the Equation 4.10 can be assumed zero, and thus the rate of adsorbed mass can be described by the following equation (Lee, 1996),

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r} \right) + \frac{\varepsilon_p}{\rho_p}\frac{D_p}{r^2}\frac{\partial}{\partial r}\left(r_2 \frac{\partial C}{\partial r} \right) \qquad (4.14)$$

Despite these model can predict the experimental results efficiently, it is very difficult to conclude which mechanism is dominant in a given adsorption system. It has been observed based on experimental results that in a low strength adsorbate solution, pore diffusion is usually the dominant intraparticle diffusion mechanism whereas in high strength solution, surface diffusion dominates the intraparticle diffusion (Furuya et al, 1989). Similarly, in a highly adsorbable solution, surface diffusion is dominant whereas in a very weakly adsorbable solution, pore diffusion is the prevailing mass transport mechanism (Suzuki, 1990)

In a multicomponent adsorption system, both the pore diffusion and surface diffusion mechanisms become very complex and the adsorption system exhibits highly non-linear functions. In such situation, a parallel pore diffusion model is often assumed with a constant parallel pore diffusion coefficient to determine the intraparticle diffusion rate. In the multicomponent adsorption system, linear driving force approximation (LDFA) model is often utilized to calculate the overall mass transfer coefficient instead of external film mass or internal pore diffusion coefficient.

Since wastewater contains several adsorbates (i.e. a multicomponent system), in this study, the LDFA model is used to describe the adsorption of organics by granular activated carbon (GAC) and powdered activated carbon (PAC).

4.3 Linear Driving Force Approximation (LDFA) Model

The linear driving force approximation model is basically a simplified expression of intraparticle diffusion of adsorbate into adsorbent particles. The model was first developed by Glueckauf and Coates (1947), and later improved by many investigators (Vermeulen, 1953; Hall et al., 1966; Do and Rice, 1986, and Yao and Tien, 1992). In this model, it is assumed that the uptake rate of adsorbate by an adsorbent particle is linearly proportional to the driving force developed due to the difference between the surface concentration and the average adsorbed phase concentration of the adsorbate (as given in Equation 4.15).

$$\frac{d\overline{q}}{dt} = k_p\left(q_s - \overline{q}\right) \tag{4.15}$$

where,

$\overline{q}$ = the average adsorbed phase concentration (on a mass basis), mg/g
q_s = Adsorbed phase concentration at the external surface of adsorbent particle, mg/g
k_p = particle phase mass transfer coefficient

For spherical particle,

$$\overline{q} = \frac{3}{R_p^3}\int_0^{R_p} r^2 q\,dr \tag{4.16}$$

where, R_p = Adsorbent particle radius
q = adsorbed phase concentration
r = radial distance measured from the centre of the particle

After some simple assumptions, Glueckauf (1955) derived a relationship between particle phase mass transfer coefficient (k_p) and effective intraparticle diffusivity (D_e).

$$k_p = \frac{15D_e}{R_p^2} \tag{4.17}$$

Here the intraparticle diffusivity, D_e can be related to effective surface diffusion coefficient (D_S) of the surface diffusion model or effective pore diffusion coefficient of the pore diffusion model or film mass transfer coefficient (k_f) when the LDFA model is used (Tien, 1994).

The overall mass transfer equation of the LDFA model is given by the Equation 4.18.

$$\frac{d\bar{q}}{dt} = \frac{15D_s}{R_p^2}\left(q_s - \bar{q}\right) \tag{4.18}$$

Equation 4.18 can be equated to the Equation 4.2. In order to calculate mass transfer coefficient in batch adsorption system, the total mass balance in the system needs to be calculated. The overall mass balance in the batch reactor is given by the Equation 4.19.

$$V\frac{dC}{dt} + M\frac{dq}{dt} = 0 \tag{4.19}$$

where,

ρ_p = Particle density of adsorbent, kg/m^3
D_s = Effective surface diffusion coefficient of organic, m^2/s
R_p = Radius of adsorbent particle, m
k_f = Film mass transfer coefficient of organic, m/s
$\bar{q}$ = Average adsorbed phase organic concentration, mg/g
q_s = Adsorbed phase concentration at the external surface of adsorbent particle, mg/g
V = Volume of the solution in batch reactor, L
M = Weight of the adsorbent, g

The equation (4.18) can be solved with the help of the mass balance equation (4.19) of the solid phase and liquid phase using finite element technique and orthogonal collocation method.

In this study, the LDFA model was used to calculate the overall mass transfer coefficient of the multicomponent system (organics in wastewater). The main reason for using the model is its simplicity and adequacy in describing the mass transfer rate. The use of lumped index parameter (TOC) to represent the overall solute composition is another main factor in the selection of the model (LDFA) in this study.

4.4 Experimental Investigation

As shown in Figure 4.1, mechanical stirrers with speed controller were employed to experimentally study the adsorption kinetics. Detailed experiments were conducted with synthetic wastewater and biologically treated effluent from a sewage treatment plant. The adsorption kinetics was studied for different GAC and PAC loadings, different mixing intensity of the mixer, and different initial organic concentration of the synthetic wastewater. In the case of biologically treated sewage effluent, the initial organic concentration was constant. The experimental results obtained were predicted by the LDFA model using the isotherm parameters. The details of the isotherm parameters are presented in Chapter 3.

The total organic carbon (TOC) was measured using the UV-persulphate TOC analyser (Dohrmann, Phoenix 8000). The GAC and PAC used in the experiments were washed 3 times with distilled water and dried in the oven at 103.5° C for 24 hours. They were kept in a desiccator before using in the experiments. The characteristics of the synthetic wastewater and the GAC and PAC are presented in Chapter 3 (Section 3.5, Tables 3.3 and 3.4).

4.5 Results and Discussion

The adsorption kinetics of the organics in synthetic wastewater and biologically treated effluent from a sewage treatment plant were studied with different GAC and PAC loading rates, different organic concentration of synthetic wastewater and different mixing intensity of the mixer. The LDFA model was used to predict the experimental results. The isotherm parameters as calculated in Chapter 3 were utilized in the simulation process to estimate the mass transfer coefficients of the adsorption kinetics for these different operating conditions. The experimental results of GAC with the synthetic wastewater and the biologically treated sewage effluent are presented and predicted in the following sections of the Chapter. The results of the adsorption kinetics study of the individual organic component of the synthetic wastewater are also discussed in this chapter. The results of the adsorption kinetics with PAC are discussed in Chapter 7 together with the application of PAC in adsorption-membrane hybrid system.

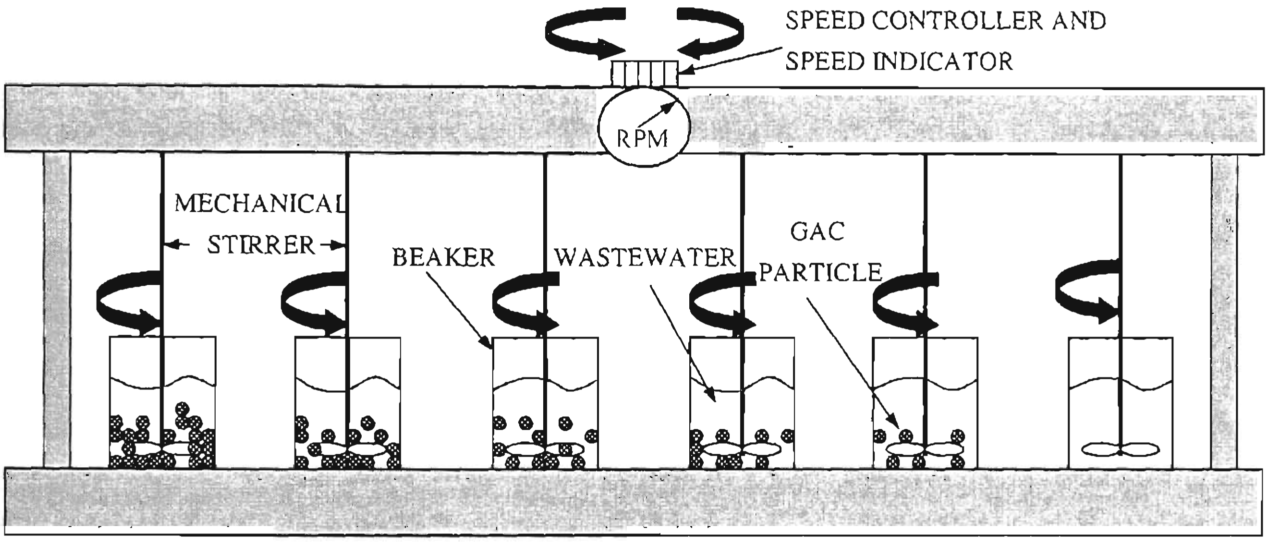


Figure 4.2 Schematic of the batch experimental set-up

(Speed controller 0-100 rpm, beaker 1 L)

4.5.1 Adsorption Kinetics of Individual Component of the Synthetic Wastewater

The synthetic wastewater used in this research consisted of three organic compounds and seven inorganic compounds (as presented in Table 3.3 in Chapter 3). Since total organic carbon (TOC) is the target pollutant to be removed, the adsorption affinity (in terms of initial mass transfer rate) of the individual organic compound with and without inorganic compounds are analysed in this section. As shown in Figures 4.3 – 4.4 (Table 4.1), the glucose is the least adsorptive and peptone is the most adsorptive compound. In the presence of inorganic compounds, the initial mass transfer rates of the organics were improved (Table 4.1). The glucose remained the least adsorptive even in the presence of inorganic compounds. The initial adsorption affinity of both yeast extract and peptone was enhanced in the presence of inorganics to 94 % and 97% respectively. It could be due to the adsorptive nature of the inorganic compounds. However, by the time the equilibrium state is reached (after 3 days as analysed in Chapter 3), the total organic adsorption onto the adsorbent (GAC) would be less in case of solution with inorganic compounds, as some of the adsorption sites would be occupied by the inorganic compounds themselves.

Table 4.1 Effect of inorganic compounds on the mass transfer coefficients of the synthetic wastewater

Organic compound	k_f without inorganic compounds	k_f with inorganic compounds
Glucose	3×10^{-6} m/s	6×10^{-6} m/s
Yeast extract	7×10^{-6} m/s	8×10^{-6} m/s
Peptone	9×10^{-6} m/s	9.9×10^{-6} m/s

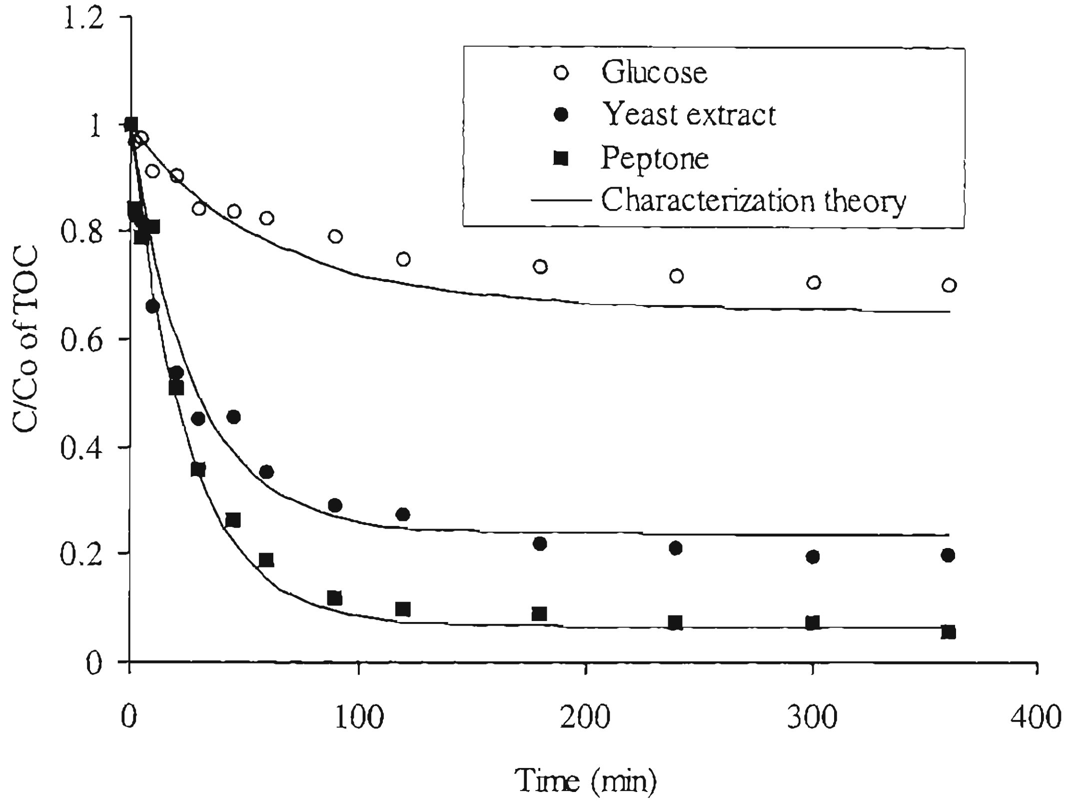


Figure 4.3 Batch adsorption of individual organic component in the absence of inorganic compounds of the synthetic wastewater (GAC dose = 5 g/L, rotational speed = 100 rpm, mixing intensity, G = 92 s^{-1}, $C_{0(glucose)}$ = 2.2 mg/L, $C_{0(yeast)}$ = 1.3 mg/L, $C_{0(peptone)}$ = 1.4 mg/L, C_o = initial organic concentration of individual organic compound)

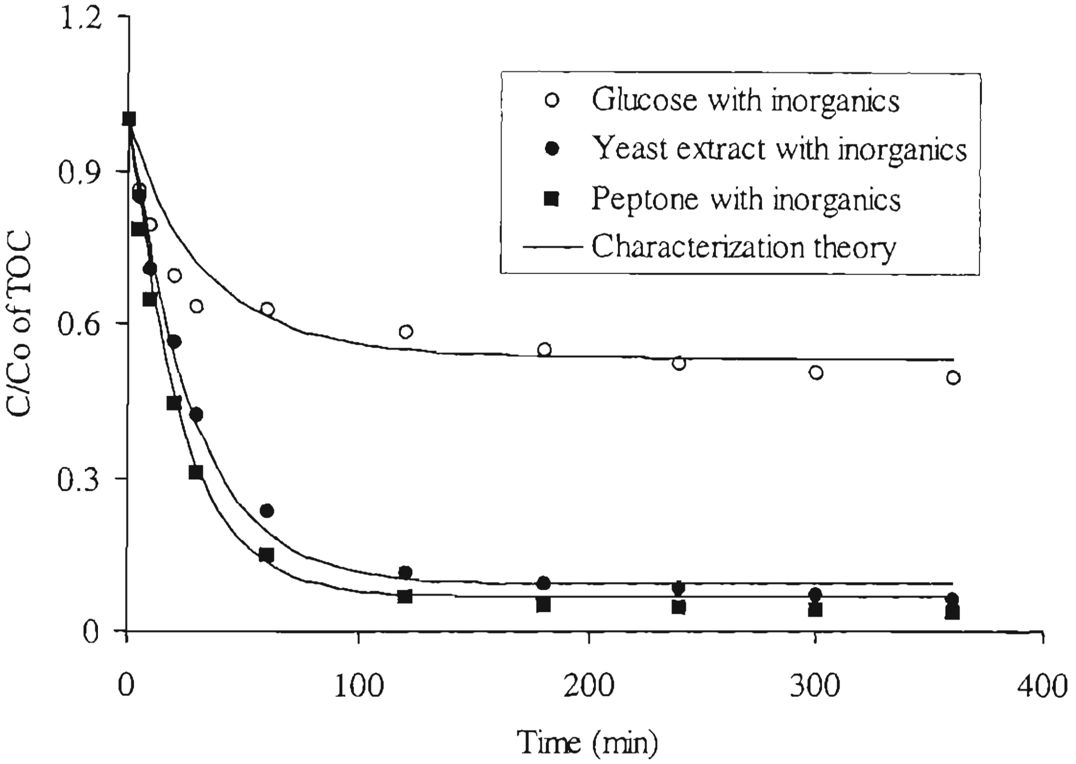


Figure 4.4 Batch adsorption of individual organic component in the presence of inorganic compounds of the synthetic wastewater (GAC dose = 5 g/L, rotational speed = 100 rpm, mixing intensity, G = 92 s^{-1}, $C_{O(glucose)}$ = 4.2 mg/L, $C_{O(yeast)}$ = 2.1 mg/L, $C_{O(peptone)}$ = 2.2 mg/L)

4.5.2 Effect of GAC Dose

The film mass transfer coefficient (k_f) was calculated using LDFA model. The film mass transfer coefficient (k_f) was directly obtained from the concentration decay curve by minimizing the mean percent deviation between experimental and calculated concentrations (Vigneswaran and Moon 1999). The film mass transfer coefficient (k_f) of the synthetic wastewater and the biologically treated sewage effluent was found to increase with the increase in the adsorbent dose. The increase in k_f may be attributed due to the increase in available adsorption sites. Higher the GAC dose, more the available adsorption sites for the organics. The mass transfer coefficients for organics in the synthetic wastewater and biologically treated effluent presented in Tables 4.2 - 4.4 (Figures 4.5-4.7).

Table 4.2 Mass transfer coefficients in the synthetic wastewater with an initial average TOC of 7 mg/L (Mixing intensity, G = 92 s^{-1} corresponding to the rotational speed of 100 rpm)

GAC dose, g/L	Overall mass transfer coefficient, m/s	
	Association theory	Characterization theory
1	3.8×10^{-6}	2.9×10^{-6}
2	5.0×10^{-6}	4.0×10^{-6}
5	5.5×10^{-6}	4.5×10^{-6}
10	5.8×10^{-6}	5.2×10^{-6}
15	6.0×10^{-6}	5.6×10^{-6}

Table 4.3 Mass transfer coefficients in the synthetic wastewater with an initial average TOC of 4.7 mg/L (Mixing intensity, G = 92 s^{-1} corresponding to the rotational speed of 100 rpm)

GAC dose, g/L	Overall mass transfer coefficient, m/s	
	Association theory	Characterization theory
0.2	2.9×10^{-6}	3.0×10^{-6}
1.0	4.0×10^{-6}	4.0×10^{-6}
2.0	5.5×10^{-6}	4.8×10^{-6}
5.0	6.0×10^{-6}	5.5×10^{-6}

Table 4.4 Mass transfer coefficients in the biologically treated effluent with an initial average TOC of 3.1 mg/L (Mixing intensity, G = 92 s^{-1} corresponding to the rotational speed of 100 rpm)

GAC dose, g/L	Overall mass transfer coefficient, m/s	
	Association theory	Characterization theory
0.1	1.0×10^{-5}	1.0×10^{-5}
1.0	1.1×10^{-5}	1.1×10^{-5}
2.5	2.0×10^{-5}	2.0×10^{-5}
5.0	2.2×10^{-5}	2.1×10^{-5}

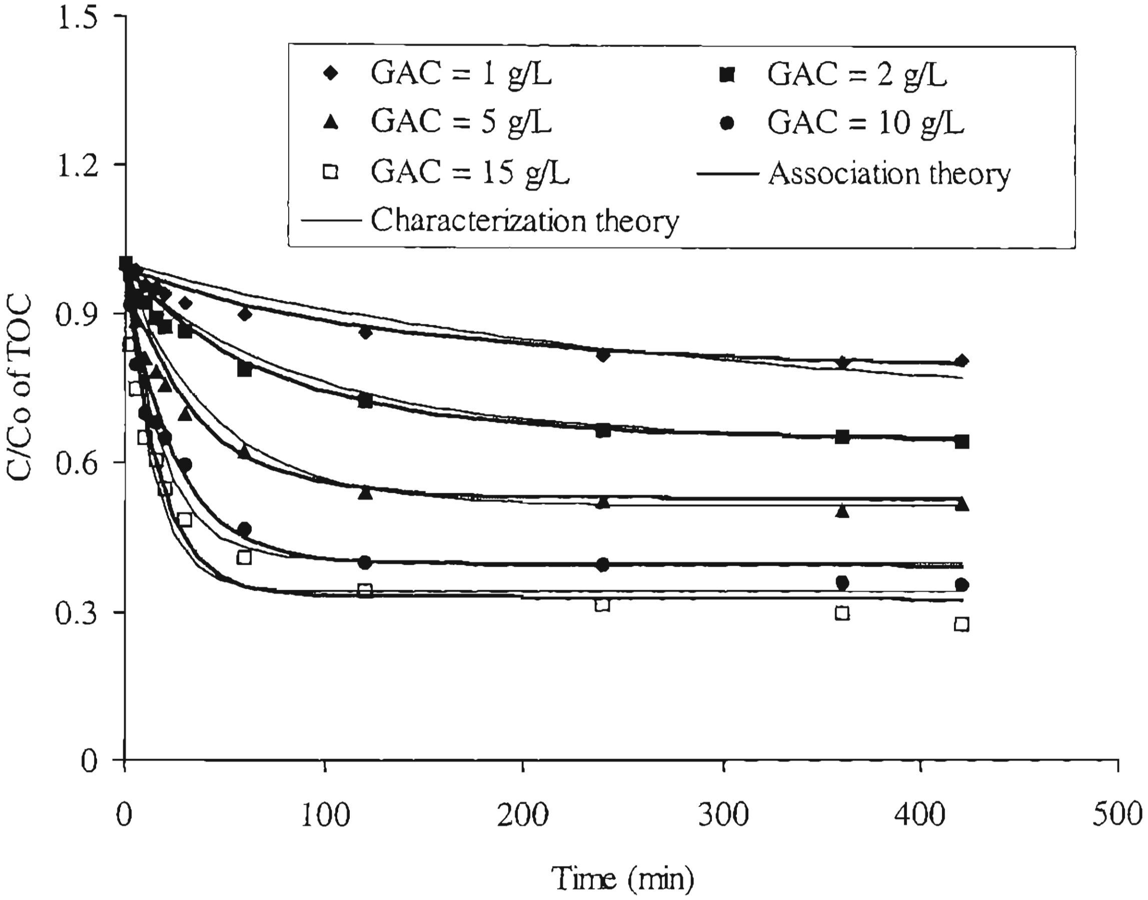


Figure 4.5 Effect of GAC dose mass transfer rate in the synthetic wastewater with an initial average TOC of 7.0 mg/L (Mixing intensity, G = 92 s^{-1})

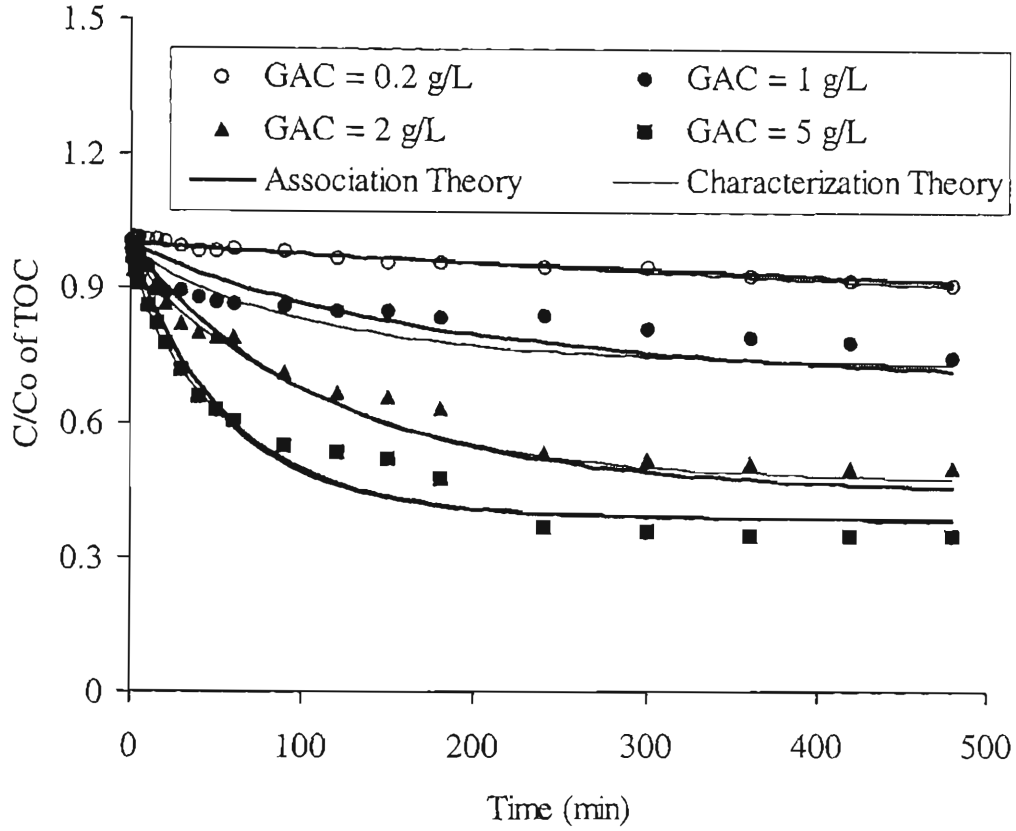


Figure 4.6 Effect of GAC dose mass transfer rate in the synthetic wastewater with an initial average TOC of 4.7 mg/L (Mixing intensity, G = 92 s^{-1})

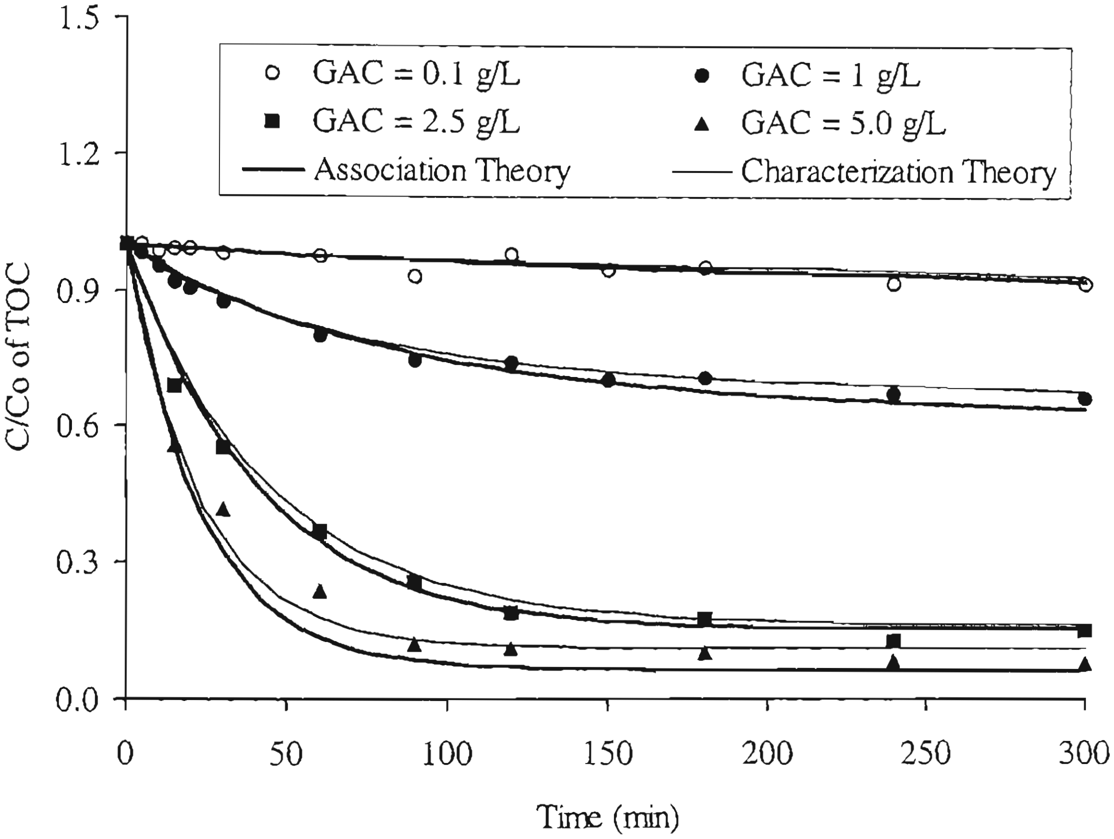


Figure 4.7 Effect of GAC dose mass transfer rate in the biologically treated effluent with an initial average TOC of 3.1 mg/L (Mixing intensity, G = 92 s^{-1})

4.5.3 Effect of Mixing Intensity (G)

The mass transfer coefficients are dependent on the mixing intensity. The mixing was provided with the help of rotational paddles in the batch experiment. Higher the rotational speed, higher is the mixing intensity and more the rate of mass transfer to the adsorbent. Increase in the mass transfer rate can be correlated to the energy dissipation (ε) in the fluid phase, which is defined as the energy consumed in the unit mass of the fluid (m^2/s^3)

$$\varepsilon = \frac{Pg_c}{\rho V} \tag{4.21}$$

where P = input power to the fluid (kg.m/s)

V = volume of the fluid (m^3)

ρ = density of the fluid (kg/m^3) and

g_c = gravity conversion coefficient ($kg.m/kg.s^2$)

For a homogeneous agitation, Pg_c is the function of stirring speed and the size of the baffle as given below,

$$Pg_c = N_p \rho n^3 d^5 \tag{4.22}$$

where n = rotation speed (1/s)

d = sweeping diameter of the impeller

N_p = power number. It varies with the configuration of the mixer. N_p takes a value of 0.35 for propeller and 6 for the six blade flat turbine)

Therefore, the higher agitation means the higher energy dissipation, thus higher mass transfer rate. In fact, high-speed agitation of fluid does not necessarily assure good contact between the adsorbate and adsorbent. Because the adsorbent particles move together with the moving fluid, it in fact reduces the relative velocity between fluid to the particles. Therefore, apart from the speed, the shape and size of the impeller play a major role in maximizing the contact between the fluid and adsorbent particles, and must be considered to improve the mass transfer rate.

Kawamura (2000), from detailed experimental studies developed an empirical relationship between mixing intensity (G) and the rotational speed of the mixer usually employed in the laboratory (Figure 4.8). In this study, the rotational speed was converted into mixing intensity (G)

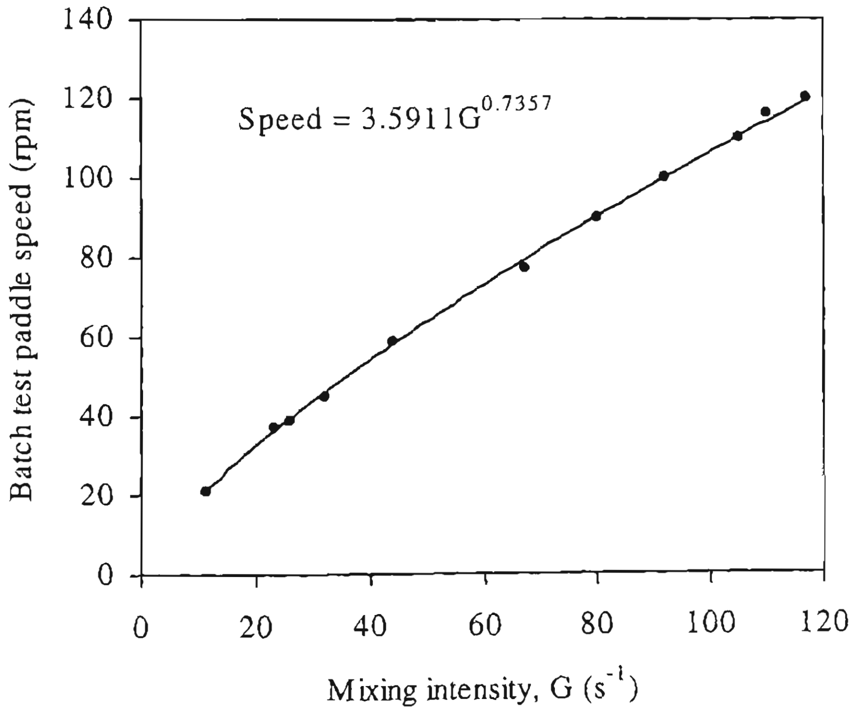


Figure 4.8 Relationship between rotational speed and mixing intensity (Kawamura, 2000)

Table 4.5 Mass transfer coefficients in the synthetic wastewater at different mixing intensities (GAC dose = 1 g/L, average initial TOC = 7.0 mg/L)

Rotational speed, rpm	Mixing intensity, s^{-1}	Overall mass transfer coefficient, m/s	
		Association theory	Characterization theory
20	10.3	1.2×10^{-6}	1.0×10^{-6}
40	26.5	2.5×10^{-6}	2.0×10^{-6}
80	67.9	4.0×10^{-6}	3.5×10^{-6}
100	92	5.6×10^{-6}	4.5×10^{-6}

Table 4.6 Mass transfer coefficients in the biologically treated effluent at different mixing intensities (GAC dose = 1 g/L, average initial TOC = 4.4 mg/L)

Rotational speed, rpm	Mixing intensity, s^{-1}	Overall mass transfer coefficient, m/s	
		Association theory	Characterization theory
20	10.3	3.0×10^{-6}	2.0×10^{-6}
50	35.9	6.0×10^{-6}	4.0×10^{-6}
80	67.9	8.0×10^{-6}	8.0×10^{-6}
100	92	10.0×10^{-6}	10.0×10^{-6}

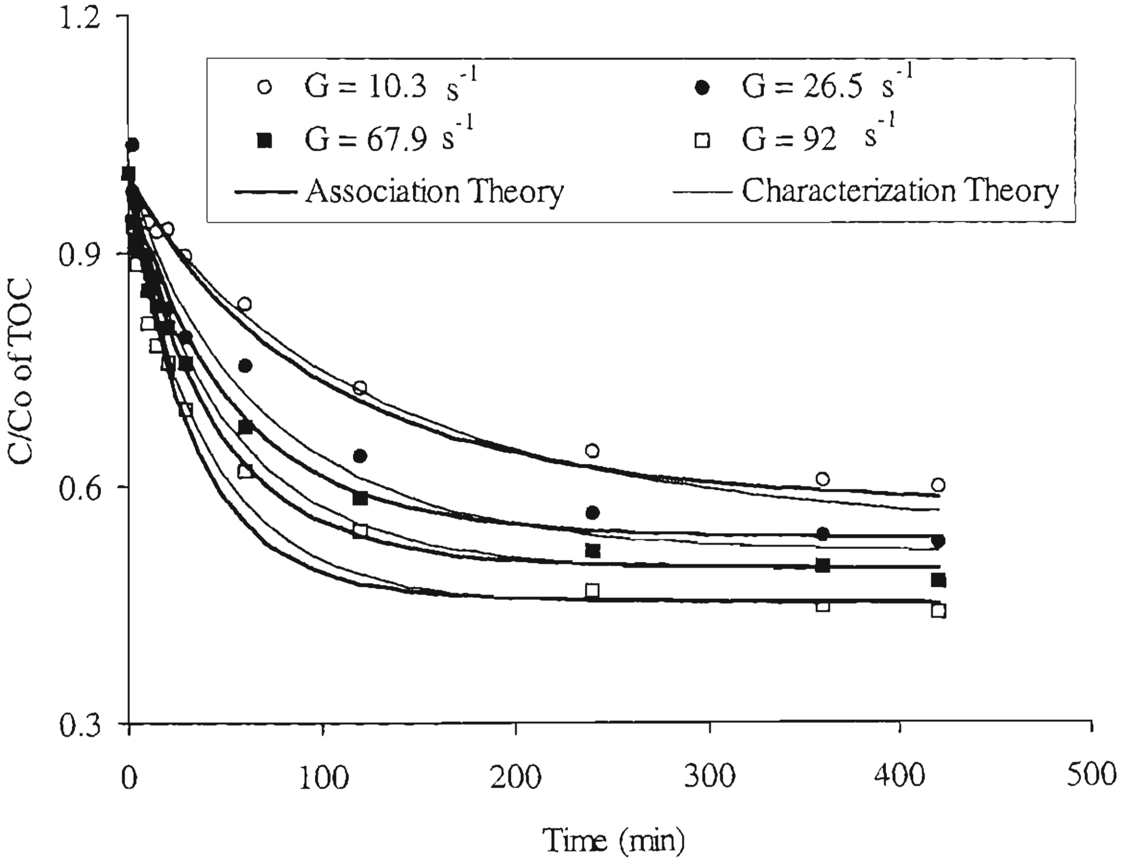


Figure 4.9 Effect of mixing intensity on mass transfer rate in the synthetic wastewater (GAC dose = 1 g/L, average initial TOC = 7.0 mg/L)

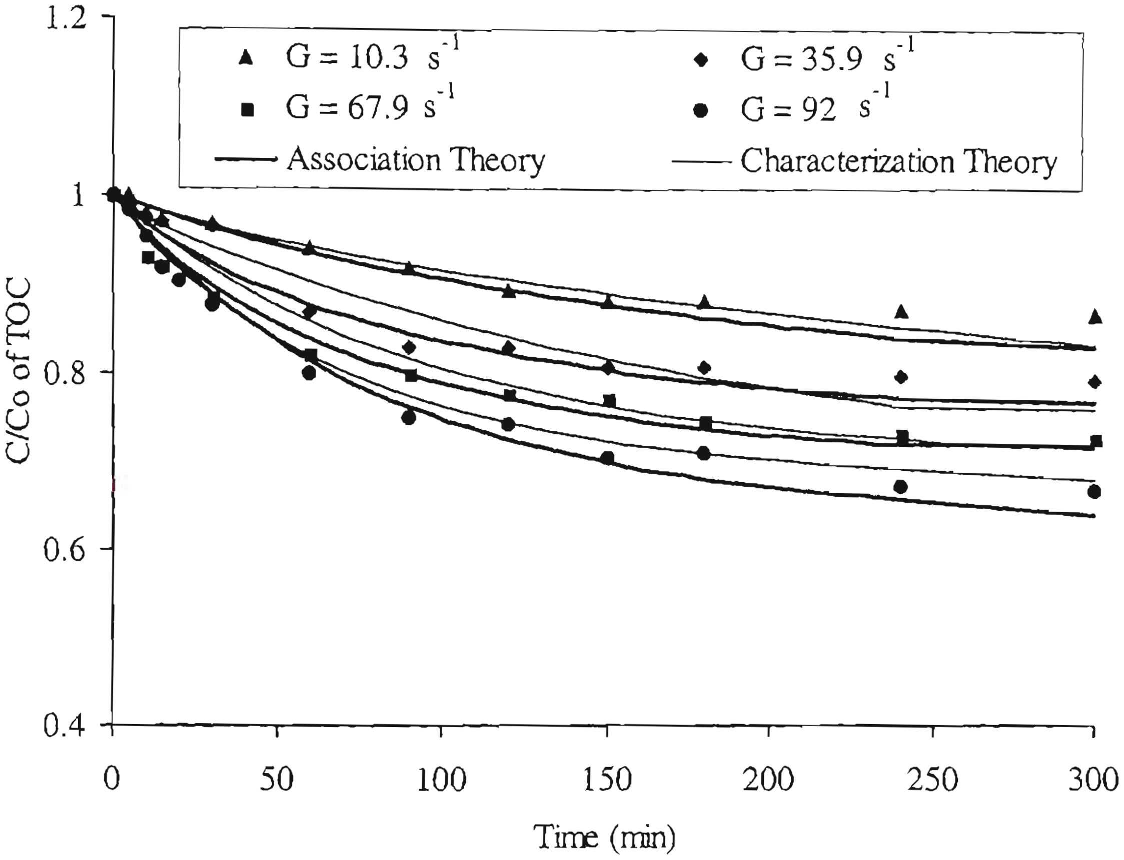


Figure 4.10 Effect of mixing intensity on mass transfer rate in the biologically treated sewage effluent (GAC dose = 1 g/L, average initial TOC = 4.4 mg/L)

4.5.4 Effect of Initial Organic Concentration

The mass transfer rate of the organics from bulk phase to the adsorbent particle was found to depend on the initial organic concentration of the solution as well. When the initial organic concentration of the synthetic wastewater was increased, the mass transfer rate of the organics from bulk phase to the adsorbent particles decreased (Table 4.7, Figure 4.11).

Table 4.7 Mass transfer coefficients in the synthetic wastewater
(GAC dose = 1 g/L, mixing intensity = 92 s^{-1})

Organic Concentration, mg/L	Overall mass transfer coefficient, m/s	
	Association theory	Characterization theory
3.2	6.5×10^{-6}	6.0×10^{-6}
7.6	5.6×10^{-6}	5.1×10^{-6}
10.4	5.0×10^{-6}	4.6×10^{-6}
13.4	4.5×10^{-6}	4.2×10^{-6}
15.5	3.3×10^{-6}	3.0×10^{-6}

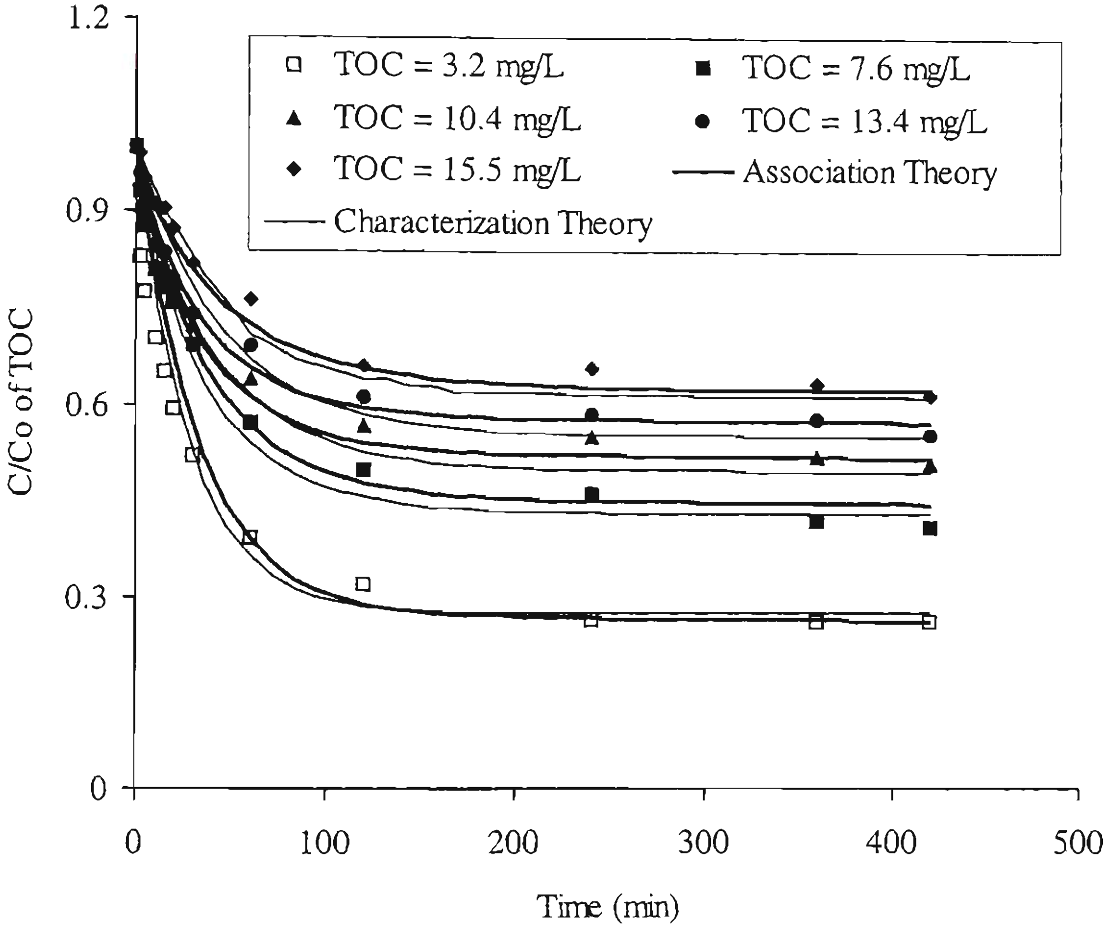


Figure 4.11 Effect of initial organic concentration on mass transfer rate in the synthetic wastewater (GAC dose = 1 g/L, mixing intensity = 92 s^{-1})

4.6 Development of Empirical Relationship for the Film Mass Transfer Coefficient

The mass transfer coefficient was calculated using LDFA model by fitting the experimental data. Thee mass transfer coefficient was related to the initial TOC concentration, rotational speed, and the GAC dose to establish empirical relationship.

The empirical relationship between mass transfer coefficient (k_f) and GAC dose, stirring speed, and initial TOC concentration of the synthetic wastewater are given in Equations 4.23 – 4.25.

$$k_f = 3.74(GAC)^{0.17} \tag{4.23}$$

$$k_f = 0.07(SPEED)^{0.91} \tag{4.24}$$

$$k_f = 10.16(TOC)^{-0.36} \tag{4.25}$$

Combining equations 4.23 – 4.25, the following Equation 4.46 was obtained.

$$k_f = 1.4(GAC)^{0.056} \cdot (SPEED)^{0.30} \cdot (TOC)^{-0.12} \tag{4.26}$$

In terms of mixing intensity, the k_f can be written as,

$$k_f = 5(GAC)^{0.056} \cdot (G)^{0.22} \cdot (TOC)^{-0.12} \tag{4.27}$$

Similarly, for the biologically treated sewage effluent, the following relationships were established,

$$k_f = 1.65(GAC)^{0.10} \cdot (SPEED)^{0.43} \tag{4.28}$$

$$k_f = 5.9(GAC)^{0.10} \cdot (G)^{0.32} \tag{4.29}$$

Since the TOC concentration was not varied during the experimentation with biologically treated sewage effluent, its effect was not incorporated in the equation 4.27. Here, the units of GAC dose, the rotational speed, mixing intensity (G) and the TOC concentration used in developing these empirical relationships are in g/L, rpm, s^{-1}, and mg/L respectively.

4.7 Conclusions

In this study, the linear driving force approximation (LDFA) model was used to calculate the overall mass transfer coefficients of organics in the synthetic wastewater and the biologically treated sewage effluent. The overall adsorption isotherm parameters were obtained from the association theory and the characterization theory, and the experimental results were fitted using LDFA model. The main reason for selecting the LDFA model is the simplicity of the model and the use of lumped parameter such as TOC to represent the liquid phase concentration of the system. The isotherm parameters obtained from both the isotherms were found equally effective in predicting the experimental results. The overall effect of the dissolved inorganic compounds in the synthetic wastewater solution was observed to enhance the mass transfer rate of the organics to the GAC particle. Similarly, the mass transfer rate was found to increase with the higher adsorbent dose and the mixing intensity of the mixer, but it decreased when the initial organic concentration of the synthetic wastewater solution was increased. The average value of the overall mass transfer rate was in the order of 10^{-6} m/s.

An empirical relationship for both the synthetic wastewater and the biologically treated sewage effluent was developed to calculate the mass transfer coefficient for different adsorbent dose, rotational speed, mixing intensity, and initial TOC concentration of the system (Equations 4.23 – 4.29). The relationship was developed based on the LDFA prediction of the experimental results.

Chapter 5

Fixed Bed Adsorption

5.1 Introduction

The application of adsorption system in practice is usually carried out in the fixed bed adsorption mode. The adsorbent, usually GAC is packed in a column and the target pollutants are passed through either end to be adsorbed by the adsorbent. In the course of adsorption, a saturated zone is formed near the inlet of the column and a zone with increasing concentration is observed at the frontal part. Despite its simple operation, the actual adsorption process in the fixed bed system is very complex and difficult to model. The adsorption process is unsteady, both adsorption and desorption or their combination can take place and the mass transfer rates are controlled by different factors such as axial dispersion coefficient. It is therefore essential to have a model that can simulate the dynamic behaviour of the fixed be system and optimise its operation. In the case of a fixed bed system, the mass transport mechanisms such as axial dispersion in the intraparticle fluid phase, fluid-to-particle mass transfer, intraparticle diffusion, and reversible adsorption in the interior of the adsorbent particle are employed to formulate the dynamic behaviour of the system. Isotherm equilibrium and mass transfer data, which can be obtained experimentally, usually provide fundamental information to verify the model. The assumptions that are usually made to formulate the dynamic behaviour of adsorption process in a fixed bed system are: (i) the column is packed with homogeneous and uniform particle and pore size, (ii) the column has uniform packing and influent distribution, (iii) all the mechanisms within the column are isothermal, (iv) the flow through the column is axial (radial flow is neglected), (v) the mass transfer coefficients are constant and independent of other components, and (v) the flow rate and adsorbate concentration of the influent solution do not change with time.

The main feature of the dynamic behaviour of a fixed bed adsorption is the effluent concentration with time as depicted in Figure 5.1. These concentration-time curves are commonly referred to as the breakthrough curves, and the time at which the effluent concentration reaches the threshold value is called the breakthrough time. The rational design of adsorption system is therefore, based on the accurate predictions of breakthrough curves for specified conditions. There are different empirical and analytical methods for predicting the breakthrough curve of the fixed bed adsorption system. Scale-up procedure based on an experimentally determined breakthrough curve (Vermeulen et al., 1973), Collins' length of unused bed (LUB) method (Collins, 1967), and the methods based on adsorption equilibrium and mass transfer are used to predict the breakthrough curve of a fixed bed adsorption system. Finite difference and orthogonal collocation methods are the most commonly used methods to solve the ordinary and partial differential equations that describe the fixed bed dynamics. The fixed bed dynamic equation and its solution are discussed in Section 5.2. It considers adsorption equilibrium and mass transfer effects. It is almost impossible to get devise an analytical solution to the fixed bed dynamics. The actual adsorption process is complex and unsteady, and the external mass transfer, intraparticle diffusion, and equilibrium relationship need to be considered in the model at the same time. Therefore, the numerical solution is preferred method to solve the dynamic equations. When an index parameter is used to represent the overall adsorbate concentration, the computational difficulties are further reduced by the use of linear driving force model (Rutheven, 1984, Vigneswaran and Moon, 1999, Lee, 1995).

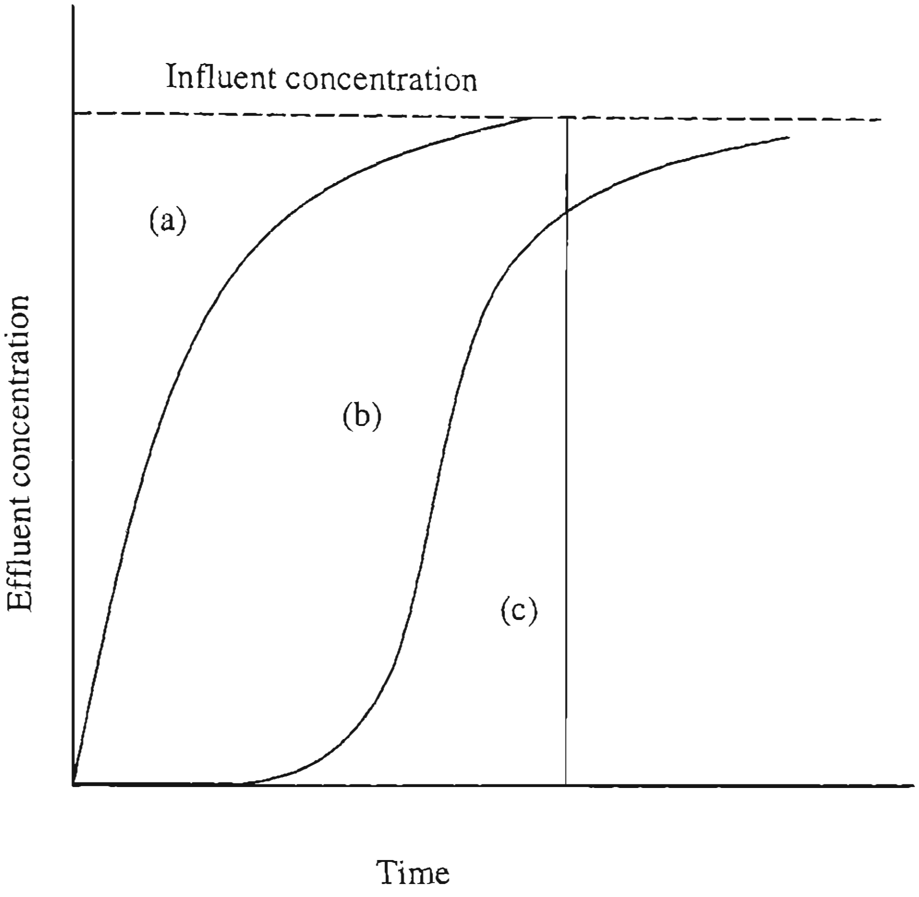


Figure 5.1 Schematic representations of breakthrough curves: (a) poorly adsorbed case, (b) commonly observed adsorption case, and (c) strongly adsorbed case with on mass-transfer effect (after Tien, 1994)

5.2 Adsorption Dynamics of the Fixed Bed System

The dynamic behaviour of the fixed bed adsorption system is described by the mass balance, and the initial and boundary conditions of the system as shown in the equations 5.1, 5.2, and 5.3 and 5.4 respectively. The flow through the bed was assumed to be linear with plug flow pattern.

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \frac{1-\varepsilon_b}{\varepsilon_b} \cdot \rho_p \cdot \frac{dq}{dt} \tag{5.1}$$

$$C(z,0) = 0 \ ; \quad q(z,0) = 0 \tag{5.2}$$

$$D_L \frac{\partial C}{\partial z}\Big|_{z=0} = -v\left(C\big|_{z=0^-} - C\big|_{z=0^+}\right) \tag{5.3}$$

$$\frac{\partial C}{\partial z}\Big|_{z=L} = 0 \tag{5.4}$$

These equations for liquid phase and solid phase concentrations were solved simultaneously by the orthogonal collocation method (OCM). The partial differential equations of the fixed bed system were first transformed into ordinary differential equations (ODEs) (Finlayson, 1972; Villadsen and Michelsen, 1978). The resulting equations were then integrated numerically in the time domain using subroutine, DVODE (Brown et al., 1989).

The isotherm constants obtained from the association theory and the Freundlich isotherm were utilized in terms of liquid phase concentration and solid phase concentration in the fixed bed simulations of the experimental results. The film mass transfer coefficient, k_f, was directly obtained from the concentration decay curve by minimizing the mean percent deviation between experimental and calculated concentrations (Vigneswaran and Moon, 1999).

5.3 Axial Dispersion Coefficient

The flow through a fixed bed column does not follow an ideal plug pattern in practice. Due to the bed porosity, there is always a tendency of axial and/or radial dispersion to occur when influent is passed through the fixed bed column. Any such mixing (axial or radial dispersion) is not desirable, as it reduces the efficiency of the system. It is obvious that the dispersion coefficients for the bed packed with porous particle would be much higher than that with nonporous adsorbent particles, and as such the minimization of the dispersion effect is one of the major operational consideration of the system. In this study, the air was first released from the voids by backwashing the bed before the commencement of the experiments. The radial dispersion effect was ignored in this study to simplify the model for practicality, and is not discussed here.

It has been observed that the axial dispersion effect is caused by both molecular diffusion and turbulent mixing. The Peclet number is very much related to the axial dispersion effect as shown in equation 5.5.

$$P_e = \frac{d_p v}{D_L} \tag{5.5}$$

There are some correlations between the Peclet number, Reynolds number, and Schmidt number reported in the literature. At lower Reynolds number regime, the axial dispersion effect is mainly due to molecular diffusion. As the Reynolds number is increased, the dispersion effect due to turbulent flow becomes prominent. Wakao's (1978) correlation for a highly favourable adsorption system is shown in equation 5.6

$$\frac{D_L}{2vR_p} = \frac{20}{\varepsilon}\left(\frac{D_m}{2vR_p}\right) + 0.5 = \left(\frac{20}{R_e S_c} + 0.5\right) \tag{5.6}$$

Similarly, Tien (1994) reported a correlation between the Peclet number, Reynolds number, and the Schmidt number as shown in equation 5.7

$$\frac{1}{P_e} = \frac{0.3}{R_e S_c} + \frac{0.5}{1 + \frac{3.8}{R_e S_c}} \tag{5.7}$$

$$0.008 < R_e < 400 \quad and \quad 0.28 < S_c < 2.2$$

The inclusion of the axial dispersion coefficient in the fixed bed adsorption model results into a differential equation dispersion model of second order (equation 5.1). Berninger (1991) also reported the similar model equations with the boundary and initial conditions of the fixed bed dynamics.

5.4 Mass Transfer in the Fixed Bed Adsorption System

The rate of mass transfer in an adsorption system depends on the adsorbate and adsorbent characteristics, and the hydrodynamic condition such as filtration velocity of the system. There are several empirical relationships reported in the literature. Some of the most widely used empirical equations often utilized in estimating the external mass transfer coefficients for the fixed bed system are as follows:

Wakaoa and Funazkri (1978):

$$k_f = \frac{D_m}{2R_p}\left(2.0 + 1.1\,\mathrm{Re}^{0.6}\,Sc^{0.33}\right) \tag{5.5}$$

Petrovic and Thodes (1968):

$$k_f = 0.355\upsilon_s\left(\frac{1-\xi}{\xi}\right)\mathrm{Re}^{-0.359}\,Sc^{-0.67} \tag{5.6}$$

Williamson et al. (1963):

$$\begin{aligned} k_f &= 0.24\upsilon_s\,\mathrm{Re}_p^{-0.66}\,Sc^{-0.58} && \mathrm{Re} = 0.08 - 125 \\ &= 0.442\upsilon_s\,\mathrm{Re}_p^{-0.31}\,Sc^{-0.58} && \mathrm{Re} = 125 - 5000 \end{aligned} \tag{5.7}$$

Ranz and Marshal (1952):

$$Sh = \frac{2k_f R_p}{D_m}\left(2.0 + 0.6\,\mathrm{Re}^{0.5}\,Sc^{0.33}\right) \tag{5.8}$$

Here, Re and Re_p are the Reynolds number and Sc is the Schmidt number.

$$\mathrm{Re} = \frac{2R_p \upsilon_s \rho_f}{\mu} \tag{5.9}$$

$$\mathrm{Re}_p = \frac{2R_p \upsilon_s \rho_f}{\xi\mu} \tag{5.10}$$

$$Sc = \frac{\mu}{D_m \rho_f \upsilon_s} \tag{5.11}$$

R_p = adsorbent particle radius

D_m = molecular diffusion coefficient

ρ_f = fluid density

ξ = void fraction

In liquid phase adsorption, there are competitive interactions among different molecules, and that makes the molecular diffusion very complex. Wilke-Chang (1955) proposed an equation to estimate the molecular diffusivity for solution of a low adsorbate concentration as follows:

$$D_m = 7.4 \times 10^{-8} \frac{(\phi M_b)^{0.5} T}{\mu V_a^{0.6}} \qquad (5.11)$$

where ϕ = association factor of the solvent = 2.6 for water

M_b = molecular weight of the solvent

V_a = molar volume of the solute at its normal boiling temperature

It has been observed that at ordinary temperature, the liquid phase diffusitivities generally remain within the range of 10^{-8}-10^{-10} m^2/s except for polymers and other very large molecules (Ruthven, 1984).

5.5 Experimental Investigation

Fixed bed experiments were conducted in a filter column of 2 cm diameter and 50 cm height. The column had ports for influent feed and effluent collection. The schematic diagram of the experimental set-up is shown in Figure 5.2. The column was packed with GAC (porosity 0.65). Constant pressure head was maintained in the filter column to keep a constant filtration rate. The filtration rate here refers to the hydraulic loading rate (volume of wastewater flow per unit of cross sectional area of adsorption column per hour). Detailed experiments were conducted with synthetic wastewater and biologically treated effluent from a sewage treatment plant at different GAC loadings, different flow rates, and different initial organic concentration (synthetic wastewater). The experimental results were predicted by LDFA model using the isotherm parameters calculated (in Chapter 3)

As mentioned in Chapters 3 and 4, the total organic carbon (TOC) was measured using the UV-persulphate TOC analyser (Dohrmann, Phoenix 8000). The GAC used in the experiments was washed 3 times with distilled water and dried in the oven at 103.5° C for 24 hours. It was kept in a desiccator before using in the experiments. The characteristics of the synthetic wastewater and the GAC have been shown in the previous chapter and therefore, they are not repeated in this chapter

Total organic carbon (TOC) was measured using the UV-persulphate TOC analyser (Dohrmann, Phoenix 8000). Basically, GAC used in the experiments was washed 3 times with distilled water and dried in the oven at 103.5° C for 24 hours. It was kept in a desiccator before using in the experiments.

The chemical composition of the synthetic wastewater and the characteristics of GAC used in this study are shown in Tables 5.1 and 5.2 respectively.

Table 5.1 Constituents of the synthetic wastewater used

Compounds	Weight (mg/L)	Compounds	Weight (mg/L)
$MnSO_4$	0.125	KH_2PO_4	1.250
$CaCl_2$	0.925	$NH_2.NH_2.H_2SO_4$	3.500
$NaHCO_3$	0.875	Glucose	16.500
NaCl	2.500	Yeast Extract	1.750
$MgSO_4.7H_2O$	3.750	Peptone	1.750

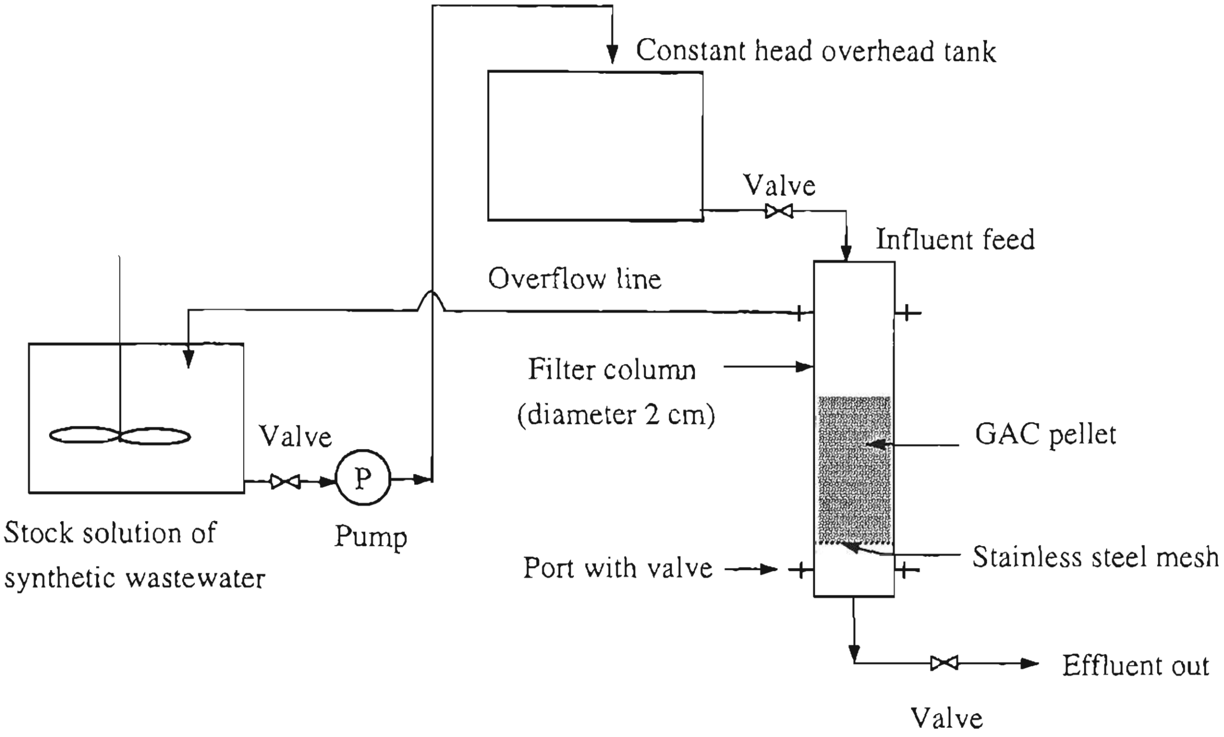


Figure 5.2 Schematic diagram of the fixed bed adsorption system

Table 5.2 Physical properties of the GAC used in the study

Specification	Estimated Value of GAC
Iodine number, mg/g.min	800
Maximum Ash content	5 %
Maximum Moisture content	5 %
Bulk density, kg/m^3	748
BET surface area, m^2/g	1112
Nominal size, m	3×10^{-4}
Average pore diameter, Å	26.14

The TOC contribution of the organics used to prepare the synthetic wastewater (glucose, peptone and yeast extract) along with inorganics were 79%, 11% and 10% respectively. This represents a well-treated secondary effluent from a biological wastewater treatment plant (TOC = 3.5 mg/L and COD = 30 mg/L) (Matsui, et al., 1998).

The physical properties of the GAC were determined using BET apparatus in the laboratory. Since the characteristics of the activated carbon change with time, its properties need to be determined at the time of experimentation.

5.6 Results and Discussion

The experimental results of the GAC fixed bed system with synthetic wastewater and biologically treated sewage effluent are discussed in the following sections of the Chapter. The experimental studies presented here were carried out at different filtration velocity, bed depth, and initial organic concentration. The mass transfer rate from the bulk solution to the GAC surface was calculated by fitting the experimental results using the dynamics of the fixed bed system as discussed at section 5.2 of the Chapter.

5.6.1 Sensitivity Analysis of the Dynamic Model

The dynamics of the model developed were analysed for the effects of the effective film mass transfer coefficient and the axial dispersion coefficient on the effluent quality of the fixed bed system. The model was found to be sensitive to the change in the film mass transfer coefficient (Figures 5.3 and 5.4). However, for the range of the operating conditions (bed depth = 4 cm and flow rate 1-5 m/h), the effect of axial dispersion coefficient on the effluent quality was not observed to be significant (Figures 5.5 and 5.6). This could be due to the small adsorbent particle size, low interstitial flow rate, and the shallow bed depth of the fixed bed system.

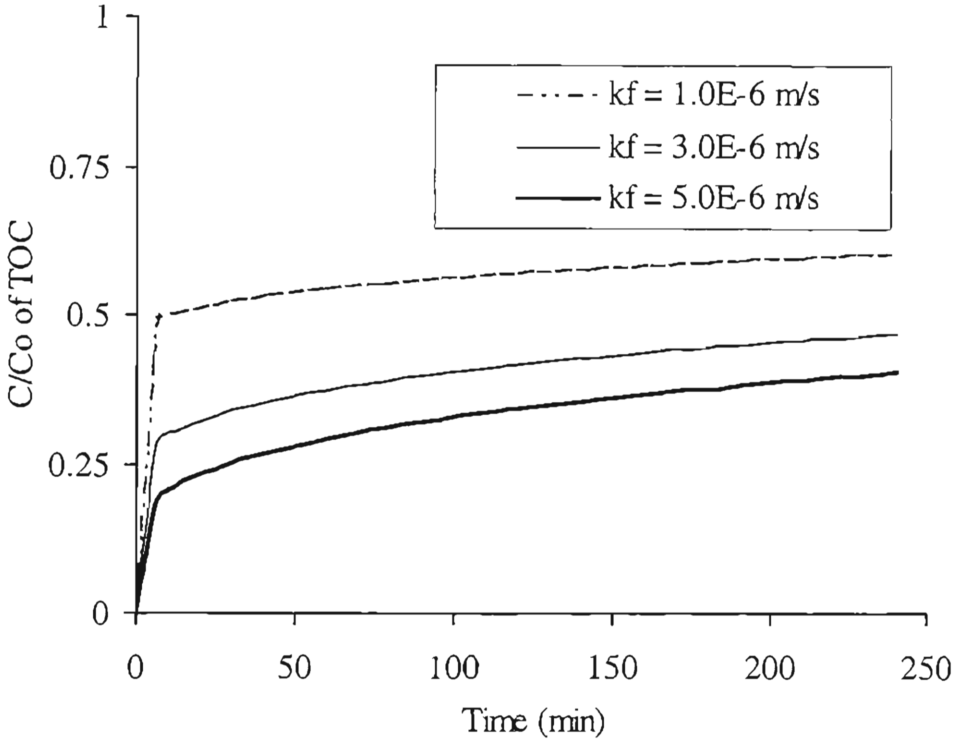


Figure 5.3 Effect of film mass transfer coefficient on the breakthrough curve of the fixed bed adsorption system (Fixed bed depth = 4 cm, filtration velocity = 1m/h, axial dispersion coefficient (D_L) = 1 x 10^{-7} m^2/s, TOC = 6.9 mg/L)

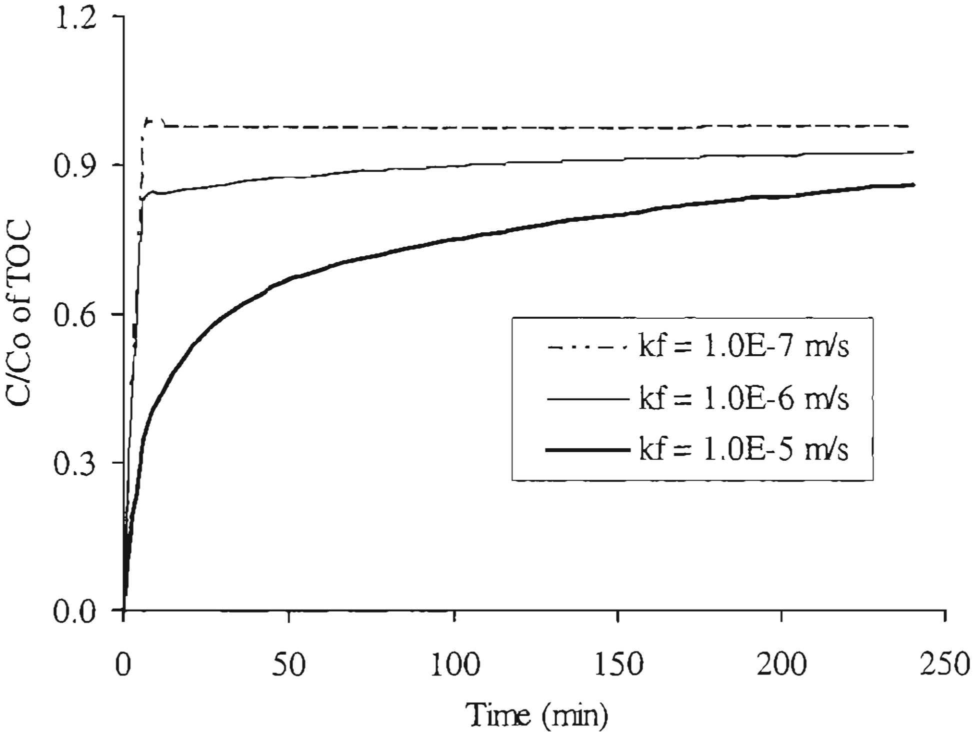


Figure 5.4 Effect of film mass transfer coefficient on the breakthrough curve of the fixed bed adsorption system (Fixed bed depth = 4 cm, filtration velocity = 5 m/h, axial dispersion coefficient (D_L) = 1 x 10^{-5} m^2/s, TOC = 3. 8 mg/L)

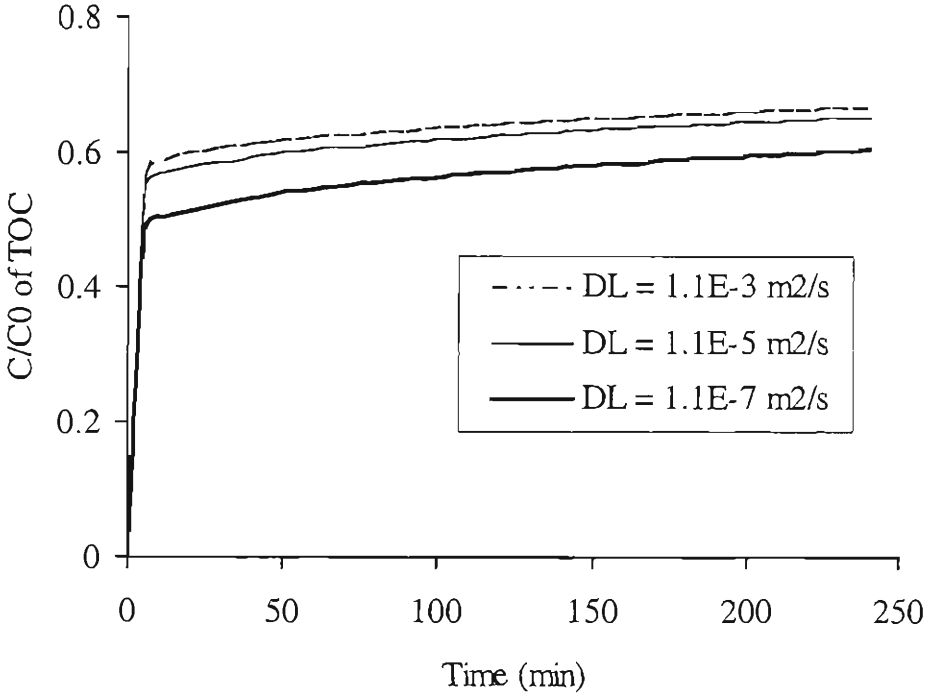


Figure 5.5 Effect of axial dispersion coefficient on the breakthrough curve of the fixed bed adsorption system (Fixed bed depth = 4 cm, filtration velocity = 1 m/h, Film mass transfer coefficient (k_f) = 1 x 10^{-6} m/s, TOC = 6.9 mg/L)

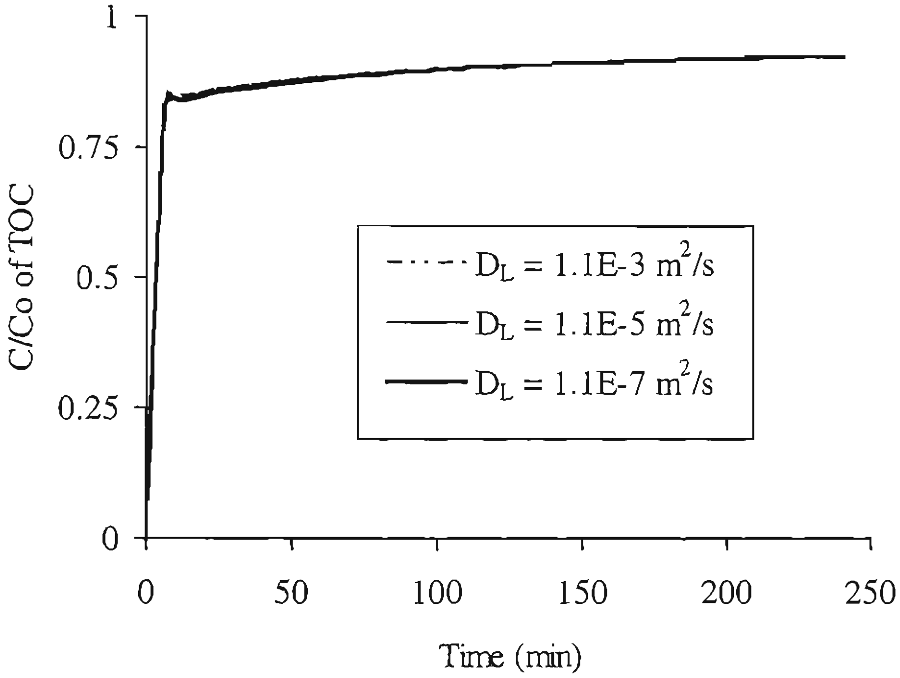


Figure 5.6 Effect of axial dispersion coefficient on the breakthrough curve of the fixed bed adsorption system (Fixed bed depth = 4 cm, filtration velocity = 5 m/h, Film mass transfer coefficient (k_f) = 1 x 10^{-6} m/s, TOC = 3.8 mg/L)

5.6.2 Effect of Bed Depth

The result of the effect of fixed bed depth on the film mass transfer coefficient (k_f) is summarized in Table 5.3. The experimental results and their predictions using the association theory and the characterization theory are presented in Figures 5.7–5.9. The effect of the bed depth was analysed at the filtration velocities of 1, 5, and 7 m/h. The synthetic wastewater was analysed with 1 and 5 m/h whereas, the biologically treated sewage effluent with 5 and 7 m/h filtration velocities. As expected, in all these three cases (of 1, 5, and 7 m/h filtration velocity), the film mass transfer coefficient (k_f) remained constant. The rate of mass transfer was higher in case of the biologically treated sewage effluent than that of the synthetic wastewater. It shows the biologically treated sewage effluent of the sewage plant contained more adsorbable organic substances than those used to prepare the synthetic wastewater in the laboratory. This result also verifies the isotherm result discussed in Chapter 3 which shows the isotherm curve is more favourable in case of the biologically treated sewage effluent.

Table 5.3 Effect of bed depth on the film mass transfer coefficient of the fixed bed adsorption

Variable (Bed depth, cm)	Film mass transfer coefficient (m/s)		Remarks
	Association theory ($x 10^{-6}$)	Characterization theory ($x 10^{-6}$)	
Synthetic wastewater			
4	2.7	2.5	v = 1 m/h, TOC = 4 mg/L
12	2.7	2.5	v = 1 m/h, TOC = 4 mg/L
4	2.9	2.6	v = 5 m/h, TOC = 3.7 mg/L
8	2.5	2.4	v = 5 m/h, TOC = 7.5 mg/L
12	2.5	2.4	v = 5 m/h, TOC = 7.5 mg/L
20	2.7	2.5	v = 5 m/h, TOC = 7.5 mg/L
24	2.7	2.5	v = 5 m/h, TOC = 7.5 mg/L
Biologically treated sewage			
4	6.0	5.4	v = 5 m/h, TOC = 4.3 mg/L
8	6.5	5.6	v = 7 m/h, TOC = 3.9 mg/L
16	6.5	5.6	v = 7 m/h, TOC = 3.9 mg/L
24	6.5	5.6	v = 7 m/h, TOC = 3.9 mg/L

Note: v = filtration velocity, TOC = total organic carbon

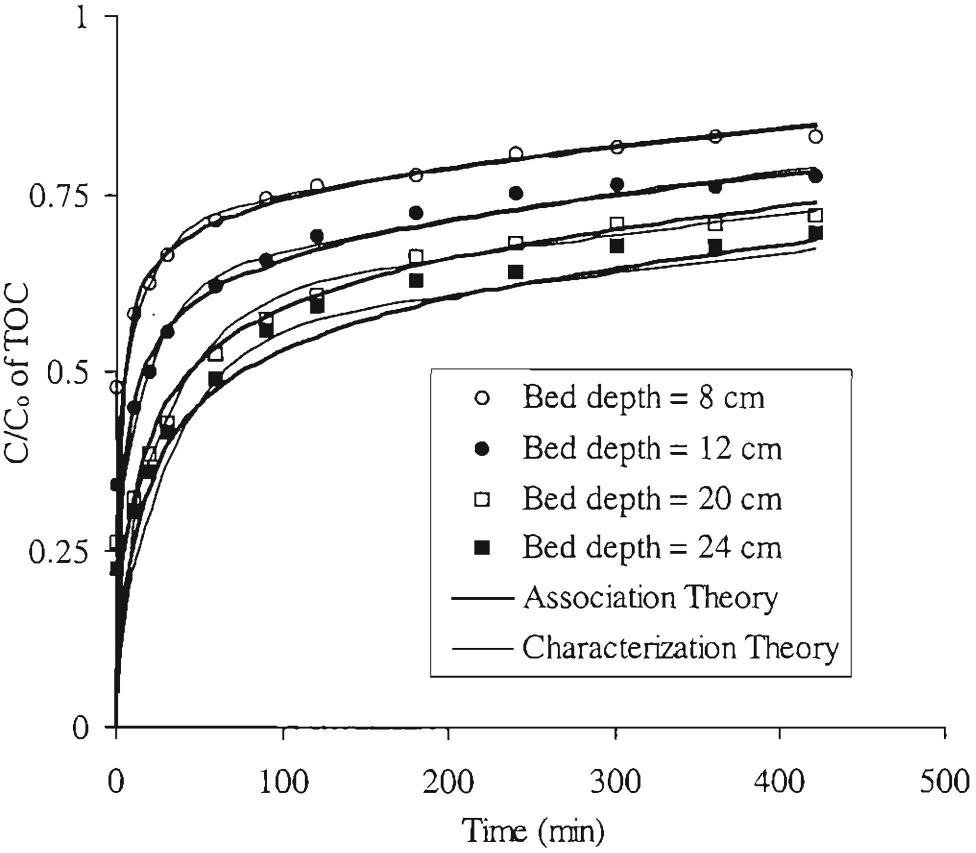


Figure 5.7 Effect of the bed depth on effluent quality from the fixed bed system (Filtration rate = 5 m/h, average initial TOC of the synthetic wastewater = 7.5 mg/L)

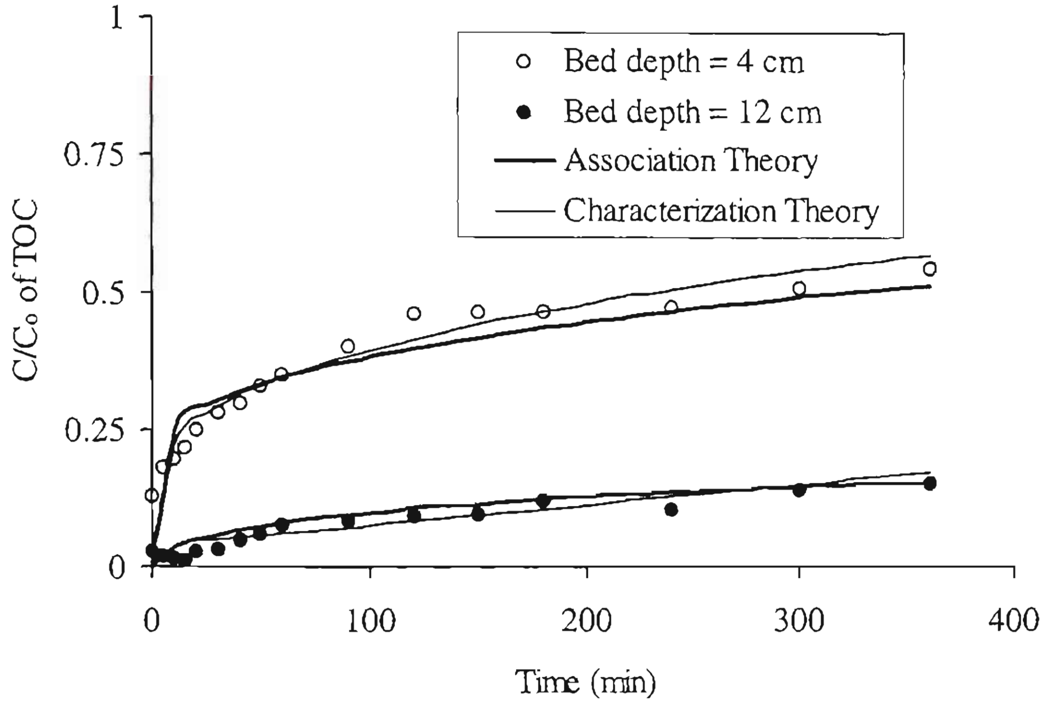


Figure 5.8 Effect of the bed depth on effluent quality from the fixed bed system (Filtration rate = 1 m/h, average initial TOC of the synthetic wastewater = 4.0 mg/L)

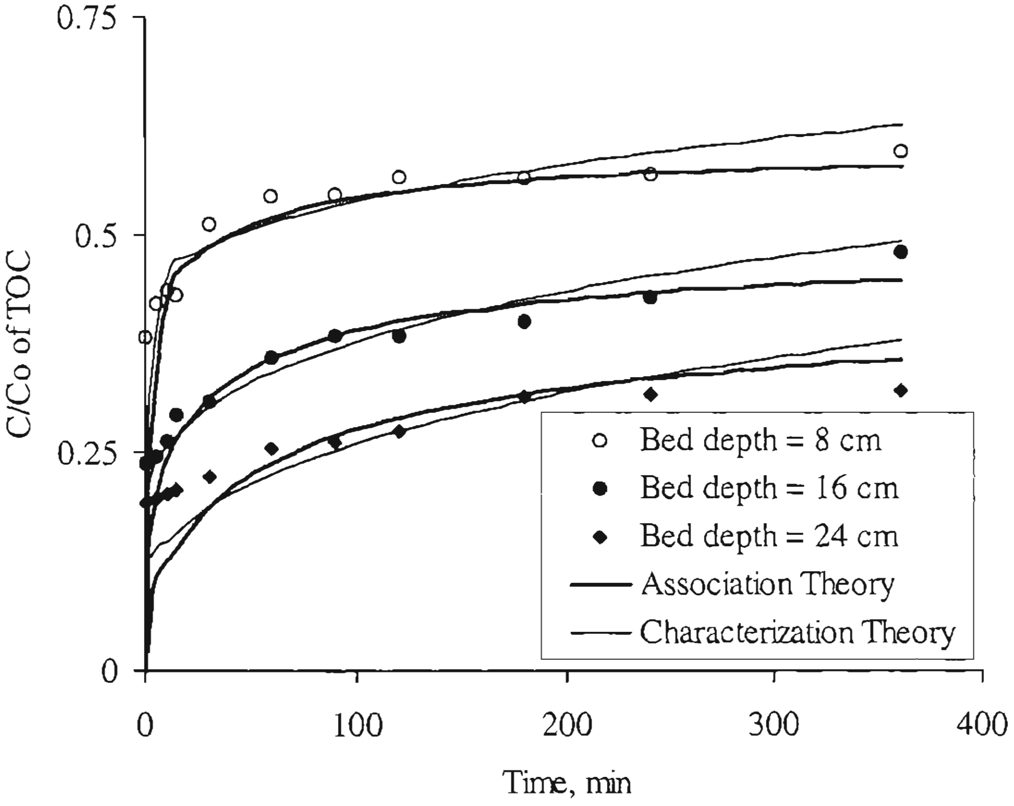


Figure 5. 9 Effect of bed depth on the effluent quality of the fixed bed system (Filtration rate = 7 m/h, average initial TOC of biologically treated sewage effluent = 3.9 mg/L)

5.6.3 Effect of Filtration Rate

The result of the effect of filtration rate on the film mass transfer coefficient (k_f) is summarized in Table 5.4. The experimental results and their predictions using the association theory and the characterization theory are presented in Figures 5.10–5.12. The effect of the filtration velocity was analysed at the fixed bed depths of 4, and 20 cm. The synthetic wastewater was analysed with 4 and 20 cm bed depth whereas, the biologically treated sewage effluent with 4 cm bed depth. The film mass transfer coefficient (k_f) was increased with the rise in the filtration velocity (volume of wastewater passing through unit area of the GAC bed). The rate of mass transfer was higher in case of the biologically treated effluent from the sewage plant than that of the synthetic wastewater. This result also shows that the organic contents of the biologically treated effluent of the sewage plant were more adsorbable than those used to prepare the synthetic wastewater.

Table 5.4 Effect of filtration rate on the film mass transfer coefficient of the fixed bed adsorption

Variable (Filtration rate, m/h)	Film mass transfer coefficient (m/s)		Remarks
	Association theory (x 10^{-6})	Characterization theory (x 10^{-6})	
Synthetic wastewater			
1	2.7	2.5	d = 4 cm, TOC = 3.7 mg/L
5	2.9	2.6	d = 4 cm, TOC = 3.7 mg/L
10	3.0	2.7	d = 4 cm, TOC = 3.7 mg/L
5	2.5	2.4	d = 20 cm, TOC = 7.0 mg/L
10	2.7	2.6	d = 20 cm, TOC = 7.0 mg/L
15	3.3	2.9	d = 20 cm, TOC = 7.0 mg/L
20	3.4	3.0	d = 20 cm, TOC = 7.0 mg/L
Biologically treated sewage			
1	4.5	3.8	d = 4 cm, TOC = 4.3 mg/L
5	6.0	5.4	d = 4 cm, TOC = 4.3 mg/L
10	6.6	6.5	d = 4 cm, TOC = 4.3 mg/L

Note: d = fixed bed depth, TOC = total organic carbon

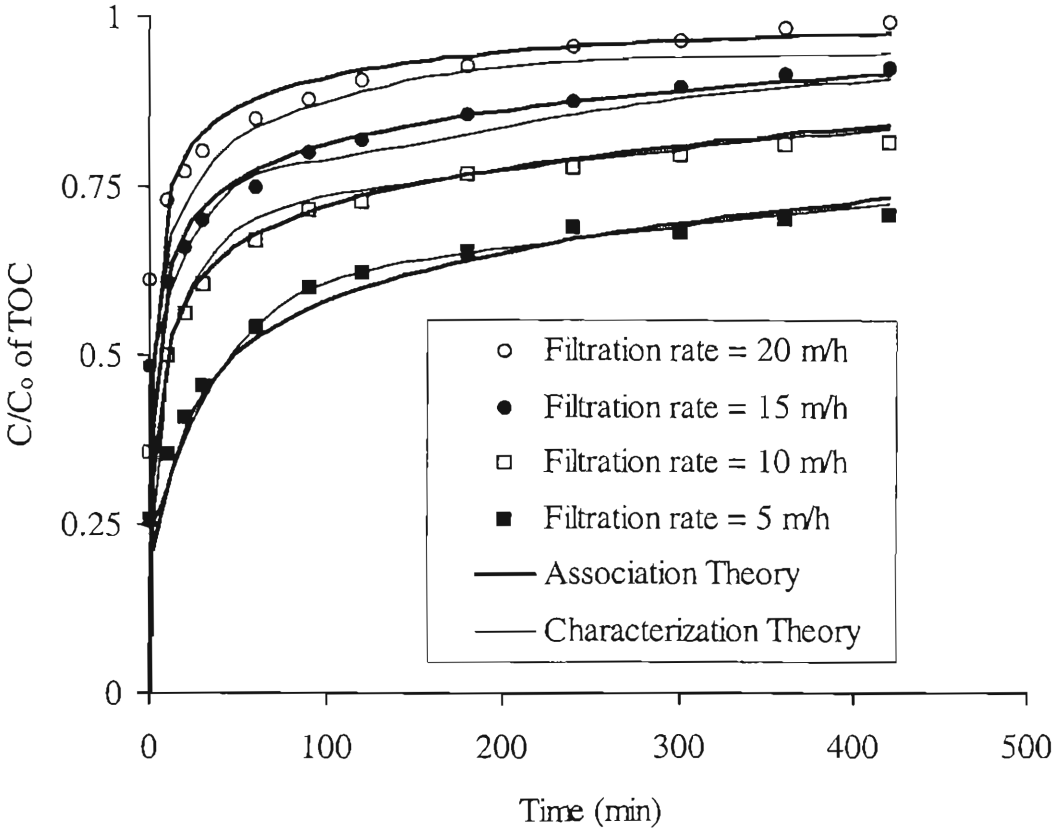


Figure 5. 10 Effect of filtration rate on the effluent quality of the fixed bed system (Bed depth = 20 cm, average initial TOC of the synthetic wastewater = 7.0 mg/L)

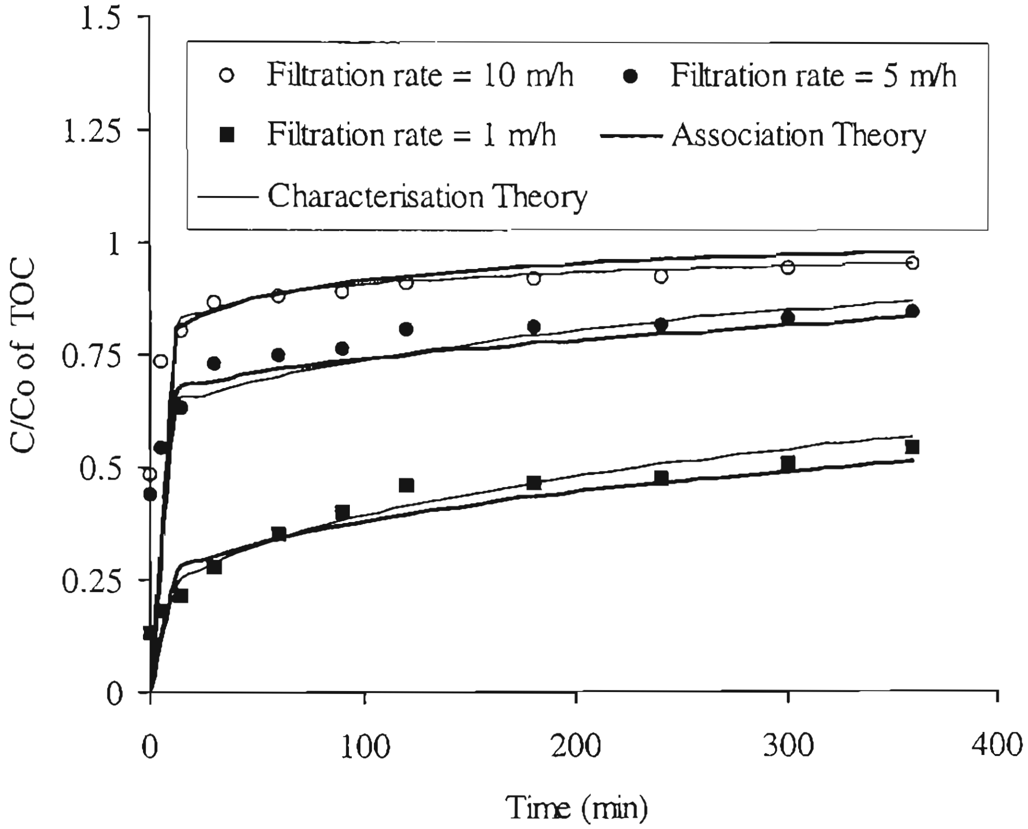


Figure 5. 11 Effect of filtration rate on the effluent quality of the fixed bed system (Bed depth = 4 cm, average initial TOC of the synthetic wastewater = 3.7 mg/L)

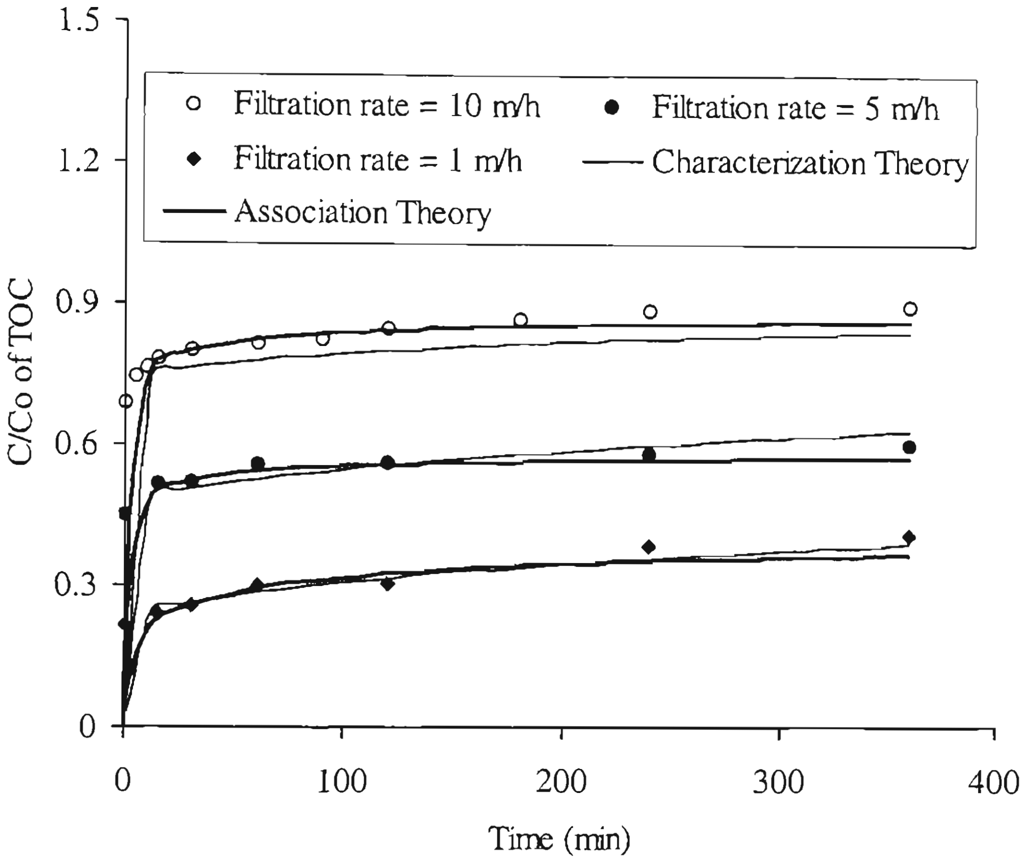


Figure 5.12 Effect of filtration velocity on the effluent quality of the fixed bed system (Bed depth = 4 cm, average initial TOC of the biologically treated sewage effluent = 4.3 mg/L)

5.6.4 Effect of Initial Organic Concentration

The result of the effect of the initial organic concentration on the film mass transfer coefficient (k_f) is summarized in Table 5.5. The experimental results and their predictions using the association theory and the characterization theory are presented in Figures 5.13 and 5.14. The effect of the filtration velocity was analysed at two different bed depths (4 and 20 cm) and filtration velocities (1 and 10 m/h). The film mass transfer coefficient (k_f) was decreased with the rise in the initial organic concentration of the feed solution. It may be due to the scarcity of the adsorption site as the organic contents of the solution are increased. The other possibility is due to the effect of inorganic substances. Since the inorganic contents of the synthetic solution was also increased proportionally, its unfavourable-for-adsorption effect (as discussed in Chapter 3) would also increase, which reduces the rate of mass transfer.

Table 5.5 Effect of initial TOC concentration on the mass transfer coefficient of the fixed bed adsorption

Variable (TOC, mg/L)	Film mass transfer coefficient (m/s)		Remarks
	Association theory (x 10^{-6})	Characterization theory (x 10^{-6})	
Synthetic wastewater			
3.7	2.7	2.5	v = 1 m/h, d = 4 cm
6.9	1.6	1.5	v = 1 m/h, d = 4 cm
3.9	2.7	2.6	v = 10 m/h, d = 20 cm
6.9	2.6	2.5	v = 10 m/h, d = 20 cm
12.2	2.2	2.0	v = 10 m/h, d = 20 cm
16.2	2.0	1.8	v = 10 m/h, d = 20 cm

Note: v = filtration velocity, d = fixed bed depth

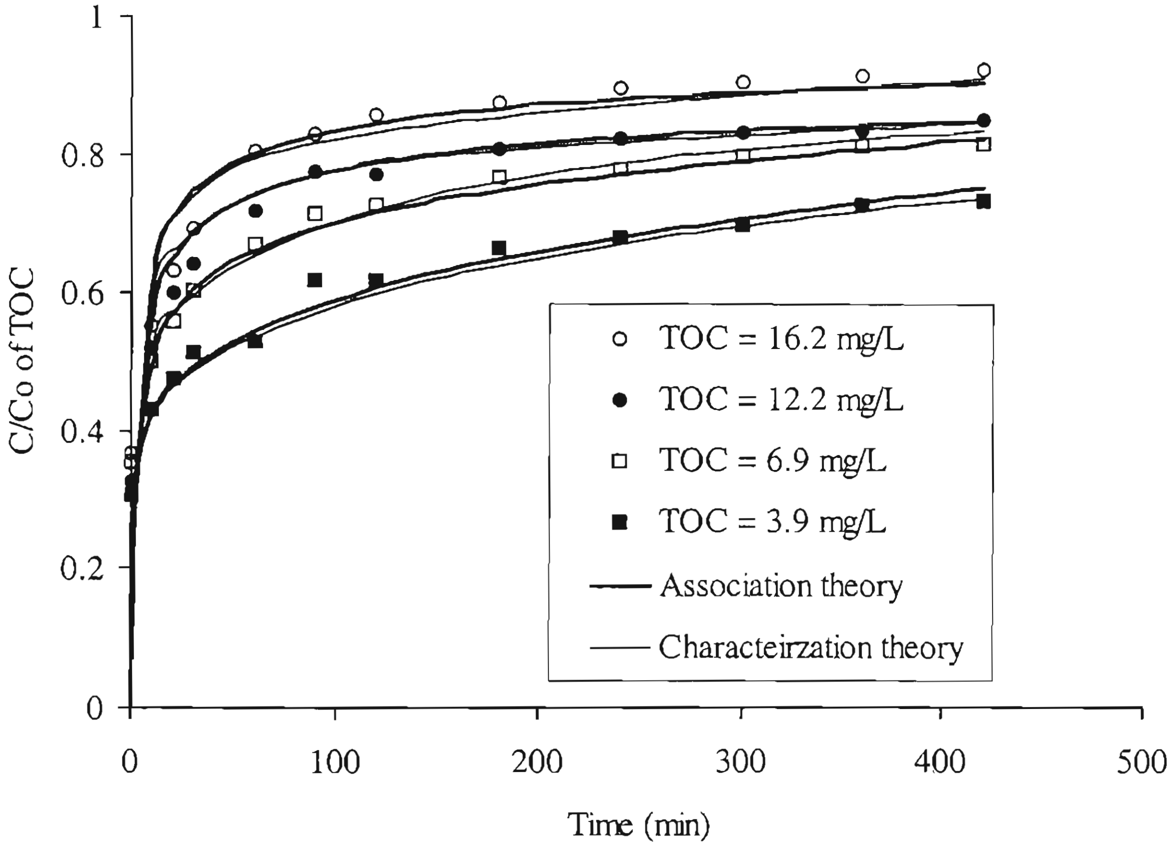


Figure 5.13 Effect of initial organic concentration of the synthetic wastewater on the effluent quality of the fixed bed system (Bed depth = 20 cm, filtration velocity = 10 m/h)

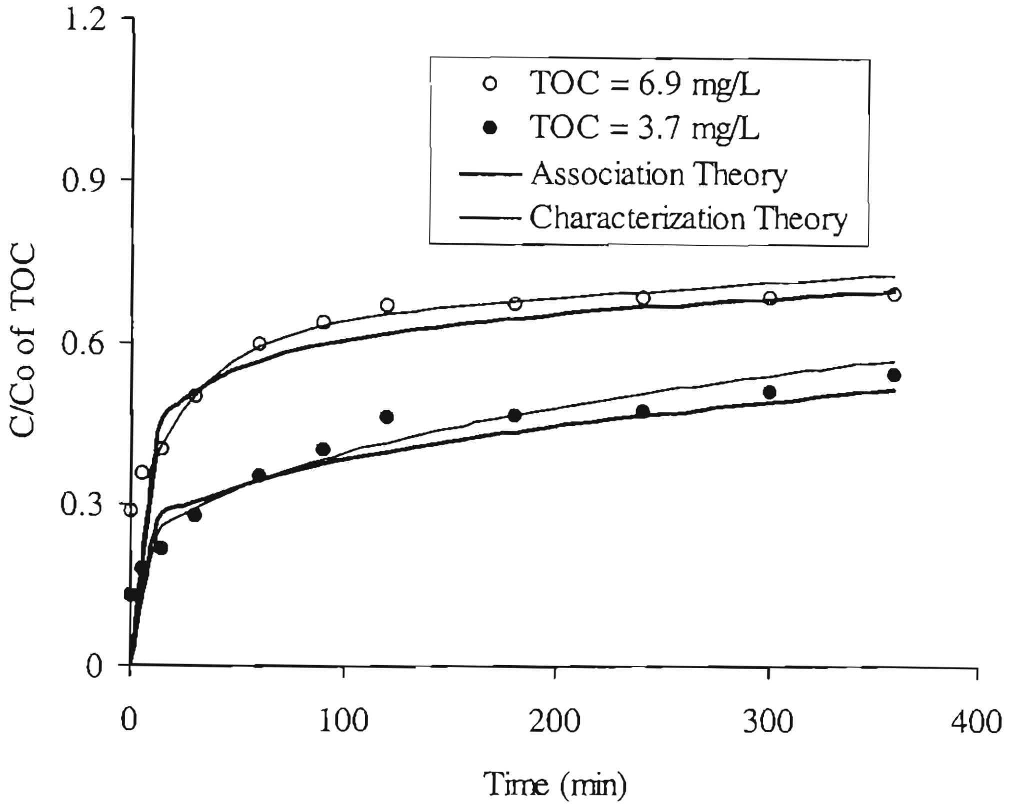


Figure 5.14 Effect of initial organic concentration of the synthetic wastewater on the effluent quality of the fixed bed system (Bed depth = 4 cm, filtration velocity = 1 m/h)

5.7 Conclusions

The GAC fixed system was effective in removing organics from the wastewater. The performance of the system was affected by several operational parameters such as fixed bed depth, filtration velocity, and initial organic concentration of the feed solution. Deeper the fixed bed depth, or lower the filtration velocity, higher was the organic removal efficiency of the system. The adsorption rate was not affected by the change in the fixed bed depth. However, it was found to increase with the rise in filtration velocity but it decreased when the initial organic concentration was increased. The adsorption rate was higher in the biologically treated effluent taken from a sewage treatment plant than that in the synthetic wastewater prepared in the laboratory. The film mass transfer coefficient determined in the fixed bed adsorption system is slightly less than that determined in the batch adsorption system. It is due to the higher mixing intensity used in batch experimentation. The adsorption parameters obtained from the association theory and the characterization theory, were effective in predicting the experimental results of the fixed bed system.

Chapter 6

Biodegradation of Organics in Granular Activated Carbon (GAC) Biofilter

6.1 Introduction

The application of adsorption system with granular adsorbent is usually implemented in the fixed bed adsorption mode. The adsorbent, usually GAC, is packed in a column and the wastewater (or water or air) with pollutants is passed through the column so that the target pollutants are adsorbed onto the adsorbent. The adsorption capacity of GAC is gradually reduced with its operational time depending on the organic and hydraulic loading rates of the wastewater through the column. However, the adsorbed organics on the surface of the GAC leads to the growth of microorganisms on the surface of the adsorbent, which can further assimilate and degradate the organic matters. The fixed bed system with attached microorganisms on the surface of the adsorbent is referred to as biofilter. In this Chapter, the performance of a GAC biofilter has been evaluated in terms of total organic carbon (TOC) removal. Synthetic wastewater and biologically treated effluent of a sewage treatment plant were used as feed solution to the GAC biofilter.

6.1.1 Biofilter in Wastewater treatment

Biofilter is one of the most important units that can be utilized in advanced sewage treatment processes to remove the majority of organics that are not removed in the secondary treatment. Biofiltration can be an alternative treatment technology and a promising treatment process to remove refractory organic matters to meet the criteria of wastewater reuse for various purposes. Due to the lower concentration of organic substances in the biologically treated secondary effluent, biofiltration is the most suitable biological treatment option in the tertiary wastewater treatment. Biofilter is also the economical and environmentally friendly solution in treating wastewater of relatively small volume (e.g. wastewater from hotel, small industries or small communities). Previous studies on biofilter have shown that it could remove organics and nutrients in significant quantities and produce high quality effluent (Yang et al., 2001; Boon et al., 1997; and Sakuma et. al., 1997). Yang et al. (2001) used three different shapes and types of filter media (plastic double cross pall rings, plastic beehive-shape plate block and crushed coke pieces) to study the efficiency of the biofilter in treating the aquaculture water for reuse. They found the characteristics of the filter media more critical than the flow scheme that can affect the efficiency of the biofilter. Boon et al. (1997) used granite and blast furnace slag as biofilter media to treat the raw wastewater. They concluded from their studies at six treatment sites that the organic loading rates (biochemical oxygen demand, ammonia) should not exceed a particular value to meet the effluent discharge criteria. The critical value of the organic loading depends on the filter media type and the depth of the filter.

6.1.2 Biofilter in Drinking Water Treatment

The conventional water treatment processes are not adequate to remove all the pollutants. It has been observed that the inner surface of water distribution pipelines carrying potable water is coated with layers of biomass in few years of service period (Van der Kooij et. al., 1982; LeChevallier and Lowry, 1990; Bouwer and Crowe, 1988). The biodegradable organic matter (BOM), NH_4^+, Fe^{2+}, Mn^{2+}, NO_2^-, dissolved H_2 and several other reduced species of sulphur are the most pertinent components that can cause bacterial mass on the water distribution pipelines (Rittmann and Huck, 1989). These substances, especially the BOM are not removed effectively in the conventional water treatment processes. Due to the "regrowth" or "aftergrowth" of the microbial mass in the pipelines, the drinking water is considered biologically not stable. Even though there is no direct evidence of its instant health hazardous side effects, use of such drinking water in long run cannot be assured to be safe. Besides the by-products of chlorine disinfections, disinfections by-products (DBPs) are often carcinogenic and harmful. Ozonation can reduce the above-mentioned DBPs, but it increases the fraction of organic matters with hydroxyl, carbonyl and carboxyl groups that can encourage bacterial regrowth in the distribution line (Goel et al., 1995). Therefore, biofilter is normally recommended to be included in the water treatment processes after ozonation. The increased organic matters after ozonation considerably enhance biological activity in the biofilter (DeWaters and DiGiano, 1990). Because of the microbial re-growth in drinking water distribution lines and more stringent regulation of disinfectants and disinfection by-products (DBPs), biological treatment especially granular activated carbon (GAC) biofilter has been assessed as an essential part of drinking water treatment (Bouwer and Crowe, 1988; Hozalski et. al., 1995; Ahmad and Amirtharajah, 1998; Carlson and Amy, 1998). It has been found that bio-filter has a high potential in removing pollutants such as biodegradable organic materials and synthetic organic compounds that produce odour and taste in drinking water. Heterotrophic bacterial masses attached to the filter media as biofilm oxidize most of the organics and use it as an energy supply and source of carbon. Removal of these organic matters not only impairs microbial regrowth but also reduces taste and odours, the amount of organic precursor (available to form disinfection by-products, corrosion potential) and other micropollutants of health and aesthetic concern.

Since the use of a biofilter has been felt necessary in both water and wastewater treatment processes, many studies have been done in last two decades especially with GAC. However, theoretically it is still difficult to explain the behaviours of a biofilter. The growth of different types of microorganisms in different working conditions makes it impossible to generalize the microbial activities in a biofilter. Therefore, it is important to evaluate the biofilter in terms of its operating conditions and the characteristics of the influent. The biofilters operated at different filtration rates and influent characteristics can have diverse efficiency for different target pollutants. That is the reason the research works on biofilters are always vital and imperative. Besides, some of the operational drawbacks of the biofilter such as performance fluctuation, maintenance of biomass, and release of microorganisms, have made the research on it more viable and important.

As the performance of a biofilter largely depends on the microbial activities, a constant source of substrates (organic substance and nutrients) is required for its consistent and effective operation. The microbial activities can vary with seasonal variation as well.

The performance of a biofilter can be better in summer than in winter. It is very important to control and maintain the biomass in the filter for its successful operation. A major concern with biological treatment is the introduction of microorganisms into the process itself. Pseudomonas, Bacillus, Azomonas, Alcaligenes, Acinetobacter and Flavobacterium are some of microorganisms reported to be attached on GAC (Cairo et al., 1979). The bacterial aggregates (heterotrophic plate count or coliform or enteropathogenic bacteria) attached to sand or GAC particles in the biofilter are more resistant to disinfections than individual bacterial cells (LeChevallier et. al. 1984). It may be due to the production of extracellular polymer by the bacteria that provides attachment to the media like sand or GAC as well as protection against disinfectants. Hence, higher disinfectants dose or longer contact time is required to effectively disinfect the effluent from a biofilter.

6.2 Major Factors Influencing the Performance of a Biofilter

6.2.1 Filter Media

The economical and efficient operation of a biofilter highly depends on the characteristics of its filter media. While selecting the filter media, one should also consider the source and concentration of targeted pollutants. For the treatment of biologically treated secondary effluent, the right choice of the filter media can be the blast furnace slag or granite or synthetic media depending upon the volume of wastewater, whereas for the treatment of tertiary wastewater or for removing offensive organic substances from the drinking water supply line, GAC or anthracite or filter coal or sand could be the better choice. Previous studies with tertiary wastewater or surface water have shown that GAC (an adsorptive media) can be a better choice than anthracite or sand (non-adsorptive media) for the removal of organic substances from tertiary wastewater or surface water (LeChevallier et. al., 1992; Wang et al., 1995). A

GAC filter might have less specific surface area (surface area per unit volume of filter) available for microbial attachment than a sand filter because the effective size of sand is usually smaller than GAC. Further the size of GAC micropores (1-100 nm) seem to be too small for microorganisms (typically greater than 200 nm in diameter) penetration inside these micropores (AWWA research and technical committee report, 1981). However, the macroporous structure and irregular surface of GAC offer more appropriate sites for biomass attachment. GAC can adsorb and retain slowly biodegradable components that can be biodegraded by the attached microbial mass leading to continuous bioregeneration of the GAC. It also provides protection from shear loss of biomass. Wang et. al. (1995) found the mesoporous GAC surface texture more suitable for biomass attachment than macroporous and microporous GAC.

6.2.2 Empty Bed Contact Time (EBCT)

The contact time, usually expressed as empty bed contact time (EBCT), is a key design and operating parameter of a biofilter. Zang and Huck (1996a) have introduced the concept of dimensionless contact time incorporating EBCT, specific surface area of the medium and substrate diffusivity and rate of biodegradation. Usually the percentage removal of organic substances increases with increase in contact time up to an optimum value. Both the filter depth and hydraulic loading can be changed to increase the EBCT. Previous studies have shown that the contact time (and not the hydraulic loading) is the key variable responsible for organic removal. For a given EBCT, organic removal is independent of hydraulic loading in the range typically used in rapid filtration (Servais et al., 1994; Carlson and Amy, 1995). Huck et al. (1994) showed that the organic removal efficiency of a biofilter could be approximated by a first-order model. It suggests that increasing EBCT will not improve the organic removal efficiency of a biofilter in proportional rate. However, Servais et al. (1992) reported a linear increase in BDOC removal with the increase in EBCT between 10 – 30 min of the biofilter. The past studies (Price, 1994; Hozalski et al. 1995), which showed very little or no effect of EBCT on organic removal efficiency of a biofilter, might be due to partial acclimatization of the biofilter.

6.2.3 Backwashing

It is important to select an appropriate backwashing technique for successful operation of a biofilter. The biomass attached to the filter media has to be carefully maintained during backwashing (Ahmad et. al, 1998; Bouwer and Crowe, 1998; Bablon et al. 1988; Graese et al. 1987). Ahmad and Amirtharajah (1998) found that biological particles (measured as heterotrophic plate counts and cellular adenosine triphosphate), which are usually hydrophobic in nature, are attached to filter media (GAC) with a greater force than non-biological clay particle (measured as turbidity). The difference in the detachment of these particles during backwashing should be taken into account while selecting or optimising the backwashing of a biofilter. Previous researches have shown no major loss of biomass during backwash of the biofilter (Ahmad et al., 1998, Lu and Huck, 1993). Servais et al (1991) backwashed the GAC biofilter with air scour and water routinely every 50-100 hours of continuous run, but no significant difference in vertical biomass profiles before and after backwash was observed.

Other factors that can influence the performance of a biofilter are the temperature and the presence of oxidants, i.e. O_3, H_2O_2, Cl_2, and NH_4Cl etc. in the influent (Urfer et al., 1997).

6.3 Fundamentals of Biological Processes in a Biofilter

Basically, three main biological processes can be assumed to occur in a biofilter, (i) attachment of microorganims, (ii) growth of microorganism and (iii) decay and detachment of microorganisms. As the success of a biofilter depends on the growth and maintenance of microorganisms (biomass) on the surface of filter media, it is necessary to understand the mechanisms of attachment, growth and detachment on the surface of the filter media. This will help to model and predict the performance of the biofilter in an accurate manner.

6.3.1 Attachment of Microorganisms

There are four main processes by which microorganisms can attach and colonize on the surface of the filter media of a biofilter, (i) transportation, (ii) initial adhesion, (ii) firm attachment and (iv) colonization (Van Loosdrecht et al, 1990). The transportation of microorganisms to the surface of the filter media can further be controlled by four main methods, (i) diffusion (Brownian motion), (ii) convection, (iii) sedimentation due to gravity and (iv) active mobility of the microorganisms. As soon as the microorganisms reach the surface, initial adhesion occurs which can be reversible or irreversible depending upon the total interaction energy, which is sum of Van der waals force and electrostatic force. The DLVO (Derjaguin-Landau-Verwey-Overbeek) theory is often used to describe the adhesion of the microorganisms on the surface of the filter media. The processes of firm attachment and colonization of microorganisms depend on influent characteristics (such as organic type and concentration) and surface properties of the filter media. The steric effects, hydrophobicity of the microorganisms, contact angle and electrophoretic mobility values are often taken into consideration to estimate the attachment of microorganisms on the surface of filter media.

6.3.2 Substrate Utilization and Biofilm Growth

A biofilm is an accumulation of microorganism attached to a surface. Since the microorganisms are attached to the surface, the supply of substrate (food) to the microorganisms in a biofilm is mainly controlled by the bulk and surface transport phenomena. The substrate must be transported from the bulk liquid to the biofilm's outer surface where it has to diffuse into the biofilm for its metabolism. Thus, at least three factors influence the rate of substrate utilization within a biofilm: (i) substrate mass transport to the biofilm, (ii) diffusion of the substrate into the biofilm and (iii) utilization kinetics within the biofilm. The other key factors that affect the performance of a biofilm process are the growth yield of the substrate and the physical factors affecting the biolfilm detachment.

Rittmann and McCarty (1978) developed a model of bacterial film kinetics incorporating liquid layer mass transport, Monod kinetics and molecular diffusion. The conceptual basis of the model is shown in Figure 6.1.

The substrate transport from the bulk liquid to the outer surface of the biofilm was described by Fick's first law (Equation 6.1),

$$J = \frac{AD(S - S_s)}{L_d} \tag{6.1}$$

where J = substrate flux into the biofilm ($mg/m^2/s$), A = surface area normal to the filter media (m^2), D = molecular diffusion coefficient for the substrate in the bulk liquid phase (m^2/s), S = substrate concentration in the bulk solution (mg/L), S_s = substrate concentration at the outer surface of the biofilm (mg/L) and L_d = diffusion layer thickness (m).

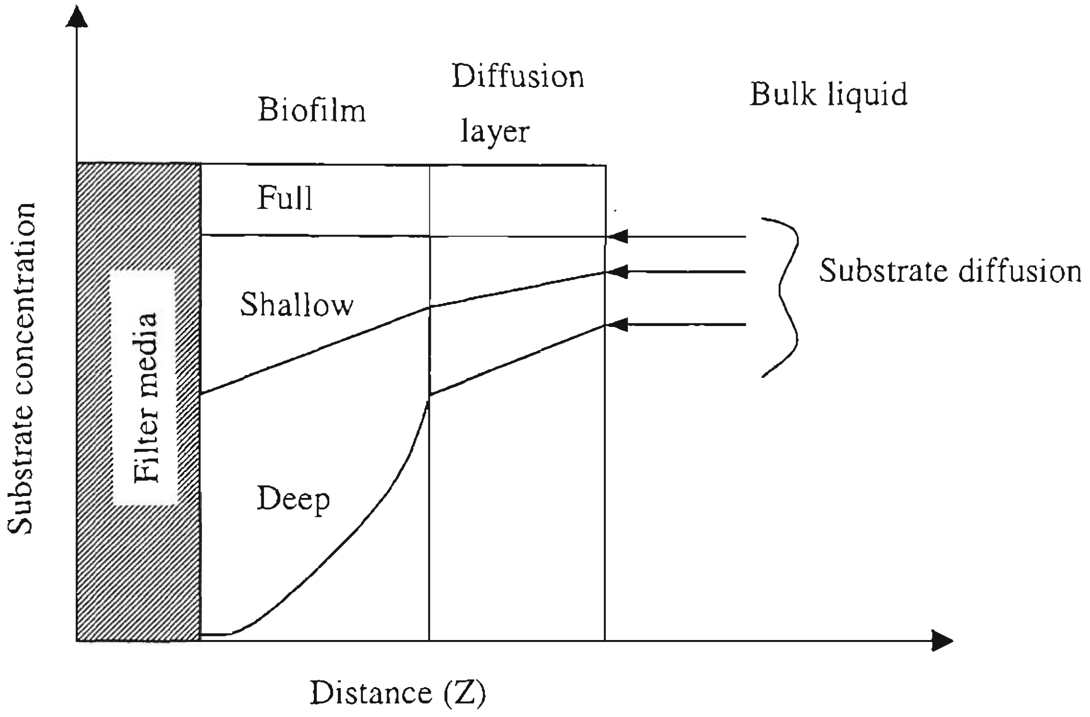


Figure 6.1 Idealized biofilm and characteristic deep, shallow, and fully penetrated profiles of the substrate concentration (after Rittmann, 1995)

The substrate transport to the microorganism inside the biofilm by molecular diffusion was described by Fick's second law (Equation 6.2), and the substrate utilization by the Monod expression (Equation 6.3).

$$r_{diff} = D_f \frac{\partial^2 S_f}{\partial Z^2} \tag{6.2}$$

$$r_{utl} = \frac{k X_f S_f}{K_s + S_f} \tag{6.3}$$

where r_{diff} = rate for substrate accumulation due to diffusion (mg/m^3/s), D_f = molecular diffusion coefficient of the substrate inside the biofilm (m^2/s), S_f = substrate concentration in the biofilm (mg/L), Z = distance normal to the biofilm surface (m), r_{utl} = rate of substrate utilization in the biofilm (mg/m^3/s), k = maximum specific rate of substrate utilization (mg of substrate /mg of biomass/s), X_f = biomass density of biofilm (mg/L) and K_s = substrate concentration for which the utilization rate is half of its maximum rate (mg/L).

In steady state, the rate of substrate diffusion equals to the rate of utilization. The model is very simple but it does not incorporate the processes of biofilm growth and biofilm loss due to shear and decay or backwashing.

Rittmann and Brunner (1984) developed a transient biofilm model incorporating biofilm growth and loss during non-steady state condition (Equations 6.4 and 6.5)

$$r_{gr} = \frac{YkX_f S_f}{K_s + S_f} A_f L_f \qquad (6.4)$$

$$r_{lss} = b_{tot} X_f A_f L_f \qquad (6.5)$$

where r_{gr} = rate of biomass growth within the biofilm (mg/s), Y = biomass growth per unit mass of substrate consumed (mg/mg), A_f = biofilm surface area (m^2), L_f = biofilm thickness (m), r_{loss} = rate of loss of biomass (mg/s) and b_{tot} = first order biofilm detachment coefficient for decay and shear (s^{-1}).

6.3.3 Detachment of Biomass

The success of a biofilter highly depends on the efficient maintenance of biomass attached to the filter media. Biomass detachment is one of the most important mechanisms that can affect the maintenance of biomass in a biofilter. Erosion, abrasion, sloughing, grazing or predation and filter backwashing are the mostly observed and literally discussed detachment mechanisms. Erosion of biomass occurs due to the fluid shear whereas abrasion of biomass is the process of scraping the biocell off the surface by collision of external particle. Similarly, large patches of biomass are detached by sloughing and a part of biomass especially on the outer surface of the biofilm may be lost due to the grazing of protozoa. Evaluation of the biomass loss due to filter backwashing is very important in operational point of view. Backwash bed expansion, mode of backwash such as air scour, chlorinated water backwash may affect biomass during backwashing. However, previous study has shown that the effective biomass is not lost during normal filter backwash (Ahmad and Amirtharatha, 1998).

Despite these many possible detachment mechanisms, most of studies have been concentrated on biomass loss due to shear stress only. A summary of the reported biomass loss due to shear stress is presented in Table 6.1.

Table 6.1 Detachment rate expressions (after Hozalski, 1996)

Detachment rate $[ML^{-2}T^{-1}]$	Reference
$k_d . X_f . L_f$	Kreikenbohm and Stephan (1985), Chang and Rittmann (1987), Rittmann (1989)
$k_d . (X_f L_f)^2$	Bryers (1984), Trulear and Characklis (1982)
$k_d . X_f . (L_f)^2$	Wanner and Gujer (1986)
$k_d . X_f . \tau$	Bakke et al (1990)
$k_d . X_f . L_f . \tau^{0.58}$	Rittmann (1982)
$L_f . (k'_d + k''_d . \mu_g)$	Speitel and DiGiano (1987)
$k_d . \mu_{gave} . X_f . (L_f)^2$	Peyton and Characklis (1993)

Where,
k_d = detachment rate coefficient (expression dependent units)
k'_d = detachment rate coefficient (M/L^3T)
k''_d = detachment rate coefficient (M/L^3)
μ_g = specific growth rate (1/T)
μ_{gave} = average specific growth rate (1/T)

All the expressions shown in Table 6.1 were derived from steady state condition except the expression reported by Speitel and DiGiano (1987). Speitel and DiGiano (1987) found that under non-steady state condition (which may usually occur due to filter backwash etc.), rate of biomass loss due to shear stress was directly proportional to the biomass growth rate and it was not significantly influenced by the amount of attached biomass.

6.4 Development of Mathematical Modelling

There are a very few researches reported in the literature to predict the performance of a biofilter. Most of the studies are based on the assumption of steady state condition (Rittmann, 1990; DiGiano and Speitel, 1993). Rittmann and McCarty (1980) first introduced a steady-state biofilm model in which, the mass transport and the microbial kinetics were expressed by Fick's second law and Monod equation respectively. In steady state, rate of substrate diffusion is equal to the rate of substrate utilization. It was assumed that minimum bulk substrate concentration (S_{min}) is required to maintain the steady-state biofilm in the filter.

$$D_f \frac{\partial^2 S_f}{\partial Z^2} = \frac{k X_f S_f}{K_s + S_f} \tag{6.6}$$

where,

D_f = molecular diffusion coefficient of the substrate inside the biofilm (m^2/s),

Z = distance normal to the biofilm surface (m),

k = maximum specific rate of substrate utilization (mg of substrate /mg of biomass/s),

X_f = biomass density of biofilm (mg/L)

K_s = substrate concentration at which the utilization rate is half of its maximum rate (mg/L).

S_f = substrate concentration in the biofilm (mg/L)

$$S_{\min} = K_s \frac{b_{tot}}{(Y q_m - b_{tot})} \tag{6.7}$$

where,

S_{min} = the minimum substrate concentration that is capable of sustaining a steady-state biofilm (mg/L)

q_m = maximum specific rate of substrate utilization (mg/mg/s)

b_{tot} = first order biofilm detachment coefficient for decay and shear (s^{-1}).
Y = biomass growth per unit mass of substrate consumed (mg/mg)

The model describes the fundamental biological processes but does not take into account the biofilm growth with time.

Chang and Rittmann (1987) developed a model for the kinetics of biofilm on activated carbon (BFAC) incorporating film mass transfer, biodegradation, and adsorption of a substrate, as well as biofilm growth. Freundlich isotherm was used to relate the bulk phase concentration to the solid (adsorbed) phase, and the mass transfer was expressed by homogeneous solid diffusion model.

$$\frac{\partial q}{\partial t} = \frac{D_s}{r_s^2}\frac{\partial}{\partial r_s}\left(r_s^2\frac{\partial q}{\partial r_s}\right) \qquad 0 \le r_s \le R \tag{6.8}$$

Boundary conditions

$$\frac{\partial q}{\partial t} = \frac{D_s}{r_s^2}\frac{\partial}{\partial r_s}\left(r_s^2\frac{\partial q}{\partial r_s}\right) \qquad 0 \le r_s \le R \tag{6.9}$$

$$R^2 D_f \left.\frac{\partial S_f}{\partial r_f}\right|_{r_f=0} = \rho_p \frac{\partial}{\partial t}\int_0^R q r_s^2 dr_s \qquad r_s = R,\ t \ge t_0 \quad \text{and} \tag{6.10}$$

Freundlich isotherm

$$q_w = K_q (S_w)^{1/n} \tag{6.11}$$

where,

q = surface concentration of adsorbed substrate (mg/mg)

D_s= surface diffusivity (m^2/s)

r_s= radial coordinate in activated carbon (m)

t = time (s)

R = radium of the carbon particle (m)

S_f = rate limiting substrate concentration in the biofilm (mg/L)

D_f = substrate diffusion coefficient in the biofilm (m^2/s)

r_f = radial coordinate in the biofilm (m)

ρ_p = apparent particle density of dry activated carbon (mg/L)

q_w = surface concentration at biofilm/activated carbon interface (mg/mg)

K_q = Freundlich isotherm coefficient

n = Freundlich exponent coefficient

S_w = substrate liquid concentration at biofilm/activated carbon interface (mg/L)

They described the non-steady state diffusion (with biological reaction) of substrate into biofilm by Fick's law and the Monod kinetics.

$$\frac{\partial S_f}{\partial t} = D_f \frac{\partial^2 S_f}{\partial r_f^2} - \frac{k S_f}{K_s + S_f} X_f \qquad 0 \le r_f \le L_f \tag{6.12}$$

Boundary condition

$$k_f (S_b - S_s) = D_f \left. \frac{\partial S_f}{\partial r_f} \right|_{r_f = L_f} \qquad t \ge t_0 \tag{6.13}$$

With the assumption that the density of the biofilm is constant, they related the growth of the biofilm to the increase in the biofilm thickness as follows:

$$\frac{d\left(L_f X_f\right)}{dt}=\int_0^{L_f}\left(\frac{YkS_f}{K_s+S_f}-b-b_s\right)X_f dr_f \tag{6.14}$$

where,

k = maximum specific rate of substrate utilization (mg/mg/s)

K_s = half-velocity concentration (mg/L)

X_f = cell density of biofilm (mg/L)

L_f = biofilm thickness (m)

S_b = substrate concentration in the bulk liquid (mg/L)

S_s = substrate concentration at liquid/biofilm interface (mg/L)

k_f = liquid-film mass transfer coefficient (m/s)

Y = true yield of biomass (mg/mg)

b = biofilm decay coefficient (s^{-1})

b_s = biofilm shear loss coefficient (s^{-1})

They utilized the model in a column reactor with high recycle flow rate for phenol removal from the synthetic wastewater. All the fundamental processes have been included in this model. However, the non-steady state condition due to backwashing, change in the filter bed porosity and hence the filter depth have not been included in this model.

Zhang and Huck (1996b) applied the steady-state biofilm model of Rittmann and MaCarty (1980) and developed the concept of dimensionless Empty Bed Contact Time (EBCT), which allows comparison of results among different surrogate parameters such as AOC and BDOC (Biodegradable dissolved organic carbon).

Wanner and Gujer (1986) developed a very general multispecies biofilm model for wastewater biofilms. The model is very general and can be easily utilized to many types of microbial interactions. Other multispecies biofilm models with similar structures were developed by Namkung and Rittmann (1987), and Rittmann and

Manem (1992). In these models, the biomass was divided into three categories, heterotrophs, autotrophs and inert particulate materials. It was also observed that the substrate removal efficiency strongly depends on the factors that confine biofilm growth such as configuration of the bioreactor and different biomass detachment mechanisms i.e. shear and sloughing. The substrate removal is directly proportional to the biofilm thickness up to a critical thickness, beyond which substrate removal no longer increases. Different critical thickness of the biofilm has been reported by the previous investigators. Harremoes (1978), La Motta (1974) and Hoehn and Ray (1973) have reported the critical thickness as 65 μm, less than 70 μm and approximately 150 μm respectively.

Billen et al. (1992) developed the CHABROL model to predict BDOC removal. The model incorporates the major microbial processes and substrates of different biodegradabilities. The model showed that BDOC removal is directly proportional to influent BDOC and EBCT. The three kinds of interaction,: (i) interaction with dissolved organic matter, (ii) interaction with the solid support, and (iii) the mortality and grazing of bacteria have been incorporated in the model to describe the dynamics of the bacterial community colonizing on the support (filter media). The model consists of six state variables, namely, H_1 and H_2 (rapidly and slowly hydrolysable biodegradable macromolecules of organic matters), S (concentration of directly usable monometric substances), B_1 (bacterial biomass actively attached to the solid support), B_2 (the bacterial biomass reversibly adsorbed to the support), and B_3 (free bacterial biomass in interstitial water. They expressed all these parameters in the mathematically as follows:

$$\frac{dH_1}{dt} = -e_{1(\max)} \frac{H_1}{H_1 + K_{H_1}} B_T + \alpha k_d B_T - \frac{1}{\tau}\left(H_1 - H_{1(0)}\right) \qquad (6.15)$$

$$\frac{dH_2}{dt} = -e_{2(\max)} \frac{H_2}{H_2 + K_{H_2}} B_T + \beta k_d B_T - \frac{1}{\tau}\left(H_2 - H_{2(0)}\right) \qquad (6.16)$$

$$\frac{dS}{dt} = e_{1(\max)} \frac{H_1}{H_1 + K_{H_1}} B_T + e_{2(\max)} \frac{H_2}{H_2 + K_{H_2}} B_T - b_{\max} \frac{S}{S + K_s} B_T - \frac{1}{\tau}(S - S_0) \tag{6.17}$$

$$\frac{dB_1}{dt} = Yb_{\max} \frac{S}{S + K_s} \left[B_2 \frac{SP - B_1}{SB} + B_1 \frac{SP - B_1}{SP} \right] - k_d B_1 \tag{6.18}$$

$$\frac{dB_2}{dt} = k_{ads} B_3 (SB - B_1 - B_2) - k_{des} B_2 - k_2 B_2 \tag{6.19}$$

$$\begin{aligned} \frac{dB_3}{dt} = {} & +Yb_{\max} \frac{S}{S + K_s} \left[B_3 + B_2 \left(1 - \frac{SP - B_1}{SB} \right) + B_1 \left(1 - \frac{SP - B_1}{SP} \right) \right] \\ & - k_{ads} B_3 (SB - B_1 - B_2) + k_{des} B_2 - k_d B_3 - \frac{1}{\tau}(B_3 - B_{3(0)}) \end{aligned} \tag{6.20}$$

where,

State variables:

H_i = macromolecular organic matter of utilization class i, (mgC/L)
S = directly utilizable monomeric substrate (mgC/L)
B_1 = biologically attached bacterial biomass (μgC/cm^3)
B_2 = reversibly adsorbed bacterial biomass (μgC/cm^3), and
B_3 = free bacterial biomass in the liquid phase (mgC/L),

Parameters related to dissolved organic matter utilization by bacteria:

$e_{i(max)}$ = maximum rate of H_i hydrolysis (h^{-1})
K_{Hi} = half saturation constant for H_i hydrolysis (mgC/L)
b_{max} = maximum uptake rate of S (h^{-1})
K_s = half saturation constant for S uptake (mgC/L)
Y = growth yield (dimensionless)

Parameters related to mortality and grazing:

k_d = overall rate of bacterial mortality (h^{-1})
α, β = fraction of bacterial biomass recycled as H_1 and H_2 respectively upon mortality (dimensionless)

Parameters related to the interactions with the solid support:

SP = maximum capacity for biological bacterial fixation (μgC/cm^3)
SB = maximum adsorption capacity for bacteria (μgC/cm^3)
k_{ads} = adsorption constant for bacteria [1/(μgC/cm^3/h)]
k_{des} = desorption constant for bacteria (h^{-1})

The model is capable of relating the macroscopic functioning of biofilters to the kinetics of the basic microbiological processes. It can predict the fixed bacterial biomass and the biodegradable organic matter in the effluent from the characteristics of influent water for a given values of contact time and temperature. The model was also calibrated and validated with pilot and full size filters run in the Neuilly-sur-Marne and Choisy-le-Roi plants.

Wang and Summers (1995) divided the biodegradable organic matter into easily and slowly biodegradable fractions. They predicted the biomass and DOC concentration along the filter depth.

Huck et al. (1994) developed a first order biofilm model. The model is more practical than accurate in predicting the performance of a biofilter. It assumes that the organic removal in a biofilter is directly proportional to the influent concentration. Boon et. al. (1997) conducted pilot-scale biofilter experiments with sewage and developed empirical equations to predict the Biochemical oxygen demand (BOD_5) and ammonia removal by the biofilters.

Hozalski and Bouwer (2001a) developed a numerical model called BIOFILT, to simulate the non-steady state behaviour of biologically active filters used for drinking water treatment. The model is capable of simulating substrate (biodegradable organic matter) and biomass (both attached and suspended) profiles in a biofilter as a function of time. The model also has capability to simulate the effects of a sudden loss in attached biomass due to filter backwash on substrate removal efficiency (Hozalski and Bouwer, 2001b). The backbone of the model is the one dimensional advection-dispersion equation with reaction as follows:

$$\frac{\partial S}{\partial t} = D'\frac{\partial^2 S}{\partial x^2} - v\frac{\partial S}{\partial x} - \frac{kSX_{susp}}{K_s + S} - \frac{a}{\varepsilon}J_f \qquad (6.21)$$

Boundary conditions:

$$vS_0 = vS_{x=x_1} - D'\frac{dS}{dx} \quad for \quad x = 0, \quad t \geq 0 \qquad (6.22)$$

$$\frac{dS}{dx} = 0 \quad for \quad x = L_b, \quad t \geq 0 \qquad (6.23)$$

Initial conditions:

$$X_{susp} = 0,\ \ S = S_0,\ \ and \quad L_f = 0 \qquad for\ \ 0 \leq x \leq L_b,\quad t = 0 \tag{6.24}$$

where,

S = substrate concentration (mg/L)

D'= dispersion coefficient (m^2/s)

v = fluid velocity (m/s)

x = distance along the biofilter length (m)

k = maximum rate of substrate utilization (mg/mg/s)

K_s = Monod half-velocity coefficient (mg/L)

X_{susp} = suspended cell concentration (mg/L)

a = specific surface area of the media (m^{-1})

J_f = flux of substrate into the biofilm (mg/m^2/s)

ε = bed porosity

They represented the transport of the suspended biomass (neglecting the dispersion, growth, and decay of biomass on suspension), and the biomass accumulation on the biofilter as follows:

$$\frac{\partial X_{susp}}{\partial t} = -v\frac{\partial X_{susp}}{\partial x} + \frac{aX_f\sigma}{\varepsilon}L_f - \frac{X_{susp}\beta}{\theta\varepsilon} \tag{6.25}$$

$$\frac{\partial L_f}{\partial t} = \frac{YJ_f}{X_f} + \frac{X_{susp}\beta}{X_f a\theta} - b_{tot}L_f \tag{6.26}$$

where,

L_f = biofilm thickness (m)

σ = biofilm shear loss coefficient (s^{-1})

β = filtration efficiency (= ratio of the effluent particle concentration to the influent particle concentration)

θ = empty bed contact time (s)

b_{tot} = overall loss rate of biomass due to both decay and fluid shear (s^{-1})

They modelled the biomass loss due to backwashing as an instantaneous reduction in biofilm thickness throughout the entire biofilter bed depth, and computed the biofilm thickness for each discrete segment of the biofilter bed after backwashing (post-BW) from the values before backwashing (pre-BW) as follows:

$$L_{f(post-BW)} = L_{f(pre-BW)}(1 - REM) \tag{6.27}$$

where,

REM = fraction of biomass removed by backwashing

The model is very practical and it incorporates most of the fundamental processes of the biofiltration. Some of the limitations of this model are as follows:

(i) It is a single substrate model.
(ii) It assumes that there is no mixing of the filter media during backwashing.
(iii) It does not incorporate the adsorption of substrate that occurs when GAC is the filter media of the biofilter.
(iv) The model requires a lot of input data to perform the simulation.

Despite these limitations, the BIOFILT is the first model that incorporates the backwashing effect in the simulation, and should be considered as the most practical model to date.

In this study, a simple mathematical model was developed to predict the organic removal efficiency of the GAC biofilter incorporating both adsorption and biological degradation. The model is based on the fundamental mechanisms of transport of substrate in the bulk liquid, biofilm growth, transport and biodegradation within the biofilm, and adsorption on activated carbon.

6.4.1 Substrate in the Bulk Liquid

The unsteady-state material balance on the substrate in the bulk liquid is represented by the advection-diffusion equation with adsorption and reaction terms (Equation 6.28)

$$\frac{\partial C}{\partial t} = D_{ax} \cdot \frac{\partial^2 C}{\partial z^2} - v \cdot \frac{\partial C}{\partial z} - \gamma_{bio} - \gamma_{ads} \tag{6.28}$$

with initial and boundary conditions,

$$C = C_0$$

$$D_{ax} \frac{dC}{dz} = -v \cdot \left(C\big|_{z=0^-} - C\big|_{z=0^+} \right) \quad at \quad z = 0$$

$$\frac{dC}{dz} = 0 \quad at \quad z = L$$

where,

C = liquid phase substrate (organic) concentration (mg/L)

D_{ax} = axial dispersion coefficient (m^2/s)

v = fluid velocity (m/s)

z = distance along the biofilter length (m)

Here, γ_{bio} and γ_{ads} are the substrate removal rates by biodegradation and adsorption respectively and can be calculated using Equations 6.28a and 6.28b.

$$\gamma_{bio} = k_{\max} \cdot \frac{C}{K_s + C} \cdot X_s \tag{6.29a}$$

$$\gamma_{ads} = (1 - \varepsilon) \cdot \frac{3N}{4 \cdot \pi \cdot a_p^3} \tag{6.29b}$$

where,

k_{max} = maximum rate of substrate utilization (mg/mg/s)
K_s = Monod half-velocity coefficient (mg/L)
X_s = suspended biomass concentration (mg/L)
a_p = specific surface area of the media (m^{-1})
N = substrate uptake rate of the biofilm ($mg/m^2/s$)
ε = bed porosity

6.4.2 Biomass Suspended in the Bulk Liquid

The suspended biomass in the bulk liquid is given by Equations 6.30.

$$\frac{\partial X_s}{\partial t} = \left(Y \cdot \frac{k_{\max} \cdot C}{K_s + C} - K_d - \frac{\beta}{\theta \cdot \varepsilon} \right) \cdot X_s + \frac{1 - \varepsilon'}{\varepsilon'} \cdot a_f' \cdot X_f \cdot \sigma \tag{6.30}$$

with initial and boundary conditions,

$X_s = X_{s0}$
$z = 0$

where,

Y = yield coefficient (mg/mg)

K_d = decay coefficient (s^{-1})

β = filtration efficiency

θ = empty bed contact time (s)

ε = bed porosity

ε' = bed porosity with biofilm

a'_f = specific surface area of the pellet with biomass (m^2)

X_f = cell density of biofilm (mg/L)

σ = biofilm shear loss coefficient (s^{-1})

6.4.3 Biofilm Diffusion and Biodegradation

Biofilm diffusion and biodegradation of the substrate is given by equation 6.31.

$$\frac{\partial S}{\partial t} = D_f \cdot \frac{\partial^2 S}{\partial x^2} - X_f \cdot \frac{k_{\max} \cdot S}{K_s + S} \tag{6.31}$$

with initial and boundary conditions,

$$S = S_0$$

$$D_f \cdot \frac{\partial S}{\partial x} = \left(\frac{a_p}{3}\right) \cdot \rho_s \cdot k_s \cdot \left(q_s - \bar{q}\right) \quad at \quad x = 0$$

$$D_f \cdot \frac{\partial S}{\partial x} = k_f \cdot (C - S) \quad at \quad x = L_f$$

where,

S = substrate concentration in the biofilm (mg/L)

D_f = molecular diffusion within biofilm (m^2/s)

a_p = radius of the pellet (m)

ρ_s = density of the pellet (mg/L)

k_s = solid phase mass transfer coefficient (m/s)

q_s = adsorbed phase concentration at pellet surface (mg/mg)

$\bar{q}$ = average adsorbed phase concentration (mg/mg)

k_f = interphase mass-transfer coefficient from liquid to biofilm (m/s)

It is assumed that the substrate diffuses through biofilm where it is biodegraded by the microorganisms.

6.4.4 Biofilm Growth and Decay

Since the biofilm growth rate is directly related to the biological activity, the cell growth rate (which is the sum of the cell production rate due to degradation and its decay rate) can be written as in Equation 6.32.

$$\frac{dL_f}{dt} = \int_0^{L_f} \left(\frac{Y \cdot k_{max} \cdot S}{K_s + S} - b_{tot} \right) \cdot dr \qquad (6.32)$$

At $t = 0$,

$x = x_0$

where,

L_f = biofilm thickness (m)

b_{tot} = total shear and decay loss (s^{-1})

x = biofilm coverage (m)

6.4.5 Support-phase Substrate Balance

The support phase substrate balance of the biofilter was done by linear driving force approximation (LDFA) model and Freundlich isotherm. The equation 6.33 describes the mass uptake rate of the adsorbent from the bulk phase solution, and the equation 6.34 the adsorption isotherm of the system.

$$\frac{\partial \bar{q}}{\partial t} = k_s \cdot \left(q_s - \bar{q}\right) \tag{6.33}$$

Here, $q_s = f\left(S\big|_{y=0}\right)$ *and* $S\big|_{y=0} = C_s$

$$q_s = K_F C^{1/n} \tag{6.34}$$

where,

k_s = solid phase mass transfer coefficient (m/s)
K_F = Freundlich adsorption coefficient
n = Freundlich exponential coefficient

6.4.6 Change in Bed Porosity, Specific Surface Area and Bed Depth

The growth of biofilm in the bed alters the bed porosity, the specific surface area, and the filter medium depth as the bioadsorption proceeds. These changes can be given by the Equations 6.35, 6.36, and 6.37 respectively.

$$\varepsilon' = 1 - (1-\varepsilon_0)\cdot\left(\left(1+\frac{L_f}{a_p}\right)^3 - \frac{n}{4}\cdot\left(\frac{L_f}{a_p}\right)^2\cdot\left(2\frac{L_f}{a_p}+3\right)\right) \quad 6.35)$$

$$a_f' = \frac{3(1-\varepsilon_0)}{2\cdot a_p}\cdot\left(1+\frac{L_f}{a_p}\right)\cdot\left((2-n)\cdot\frac{L_f}{a_p}+2\right) \quad (6.36)$$

$$\frac{L}{L_0} = \left(\frac{1-\varepsilon_0}{1-\varepsilon'}\right)\cdot\left(\left(1+\frac{L_f}{a_p}\right)^3 - \frac{n}{4}\cdot\left(\frac{L_f}{a_p}\right)^2\cdot\left(2\frac{L_f}{a_p}+3\right)\right) \quad (6.37)$$

where,

ε_o = initial bed porosity
a_p = radius of the pellet
L_f = biofilm thickness (m)
ε' = bed porosity with biofilm
a_f' = specific surface area of the pellet with biomass (m^2)
L = bed depth with biofilm (m)
L_o = initial bed depth (m)

The bed porosity depends on the number of particles in contact with a single particle (n). Alonso et al.(1998) reported an empirical relationship to calculate the bed porosity from the number of particles in contact (n).

$$\varepsilon_0 = 1.072 - 0.1193\cdot n + 0.004312\cdot n^2 \quad (6.38)$$

In this study, n is taken as 5.

It is almost impossible to solve the set of these coupled parabolic second-order partial differential equations analytically. Numerical methods are generally employed to solve the complex equations. In this study, the partial differential equations were first discretised by orthogonal collocation method (OCM) to form a set of first-order ordinary differential equations (ODEs). The resulting set of ODEs was then solved using the subroutine DVODE (Brown et al., 1989).

6.4.7 Sensitivity Analysis of the Model

The model simulation indicated that the model is sensitive to several parameters such as biofilm thickness (L_f), yield coefficient (Y), decay coefficient (k_d), shear loss coefficient (σ), substrate utilization rate(N), molecular diffusivity (D_f) etc. All these parameters are very much dependent on the characteristics and the concentration of the wastewater (the feed solution), filter media and filtration rate. The effects of biofilm thickness and decay coefficient are shown in Figures 6.2 and 6.3 respectively. Here C and C_0 are the effluent and influent organic concentrations measured in terms of total organic carbon (TOC). As shown in Figure 6.2, the organic removal efficiency of the biofilter was improved with the increase in biofilm thickness. It means that the filter media, which has capacity of holding more biomass, will produce better organic removal. It is therefore important to maintain of the biomass for the efficient and long-term operation of the biofilter. The decay of the biomass impairs the efficiency of the filter (Figure 6.3). As the biomass detachment is caused by the sloughing action, it is important to optimise the operating parameters of the filter to maintain the optimum biofilm thickness.

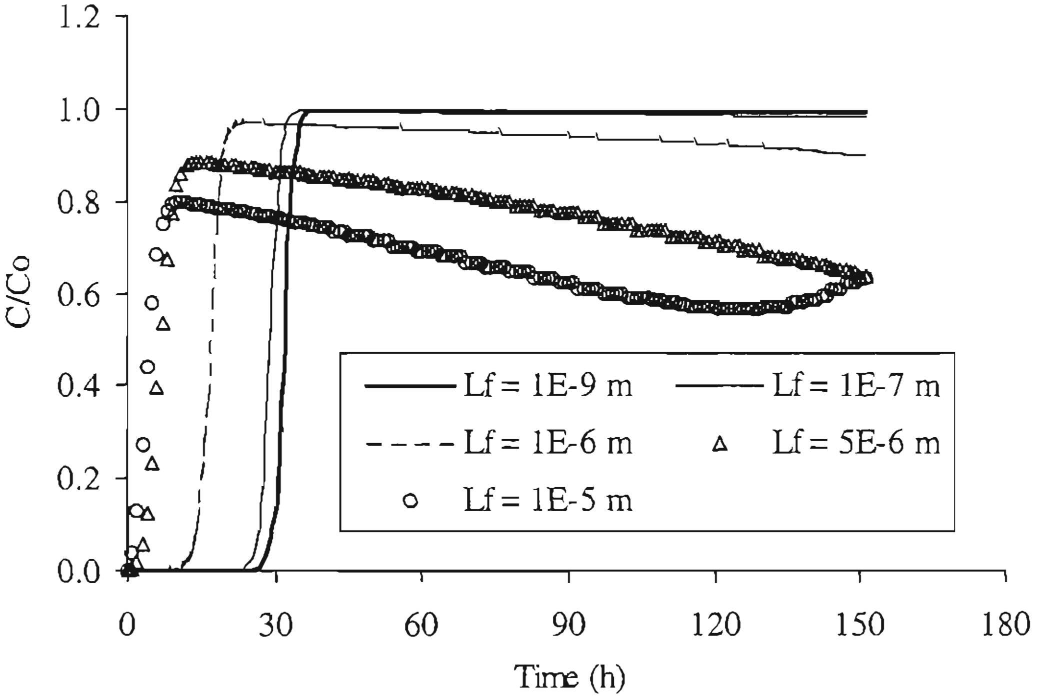


Figure 6.2. Effect of initial biofilm thickness (L_f) on the effluent organic concentration. (X_s = 1.0E-7 mg/L, K_d = 5.0E-6 s^{-1}, σ = 1.16E-6 1/s, β = 10000, Y = 0.34 mg/mg, and X_f = 6.44E+3 mg/L)

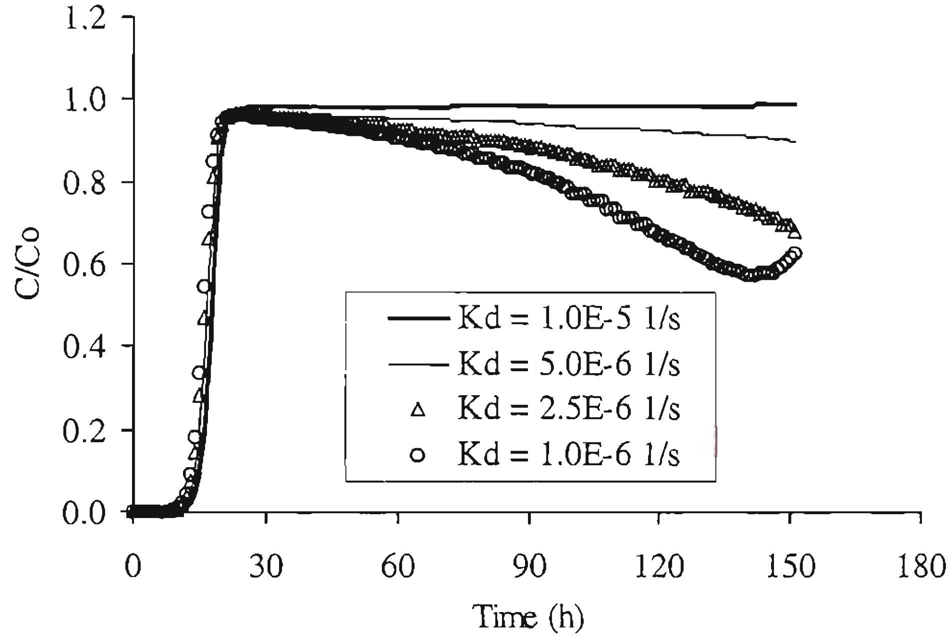


Figure 6.3. Effect of decay coefficient (K_d) on the effluent organic concentration. (X_s = 1.0E-7 mg/L, L_f = 1.0E-6 m, σ = 1.16E-6 s^{-1}, β = 10000, Y = 0.34 mg/mg, and X_f = 6.44E+3 mg/L)

6.4.8 Estimation of the Model Parameter

The parameters of the biofilter model are summarized in Table 6.2. Although these parameters were estimated from the previous studies (Hozalski and Bouwer, 2001b; Alonso et al. 1998), it is necessary to calculate these parameters from detailed experiments in different operating conditions of the biofilter for an accurate prediction of the behaviour of the biofilter.

Table 6.2. Biofilm parameters of the model

Parameter	Value
Influent organic concentration, mg/L	3.5
Biomass density, X_f (mg/L)	1.4×10^3
Decay coefficient, K_d (s^{-1})	5.0×10^{-6}
Biofilm thickness, L_f (m)	1.0×10^{-6}
Maximum growth rate, k_{max} (s^{-1})	1.6×10^{-4}
Monod kinetic constant, K_s (mg/L)	0.24
Shear loss coefficient, σ (s^{-1})	1.2×10^{-6}
Yield coefficient, Y (mg/mg)	0.34
Suspended cell concentration, X_s (mg/L)	1.0×10^{-8}
Filtration efficiency, β	1×10^4
Bed porosity, ε_0	0.6
Diffusivity in biofilm, D_f (m^2/s)	1.7×10^{-10}

6.5 Experimental Investigation

Detailed column experiments were conducted using low strength synthetic wastewater at Environmental R&D laboratory, University of Technology, Sydney (UTS). The characteristic of the synthetic wastewater corresponds to the biologically treated sewage in terms of TOC. The main objective of the study was (i) to evaluate the long-term performance of the GAC bed filter, (ii) to assess the effect of backwashing on the organic removal efficiency of the filter, and (iii) to estimate the attached biomass on GAC media. Six filter columns were employed. The columns had ports for influent feed, effluent collection and backwashing. The columns were packed with 5 g (bed depth 4 cm and porosity 0.65) of granular activated carbon (GAC). Shallow bed depth was chosen to attain quick biofilm acclimatization. The GAC bed was acclimatized at constant filtration rate of 1 m^3/m^2.h. The filters were backwashed at 30% bed expansion for approximately 5 minutes every 24 hours of filtration run. Total organic carbon (TOC) was measured on a daily basis using the UV-persulsuphate TOC analyser (Dohrmann, Phoenix 8000). Total adsorbed biomass (as dry weight) was calculated every week. The physical properties of the GAC are shown in Table 6.3. The GAC used in the experiments was initially washed 3 times with distilled water and dried in the oven at 103.5° C for 24 hours. It was kept in desiccators before packing into the column. To measure the biomass, after a week of continuous operation, the GAC was taken out of the filter column and washed 3 times with distilled water to remove the suspended mass. The GAC with the retained biomass was then dried in an oven at 103.5° C for 24 hours and desiccated prior to the measurement of the total adsorbed biomass (as dry weight).

Table 6.3. Physical properties of GAC used

Specification of the GAC	Estimated Value
Iodine number, mg /(g.min)	800
Maximum Ash content	5 %
Maximum Moisture content	5 %
Bulk density, kg/m^3	748
BET surface area, m^2/g	1112
Nominal size, m	3 x 10^{-4}
Average pore diameter, Å	26.14

The chemical composition of the synthetic wastewater used (Table 6.4) was representative of the biologically treated sewage effluent in terms of TOC concentration. The TOC contribution of the Glucose, Peptone and Yeast extract with inorganics are 79%, 11% and 10% respectively.

Table 6.4. Constituents of the synthetic wastewater used

Compounds	Weight (mg/L)	Compounds	Weight (mg/L)
$MnSO_4$	0.125	KH_2PO_4	1.250
$CaCl_2$	0.925	$NH_2.NH_2.H_2SO_4$	3.500
$NaHCO_3$	0.875	Glucose	16.500
NaCl	2.500	Yeast Extract	1.750
$MgSO_4.7H_2O$	3.750	Peptone	1.750

6.5.1 Biofilter Parameters and its Measurement

Biofilters are used for many purposes. It can be used for the treatment of primary wastewater, tertiary wastewater or for the treatment of potable water. Measurement of biofilter parameters depends on the purpose of the use of the biofilter. If the purpose of the biofilter is to treat the primary wastewater, then the parameters that should be measured are BOD, COD, SS etc. However, when the biofilter is used for the tertiary wastewater treatment, then the organic level such as TOC could be an appropriate parameter to be measured. Similarly, the main purpose of the use of a biofilter in potable water treatment is to reduce the chlorine demand or disinfection by-product formation potential and the bacterial re-growth potential, and its measurements are expressed in terms of BDOC and AOC. Since the measurement of AOC or BDOC is of specific nature, precise measurement methods are required. Some of the commonly used methods for the measurement of AOC or BDOC are: (a) Van der Kooij method, (b) Kemmy method, (c) US-EPA method, (d) Werner method, (e) Jago-Stanfield method, and (f) Billen-Servais method. In Van der Kooij method, the AOC concentration is expressed as μg acetate C eq/L, whereas in Kemmy and US-EPA methods, colony-forming units (cfc/ml) is measured and then converted into AOC μg/L and coliform growth response (CGR) respectively. In Werner and Jago-stanfield methods, the bacterial cell is measured in terms of turbidity and adenosine triphosphate (ATP) concentration respectively. Billen-Servais method measures the biodegradable dissolved organic carbon (BDOC).

6.5.2 Estimation of the Biomass Growth

The performance of a biofilter depends on the biomass attached to the filter media. The biomass growth and its maintenance over the surface of the filter media, on the other hand, depend mostly on the surface characteristics of the filter media itself. As mentioned earlier, different media can have different biomass growth rate and biomass retention capacity. GAC, sand, anthracite, blast-furnace slag and floating polyproperlyne pellets are some of the common biofilter media used in the water and wastewater treatment. Other factors that can affect the biomass accumulation are the filtration rate, filter backwashing techniques, and the organic content of the influent wastewater.

Several methods are adopted in practice to measure the biomass attached to the filter media depending on the availability of the analytical facilities. Usually for the biofilter used in water treatment facilities, the amount of biomass is relatively small (in microgram) and hence precise methodology for the biomass measurement is required.

Ahmad et al. (1998) however, used heterotrophic plate count (HPC) to measure the biomass growth in the biofilter. The heterotrophic bacteria were enumerated by using the spread plate method according to the STANDARD METHODS (1989) section 9215C. The growth medium used was R2A agar, and incubation conditions were 20°C for seven days.

Wang et al. (1995a) used Phospholipid analysis to estimate the biomass in the biofilter. About 0.5 g of GAC filter media with attached biomass were taken from the filter, and washed with dechlorinated tap water to remove the suspended solids so that the measured mass would be only the attached biomass. Basically, the method is to extract the organically bound phosphorous and then it is digested to inorganic phosphate which can be quantified by colorimetric measurement. Wang et al. (1995a) extracted the phospholipids by a chloroform-methanol-water mixture with a volume ratio of 1:2:0.8 in around 2- 24 hours time. The extracted mixture was then separated into a lipid-containing chloroform phase, and a methanol-water aqueous phase by adding more chloroform and water so that the chloroform-methanol-water ratio reached 1:1:0.9. A portion of the lipid containing chloroform (sample) was taken in a 5-ml ampule and then evaporated using nitrogen gas. Around 0.9 ml of potassium persulfate reagent (5 g of potassium persulfate in 100 ml of 0.36 N sulphuric acid solution) was then added into the ampule, and then the sample was digested (with potassium persulfate) at 102°C for 2 h to release phosphate. After that, ammonium molybdate [2.5 % $(NH_4)_6Mo_7O_{24}.4H_2O$ in 5.72 N H_2SO_4)] and malachite green [0.011 g of malachite green in 100 ml of 0.111 % polyvinyl alcohol solution) were added to form a coloured compound which was then measured colourimetrically at a wavelength of 610 nm. The absorbance of each sample was compared with a standard curve (derived from standard solution 0.1 mM KH_2PO_4) to determine the concentration of lipid phosphate. The amount was biomass was reported as nmol lipid-P/g dry filter media (1 nmol lipid-P is equivalent to about 10^8 bacteria of the size of E.coli).

Servais et al. (1994) suggested that it would not be possible to enumerate the bacteria attached onto activated carbon due to size and surface irregularity of the GAC, and developed a new approach to estimate the bacterial biomass. In this method, bacterial activity is measured under standard conditions, and then it is related to size of active bacterial population as follows: (a) one millilitre of ^{14}C-glucose solution (1 mmole glucose containing 0.1-1 μCi) was added to a 2-ml GAC sample in a penicillin flask closed with a rubber septum, (b) the sample was incubated at 20°C for 3 hr, and then it was acidified by 2 ml of 10% H_2SO_4 through the septum, (c) the sample was bubbled for 10 min to extract CO_2, which was trapped in a mixture of carbo-sorb and lipoluma (0.25:1 by volume), (d) radioactivity was determined by liquid scintillation with a packard tri-carb scintillation counter, and the amount of glucose mineralised was expressed in nano-moles of glucose respired per hour, (e) the respiration rate was correlated to μg C of biomass by a conversion factor of 1.1μg C of bacterial biomass per nanomole of glucose respired per hour (Servais et al. 1991).

Since the biomass growth with synthetic wastewater used in this study was significantly large, the method of total dry weight of the adsorbed mass is sufficiently accurate for the measurement of biomass. Thus, the method of total dry weight was used in this study. This method is simple and more practical.

As shown in Figure 6.4, after 6 weeks of continuous operation, a decline in the biomass was observed. Maximum biomass measured was 0.09 g per g of GAC after 42 days of operation. Most of the studies with natural surface water showed that 3-months period are required for a GAC filter to retain maximum amount of biomass (Servais et al., 1994; Ahmad and Amirtharajah, 1998). A minimum biomass concentration of 0.036 g per g of GAC was observed after 63 days of continuous operation. Another set of experiments conducted with filtration rate of 2.5 m/h showed a biomass concentration of 0.1 g per g of GAC in 30 days of continuous filter run. The amount of biomass accumulation was found to be dependent on hydraulic loading rate (HLR) and the organic concentration. Carlson and Amy (1998) also found the biomass concentration profile as a function of HLR. The higher the loading rate, the greater was the initial biomass and deeper the penetration into the filter bed. The biomass concentration profile thus appears to be the most critical parameter in the design of biofiltration system.

Two important changes due to the biomass coating on the outer surface of the GAC pellet were: (i) a decrease in the fixed bed porosity, and (ii) an expansion of the GAC bed of the biofilter. The maximum bed expansion (1.14 cm) was observed after 42 days continuous operation of the filter.

A study of GAC biofilter at Neuilly-sur-Marne (France) water treatment plant (Servais et al., 1994) showed that for a given empty bed contact time (EBCT), biological removal of organic matter in GAC filters is independent of filtration rate in the range of 6-18 m/h. They also found some decrease in biomass after 100 days of operation. However, the average biomass in the filter operating at different filtration rates but at identical contact times remained almost constant.

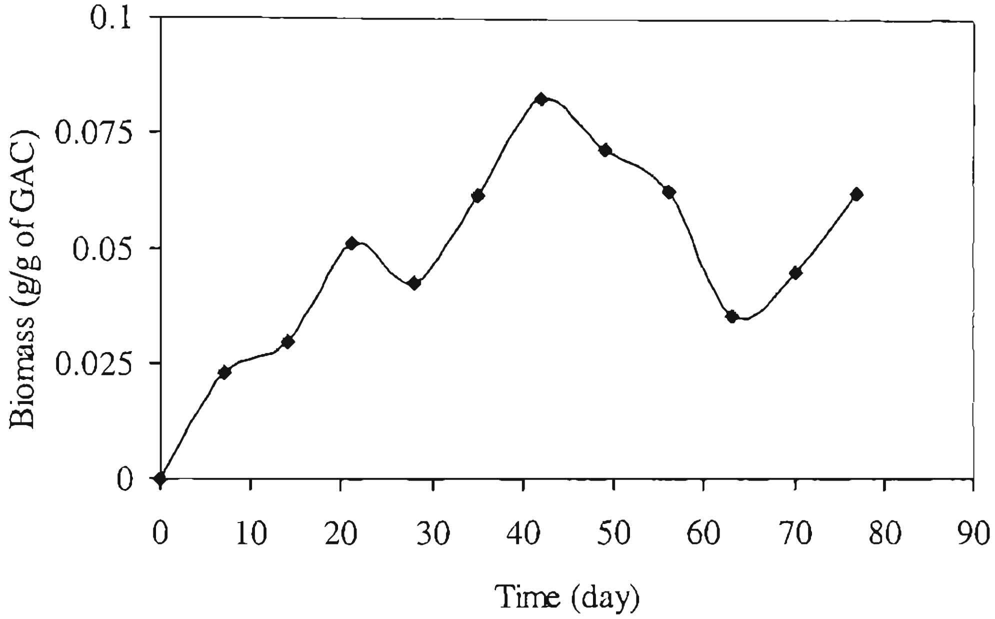


Figure 6.4 Biomass accumulations in the GAC biofilter

(Filtration rate = 1 m/h, GAC = 5 g, average influent TOC = 3.5 mg/L)

Ong et al. (1999) through their work with high strength wastewater (BOD_5 = 389 mg/L) in an ultra-compact biofilm reactor observed 52.5 % and 32.8 % decrease in biomass after 38 days and 94 days of filter run respectively. The decrease in biomass during the 7th to 9th week of the operation in this study may be due to die-off of microorganisms and its subsequent removal in backwashing. Despite the decrease in the biomass, the removal efficiency of the filter was not impaired, and it continued to produce consistent quality of effluent.

6.5.3 Long-term Performance of the Biofilter

The TOC removal efficiency of a long-term run of the biofilter is presented in Figure 6.5. The results in terms of TOC removal show that the GAC biofilter can be operated for a long time without regeneration of GAC. The organic removal efficiency of the filter remained constant at 50-55% even after 77 days of continuous run. Servais et al. (1994) found 49-56% of BDOC removal in the four pilot-scale GAC biofilter during first year of operation. An investigation of the GAC system at the Palo Alto Reclamation Facility by Summers and Roberts (1984) revealed that biofilter could have pseudo-steady state removal of 50% for the first year, 24% for the second year and 14% for the third year.

The daily backwash adopted to avoid the physical clogging of the biofilter did not seem to affect the organic removal efficiency of the filter. Adsorption of organics and biological degradation of the organics adsorbed onto the activated carbon are two major mechanisms for the consistent removal of organics in the GAC biofiltration system. From the laboratory-scale filter study, Hozalski and Bouwer (1998) also found that biomass accumulation is not impaired by backwash with water. In their experiments, the organic removal efficiency of the biofilter was found to be unchanged after the backwash. Some of the biomass may naturally be lost during backwashing of the filter but the loss of biomass can create more sites for adsorption of organics and thus impairment is balanced. This can happen when the adsorption capacity of GAC is not fully exhausted.

The organic removal efficiency of the biofilter could be improved by employing a larger depth of GAC in the column.

An attempt was made to predict the organic removal efficiency of the biofilter using the mathematical model described in section 6.4 (Figure 6.5). The model describes the organic removal mechanism at the earlier stage by adsorption and then by biodegradation as the biomass is gradually developed on the GAC surface (and the adsorption capacity of the GAC is gradually exhausted). Since only one sample was taken each day, and the backwash was provided on a daily basis, the adsorption part is not well presented experimentally in the Figure 6.5. Also due to the lack of the data on the model parameters, the values estimated from the earlier studies were used in the prediction (Table 6.1).

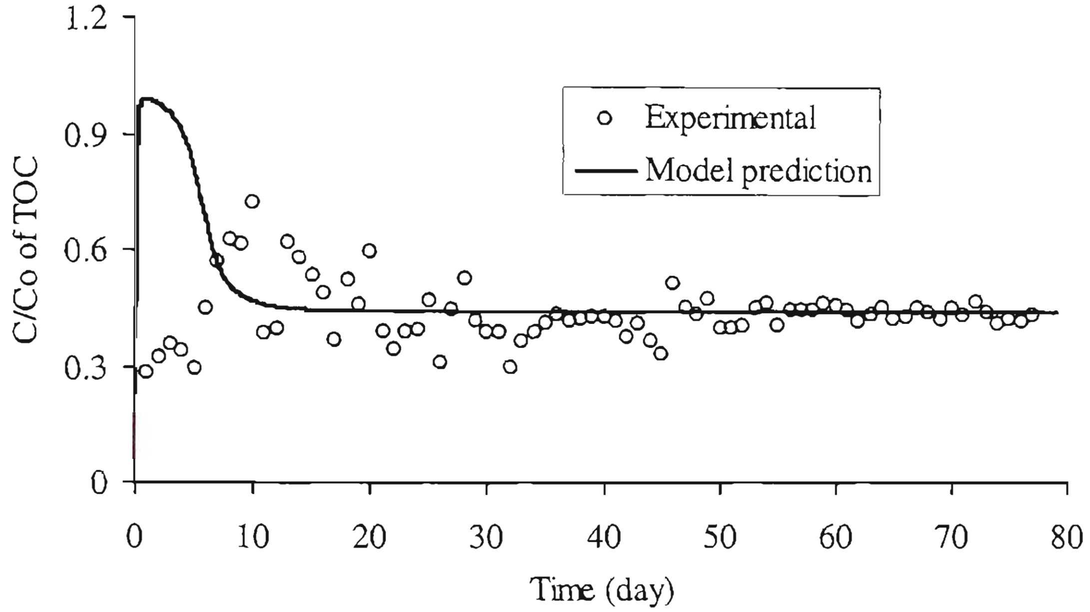


Figure 6.5. TOC removal efficiency of the GAC biofilter and model prediction (Filtration rate = 1 m/h, filter depth = 4 cm, average influent TOC = 3.50 mg/L) (X_s = 1.0E-8 mg/L, L_f = 1.0E-6 m, σ = 1.16E-6 s^{-1}, β = 10000, Y = 0.34 mg/mg, X_f = 1.44E+3 mg/L, and K_d = 5.0E-6 s^{-1})

Note: The effluent was taken after filter backwash considering influent residence time.

6.5.4 Effect of Filtration Rate and Influent Organic Concentration

The effects of both influent organic concentration and filtration rate on the organic removal efficiency of the biofilter were experimentally investigated. As can be seen from Figure 6.6, with increased filtration rates, the effluent quality became inferior to that with lower filtration rate (at which the filter was acclimatized) but the organic removal pattern remained unchanged with time. It might be due to the fact that when the hydraulic loading rate of the biofilter was increased, the EBCT is decreased and the increased organic mass loading exceeded the ability of the biomass to assimilate the available biodegradable organic substances resulting in substandard effluent quality. It should be noted that the filter column was acclimatized with relatively low concentration of organics (TOC of 3.5 mg/L) and low filtration rate of 1 m/h for the gradual growth of biomass in the filter media.

Previous researchers have also observed the decreases in the organic carbon removal with the decrease in EBCT (LeChevallier et al., 1992 and Prevost et al., 1992). LeChevallier et al. (1992) found an increase in TOC removal from 29 to 51.2 percent when EBCT was increased from 5 to 20 min i.e. when the filter rate was decreased by four times. However, Carlson and Amy (1998) have reported from their pilot scale experimental studies that organic removal in a biofilter is limited either by biodegradable organic matter (BOM) formation or biomass concentration, not by filter operating parameters. They also found that optimum organic removal efficiency of the biofilter was at the loading rate to which the filter was acclimatized, and if the steady-state biomass conditions were allowed to develop, even at higher hydraulic loading rate, the removal efficiency of biofilter would increase to that found at the lower hydraulic loading rate (at which the filter was first acclimatized).

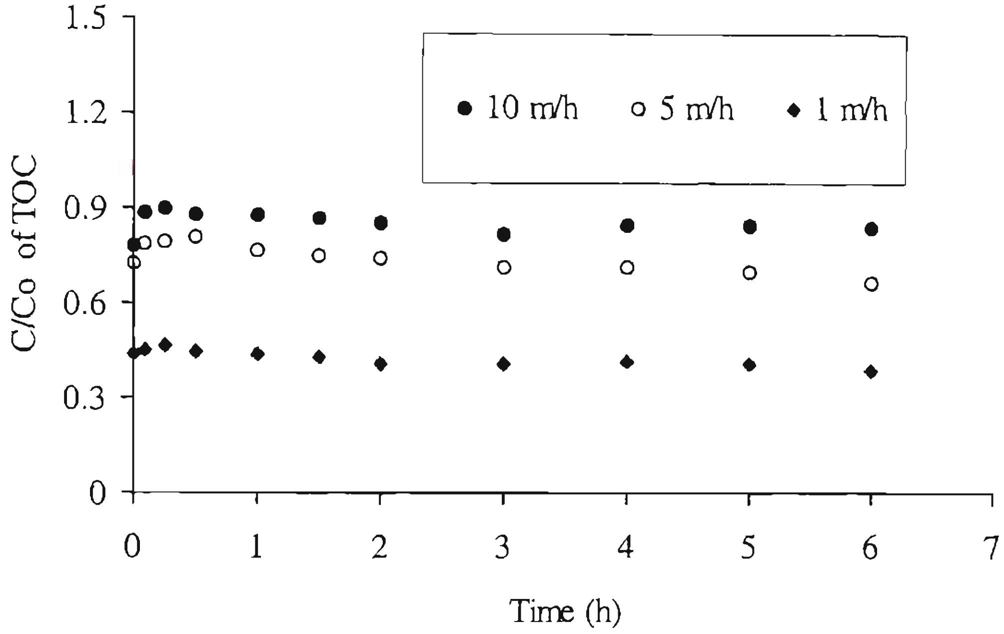


Figure 6.6 Effect of filtration rate on the performance of GAC biofilter after acclimatization period (Acclimatization period = 77 days at 1 m/h, Average influent TOC = 3.5 mg/L, GAC = 5 g, C and Co are the effluent and influent TOC concentration)

As shown in Figure 6.7, the removal efficiency of the filter improved slightly when the influent TOC concentration was increased to 6.8 mg/L. The obvious reason for this improvement is the increased biological activity of the microorganism. The first order steady-state model developed by Huck et al. (1994) also showed that the organic removal efficiency of the biofilter is approximately directly proportional to the influent organic concentration. However, when the influent concentration was increased from 6.8 mg/L to 11.2 mg/L, the removal efficiency of the filter was higher initially and then decreased with time.

The experimental results thus indicated that the biomass profile is the most critical parameter in the design of a biofiltration system, and that the biofilter should be operated as close to steady-state conditions as possible to achieve optimum organic removal efficiency. The sudden increase in the flow rate and influent concentration can change the efficiency of the biofilter temporarily, but as mentioned earlier, if the steady-state biomass condition is allowed to develop, the organic efficiency of the biofilter would be equivalent to that of the organic or hydraulic loading rate at which the filter is first acclimatized.

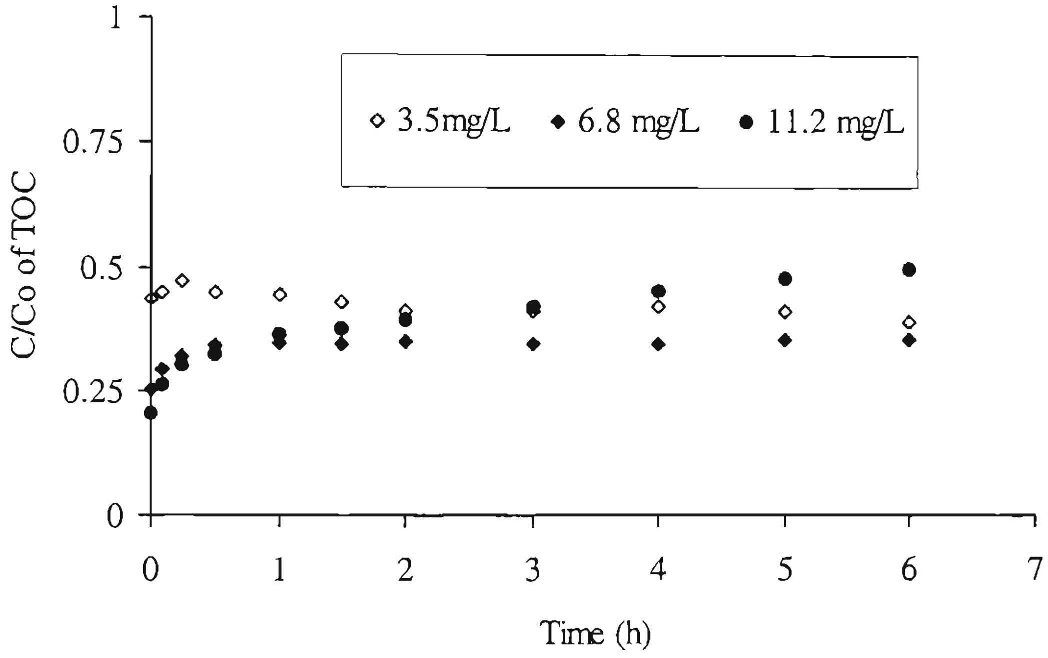


Figure 6.7 Effect of influent organic concentration on the performance of GAC biofilter after acclimatization period (Acclimatization period = 77 days at 1 m/h, Filtration rate = 1 m/h, GAC = 5 g)

6.6 Conclusions

- GAC biofilter can effectively be used for an extended period of time without the need of GAC regeneration.
- The biological activity led to a consistent effluent organic concentration over a long period of time. The daily backwash adopted did not affect the biological mass growth, thus the effluent quality. Its performance however, was affected by the filtration rate and the influent organic concentration, suggesting that the biofilter should be operated in the same conditions at which it was acclimatized for its optimum and consistent organic removal efficiency.
- Although higher filtration rates led to inferior effluent quality, the TOC removal efficiency was maintained constant with filtration time. A correct choice of filtration rate and GAC medium depth with appropriate backwash can lead to a long-term operation with consistent and superior effluent quality.
- The mathematical model proposed in this study could predict the steady rate organic removal efficiency of the biofilter reasonably well.
- It is important to estimate the biofilter parameters for different operating conditions (such as acclimatization filtration rate and initial organic concentration) to verify the versatility and adaptability of the model in practice. In this study, however, the biofilter parameters used in the model prediction were estimated from the previous studies.

Chapter 7

Adsorption-Membrane Hybrid System

7.1 Introduction

As global supplies of clean, fresh water dwindle and demand for water rises, wastewater reuse is becoming an international focus for the rational use of scarce water resources, and as a means of safeguarding aquatic environments from the harm caused by wastewater disposal. Conventional sewage treatment includes primary treatment to remove the majority of suspended solids, secondary biological treatment to remove the biodegradable dissolved organics and nitrogen, and tertiary treatment to remove most of the remaining organics, solids, and pathogenic microorganisms. Although the effluent from this treatment can be discharged into a waterway, it cannot for reasons of health and safety be recycled. To obtain water of recyclable quality, physico-chemical processes such as flocculation, sedimentation, filtration and adsorption were initially tried. With technological advances and the ever-increasing stringency of water quality criteria, membrane processes are becoming a more attractive solution to the challenge of water reuse. The use of membrane technology in water and wastewater treatment (particularly in wastewater reuse application) has received increased attention since early 1990s. The necessity of its application in drinking water treatment has been felt due to the anticipation of growing stringent water quality regulations whereas its application in wastewater treatment has been expected to be an innovated treatment process. However, the practical application of the membrane technology in the field has been limited to Japan, Australia, some parts in Europe and North America only. It is firstly due to the higher installation cost and secondly very little know-how of its operational and maintenance procedures. Membrane technologies currently used in many industries include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, pervaporation, dialysis and electrodialysis.

Membrane filtration is basically, a pressure driven process in which membrane acts as selective barriers to restrict the passage of pollutants such as organics, nutrients, turbidity, microorganisms, inorganic metal ions and other oxygen depleting pollutants. The membrane processes and the representative particle sizes removed by them are shown in Figure 7.1. In general, microfiltration refers to the membrane size between 0.1 to 10 μm. However, depending on the types of solids to be separated and the aim of the membrane processes, membrane sizes from 0.02 to 20 μm are also called microfiltration (Gunder, 2001). Efficiency of the membrane system depends on several other physico-chemical, biological and operational factors such as temperature, pressure and chemical resistivity, adsorption qualities, size and stability of hydraulic performance.

Microfiltration alone cannot remove dissolved organic substances due to its larger pore size. Due to the need for removing the persistent organic pollutants in an economic manner and to reduce the membrane clogging (fouling) problem, the use of powdered activated carbon (PAC) to membrane filtration system, either microfiltration or ultrafiltration (known as adsorption-membrane filtration hybrid system) is being emerged as an innovative water and wastewater treatment technology (Vigneswaran et al., 1991, Seo et al., 1996, 1997; Snoeyink et al., 2000; Kim et al., 2001; Matsui et al., 2001a, 2001b). In this process, the pollutants (particularly the dissolved organics) are first adsorbed onto PAC and thus the direct loading of the pollutants to the membrane is greatly reduced. The use of PAC in the system not only increases the permeate flux (effluent filtration rate) through the membrane; it also prolongs the life of membrane application.

7.1.1 Application of membrane without PAC

Many studies have been done on the application of membrane technology in water and wastewater treatment without PAC. Yamamoto et al. (1989) investigated the application of direct membrane separation in activated sludge process with synthetic wastewater. A hollow fibre membrane module with a pore size of 0.1 micron was immersed in the aeration tank and the treated water was filtered through the membrane by suction. The chemical oxygen demand (COD) and total organic carbon (TOC) removal efficiencies of the membrane separation system were found to be 95% and 97% respectively from the synthetic wastewater. They suggested an intermittent and low-pressure operation to reduce the membrane clogging.

Jacangelo et al, (1995) observed that the MF and UF membrane systems were very effective in removing cryptosporidium, giardia and MS2 virus from drinking water. The virus removal efficiency of the system was found to range from 0.6 log to 6 log depending upon the membrane pore size. Pankhania (1999) found the COD removal efficiency of a hollow fibre membrane bioreactor 89 % and 86 % when operated as a completely mixed reactor and as a plug flow reactor respectively using synthetic wastewater. Oh et al. (2000) employed three types of membranes (hollow fibre, tubular and spiral wound) to reuse the primarily treated sewage, and found a remarkable decline in the initial permeate flux. The permeate flux decline in hollow fibre module was the most severe. Even the chemical cleaning was not found so effective in restoring the permeate flux. Similar results were also obtained by Zhu and Elimelech (1995), and Gosling and Brown (1993). The initial decrease in the permeate flux is mainly due to rapid, irreversible adsorption of organic substances on the membrane surface (Ben Aim et al., 1993). Therefore, it is necessary to provide a pre-adsorption of organics before passing the wastewater solution through the membrane, and the PAC-membrane hybrid system is a very effective solution to this problem.

7.1.2 Application of membrane with PAC

Most of the previous studies of the PAC-membrane hybrid system have been concentrated on the removal of a targeted pollutant. Kim et al. (2001) found the PAC-membrane hybrid system very effective in removing coliphase-Qβ and total organic carbon (TOC) from the synthetic secondary wastewater. They used a submerged hollow fibre membrane with predetermined PAC dose, and they found 99.9 % and 95% removal of coliphase-Qβ and TOC respectively for a PAC dose of 40 g/L. Matsui et al. (2001) applied the PAC-UF system to remove the synthetic organic substance namely simazine. Suzuki et al. (1998) studied the long-term (250 days) performance of the PAC-membrane hybrid system by circulating PAC-sludge in a pilot scale experimental unit in removing turbidity, natural organic matter, manganese and ammonia nitrogen from a river water. They used a submerged hollow fibre membrane and recirculate the PAC-sludge from the bottom to the influent tank. For a water temperature higher than 5°C, they found almost 100 % removal of soluble manganese and ammonia. Seo et al. (1996) from their experimental study found that the biological powdered activated carbon (BPAC)-MF hybrid system could remove 83 % of TOC and 99.99 % of coliphase-Qβ in with a the PAC dose of 20 g/L. They provided a contact time of 1 h for PAC with the wastewater.

It is important that the effectiveness of the hybrid system should be evaluated using real wastewater before its implementation in practice. Further, the initial adsorption in this system has to be optimised through the correct choice of PAC and its dose. In this study, wood-based PAC was used as an adsorbent. Both (1) the cross-flow microfiltration system with external loop flat-plate membrane, and (2) the submerged hollow fibre membrane system with online PAC adsorption were studied to evaluate the organic removal efficiency of the system. Biologically treated sewage effluent from a sewage treatment plant in Sydney was used as the wastewater. The hybrid systems were also tested using low strength synthetic wastewater. A simple and practical mathematical model was developed for the submerged hollow fibre membrane hybrid system to predict the effluent quality of the system.

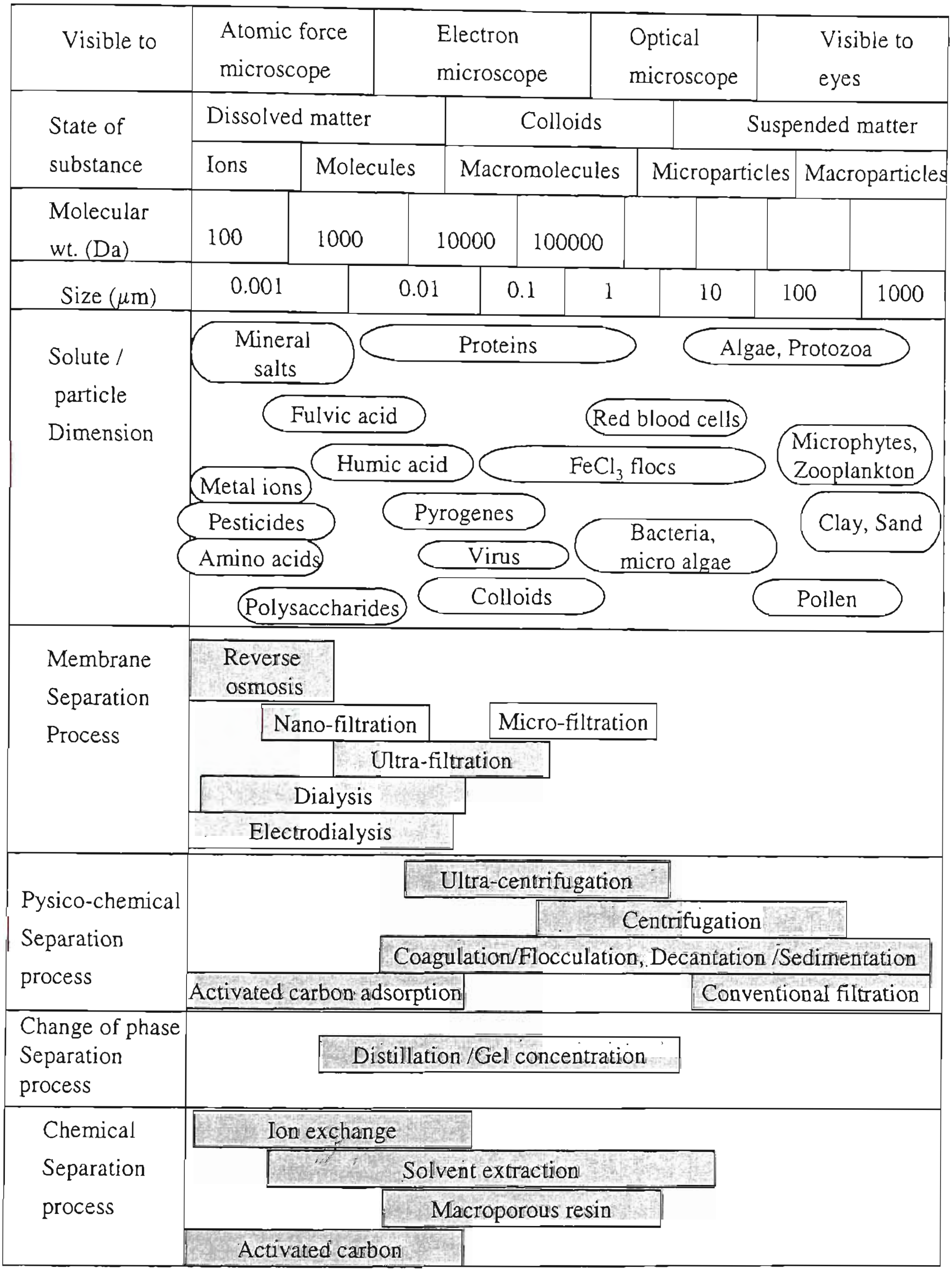


Figure 7.1 Membrane separation process compared to other treatment processes, and solute / particle dimension (after Schafer, 2001)

7.2 Microfiltration Process

The microfiltration process can be either crossflow type or dead-end type. In the crossflow filtration, the inflow of the solution is parallel to the membrane surface. The crossflow velocity generates cleaning effects due to shear force and hence there is relatively less cake formation on the surface of the membrane (Figure 7.2a). In the steady state condition, equilibrium between cleaning effects and cake deposit effects is established and the thickness of the cake layer on the membrane surface remains constant. In the dead-end procedure, the flow direction of the solution is orthogonal to the membrane surface, and therefore, all the substances rejected by the membrane remain on the surface and contribute to the formation of relatively thicker cake layer on the membrane surface. The thickness of the cake layer increases proportionally to the flow velocity, and the permeate flow decreases accordingly (Figure 7.2a). Periodic backwash system is required to remove the cake layer from the membrane surface for continuous functioning the membrane system. Previous studies have shown that pretreatment of organics by adsorption onto PAC prior to subjecting the solution to microfiltration process is a very effective way to reduce the membrane clogging (Vigneswaran et al., 1991). The pretreatment by adsorption reduces the organic loading to the membrane surface and hence the membrane fouling, and prolongs the operational life of the microfiltration system.

7.2.1 Permeate Flux

The permeate flux (J_p) of a membrane filtration system is the permeate volume flow (Q_p) per unit membrane surface area (A_m). A typical variation pattern of permeate flux is shown in Figure 7.2b. The steady state flux can be measured at any time. In the case of non-steady state condition which occurs at the early stage of membrane filtration, normally only average flux is specified, and it is determined by measuring the permeate volume (ΔV_p) for a sufficient long period of time (Δt).

$$J_p = \frac{Q_p}{A_m} = \frac{1}{A_m} \cdot \frac{\Delta V_p}{\Delta t} \qquad (7.1)$$

The permeate flux characterizes the hydraulic performance of membrane system.

7.2.2 Transmembrane Pressure

The transmembrane pressure (ΔP) is defined as the average of the feed and concentrate pressure (P_F, P_C) minus the pressure on the permeate side (P_p) (Figure 7.2a).

$$\Delta P = \frac{P_F + P_C}{2} - P_p \qquad (7.2)$$

In submerged membrane, the transmembrane pressure is calculated using the following equation.

$$\Delta P = -P_p - \rho \cdot g \cdot \Delta Z \qquad (7.3)$$

Here, ΔZ refers to the level difference between the water level in the tank and the pressure measurement point. The measured permeate pressure (P_p) gives the negative value, as it is the suction pressure.

The transmembrane pressure in both crossflow microfiltration and the submerged hollow fibre microfiltration is illustrated in the following diagram (Figure 7.2a).

In crossflow microfiltration, Cake Layer model, often known as resistance model is widely used in the literature. According to this model, the permeate flux microfiltration is defined as:

$$J_p = \frac{\Delta P}{\mu R_T} \tag{7.4}$$

where J_p is the permeate flux, μ is the viscosity of the permeate and R_T is the total resistance to the filtration, which is the function of intrinsic membrane resistance (R_m), polarization layer resistance caused by the concentration gradient (R_p), external fouling resistance formed by deposited cake layer (R_f) and internal resistance due to adsorbed substances into the pores (R_i). Thus equation 7.4 can be written as:

$$J_p = \frac{\Delta P}{\mu(R_m + R_i + R_e)} = \frac{\Delta P}{\mu(R_m + R_i + \beta \cdot \Delta P)} \tag{7.5}$$

where R_e is the total external resistance (= $R_p + R_f$) and β is the function that relates compressibility and hence the resistance caused by the cake layer, R_e to the pressure applied

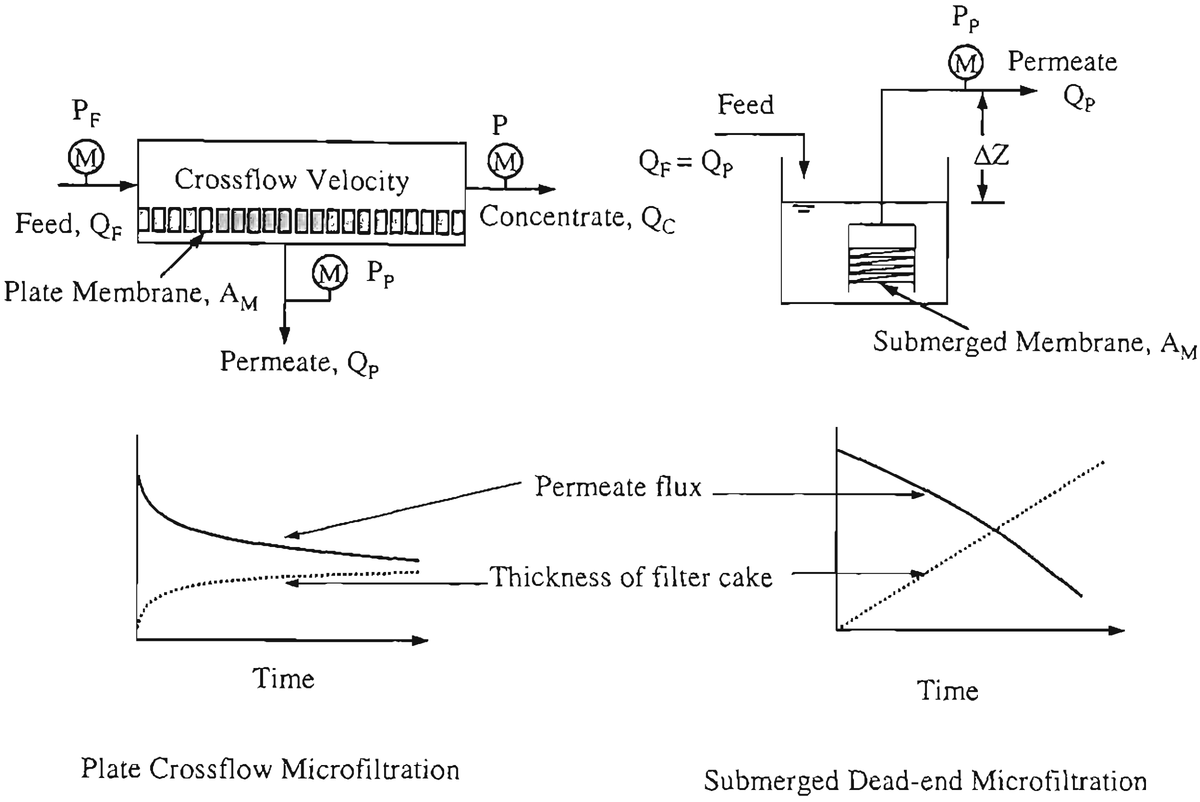


Figure 7.2a Illustration of flow patterns, flux decline, filter cake formation, and transmembrane pressures in dead-end filtration and crossflow filtration (after Gunder, 2001)

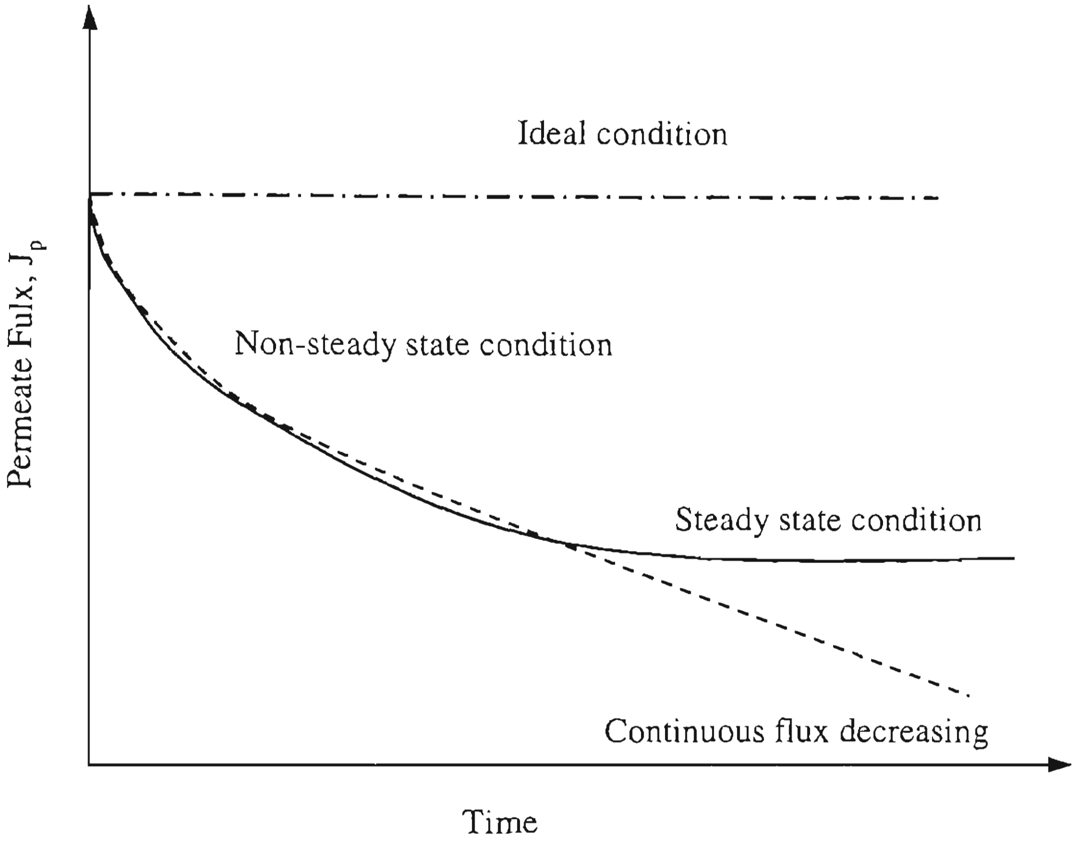


Figure 7.2b Variation of permeate flux with time (after Vigneswaran et al. 1991)

7.2.3 Membrane Fouling

In a membrane filtration system, a decline in the permeate flux due to blockage of the pores of the membrane surface is defined as membrane fouling. Membrane fouling can be reversible or irreversible in nature, and it is considered as one of primary problems of membrane process application. The reversible fouling can be restored through chemical cleaning, backwashing or hydrodynamic scouring (surface washing). In the case of irreversible fouling, the membrane must pass through extensive chemical cleaning. Reversible fouling is caused mainly by cake formation and the irreversible fouling mainly due to organic adsorption. Fouling can occur at the external surface or inner pore surface of the membrane, and it can be caused by many factors such as (Gunder, 2001):

- Adsorption of macromolecules or colloidal matters
- Adhesion and growth of biofilms (biofouling)
- Precipitation of solvents (scaling), and
- Aging of the membrane (polymerisation)

Since the fouling is caused by the interaction between substances in the fluid and membrane surface and the membrane itself due to aging, selection of membrane material for specific purpose is important for economical operation of membrane filtration.

Membrane fouling can be controlled by altering the operating conditions, by chemical addition, or by pretreatment. If the feed solution contains a large amount of colloidal particles, then severe fouling is expected to occur. It can be controlled by operating the system under critical flux (the flux below which, there is no deposition on the membrane or there is no transmembrane pressure increase). Similarly the inorganic fouling or scaling, which is mainly caused by calcium, magnesium, carbonate, sulphate, silica, and iron, can be controlled by adding some chemicals (anti-scalants) or by simply adjusting the pH to a lower value to prevent the precipitation on the membrane surface. In practice, however, pretreatment is always incorporated prior to membrane filtration. Conventional coagulation/flocculation and filtration are often used to reduce the membrane fouling (Ben Aim et al, 1988, Vigneswaran et al, 1991). Addition of powdered activated carbon on the membrane filtration system especially for wastewater treatment is gaining great attention nowadays due to its ability to remove persistent organic pollutants (POPs) and the potential long-term use of PAC and membrane in the system (Kim et. al. 2001)

7.3 Mathematical Modelling of the Microfiltration Hybrid System

Two mathematical models are described in this chapter: (a) membrane fouling models that describe the flux decline with time, and (b) the model that describes the dynamics of adsorption–filtration characteristics of the membrane.

7.3.1 Flux Decline and Fouling Models

Flux decline is one of the major obstacle in wide spread implementation of the membrane technology in water and wastewater industry. Three main phases of flux decline has been reported in the literature (Fane et. al., 1983; Turker and Hubble, 1987; Aimar et al., 1988; Hallstrom et al, 1989), (i) rapid drop in the flux due to concentration polarization , (ii) monolayer particle deposition and surface layer build-up, and (iii) development of a quasi-steady state due to further deposition of particles and consolidation of the build-up layer.

The concentration polarization is the development of the concentration gradient of the retained components near the membrane surface. The membrane porosity is not directly affected by the concentration polarization. It causes only the external fouling of the membrane as the solutes being filtered is carried to the membrane by the permeate flow and then they are rejected by the membrane surface. The various factors that affect the flux decline are (i) the characteristics of the solution such as particle size and its distribution, concentration, pH and ionic strength, (ii) the characteristics of the membrane material such as charge effects, porosity and pore size distribution, and (iii) the operational variables such as transmembrane pressure, filtration velocity, temperature etc.

The cake filtration model (CFM) is the most commonly used model to characterize such hydrodynamic behaviour of the membrane. In the case of internal membrane fouling, the attachment of the solutes directly on the membrane surface or pores due to adsorption, adhesion, or precipitation reduces the porosity of the membrane significantly. There are two main blocking phenomena, the standard blocking (SB) and the pore blocking (PB). The SB assumes that the flux decline is due to the deposition of solutes on the walls of the pores whereas the PB is based on the assumption that the flux decline is due to the complete blocking of some of the pores while the rest remain unaffected by the solute particles. In practice however, the pore constriction and the pore blocking of the membrane may occur simultaneously. Depending on the particle size in the influent, the four different modes of membrane filtration models are defined as follows (Hermia, 1982):

7.3.1.1 Cake Filtration Model (CFM)

The Cake filtration model (CFM) describes the filtration of particles, which are much larger than the membrane pore size. All the particles are assumed to be deposited due to concentration polarization on the membrane surface contributing to the development of boundary layer resistance.

$$\frac{d^2t}{dV^2} = k_c$$

$$\frac{t}{V} = \frac{k_c}{2}V + \frac{1}{J_o} \tag{7.6}$$

where, V = volume filtered in time t , J_0 = the initial filtration (permeate) flux, and k_c = cake formation filtration constant

7.3.1.2 Standard Blocking Model (SBM)

The standard blocking model (SBM) is the pore constriction model. It describes that particles which are smaller than the membrane pore size pass through the pores and get deposited on the wall surface of the pores, thus decreasing the pore volume and hence the filtrate volume with time.

$$\frac{d^2t}{dV^2} = k_s\left(\frac{dt}{dV}\right)^{\frac{3}{2}}$$

$$\frac{t}{V} = \frac{k_s}{2}t + \frac{1}{J_o} \qquad (7.7)$$

where, k_s = standard blocking filtration constant

7.3.1.3 Intermediate Blocking Model (IBM)

The intermediate blocking model (IBM) basically describes the flux decline due to very slow and long-term adsorption.

$$\frac{d^2t}{dV^2} = k_i\left(\frac{dt}{dV}\right)$$

$$k_iV = \ln(1 + k_i t J_0) \qquad (7.8)$$

where, k_i = intermediate blocking filtration constant

7.3.1.4 Complete Blocking Model (CBM)

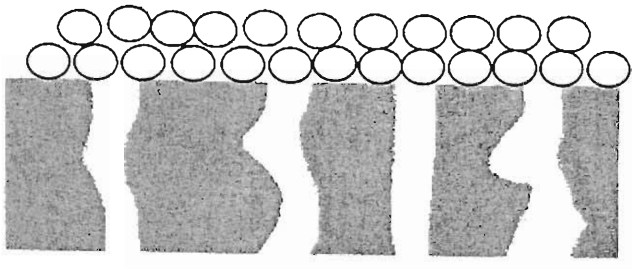
The complete blocking model (CBM) is the pore-blocking model. It is valid for the particles, which are of similar size of the membrane pores. It assumes that the particles seal the pores of the membrane resulting in sharp decline in the flux.

$$\frac{d^2t}{dV^2} = k_{ct}\left(\frac{dt}{dV}\right)^2$$

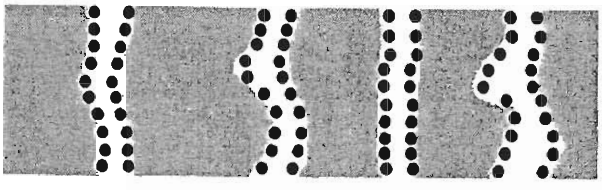
$$V = J_0(1 - e^{-k_{ct}t}) \tag{7.9}$$

where, k_{ct} = complete blocking filtration constant

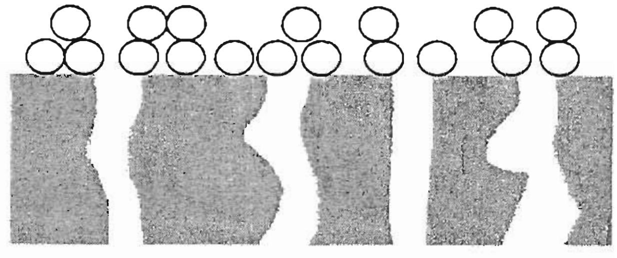
The solute rejection mechanisms of all these four types of models are illustrated in figure 7.3. When the solute particles of the feed solution are much larger than the membrane pore size then a porous cake layer is formed, which is described by cake filtration block model. Complete blocking occurs when the size of the particles is of similar size to the pores of the membrane, and thus they plug the pores. Similarly, when the particle size is much smaller than the size of the membrane pores, the standard blocking occurs. The intermediate blocking is the modified fouling mechanism, which falls between cake filtration and complete blocking modes.



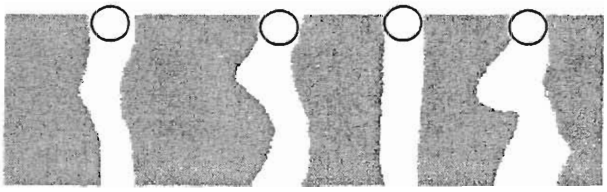
Cake Filtration (boundary layer resistance)



Standard blocking (direct adsorption)



Intermediate blocking (long term adsorption)



Complete blocking (pore blocking)

Figure 7.3 Different particle retention mechanisms (Vigneswaran et al., 1991)

7.3.2 Adsorption Model for the Submerged Membrane Hybrid System

Application of PAC-membrane hybrid system in water and wastewater treatment processes is relatively new. The membrane processes such as microfiltration (MF) and ultrafiltration (UF) can remove the suspended matters and produce very clean effluent, however, these membrane processes cannot remove the dissolved organic matters efficiently. Application of PAC in the system not only removes the dissolved organic matters, it also prolongs the operational life of the membrane by reducing the organic loading and hence membrane fouling. In PAC-membrane hybrid system, dissolved organic compounds are adsorbed onto PAC particles, which are eventually separated by the membrane filtration process. Previous studies have shown that the addition of PAC to the membrane filtration system is a simple and cost-effective way to remove the dissolved organic (natural and synthetic) compounds (Pirbazari et al., 1992; Clark et al., 1996).

The treatment efficiency of the processes depends on the reactor configuration, operating modes, carbon dose and adsorptive capacity and influent characteristics. Depending on the operational mode, continuous-flow stirred tank reactor (CSTR) and plug-flow reactor (PFR) are two main models used to facilitate the design of the membrane hybrid system.

Extensive research has been done in the mathematical modelling of the adsorption kinetics of dissolved organic compounds by PAC (Najm et al., 1990; Roy et al., 1993; Qi et al., 1994). Najm (1996) applied homogenous surface diffusion model (HSDM) and Freundlich isotherm to model the CSTR and PFR modes of the adsorption system. He presented an easy-to-use model for the PAC adsorption system using non-linear equation-solving techniques such as Newton's method and developed a non-dimensional parameter, $\lambda = (\tau . D^2)/R^2$ to evaluate the efficiency of the PAC adsorption process. Larger the value of λ, greater is the efficiency of the system. Here τ is the hydraulic retention time, D_s is the surface diffusion coefficient and R is the radius of the carbon particle.

The mathematical representation of HSDM with no film diffusion limitation is given by equations 7.10-7.13.

$$\frac{\partial q}{\partial t} = D_s \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial q}{\partial r} \right) \tag{7.10}$$

with the initial condition,

At $t = 0, 0 \leq r \leq R$: $q = 0$ (7.11)

And boundary conditions,

$$\text{at } r = 0,\ t \geq 0\text{: } \frac{\partial q}{\partial r} = 0 \text{ and} \tag{7.12}$$

$$\text{at } r = R,\ q_s = K \cdot C_s^{\frac{1}{n}} \tag{7.13}$$

Here, equation 7.10 describes the rate of change of surface concentration (q) with time (t) at any distance (r) from the centre of carbon particle during adsorption. The surface diffusion coefficient (D_s) represents the rate of diffusion of the adsorbate (the target compound) along the surface of the adsorbent (PAC particle). The boundary conditions (equations 7.12 and 7.13) state that at the centre of the adsorbent, the rate of change of q with time is equal to zero, and that the surface concentration at the outer surface of the adsorbent q_s is in equilibrium with the liquid-phase concentration at the surface of the adsorbent C_s.

It is important to use the adsorption kinetics of the PAC in the PAC-membrane hybrid system. There are very few studies reported in the literature on the integration of the PAC adsorption modelling into the membrane filtration system. Campos et al. (2000a, 2000b) utilized HSDM model with no external mass transfer limitations and developed an integrated mathematical model to predict the removal of organic compounds in the PAC-membrane hybrid system. They considered four cases of adsorption: (i) membrane reactor fed with step input of fresh PAC, (ii) CSTR-membrane system fed with step input of fresh PAC, (ii) PFR-membrane system fed with step input of fresh PAC, and (iv) the membrane reactor fed with pulse input of fresh PAC. Model predictions were based on a single set of equilibrium and kinetic parameters independently determined from the results obtained in bench-scale experiments.

Kim at al. (2001) used PAC-MF (submerged membrane) system to evaluate the removal efficiency of coliphase Qβ and organic matter from a synthetic secondary effluent. They assumed a first order driving force model, and proposed the equations 7.14 for the rate of Qβ concentration change in the reactor.

$$\frac{dC_r}{dt} = -k(C_r - C_r^{\infty}) \qquad (7.14)$$

where, C_r = Qβ concentration in the bulk phase

C_r^{∞} = equilibrium concentration of Qβ in the bulk phase, and

k = the first order reaction coefficient.

A correlation between log (k) and log (PAC concentration) raised to the power 1.69 was found to be in good agreement with experimental batch kinetics data. They further purposed a dynamic mass balance equation for the long-term performance of the membrane hybrid bioreactor as follows:

$$V\frac{dC_r}{dt} = Q(C_i - C_e) - k_a V(C_r - C_r^{\infty}) - k_m V(C_r - C_e) - k_d V C_r - k_e q W V \qquad (7.15)$$

where, V = volume of the reactor,

Q = flow rate,

C_i = influent concentration

C_e = effluent concentration

q = amount of Qβ absorbed onto PAC

W = PAC dose, and

k_a, = coefficient for adsorption onto PAC

k_m = coefficient for attachment to the membrane

k_d = coefficient for the bacterial decay, and

k_e = coefficient for inactivation due to the desorption of Qβ from PAC

These models are capable of predicting the organic removal efficiency of the system. However, they do not incorporate the characteristics of the influent and explicitly the membrane properties. Both parameters are very likely to be changed during the operation of the hybrid system.

In this study, a simple mathematical model using the concept of a continuous flow stirred tank reactor (CSTR) was developed. Membrane packing density (A_M/V_M) and membrane correlation coefficient (MCC) were incorporated into adsorption model. The model can be further expanded to incorporate the biodegradation of the organics by microbial community on the adsorbent. The later is the most important mechanism to occur in long-term use of the hybrid system. Since the filtration flux is very low (less than the critical flux), decline in flux is not considered in this model.

The mass balance of the system is described by equation 7.16.

$$\frac{dC_b}{dt} = \frac{Q}{V}\cdot\left(C_0 - C_b\right) - \frac{M}{V}\cdot\frac{dq}{dt} - \frac{A_M}{V_M}\cdot MCC\cdot C_b - BIO \tag{7.16}$$

where,

C_b = organic concentration in the bulk phase in the reactor, mg/L

Q = flow rate, m^3/s

V= volume of the bulk solution in the reactor, m^3

C_0 = organic concentration in the feed tank, mg/L
M = weight of PAC used, g
A_M = surface are of the membrane, m^2
V_M = volume of the membrane, m^3
MCC = membrane correlation coefficient,
BIO = Biodegradation by the microbial community

The second term,[(M/V) · (dq/dt)] in the right hand side of the equation 7.16 represents adsorption of the organics onto PAC, and the third term, [(A_M/V_M) · MCC · C_b] represents the adsorption on membrane surface. The fourth term [BIO] of the equation is introduced to account for the removal of organics by microbial biodegradation. Here the term, A_M/V_M represents the packing density of the membrane. The membrane correlation coefficient (MCC) can be defined as the adsorption coefficient of the membrane. It is an empirical coefficient, and it was introduced in the model to account for the adsorption of organics on the membrane surface and retention of PAC (associated with organics adsorbed on it) on the membrane. Higher the value of MCC, better the organic removal efficiency of the membrane hybrid system. In this study, since only the short-term experiments were carried out, the term BIO is omitted from the model. Further research is required to extend the model by incorporating the biodegradation of organics in the system.

The mass transfer rate inside the particle was described by linear driving force approximation (LDFA) model as shown in equation 7.17. The model assumes that the rate of mass transfer is directly proportional to the concentration gradient developed between the surface concentration and the average adsorbed phase concentration of the adsorbate. The model and its appropriateness in multicomponent adsorption system has been explained in detail in Chapter 4.

$$\frac{dq}{dt} = k_s \cdot (q_s - q) \qquad (7.17)$$

The initial conditions for mass balance in bulk phase and solid phase are: $C = C_0$ and $q = 0$ respectively.

Here, q is the adsorbed phase organic concentration at any time (t), q_s is the equilibrium adsorbed phase organic concentration, and k_s the film mass transfer coefficient.

The adsorption condition equilibrium is represented by Freundlich isotherm (equation 7.18)

$$q_s = K_F \cdot C^{\frac{1}{n}} \tag{7.18}$$

Here, K_f and n are the Freundlich adsorption coefficient and exponential coefficient respectively, and C is the equilibrium bulk phase organic concentration.

The differential equations were solved using DVODE (Brown et al., 1989). The sensitivity of the model for different adsorption and membrane parameters is discussed in the following section. The experimental results and the model predictions are given in section 7.4.3.

7.3.3 Sensitivity Analysis of the Adsorption Dynamics Model

The model developed for the membrane hybrid system was tested for the various parameters such as membrane correlation coefficient, solid mass transfer coefficient, filtration rate, and influent organic concentration used in the model. The performance of the model was found to be dependent mainly on membrane correlation coefficient

(MCC) and the filtration flux (Figure 7.4 and 7.6). Higher the value of MCC, better is the organic removal efficiency of the system. However, as anticipated, the organic removal efficiency of the system decreases, when the filtration rate is increased. The model was sensitive neither to the solid mass transfer coefficient (K_s) (Figure 7.5) nor to the influent organic concentration (C_0) (Figure 7.7). It may be due to the fact that the effects of K_s and C_0 are taken into account by the PAC dose and the isotherm constant respectively. As discussed in Chapter 3, the isotherm parameters are dependent on the initial organic concentration (C_0). Similarly, the value of k_s depends on the adsorbent dose (Chapter 4).

Since in this analysis, the PAC dose and the isotherm parameters are constant, no direct effect of C_0 and K_s could be observed.

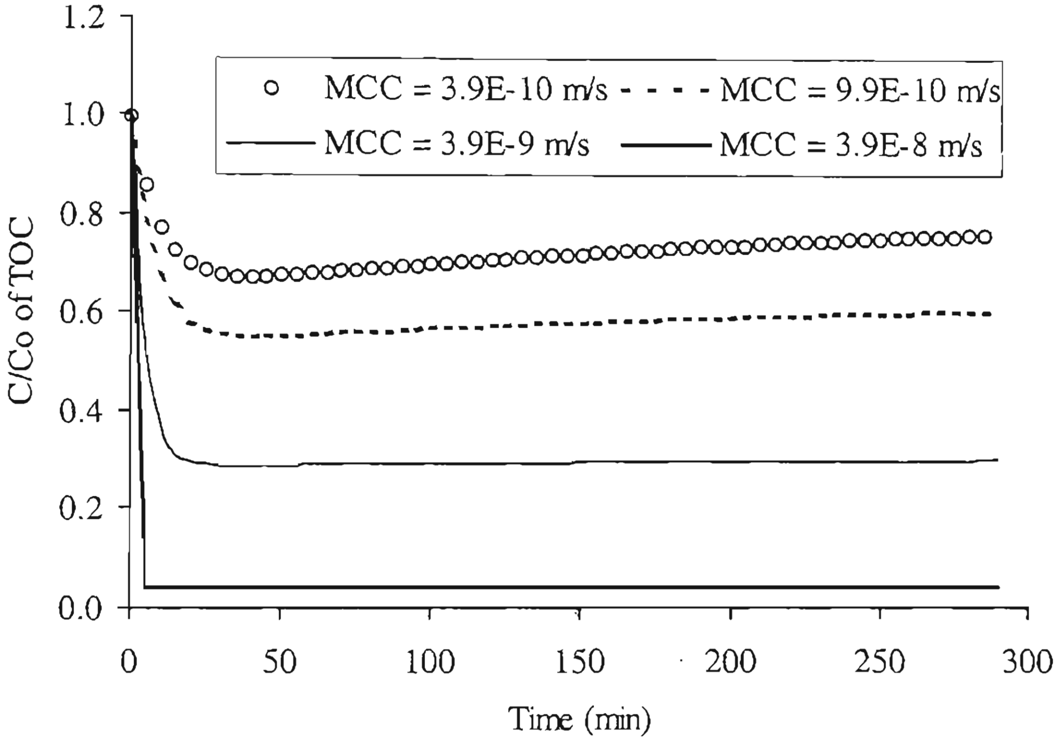


Figure 7. 4 Effect of membrane correlation coefficient on the effluent TOC (PAC dose = 200 mg/L, Influent TOC = 2.6 mg/L, ks = 1.6E-6 m /s, filtration flux = 3 x 10^{-3} L/s/m^2, K_f = 13.2, 1/n = 1.5, C = effluent TOC concentration, mg/L and C_0 = influent TOC concentration, mg/L)

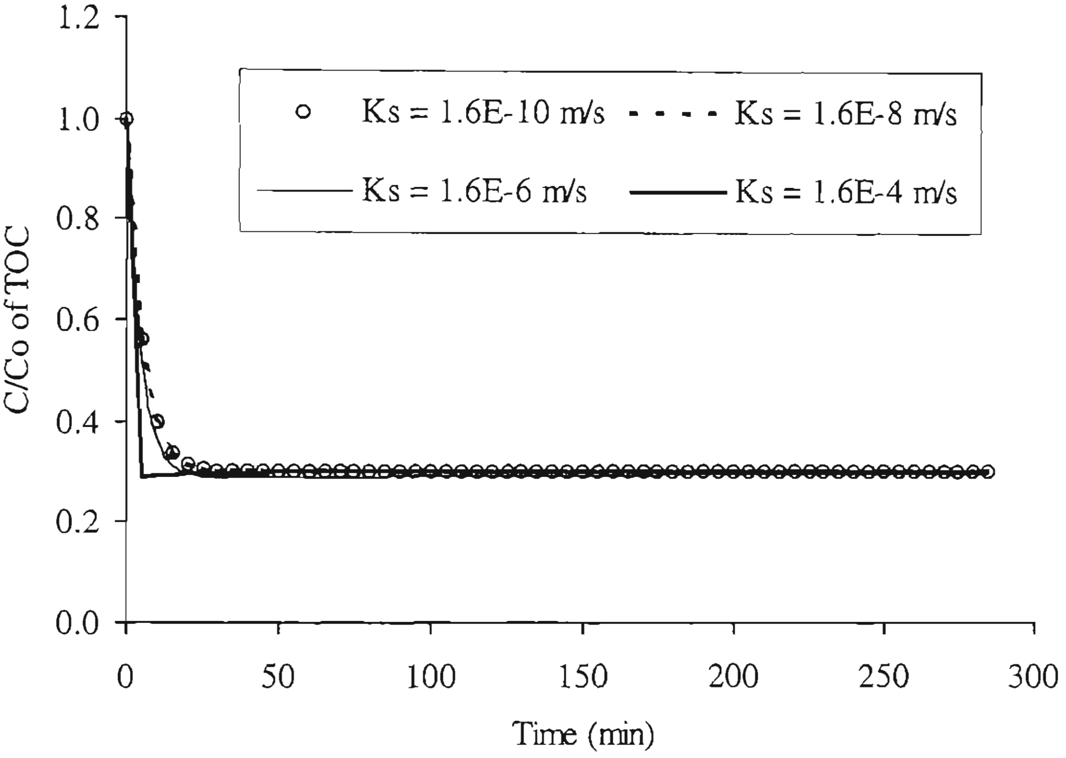


Figure 7. 5 Effect of solid mass transfer rate (k_s) on the effluent TOC (PAC dose = 200 mg/L, Influent TOC = 2.6 mg/L, MCC = 3.9E-9 m /s, filtration flux = 3 x 10^{-3} L/s/m^2, K_f = 13.2, 1/n = 1.5, C = effluent TOC concentration, mg/L and C_0 = influent TOC concentration)

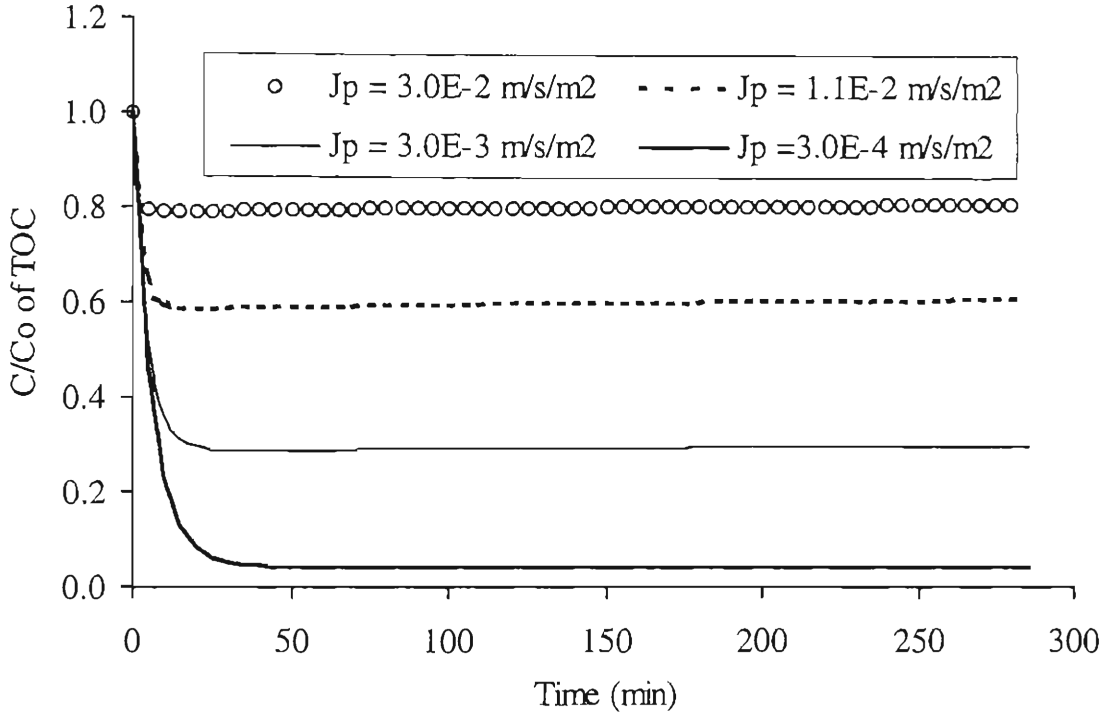


Figure 7. 6 Effect of filtration flux on the effluent TOC

(PAC dose = 200 mg/L, Influent TOC = 2.6 mg/L, MCC = 3.8 x 10^{-9} m /s, k_s = 1.6 x 10^{-6} m/s, K_f = 13.2, 1/n = 1.5, C = effluent TOC concentration, mg/L and C_0 = influent TOC concentration)

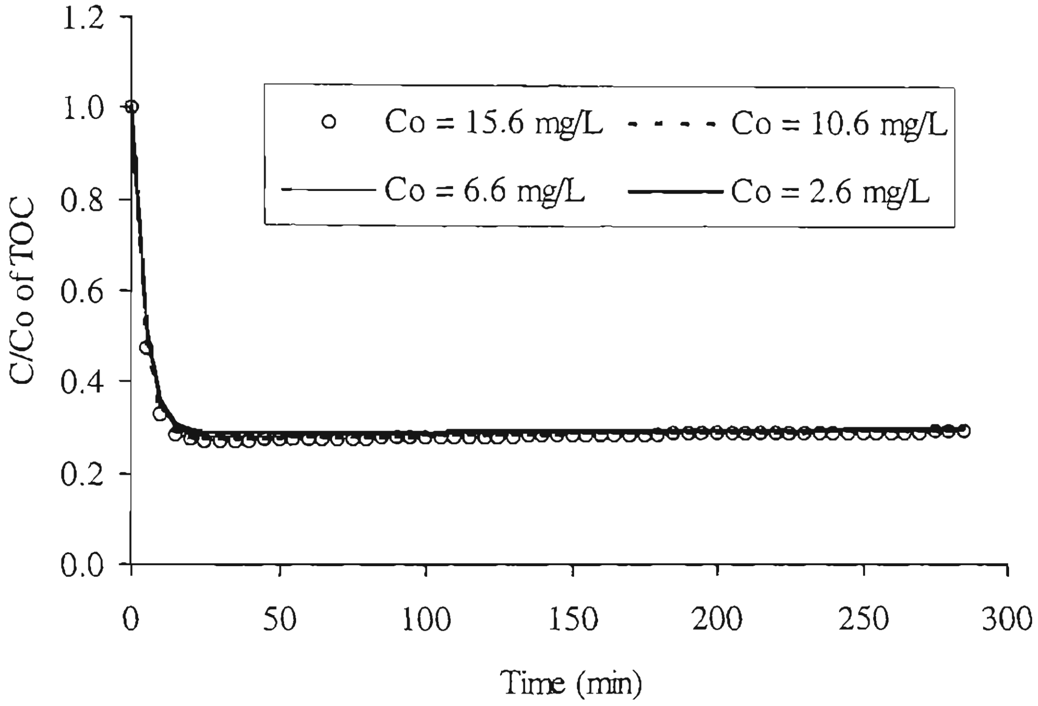


Figure 7. 7 Effect of Influent TOC concentration on the effluent TOC (PAC dose = 200 mg/L, Filtration flux = 3 x 10^{-3} L/s/m^2, MCC = 3.9 x 10^{-9} m /s, k_s = 1.6 x 10^{-6} m/s, K_f = 13.2, 1/n = 1.5, C = effluent TOC concentration, mg/L and C_0 = influent TOC concentration)

7.4 Experimental Investigation

The experimental investigation consists of four experimental processes namely, (i) isotherm equilibria, (ii) batch kinetics, (iii) experiments with submerged hollow fibre membrane, and (iv) the experiments with external loop cross-flow microfiltration. The isotherm and the batch kinetics studies were carried out to determine the adsorption characteristics of PAC in the membrane hybrid system.

7.4.1 Adsorption Equilibrium with PAC

7.4.1.1 Experimental Investigation

The methodology to carry out the isotherm experiments of the synthetic and real secondary wastewater with PAC was similar to that mentioned in chapter 3. Isotherm adsorption experiments were conducted using 250 ml of synthetic wastewater and real wastewater solutions in flasks. The amount of PAC used for the study varied from and 0.1 g to 1.7 g. The flasks were kept shaking continuously for 7 days at 130 rpm at 25°C. Total organic carbon (TOC) was measured using the UV-persulphate TOC analyser (Dohrmann, Phoenix 8000). The PAC used in the experiments was washed 3 times with distilled water and dried in the oven at 103.5° C for 24 hours. It was kept in the desiccator before using in the experiments.

The chemical composition of the synthetic wastewater used is shown in Table 3.1, which yields the total organic carbon (TOC) concentration of 3.5 mg/L. The TOC concentration of the biologically treated sewage effluent used in this study remained fairly stable between 3 – 4.5 mg/L. The physical properties of the PAC are shown in Table 3.2.

7.4.1.2 Results of the Adsorption Equilibrium Study

The adsorption isotherm results of the synthetic wastewater and the secondary effluent from the St Marys sewage treatment plant are shown in figures 7.8 and 7.9 respectively. The Freundlich isotherm was used to describe the isothermal adsorption behaviour of the system. The results are summarized in Table 7.1.

Table 7.1 Isotherm parameter values

Freundlich	Synthetic wastewater of initial concentration (C_0)			Secondary effluent
Parameter	4.2 mg/L	11.7 mg/L	15.3 mg/L	(C_0 = 3.5 mg/L)
k	0.006	0.0054	0.002	13.2
1/n	0.15	0.14	0.12	1.5

The adsorption was more unfavourable in the case of synthetic wastewater solution than that of secondary sewage. For all three different initial TOC concentration, the adsorption constant, k of the Freundlich isotherm was very low whereas the exponential constant (1/n) was greater pushing the tendency of the system towards unfavourable adsorption zone in the case of synthetic wastewater as shown in the Table 7.1.

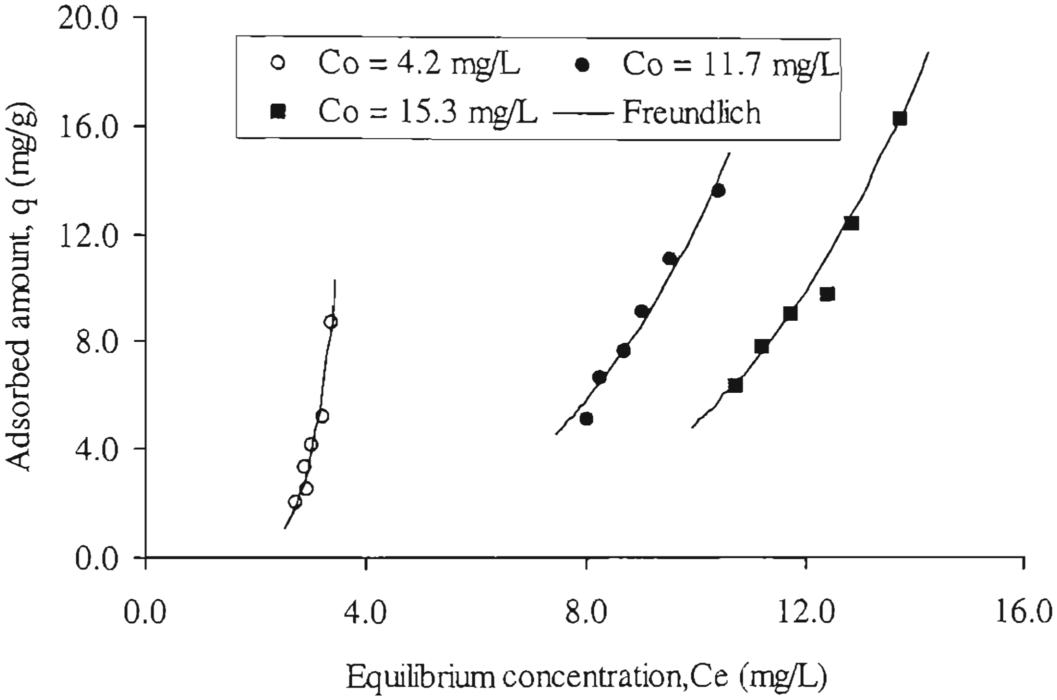


Figure 7.8 Overall adsorption isotherm of the synthetic wastewater at three different initial organic concentrations

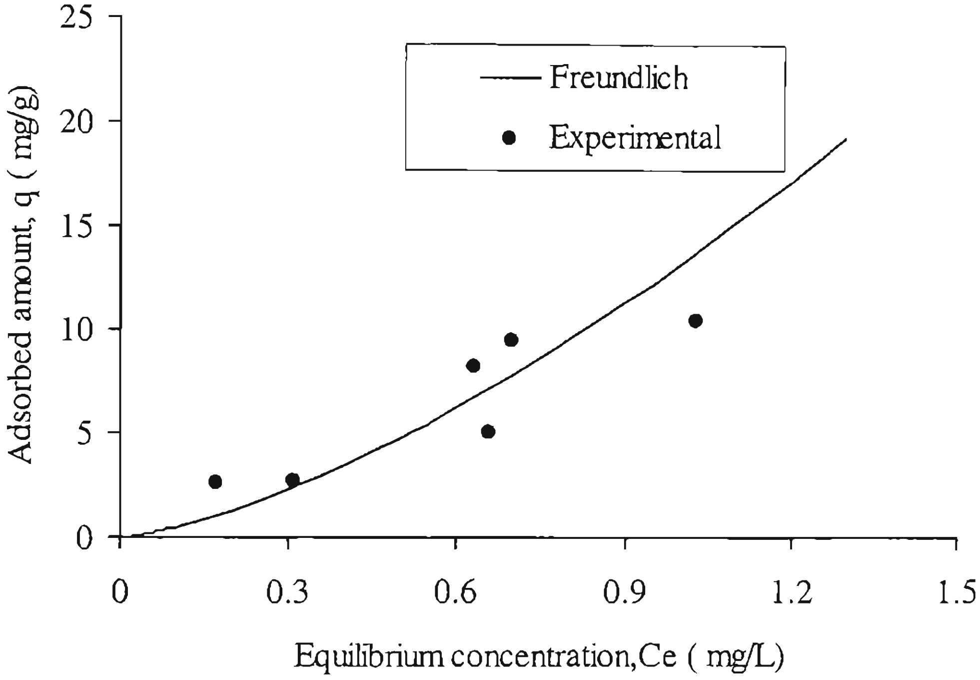


Figure 7.9 Overall adsorption isotherm of the biologically treated sewage effluent (Initial TOC = 3.5 mg/L)

7.4.2 Adsorption Batch Kinetics with PAC

7.4.2.1 Experimental Investigation

As described in detail in chapter 4, the batch experiments of the synthetic and real wastewater (biologically treated sewage effluent) with PAC were conducted using 2 L of solution at the laboratory and at the sewage treatment plant site. The PAC dose was varied from 50 to 500 mg/L and the stirring speed was maintained at 100 rpm. The total organic carbon (TOC) was measured using the UV-persulphate TOC analyser (Dohrmann, Phoenix 8000). The PAC used in the experiments was washed with distilled water and dried in the oven at 103.5° C for 24 hours. It was kept in desiccators before using in the experiments.

The chemical composition of the synthetic wastewater, and the physical properties of the PAC are shown in Tables 3.1 and 3.2 in Chapter 3. The TOC concentration of the synthetic wastewater was around 3.5 mg/L, and that of the biologically treated sewage effluent was in between 3 – 4.5 mg/L.

7.4.2.2 Results of the Adsorption Batch Kinetics Study

Wood based PAC was used to study the mass transfer rate from the wastewater bulk solution to the PAC surface. The mass transfer rate was calculated by fitting the experimental using linear driving force approximation (LDFA) model. The details of the LDFA model are given in chapter 4. It is a simplified adsorption model, which assumes the mass transfer rate is proportional to the concentration gradient developed between the bulk phase and adsorbed phase organics. The mass transfer rate with PAC was found to be higher and faster than that with GAC (as compared with the results with GAC in chapter 4). The film mass transfer (k_f) in the secondary sewage solution was estimated to be almost constant at 12.5 x 10^{-5} m/s for the PAC dose of 100-400 mg/L. Similarly in the synthetic wastewater solution, the mass transfer (k_f) was at the range of 9.5 x 10^{-6} m/s for the PAC dose of 50-500 mg/L. The TOC removal efficiency of the PAC from the wastewater was not proportionally increased when the PAC dose was increased from 50 - 500 mg/L and 100 - 400 mg/L in case of the synthetic wastewater and the secondary sewage respectively. The TOC removal efficiency of the PAC from the secondary sewage was higher than that from the synthetic wastewater. From the figures 7.8 and 7.9, it is also obvious that the adsorption is relatively more isothermally favourable in case of biologically treated sewage effluent than that of the synthetic wastewater solution.

The experimental results and the LDFA model prediction with the synthetic wastewater and the secondary sewage are shown in figures 7.10 and 7.11 respectively.

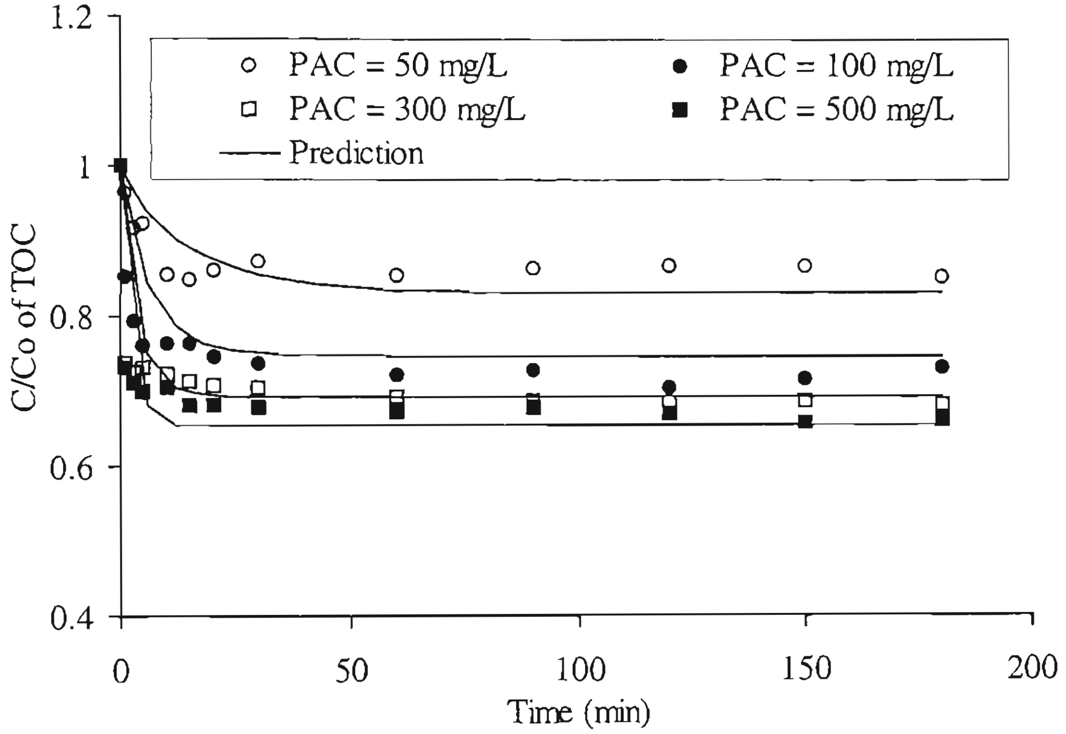


Figure 7.10 Mass transfer at different PAC doses

(Mixing intensity, $G = 92\ s^{-1}$, average initial TOC concentration of the synthetic wastewater = 3.8 mg/L, C = effluent TOC concentration, mg/L and C_0 = influent TOC concentration)

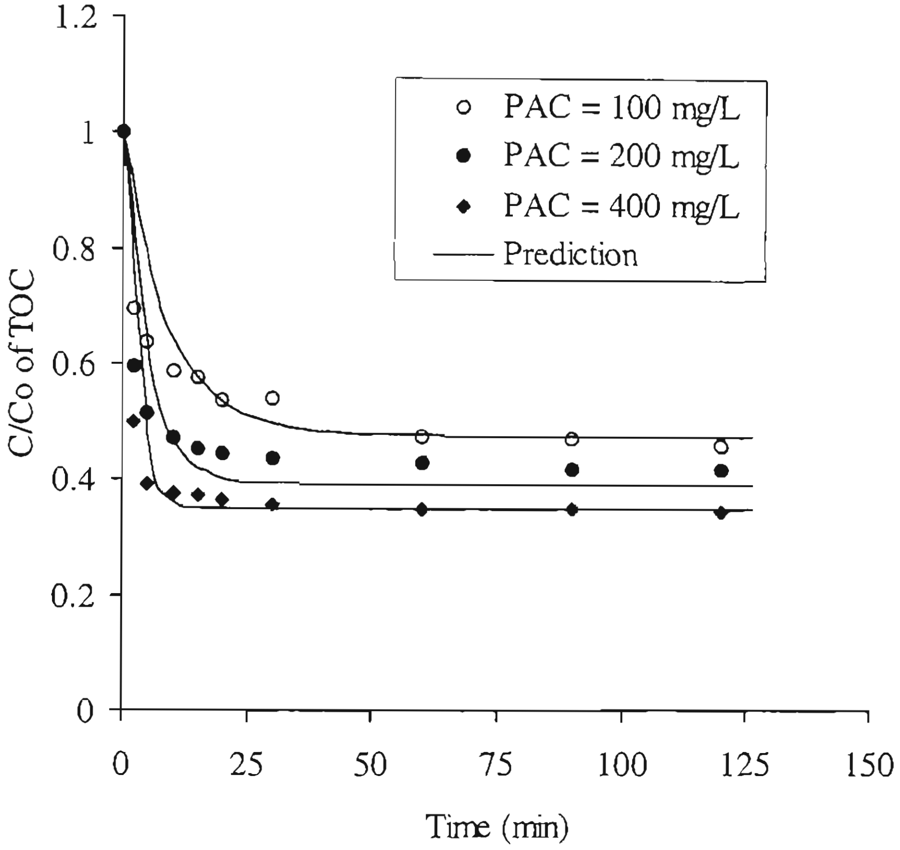


Figure 7.11 Mass transfer at different PAC doses

(Mixing intensity, G = 92 s^{-1}, average initial TOC concentration of the secondary sewage = 3.6 mg/L, C = effluent TOC concentration, mg/L and C_0 = influent TOC concentration)

7.4.3 Experimental Investigation on the Submerged Membrane-PAC Adsorption Hybrid System

The schematic diagram of the submerged hollow fibre microfiltration system is shown in Figure 7.12. Wastewater was pumped into the reactor (9L) using feed pump. The feed pump was used to control the influent and effluent flow rate. A predetermined amount of PAC was added into the tank to adsorb the dissolved organic substances, which was subsequently separated by the membrane filtration imposed by the suction pump. The inflow and outflow were kept equal to maintain the constant volume of wastewater in the reactor. Level sensor compensates the level difference that may arise due to membrane fouling. The pressure gauge is used to measure the transmembrane pressure of the hybrid system. Air diffuser was used to maintain the PAC in suspension. It also provides the dissolved oxygen necessary to maintain the microbial community in the reactor when the system is used for long-term operation. This study was limited to the short-term adsorption-membrane filtration only. The properties of the submerged hollow fibre membrane are shown in Table 7.2.

Table 7.2 Properties of the membrane

Properties	Hollow fibre membrane
Total Surface area (m^2) (320 fibres with 12 cm length)	0.05
Pore size (μm)	0.1
Material	Polyethylene
Inner diameter (mm)	0.27
Outer diameter (mm)	0.41

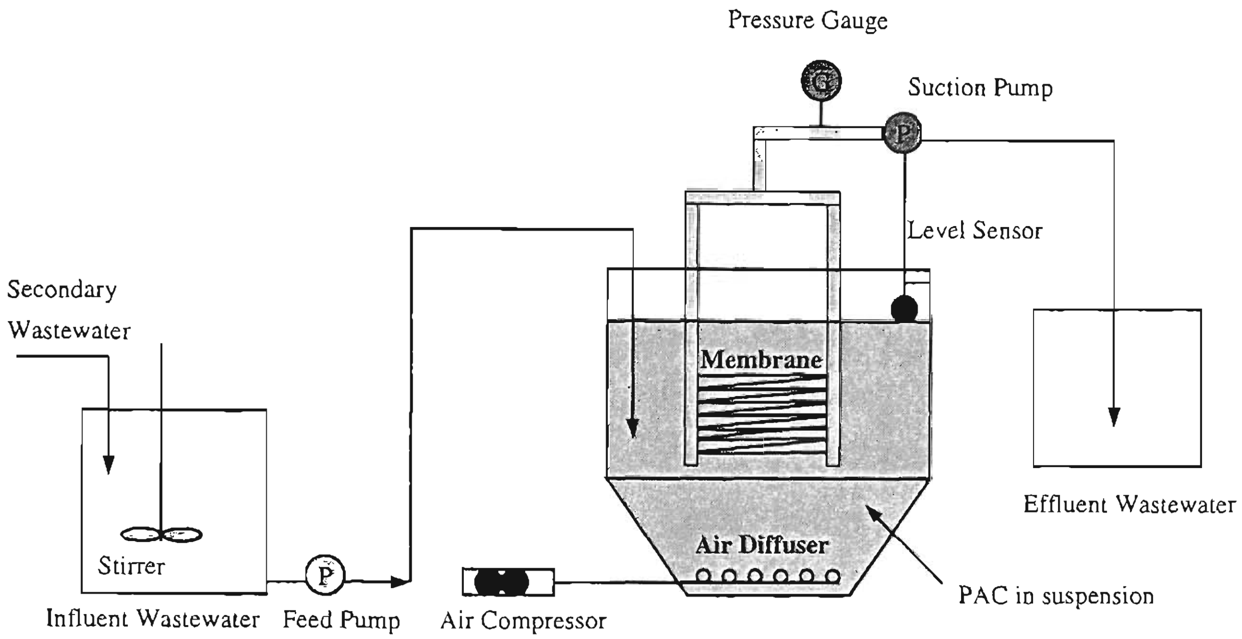


Figure 7.12 Schematic diagram of submerged hollow fibre membrane filtration hybrid system

7.4.3.1 Membrane Cleaning Procedure

The fouling of the submerged membrane can be reduced by providing aeration to the suspension of wastewater and/or pretreatment to the wastewater solution (such as PAC adsorption). However, the membrane fouling cannot be completely avoided, and therefore, a suitable membrane cleaning must be provided for an efficient and economical operation of the membrane system. The cleaning of the membrane depends on the fouling type. If the fouling of the membrane is external, then simple backwashing technique by air or water can clean the membrane surface for fresh operation of the system. However, in the case of internal fouling which is usually caused by organics, the membrane needs chemical cleaning. Since the membrane clogging in this study was mainly due to the organics, the membrane was submerged in 0.4% NaOCl and 4% NaOH solution for 2 hours, 2 times for chemical cleaning. Normally, 1% HCl is used 2-5 times to remove calcium attachment, and 2% citric acid for 2 hours, 1-2 times to remove iron, aluminium and manganese attachments from the membrane. However in the present experiments, there was no need for chemical cleaning as the organics were removed by in-line PAC adsorption and the duration of the experiments was short.

7.4.3.2 Effect of PAC Dose on the Effluent TOC Profile

The effect of PAC dose on the TOC concentration profile of the effluent of the hybrid system is shown in Figures 7.13, 7.14 and 7.15. As expected, the organic removal efficiency of the system increased with the increase in PAC dose. The solid mass transfer coefficient of the system was observed to be insensitive to the PAC dose and remained almost constant. However, the membrane correlation coefficient of the system increased when higher dose of the PAC was fed into the system. The relationship between PAC doses, filtration flux and membrane correlation coefficient (MCC) is shown in Figure 7.16. The MCC was also found to increase marginally with higher filtration flux.

A long-term operation of the PAC-membrane hybrid system for 47 days showed that the system could be effectively used in practice without interruption or cleaning (Figure 7.17). It should be noted that a second and third PAC doses of 1 g/L each time was added at the end of 27th and 43rd days respectively. This periodic addition of PAC helped to keep the organic removal efficiency constant. If higher dose of PAC is fed into the reactor, it is obvious that the system can be used continuously for longer period of time. Kim et al. (2001) found that the organic removal efficiency of the submerged hybrid system from a synthetic secondary effluent was more than 95% and 90% for 40 g and 10 g of PAC respectively for more than 40 days. In addition to the improved water quality, it was also observed that the high PAC dose in the membrane reactor extensively decelerated the membrane fouling process.

Filtration Flux = 3 x 10^{-3} L/s/m^2 (Biologically treated sewage effluent)

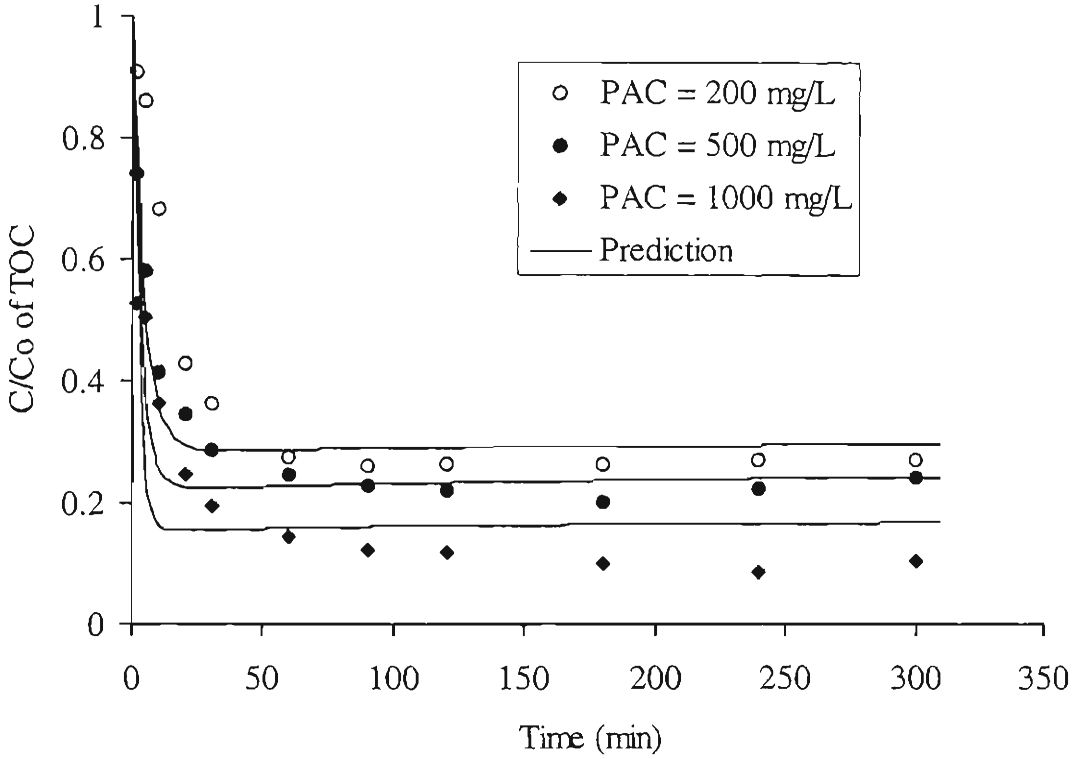


Figure 7.13 Effect of PAC dose on the performance of the submerged membrane (Filtration flux = 3 x 10^{-3} L/s/m^2, average influent TOC of biologically treated sewage effluent = 2.9 mg/L, C = effluent TOC concentration, mg/L and C_0 = influent TOC concentration)

Filtration Flux = 1.7 x 10^{-3} L/s/m^2 (Biologically treated sewage effluent)

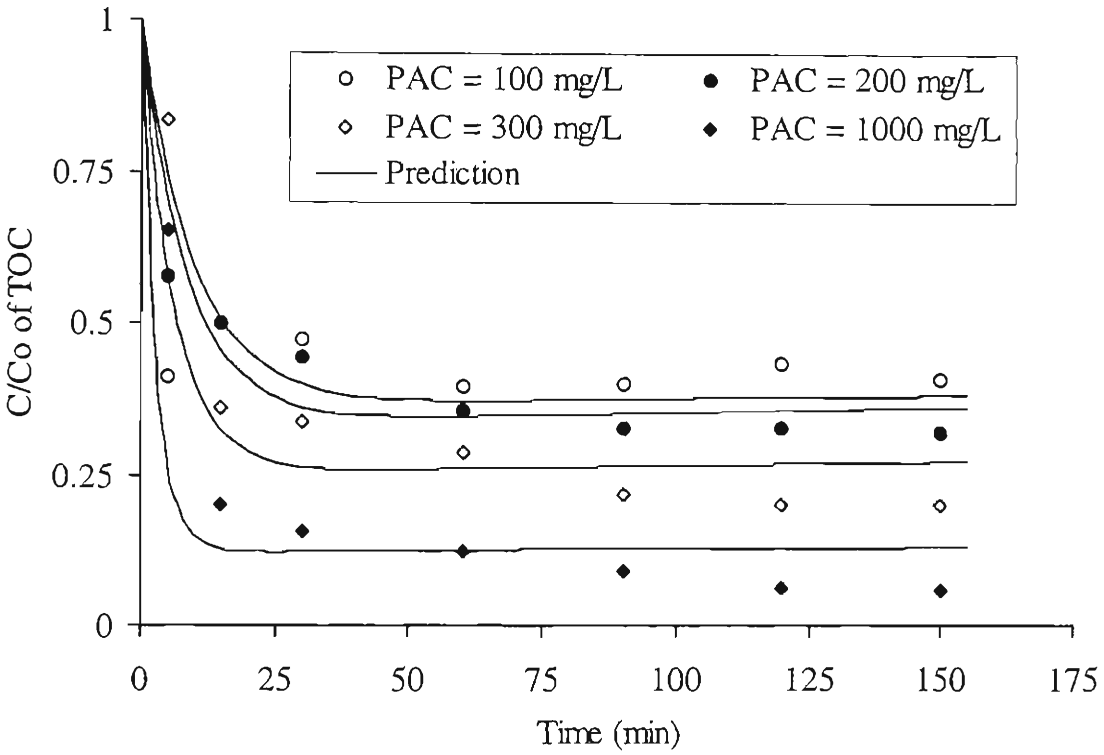


Figure 7.14 Effect of PAC dose on the performance of the submerged membrane (Filtration flux = 1.7 x 10^{-3} L/s/m^2, average influent TOC of biologically treated sewage effluent = 3.0 mg/L, C = effluent TOC concentration, mg/L and C_0 = influent TOC concentration)

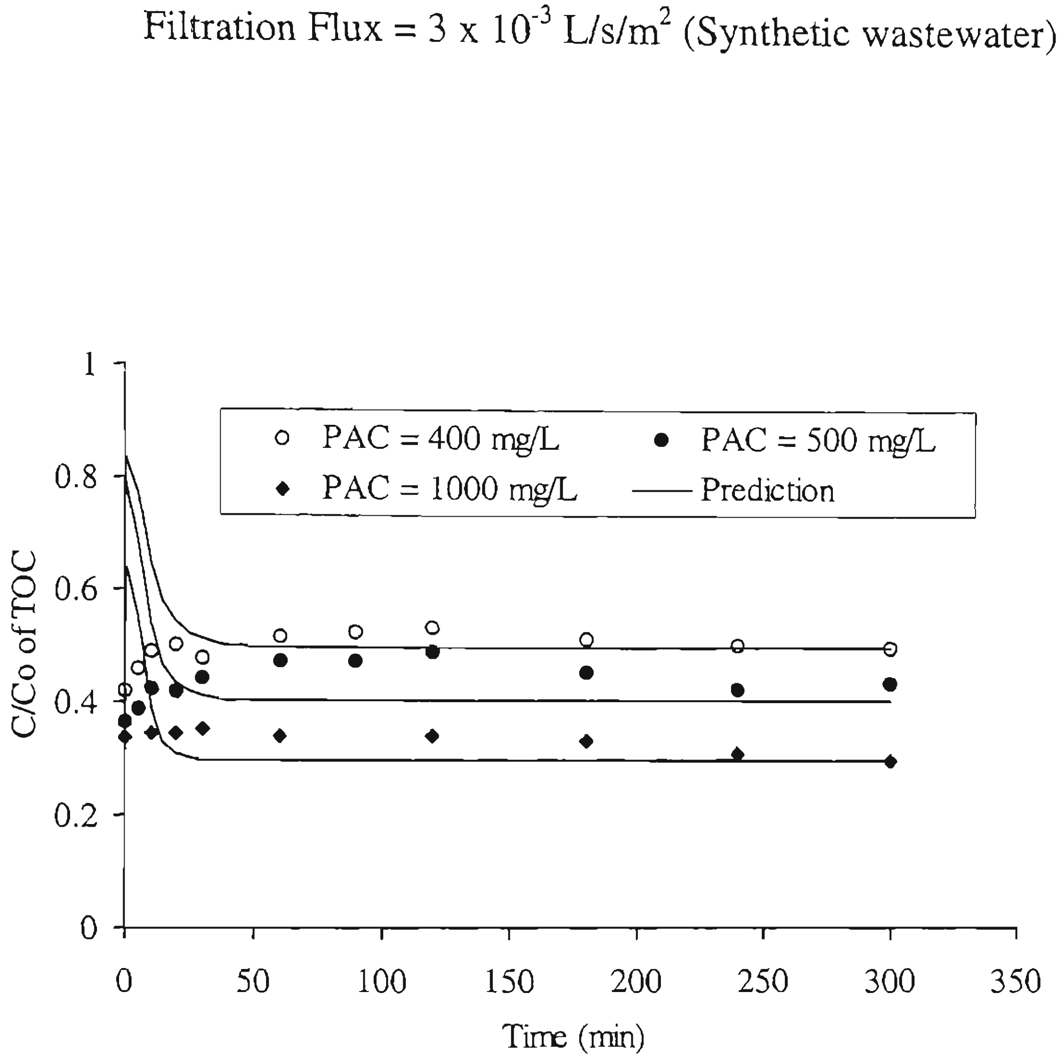


Figure 7.15 Effect of PAC dose on the performance of the submerged membrane (Filtration flux rate = 3 x 10^{-3} L/s/m^2, average influent TOC of the synthetic wastewater = 4.2 mg/L, C = effluent TOC concentration, mg/L and C_0 = influent TOC concentration)

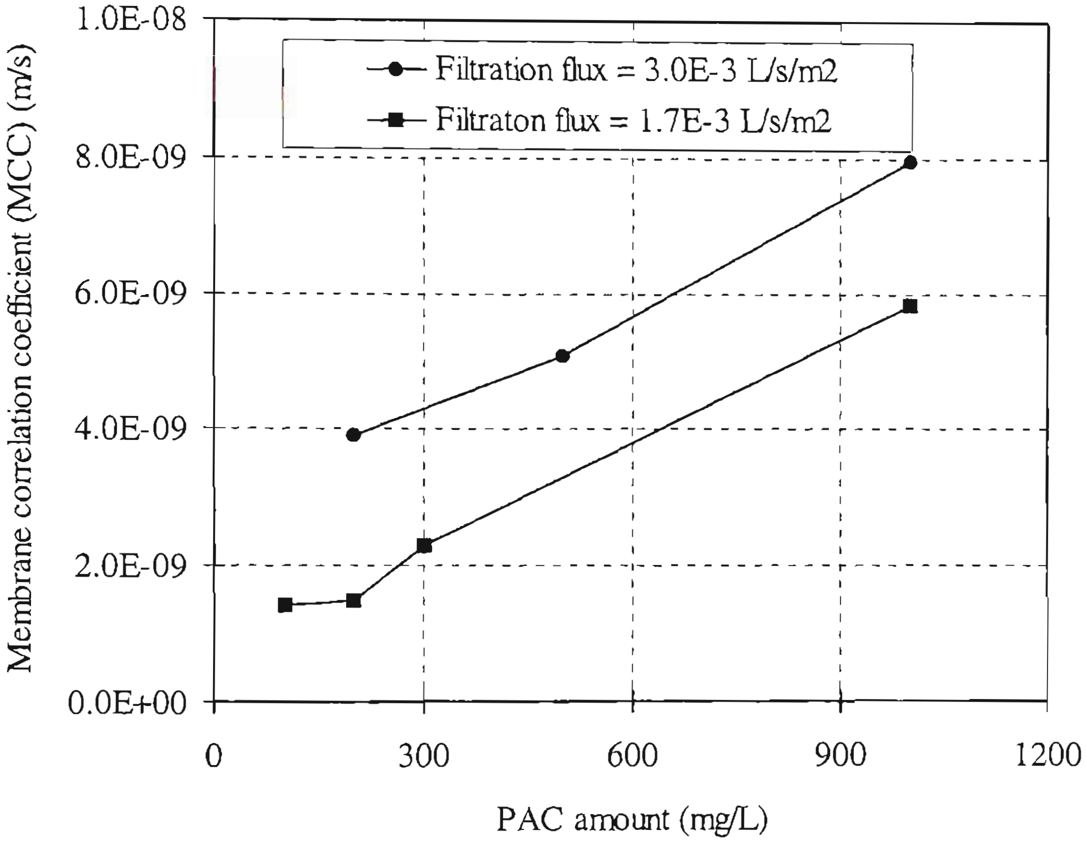


Figure 7.16 Relationship between membrane correlation coefficient (MCC), filtration flux, and PAC dose (Average influent TOC of secondary sewage = 2.95 mg/L)

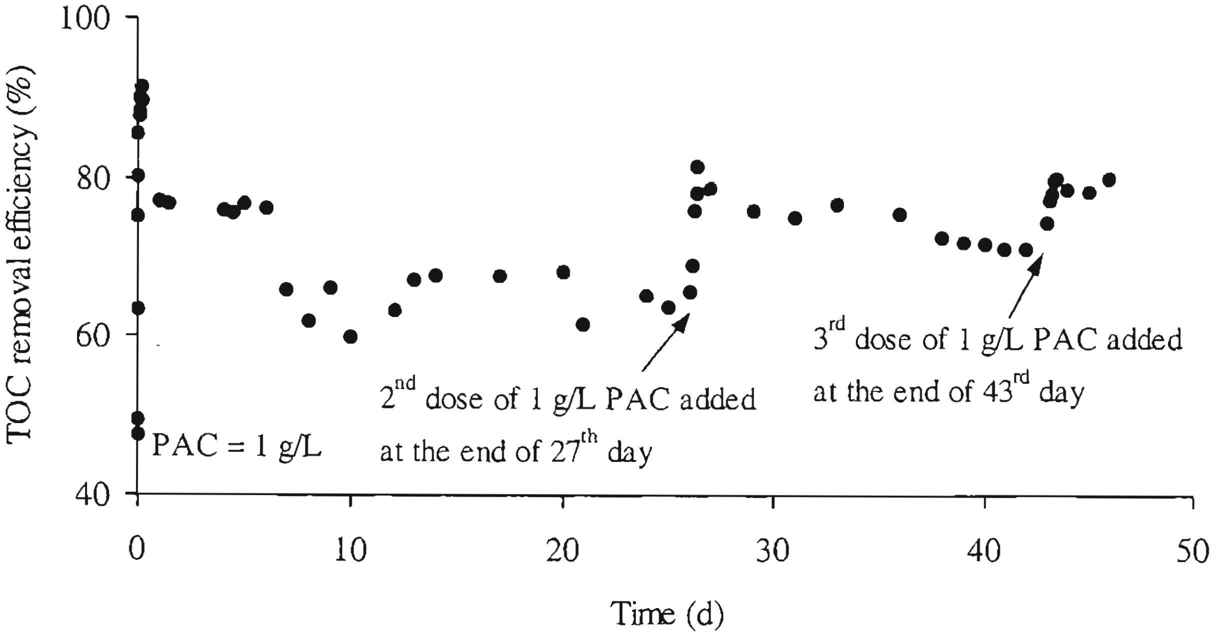


Figure 7.17 Long-term performance of the submerged membrane hybrid system (Average influent TOC of the biologically treated sewage effluent = 3.0 mg/L, C = effluent TOC concentration, mg/L and C_0 = influent TOC concentration)

7.4.4 Experimental Investigations with the External Loop Cross-flow Microfiltration System

In crossflow microfiltration, two separate tanks were used; one for the PAC slurry and another for the wastewater. The flow rate of the feed pumps was regulated to maintain the required wastewater flow and the PAC concentration to the helicoidal tube mixer (where adsorption of organics onto PAC surface takes place). The crossflow velocity through the membrane was maintained by controlling the transmembrane pressure.

The membranes used were hydrophilic poly-vinylidene fluoride (PVDF) supplied by Millipore and is referred to as GVLP with the MPS (membrane pore size) of 0.1, 0.22 and 0.45 μm. The pressure of the membrane was controlled at 20 kPa by two valves (V1 and V2) and pressure transducers (G1 and G2) at two points. The permeate flux was measured by recording the permeate volume and time of filtration. The dimensions of the filtration channel in the CFMF cell were of 6 cm length, 0.6 cm width, and 0.036 cm of thickness. The CFMF cell had 9 filtration channels which matched and the total membrane area at 3.24×10^{-3} m^2. In each experiment, a new membrane was used to obtain reproducible results. The schematic diagram of the cross-flow microfiltration is shown in figure 7.18.

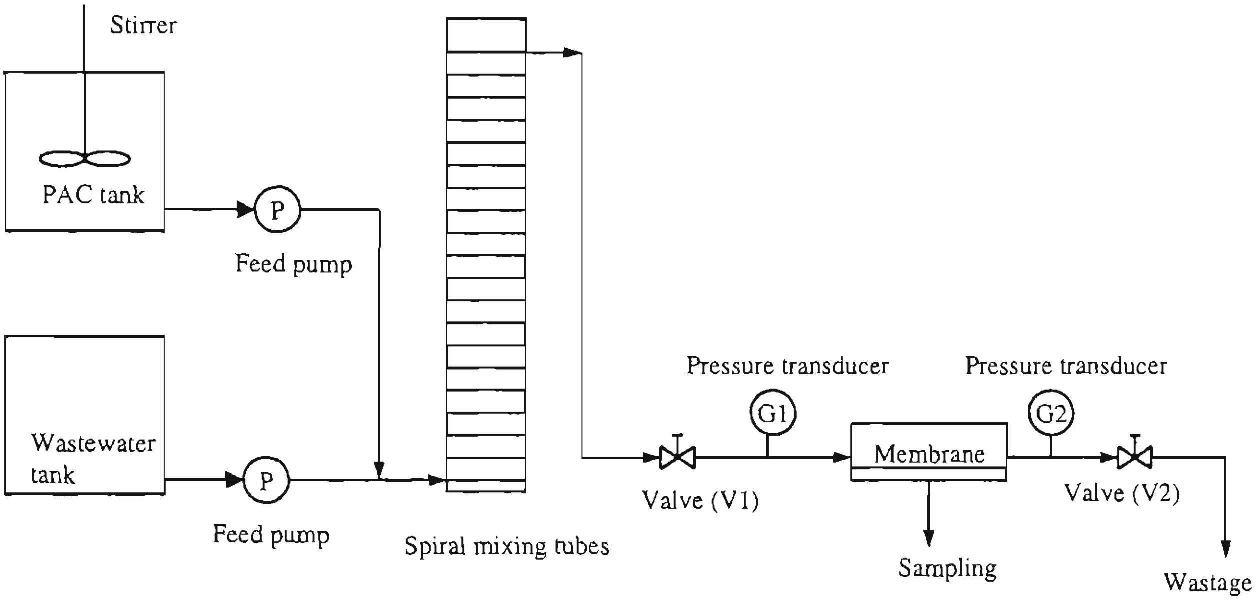


Figure 7.18 Schematic diagram of the crossflow microfiltration hybrid system

7.4.4.1 Effect of PAC Dose and the TMP on Permeate Flux

The effect of PAC dose on the permeate flux of the cross-flow microfiltration system is shown in Figures 7.19 and 7.20. It is obvious that the use of PAC in the system reduces the sharp decline in the permeate flux. In other words, the PAC adsorbs the organic and inorganic substances, and thus the membrane fouling by direct deposition of organics on membrane is controlled. When the membrane pore size was increased, as anticipated, the permeate flux also increased for the same transmembrane pressure (TMP). However, the permeate flux depends on the operating transmembrane pressure and the duration of the experiment. At lower TMP, the permeate flux is low, and thus the filtration operation is longer, as there will be a thin deposition of cake layer (of PAC) on membrane. However, when the TMP is increased, the thickness of the deposition of the organic laden PAC particles on the membrane increases, and they can block the pores of the membrane resulting in a rapid reduction in the permeate flux in a short period of operation. As shown in Figures 7.19 and 7.21, the initial permeate flux from the hybrid system decreased when the PAC was added. The obvious reason is the deposition of the PAC particles on the membrane surface. However, within few minutes of time, the permeate flux with PAC is higher than that without PAC. It shows that the effect of membrane fouling due to adsorption of organic or inorganic substances is more crucial in the design of the hybrid system than the effect of the membrane pore blocking by PAC. It may be due to the fact that when PAC is added to the system, the organics are adsorbed onto the PAC, and PAC adsorbed with organics deposit onto the membrane surface. Unlike the organics alone, the organic laden PAC cannot penetrate through the membrane pores, and get deposited on the membrane surface. Thus the flux decline in the PAC-membrane hybrid system is due to the deposition of the cake layer of organic laden PAC particles. However, the flux decline with the addition of PAC is smaller with filtration compared to the that without PAC. The fouling most likely is the external and reversible. However, when the system is run without PAC, the flux decline is due to the direct adsorption of organic and inorganic substances on the membrane surface, which may results in blocking the pores of the membrane. The nature of the fouling most likely is the internal and irreversible one.

The TOC profile of the effluent from the hybrid system is presented in Figure 7.22. The TOC removal efficiency of the hybrid system was only 25%. The lower TOC removal is due to relatively low amount of PAC and most importantly very short contact time of wastewater with PAC (only 7 mins). The film mass transfer coefficient of organic as calculated by linear driving force approximation (LDFA) model was 6 x 10^{-6} m/s. The Freundlich isotherm was employed to calculate the mass transfer coefficient in the hybrid system. The main function of the membrane was to separate the PAC from the stream and produce clear water. The adsorption of organic on the membrane surface was ignored in the LDFA model, because when the wastewater solution (without PAC addition) was passed through the membrane, practically no TOC (total organic carbon) removal was observed. The organic removal efficiency of the system was assumed to be totally dependent on the adsorption of organics onto the PAC. As can be seen from Figures 7.19 - 7.22, the application of PAC not only reduce the organic level of the effluent (Figure 7.22) but also help in minimizing the permeate flux decline with time (Figures 7.19-7.21).

The mechanisms by which the PAC reduces the flux decline rate in the hybrid system can be described as follows: (i) the PAC particle may have a scouring effect on the membrane surface resulting in reducing the thickness of the cake layer deposited on the membrane, and (ii) the PAC may have a filtration aid effect on the membrane surface resulting in reducing the hydrodynamic resistance on the cake layer (Adam, 1993). The crossflow operation mode usually generates a shearing force and/or turbulence over the membrane surface limiting the thickness of the cake layer. Since the PAC particles are big enough, there is possibility that deposited PAC particles are often washed away from the membrane surface by the crossflow velocity, and thus the flux decline rate is reduced.

With membrane pore size (MPS) = 0.11 μm

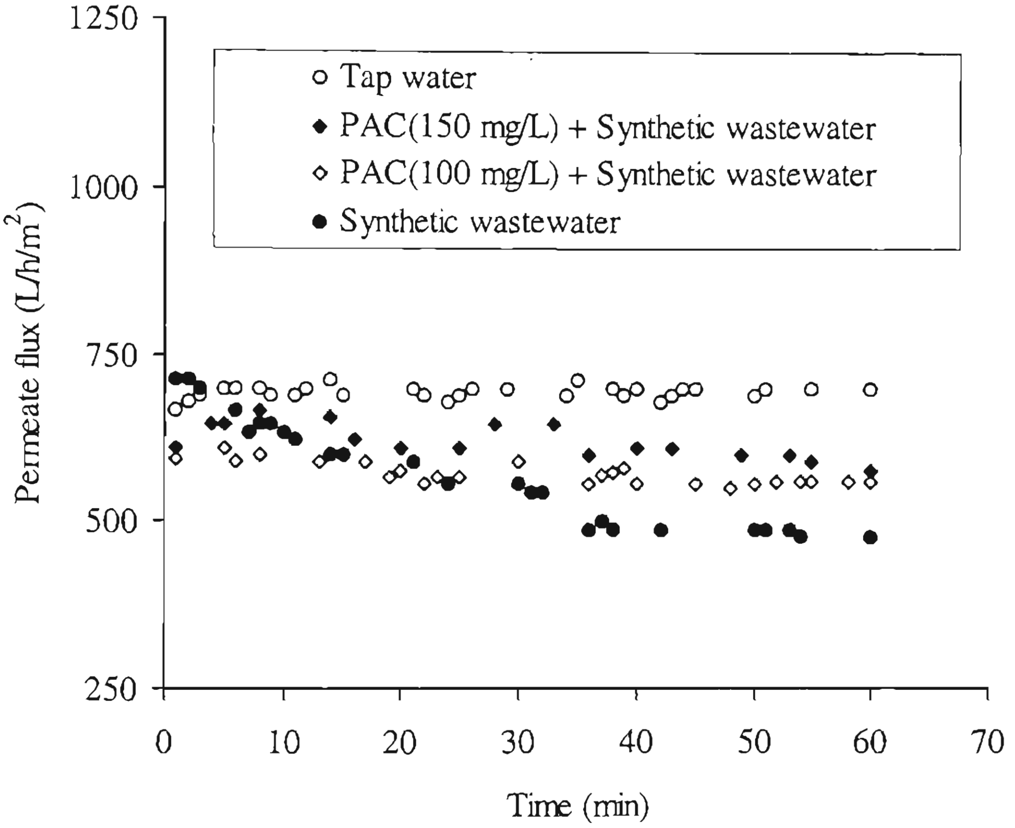


Figure 7.19 Effect of PAC dose on the permeate flux from the CFMF hybrid system (Membrane pore size = 0.11μm, TMP = 20 KPa, mixing intensity, G = 110.2 1/s, mixing time = 6.6 min, initial TOC of the synthetic wastewater = 4.1 mg/L, initial turbidity = 0.75 NTU)

With membrane pore size (MPS) = 0.22 μm

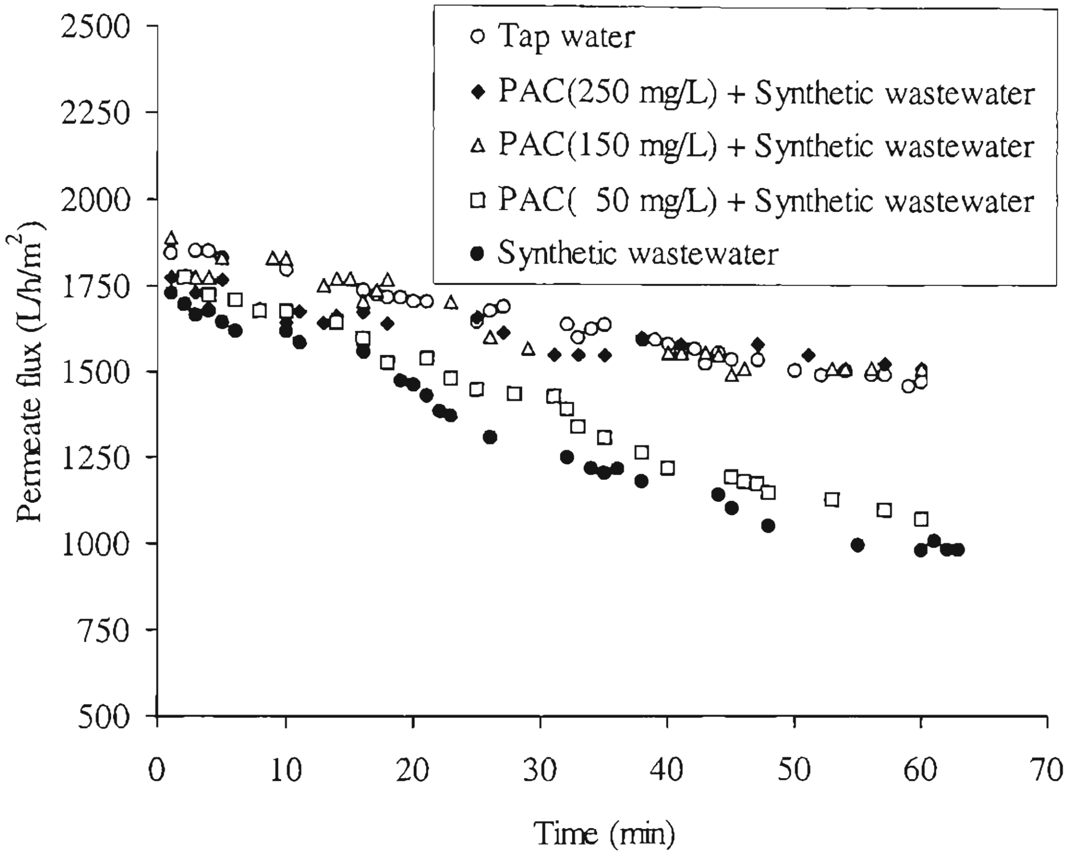


Figure 7.20 Effect of PAC dose on the permeate flux from the CFMF hybrid system (Membrane pore size = 0.22μm, TMP = 20 KPa, mixing intensity, G = 110.2 1/s, mixing time = 6.6 min, initial TOC of the synthetic wastewater = 4.1 mg/L, initial turbidity = 0.75 NTU)

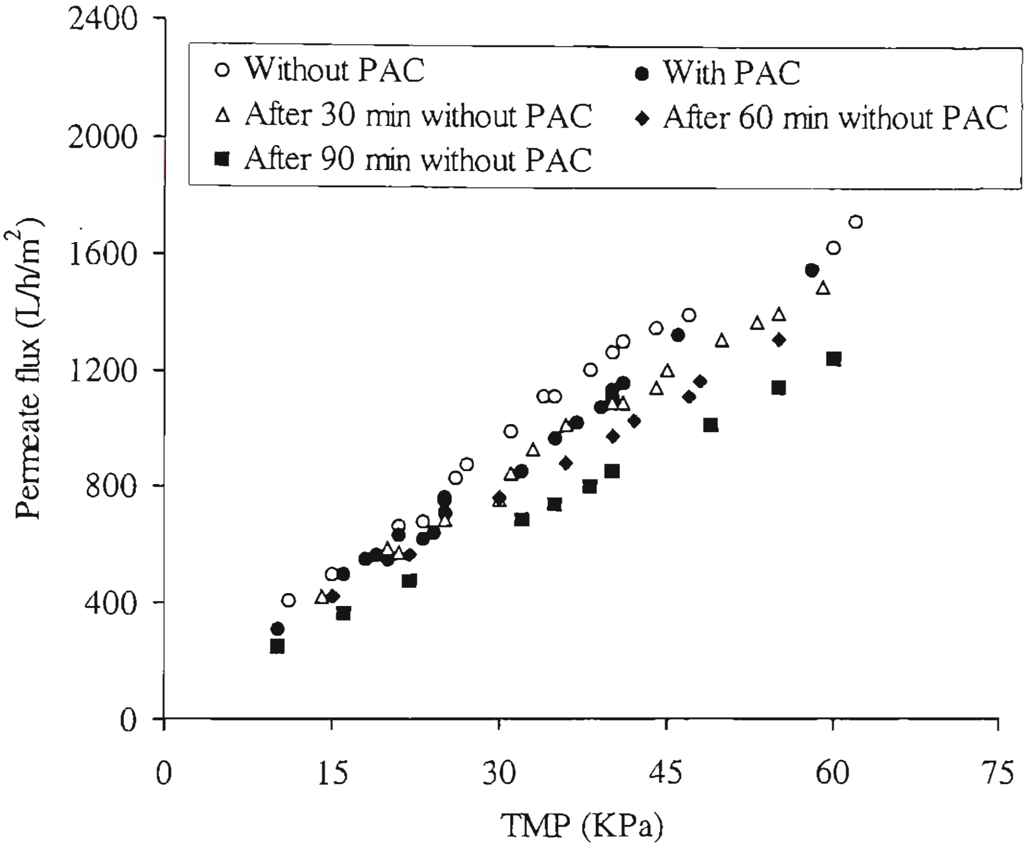


Figure 7.21 Effect of PAC dose and the TMP on the permeate flux from the CFMF hybrid system (Membrane pore size = 0.11μ m, PAC dose = 150 mg/L, mixing intensity, G = 110.2 1/s, mixing time = 6.6 min, initial TOC of the synthetic wastewater = 4.1 mg/L, initial turbidity = 0.75 NTU)

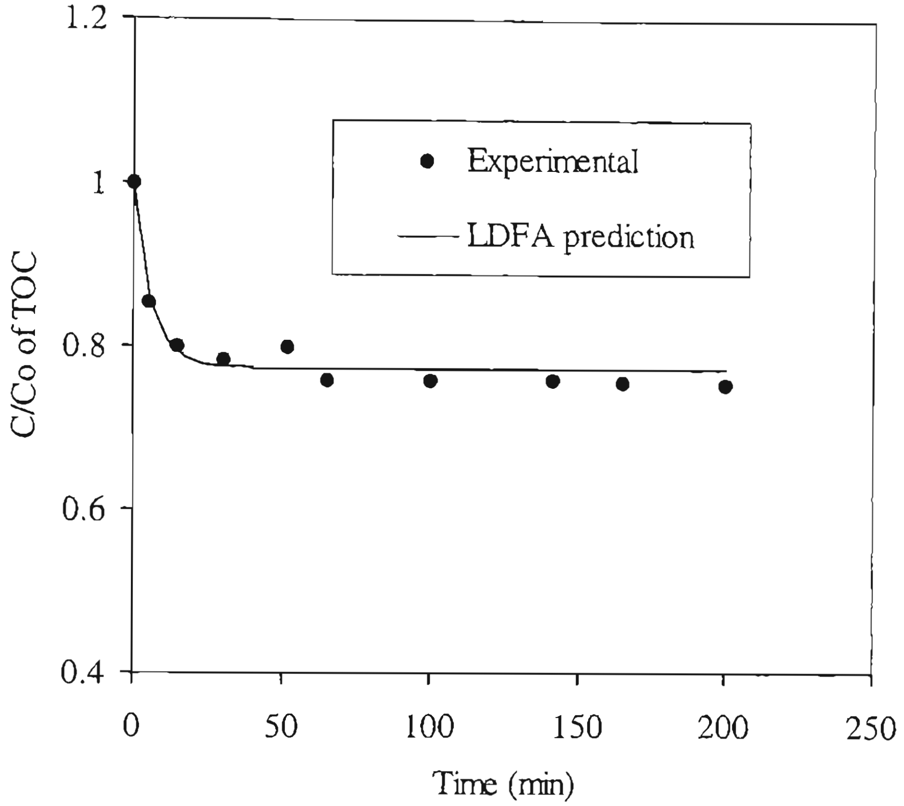


Figure 7.22 TOC profile of effluent from the CFMF hybrid system

(Membrane pore size = 0.22μ m, PAC dose = 150 mg/L, mixing intensity, G = 110.2 1/s, mixing time = 6.6 min, $k_f = 6 \times 10^{-6}$ m/s, initial TOC of the synthetic wastewater = 4.1 mg/L, initial turbidity = 0.75 NTU, C = effluent TOC concentration, mg/L and C_0 = influent TOC concentration)

7.4.4.2 Membrane Fouling Mechanisms

There are basically four constant pressure membrane filtration models as described in the Section 7.3 of the chapter. Since the organic substances used in the synthetic wastewater contain larger molecules, the fouling mechanism was assumed to be mainly due to the formation of cake layer on the membrane surface. The physical sieving, electrostatic interactions, concentration polarization, dispersion forces, and hydrophobic bonding are some of the major factors that encourage the cake deposition depending on the characteristics of the targeted solution. In this section, cake filtration model (CFM) and standard blocking model (SBM) were used to predict the permeate volume from the flat-plate membranes of pore sizes 0.11 μm, 0.22 μm, and 0.45 μm. As can be seen from Table 7.3, the CFM model is more accurate in predicting the flux volume from the hybrid system than the SBM model. The CFM and SBM predictions for membranes of different pore sizes are presented in Figures 7.23 to 7.25. The mode equations are given in Section 7.3 (equations 7.6 and 7.7 for CFM and SBM respectively).

Table 7.3 Percentage error of the model prediction

Membrane pore size (μm)	Percentage error in the prediction by	
	Cake filtration model (CFM)	Standard blocking model (SBM)
0.11	0.08	0.17
0.22	0.08	0.56
0.45	0.25	0.95

In practice, both the cake formation and the pore blocking can occur simultaneously. However, as expected, the above result (Table 7.3) shows that the membrane fouling is mainly due to the formation of filter cake layer on the membrane surface.

With membrane pore size (MPS) = 0.11 μm

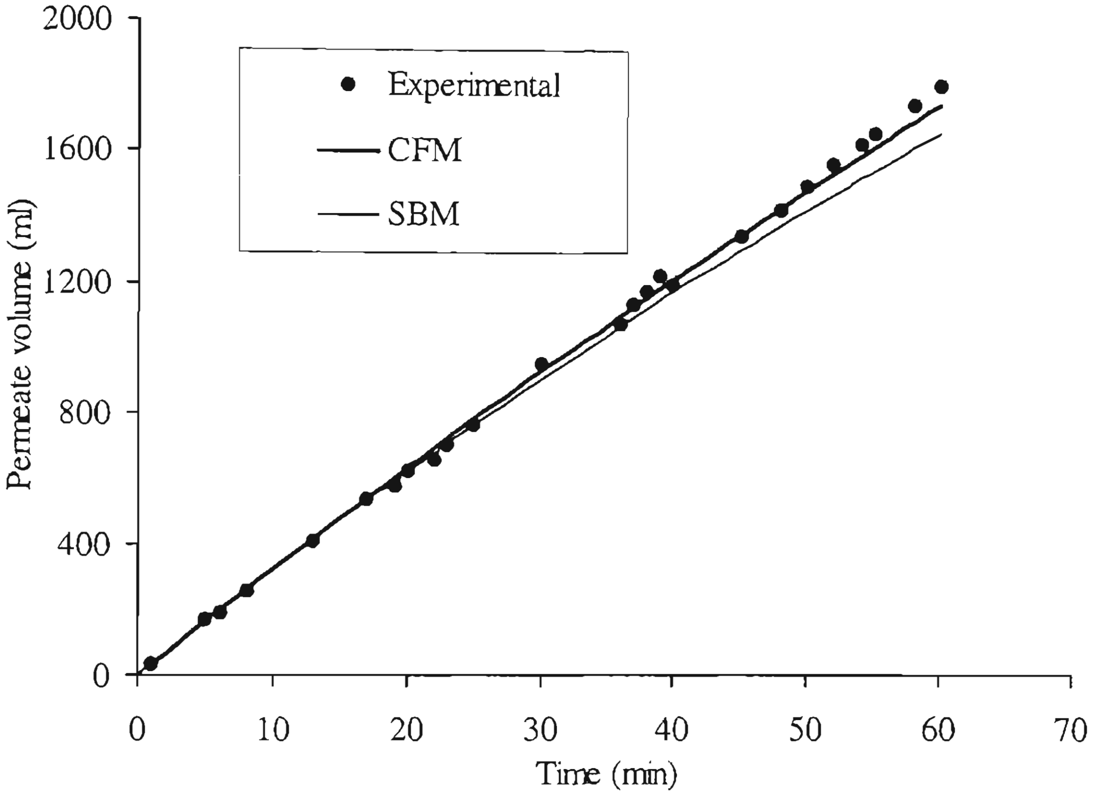


Figure 7.23 Permeate volume with time and its prediction

(Membrane pore size = 0.11μ m, PAC dose = 150 mg/L, mixing intensity, G = 110.2 1/s, mixing time = 6.6 min, TMP = 20 Kpa, $k_c = 8 \times 10^{-2}$ h/L^2, $k_s = 1 \times 10^{-1}$ 1/L, $J_0 = 2$ L/h)

With membrane pore size (MPS) = 0.22 μm

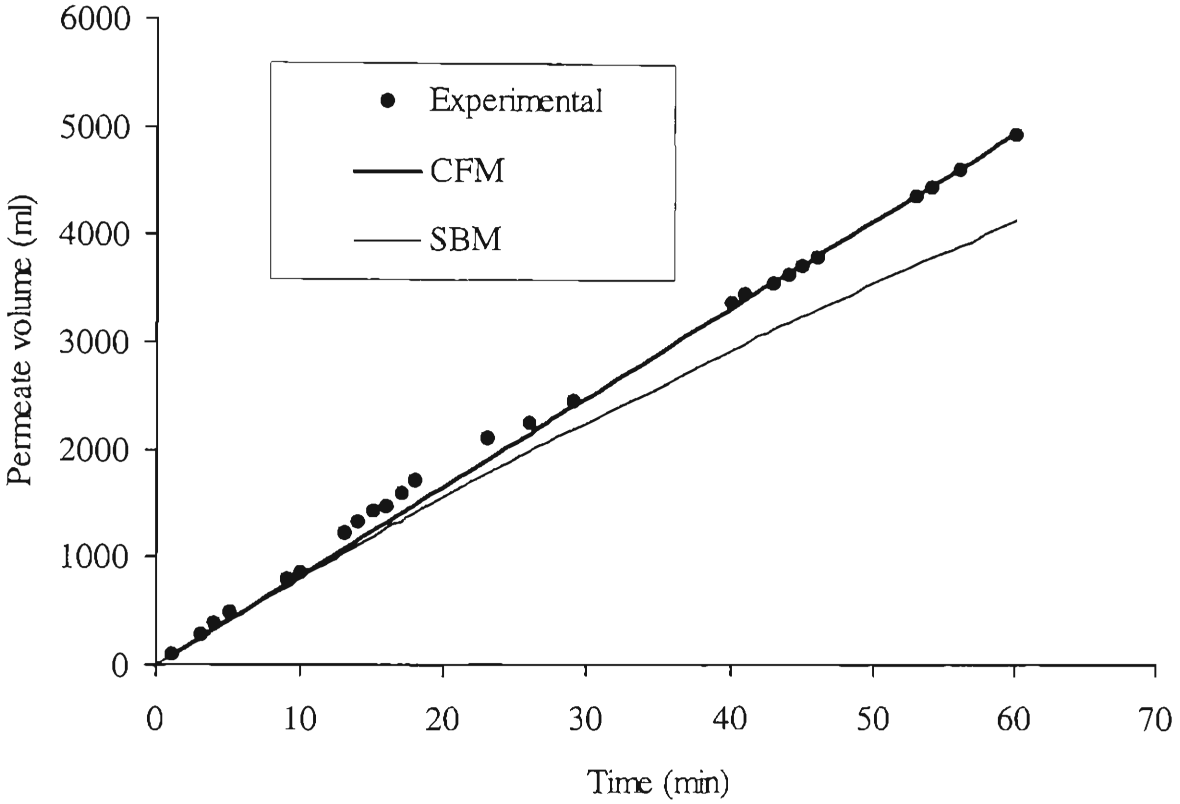


Figure 7.24 Permeate volume with time and its prediction

(Membrane pore size = 0.22 μ m, PAC dose = 150 mg/L, mixing intensity, G = 110.2 1/s, mixing time = 6.6 min, TMP = 20 Kpa, $k_c = 8 \times 10^{-5}$ h/L^2, $k_s = 4 \times 10^{-2}$ 1/L, $J_0 = 5$ L/h)

With membrane pore size (MPS) = 0.45 μm

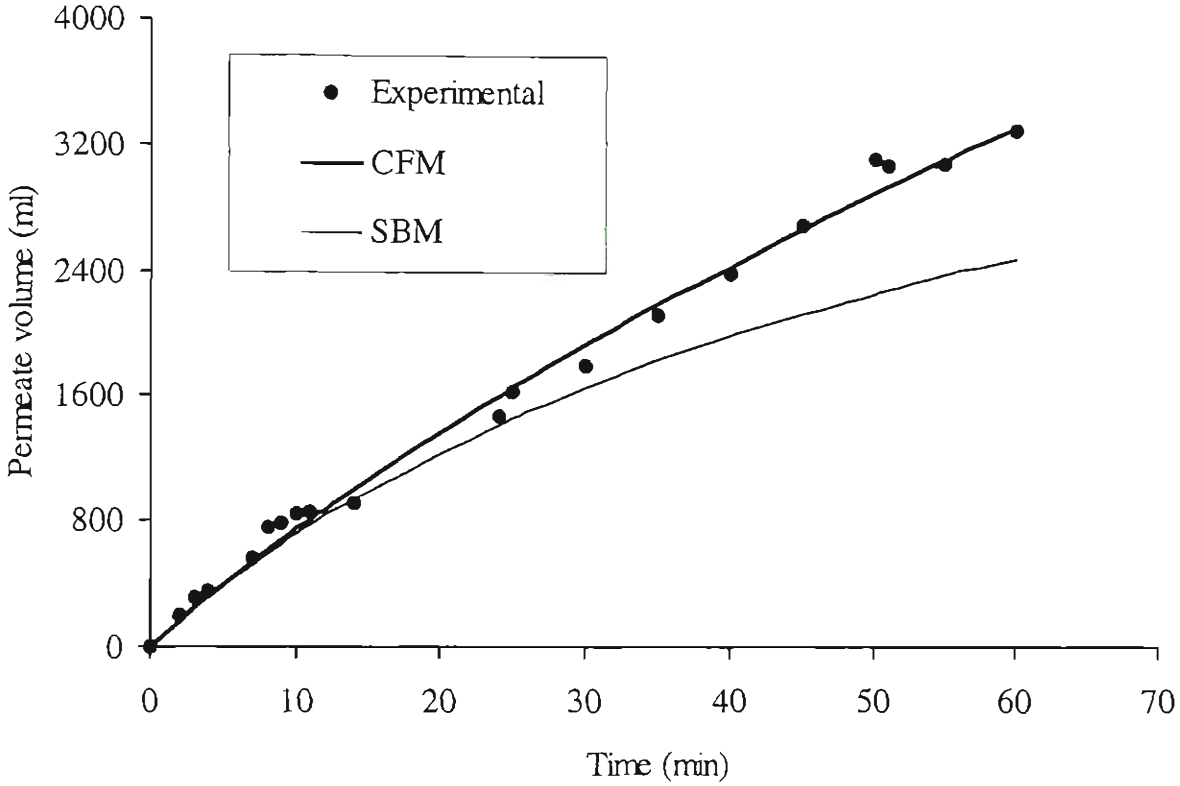


Figure 7.25 Permeate volume with time and its prediction

(Membrane pore size = 0.45 μ m, PAC dose = 150 mg/L, mixing intensity, G = 110.2 1/s, mixing time = 6.6 min, TMP = 20 Kpa, $k_c = 6 \times 10^{-2}$ h/L^2, $k_s = 2 \times 10^{-1}$ 1/L, $J_0 = 5$ L/h)

7.5 Conclusions

The submerged PAC-Membrane hybrid system was found to be effective in removing dissolved organic substances from the synthetic wastewater and the biologically treated sewage effluent. The system has potential for its long-term application in the treatment of wastewater without the need of frequent membrane cleaning. This preliminary study showed that the PAC-membrane hybrid system could be used for a long time effectively (over 47 days). At the initial stage of operation, the organic removal is mainly due to adsorption as discussed in this chapter, but in long term use of the system, the adsorption capacity of the PAC is exhausted gradually and the organic removal will be due to the biodegradation of the organic substances. The microbial communities developed on the PAC, in the suspension of the reactor, and on the membrane surface will biodegrade the organics. A periodic addition of PAC helped to maintain the effluent quality constant.

A simple and practical mathematical model was developed for the submerged hollow fibre membrane hybrid system. The model predicted the organic removal efficiency of the system effectively. An empirical term, membrane correlation coefficient (MCC) was introduced to account for the adsorption of organics onto membrane surface. The MCC and the filtration rate were found to be the main model parameters that control the quality of the effluent from the system. Greater the value of MCC, better the organic removal efficiency of the system. The MCC value was found to increase with the increase in the PAC dose to the system. Since only the short-term experiments were conducted in this study, the biological degradation of the organics was not included in the model. It is however necessary to incorporate the biological degradation part in the model to predict the long-term efficiency of the system.

The cross-flow microfiltration system with external loop was also tested using synthetic wastewater. This study showed that the use of PAC was very much favourable for the long-term operation of the membrane hybrid system. The use of PAC could increase the operational life the membrane hybrid system by reducing the membrane fouling. The conventional pressure filtration models (CFM, and SBM) were found to predict the experimental results effectively. Since CFM was more effective in predicting the volume of the permeate flux from the hybrid system, it can be concluded that fouling mechanism of the membrane was mainly due to the formation of cake layer on the membrane surface.

The organic removal efficiency of the PAC-membrane hybrid system was only 25%. The lower organic removal efficiency is attributed to the smaller PAC dose (of 150 mg/L) and shorter contact time of PAC with the wastewater (only 7 mins). The PAC-membrane hybrid system can also produce a high quality of water depending upon the PAC dose, contact time, and the filtration flux.

Chapter 8

Conclusions and Recommendations

8.1 Conclusions

In this study, batch and fixed bed adsorption, fixed bed biofiltration, and adsorption-membrane hybrid system were evaluated in terms of organic removal from the synthetic wastewater and biologically treated effluent from a sewage treatment plant. The following conclusions were drawn from the study:

8.1.1 Batch Equilibrium Adsorption Study

- The adsorption equilibrium study showed that the initial organic concentration had substantial impacts on the isotherm parameters. Hence, it is necessary to estimate the isotherm parameters of models covering wide range of initial organic concentrations (as wastewater contains a wide range of organics at different concentrations).
- Biodegradation of the organics is one of the important aspects that should be considered in the adsorption modelling. In this study, the average biodegradation rate of the synthetic wastewater was 0.0178 h^{-1} and 0.0072 h^{-1} with and without inorganics respectively.
- The synthetic wastewater comprised three organic and seven inorganic substances. The detailed adsorption equilibrium study of the individual organic with and without inorganics indicated that the overall effect of the dissolved inorganics was unfavourable for the adsorption of the dissolved organics in the synthetic wastewater.
- The Freundlich isotherm, the association theory, and the characterization theory were used to describe the adsorption equilibrium results. The association theory and the characterization theory described the adsorption equilibrium results of the wastewater system more accurately than the commonly-used Freundlich isotherm.

- A multicomponent system was assumed in the adsorption modelling due to the presence of different components in the wastewater. The number of active and optimum components controlling the adsorption phenomenon was four and eight in the synthetic wastewater and the secondary treated effluent respectively. The synthetic wastewater contained 40-50% non-adsorbable fractions of total organic carbon whereas the secondary treated effluent had negligible fraction of non-adsorbable organics.

8.1.2 Batch Kinetics Adsorption Study

- The adsorption film mass transfer coefficient was calculated using the linear driving force approximation (LDFA) model. The main reason for using the model is its simplicity and adequacy in describing the mass transfer rate. The overall adsorption isotherm parameters were obtained from the association theory and the characterization theory, and the batch kinetics experimental results were fitted using LDFA model. The isotherm parameters obtained from both the theories were found equally effective in predicting the batch kinetics results.
- The dissolved inorganic compounds in the synthetic wastewater solution increased in the film mass transfer coefficient of adsorption of organics. The increase in the mass transfer rate might be due to the adsorption of inorganics onto activated carbon.
- The mass transfer rate increased with the increase in the adsorbent dose and the mixing intensity of the batch experiments. However, it decreased when the initial organic concentration of the wastewater solution was increased. The average value of the overall mass transfer rate was in the order of 10^{-6} m/s.
- The mass transfer coefficient was found to be a function of adsorbent dose, mixing intensity, and initial TOC concentration of the batch adsorption system.

8.1.3 Fixed Bed Adsorption Column System

- The GAC fixed bed system was effective in removing organics from the wastewater. The performance of the system was influenced by several operational parameters such as GAC bed depth, filtration velocity, and initial organic concentration of the feed solution. Deeper the GAC bed depth, or lower the filtration velocity, higher was the organic removal efficiency of the system.
- The adsorption mass transfer rate was not affected by the change in the fixed bed depth. However, it increased with the increase in filtration velocity, and it decreased with the increase in the initial organic concentration.
- The adsorption mass transfer rate was higher in the biologically treated sewage effluent than that in the synthetic wastewater prepared in the laboratory. The film mass transfer coefficient determined in the fixed bed adsorption system was slightly less than that determined in the batch adsorption system. It could be due to the higher mixing intensity used in batch experimentation.
- The fixed bed adsorption phenomenon was described by a dynamic adsorption model. The isotherm parameters obtained from the association theory and the characterization theory were used to predict the experimental results of the fixed bed system.
- The GAC fixed bed adsorption system produced better effluent quality.

8.1.4 Biofiltration System

- The biofilm growth on the GAC surface was observed after few weeks of operation of the GAC column. This growth of the biofilm on the surface of the GAC turned the adsorption system into biosorption or biofiltration system. The biological activity resulted in a consistent effluent organic concentration over a long period of time. For example a 4 cm GAC column resulted in 50-55% removal of organics over a period of 77 days.
- The GAC column was acclimatized with biomass at the filtration velocity of 1 m/h. The biomass growth was 0.09 g per g of GAC (maximum) after 42 days and 0.036 g per g of GAC (minimum) after 63 days of continuous operation.

- The daily backwash adopted did not affect the biological mass growth, thus the effluent quality of the biofiltration system. Its performance however, was affected by the change in filtration velocity and the influent organic concentration. Thus the biofilter should be operated in the same conditions at which it was acclimatized to achieve optimum and consistent organic removal efficiency.
- Although the higher filtration velocity led to inferior effluent quality, the TOC removal efficiency of the biofiltration system was consistent during the filtration run. A correct choice of filtration velocity and GAC bed depth with appropriate backwash can lead to a long-term operation with consistent and high effluent quality.
- A practical mathematical model proposed in this study predicted the organic removal efficiency of the GAC biofiltration system reasonably well. Both adsorption and biodegradation of organics were incorporated in the model. It is important to estimate the biofilter parameters for different operating conditions (such as acclimatization filtration velocity and initial organic concentration) to verify the versatility and adaptability of the model in practice.

8.1.5 Adsorption-membrane Hybrid System

- The adsorption-membrane hybrid system was evaluated using external loop flat-plate membrane and submerged hollow fibre membrane. This study showed that the use of PAC was useful in achieving significant organic removal by adsorption and hence it is suitable for the long-term operation of the membrane hybrid system.

8.1.5.1 External Loop Flat Plate Membrane

- The conventional pressure filtration models, cake filtration model (CFM) and standard blocking model (SBM) were found to successfully predict the experimental results of the external loop flat-plate membrane hybrid system. Since CFM was better in predicting the volume of the permeate flux from the hybrid system, it can be concluded that fouling mechanism of the membrane was mainly due to the formation of cake layer on the membrane surface.

- The organic removal efficiency of the plate membrane hybrid system was 25% for the PAC dose of 150 mg/L. The low efficiency may be due to the low dose of PAC and insufficient contact time of PAC with the wastewater. However, the use of PAC in the system was effective in reducing the fouling and thus maintaining the permeate flow practically constant with time.

8.1.5.2 Submerged Hollow-fibre Membrane

- The performance of the submerged membrane hybrid system in removing dissolved organic substances from the synthetic wastewater and the biologically treated effluent of a sewage treatment plant was remarkable. The system has potential for its long-term application in the treatment of wastewater without the need of frequent membrane cleaning. This preliminary study showed that the PAC-membrane hybrid system could be used for a long time effectively (over 47 days). A PAC dose of 1 g/L and a filtration flux of 1.7E-3 L/s/m^2 were used in this study. At the initial stage of operation, the organic removal is mainly due to adsorption, but in long-term use of the system, the adsorption capacity of the PAC is exhausted gradually and the organic removal will be due to the biodegradation of the organic substances. The microbial communities developed on the PAC, in the suspension of the reactor, and on the membrane surface assisted in the biodegradation of the organics.
- A conceptual mathematical model was developed for the submerged hollow-fibre membrane hybrid system. The model predicted the organic removal efficiency of the system effectively. A new term, membrane correlation coefficient (MCC) was introduced to account for the removal of PAC with organics adsorbed on it, and the adsorption of organics onto membrane surface. The MCC and the filtration rate were found to be the main model parameters that control the quality of the effluent from the system. Greater the value of MCC, better the organic removal efficiency of the system. The MCC value increased with the increase in the PAC dose to the system.

8.2 Recommendation

This study has prompted for the following recommendations for any future study:

- The adsorption study with different GAC and PAC is necessary to evaluate the effect of particle size and other physical properties on adsorption.
- The wastewater contains a matrix of dissolved organics and inorganics. Detailed physical and chemical characterization of the background organics of the wastewater would be helpful to assess the effect of molecular weight and the nature of the organics on adsorption.
- The biofiltration system can be acclimatized at different filtration velocity and influent organic concentrations to estimate the rate of biomass growth and the organic removal efficiency. This will enable to find the necessity of acclimatizing the biofilter at the specific conditions of operation.
- It is important that the biofilter model parameters are estimated from the detailed experimental investigation.
- Studies on the change in membrane properties when operated with and without PAC can give a new dimension in mathematical modelling of the membrane hybrid system.
- It is important that the membrane correlation coefficient (MCC) is determined experimentally.
- Pilot-scale studies with wastewater in field may produce a more reliable set of data to effectively design the adsorption, biofiltration, and membrane hybrid systems.
- The use of GAC and PAC were effective in reducing organics from wastewater. Long-term experimental studies of these systems are required to evaluate and compare these systems with other alternative systems.
- There is possibility of developing a practical mathematical model for the submerged membrane hybrid system in long run (i.e. membrane bioreactor).

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Appendix -1

(a) Effect of Pretreatment on Adsorption of Organics

(b) Adsorption of Organics in Spiral Mixing System

(a) Effect of Pretreatment on Adsorption of Organics

A1.1 Introduction

The treatment system, in practice, is and integration of different treatment processes. Any single process of the treatment system is inadequate, and every process has a great influence of the preceding treatment process. In this chapter, the effect of flocculation on adsorption was evaluated in terms of TOC removal efficiency. The flocculation process was selected because of its universal use in both water treatment and advanced wastewater treatment processes. The flocculation was carried out by $FeCl_3$, pre-filtration by floating media filter and adsorption by GAC and PAC.

The physical properties of GAC and PAC are shown Table 3.4 in Chapter 3. The floating medium of 1.9 mm diameter, and 50 kg/m^3 of density was used as a prefilter in a column of 9 cm diameter. The bed depth of the floating medium (polystyrene beads) was 1 m and porosity of 0.36.

A1.2 Experimental Investigation

Batch experiments were carried out in standard mechanical stirring device using GAC. Fixed bed experiments were conducted in a filter column of 2 cm diameter and 50 cm height. The column had ports for influent feed and effluent collection. The column was packed with GAC (porosity 0.65). Constant pressure head was maintained in the filter column to keep a constant filtration rate. The filtration rate here refers to the hydraulic loading rate (volume of wastewater flow per unit of cross sectional area of adsorption column per hour). The spiral tube adsorption was conducted in standard 6 mm tube of varying length spirally fixed in the outer surface of a column of radius 10 cm for mixing in the tube length.

As mentioned in Chapter 3 and 4, the total organic carbon (TOC) was measured using the UV-persulphate TOC analyser (Dohrmann, Phoenix 8000). The GAC and PAC used in the experiments was washed 3 times with distilled water and dried in the oven at 103.5° C for 24 hours. It was kept in a desiccator before using in the experiments.

A1.3 Results and Discussion

In this section, the experimental results of batch kinetics and fixed bed column with GAC, and spiral mixing tube adsorption system with PAC were investigated with and without the flocculent, $FeCl_3$.

A1.3.1 Effect of Pre-flocculation on Batch Kinetics

The batch experiments of the wastewater from Homebush Bay treatment plant with and without $FeCl_3$, were carried out to investigate the effect of flocculation on adsorption. In this process, on-line flocculent dose of $FeCl_3$ of 90 mg/L was added to the influent of the floating medium filtration. The dose of 90 mg/L of $FeCl_3$ was the optimum flocculent dose for the removal of COD, phosphorous and nitrogen. The effluent from the filter was collected and further treated in batch experimental system with GAC. It was observed that the pretreatment is very favourable for the subsequent adsorption process (Table 8.1). The suspended particles are generally removed by flocculation, which eases the organic loading on the subsequent adsorption process. It is obvious that the pre-flocculation process improves the mass transfer rate.

Table A1.1 TOC removal efficiency of the batch experimental system with and without flocculation.

GAC dose g/L	With pre-flocculation % of TOC removal	Without pre-flocculation % of TOC removal
1.0	75	60
2.0	90	80
3.0	95	85

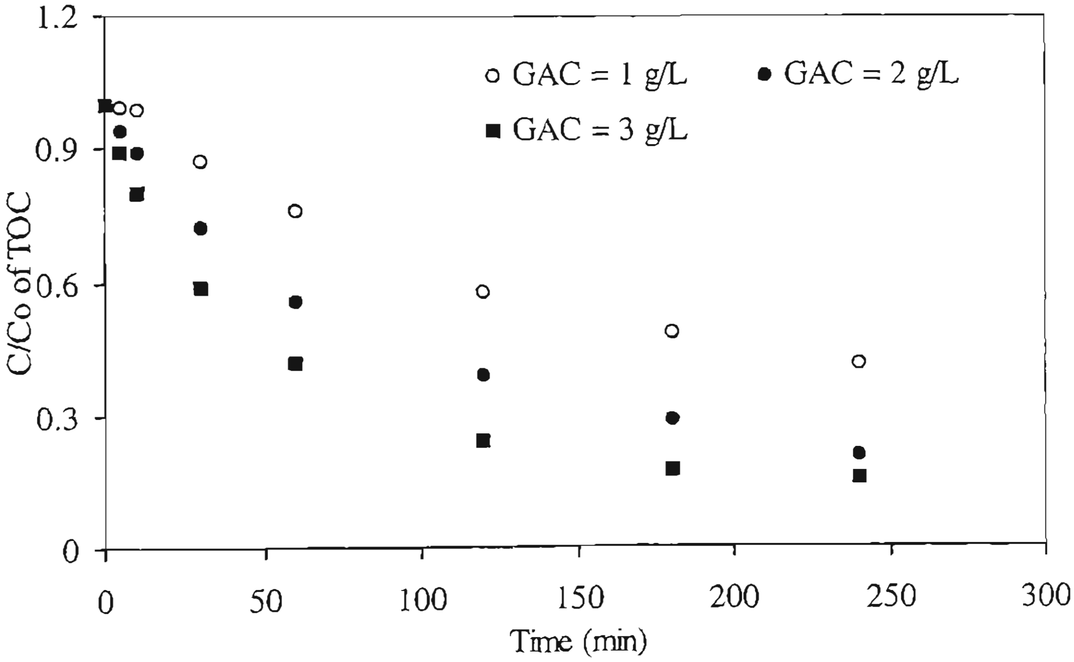

Figure A1.1 Effect of GAC dose on batch kinetics of the raw wastewater (Average initial TOC = 2.1 mg/L, stirring speed = 100 rpm)

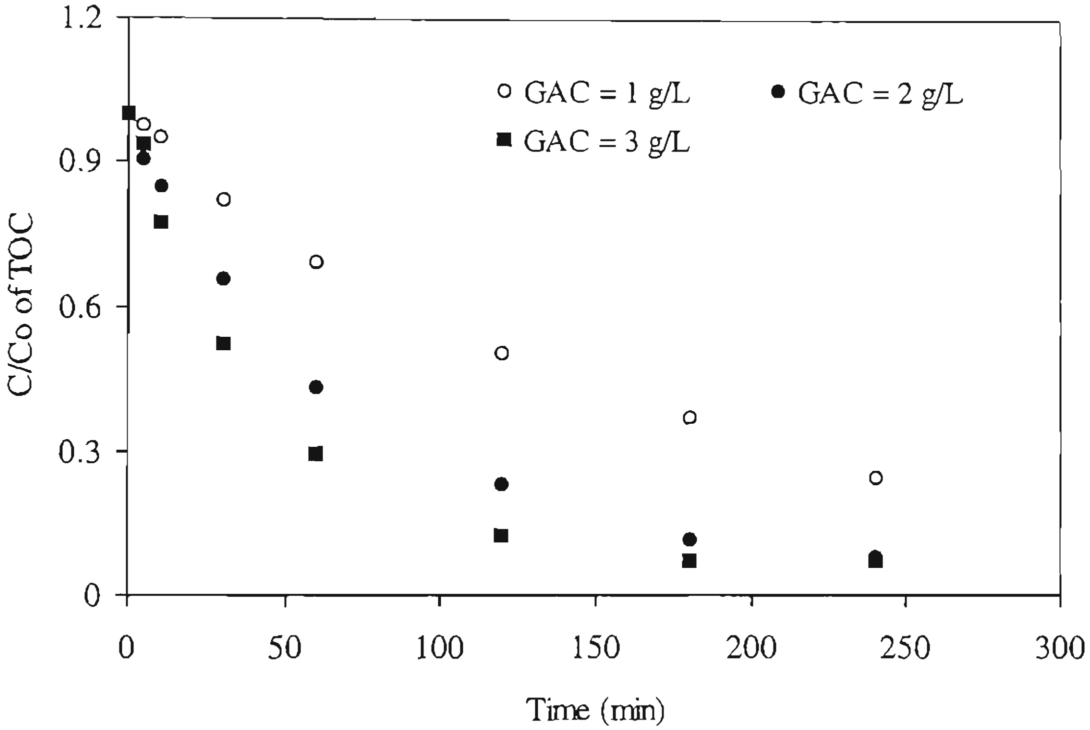

Figure A1.2 Effect of GAC dose on batch kinetics of the online- pre-flocculated wastewater (Average initial TOC = 1.4 mg/L, stirring speed = 100 rpm, $FeCl_3$ = 90 mg/L, floating medium flocculation-filtration rate = 30 m/h)

A1.3.2 Effect of Online-pre-flocculation on the Fixed Bed Effluent Profile

The fixed bed experiments using the wastewater from Homebush Bay treatment plant with and without $FeCl_3$, were carried out to investigate the effect of flocculation on adsorption. In this process, on-line flocculent dose of $FeCl_3$ of 90 mg/L was first added to the influent of the floating medium filtration. The effluent from the filter was collected at the rate of 30 m/h, and it was further passed through GAC column. It was observed that the pretreatment is very favourable for the subsequent adsorption process. The removal of the suspended particles by pre-flocculation-filtration not only eases the organic loading on the subsequent adsorption process, it improves the mass transfer rate, and also the operational life of the adsorption system. The TOC removal efficiency of the system was improved by 10-15% when pre-flocculation of the wastewater with $FeCl_3$ was done prior to adsorption (Figures 8.3-8.5).

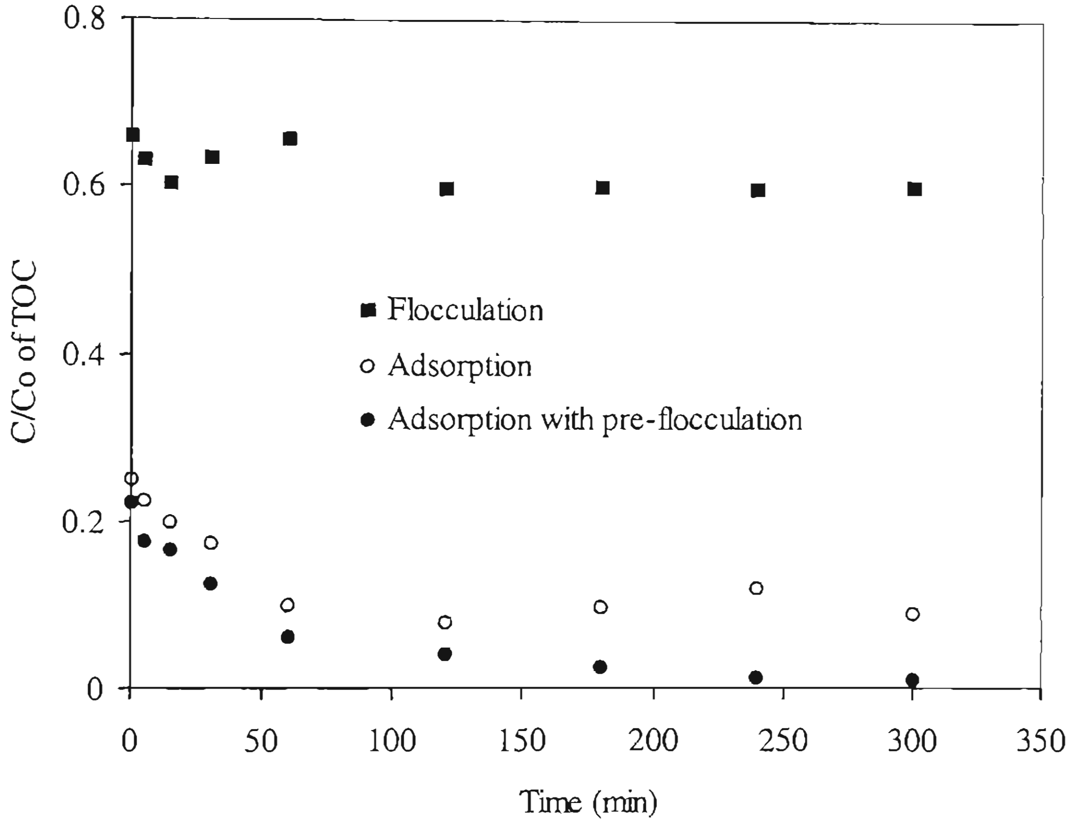

Figure A1.3 Effect of the online- pre-flocculation on the fixed bed effluent profile (Average initial TOC = 1.9 mg/L, adsorption-filtration rate = 1 m/h, $FeCl_3$ = 90 mg/L, floating medium flocculation-filtration rate = 30 m/h)

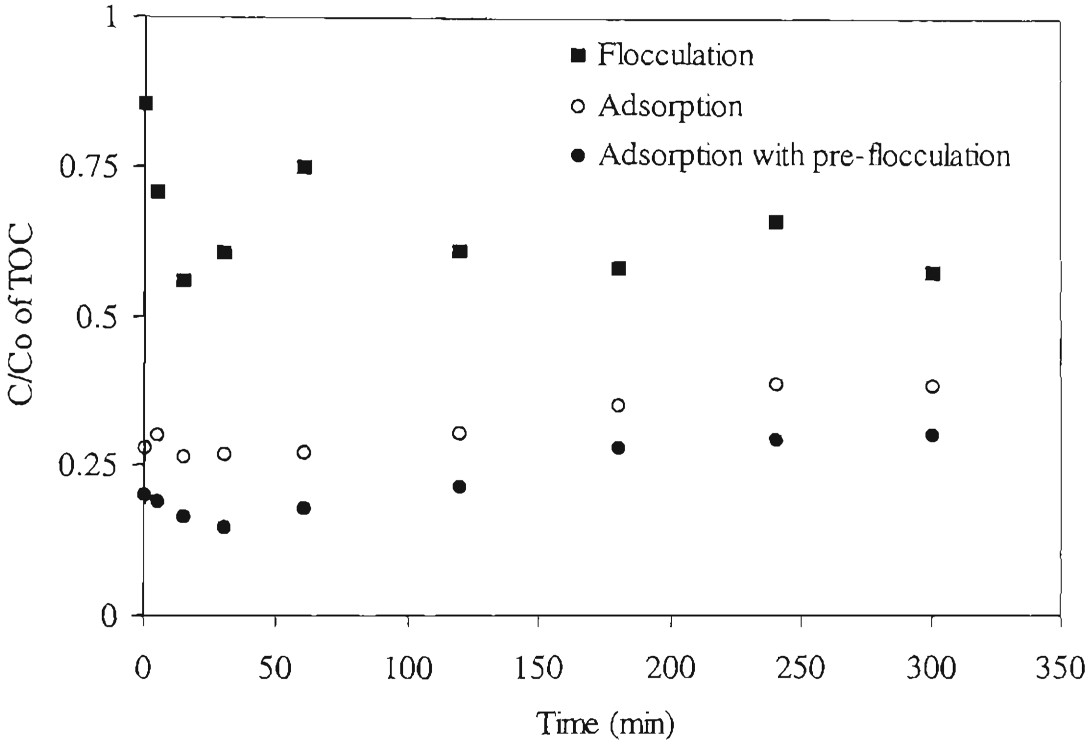

Figure A1.4 Effect of the online- pre-flocculation on the fixed bed effluent profile (Average initial TOC = 1.7 mg/L, adsorption-filtration rate = 5 m/h, bed depth = 4 cm, $FeCl_3$ = 90 mg/L, floating medium flocculation-filtration rate = 30 m/h)

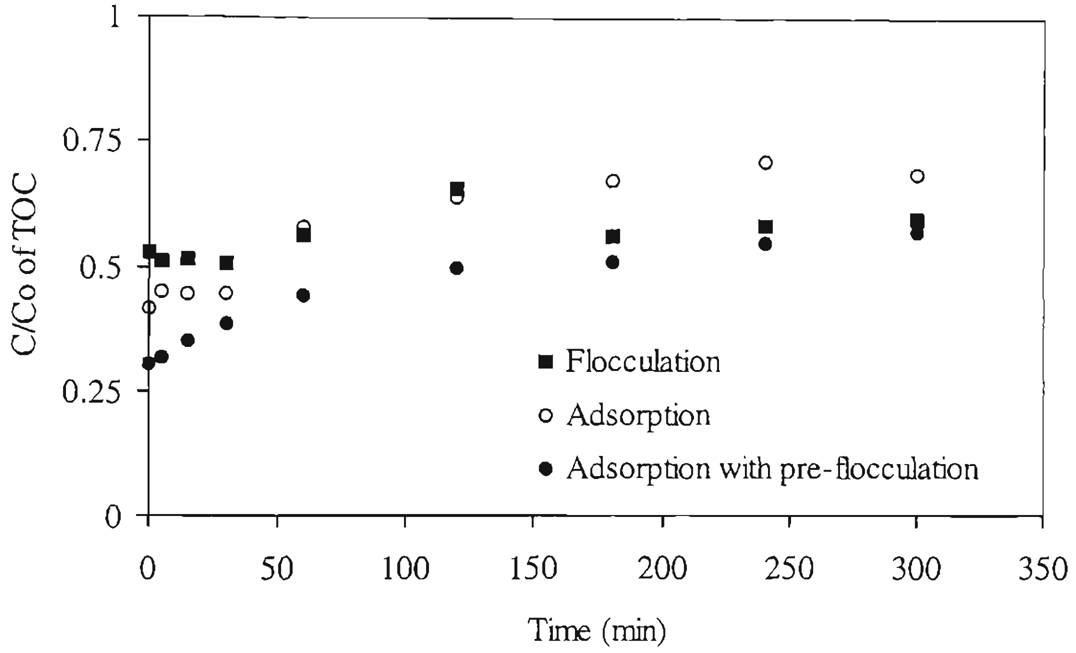

Figure A1.5 Effect of the online- pre-flocculation on the fixed bed effluent profile (Average initial TOC = 1.8 mg/L, adsorption-filtration rate = 10 m/h, bed depth = 4 cm, $FeCl_3$ = 90 mg/L, floating medium flocculation-filtration rate = 30 m/h)

A1.3.3 Effect of Flocculent on Spiral-tube Adsorption

The effect of flocculent, $FeCl_3$ on spiral tube adsorption was investigated using secondary sewage from St Marys sewage treatment plant. A series of experiments were conducted to find the optimum G-value, contact time, and PAC dose. The optimum value for G-value, contact time, and PAC dose were found to be 160.4 1/s, 20 mins and 100 mg/L respectively. In this optimum spiral tube length adsorption system, the TOC removal efficiency of $FeCl_3$ with and without PAC was measured, and it was found that the addition of $FeCl_3$ was not favourable for the removal of TOC from the wastewater. It is due to the formation of flocs, which cover the surface of PAC thus stopping the organic molecules to be adsorbed onto PAC particles. The TOC removal efficiency of the spiral system was found to be 37% with PAC (100 mg/L), 15% with $FeCl_3$ (30 mg/L), and only 4% when both PAC and $FeCl_3$ were fed together to the system (Figure A1.6).

Since the results of the batch kinetics and fixed bed adsorption showed that pre-flocculation improved the TOC removal efficiency of the adsorption system, it is obvious that the flocs particles should be removed prior to the adsorption processes, so that only the dissolved organic substances are adsorbed without blocking the pore of the activated carbon and thus the adsorption capacity of the activated carbon is effectively utilized.

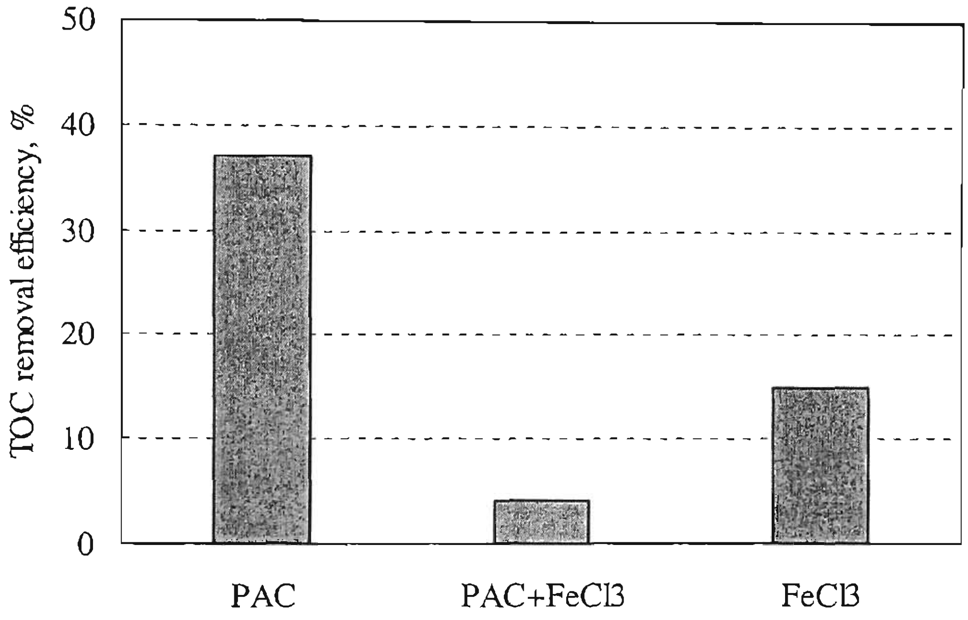

Figure A1.6 Effect of the online-flocculation on spiral tube adsorption of secondary sewage (Average initial TOC = 4 mg/L, optimum G value = 160.4 1/s, $FeCl_3$ = 30 mg/L, PAC = 100 mg/L, contact time = 20 min.)

A1.4 Conclusions

The pre-flocculation with $FeCl_3$ was favourable for adsorption process in both batch and fixed bed adsorption system. The TOC removal efficiency of the adsorption systems were found to increase by 10-15% when the wastewater was passed through pre-flocculation-filtration system prior to adsorption process. The ineffectiveness of the flocculent, $FeCl_3$ on spiral tube adsorption system was due to blockage of PAC surface by the flocs formed during flocculation. The result suggests the importance of pre-filtration system prior to adsorption process. The flocs formed during flocculation should be removed in pre-filter so that only the dissolved organic substances can most effectively, be adsorbed onto activated carbon..

(b) Adsorption of Organics in Spiral Mixing System

In crossflow microfiltration hybrid system, powdered activated carbon (PAC) is mixed with the influent solution prior to its feed to membrane system. The PAC slurry is usually mixed in on-line feeding system (refer to the Figure 7.18) in spiral mixing tubes. In this study, the adsorption of organics of the secondary treated effluent was investigated at different mixing intensity (G value), different PAC dose, and different contact time. The optimum values of the mixing intensity, the contact time, and the PAC dose were 160.4 s^{-1}, 20 mins, and 100 mg/L respectively.

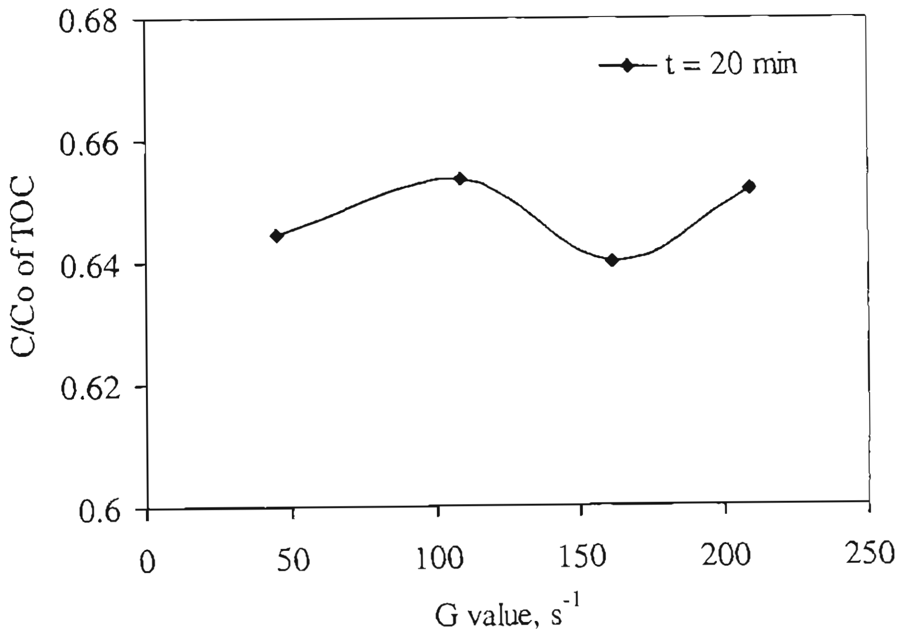

Figure B1.1 Effect of mixing intensity on adsorption of organics
(Initial TOC = 3.5 mg/L, contact time = 20 mins, PAC dose = 100 mg/L)

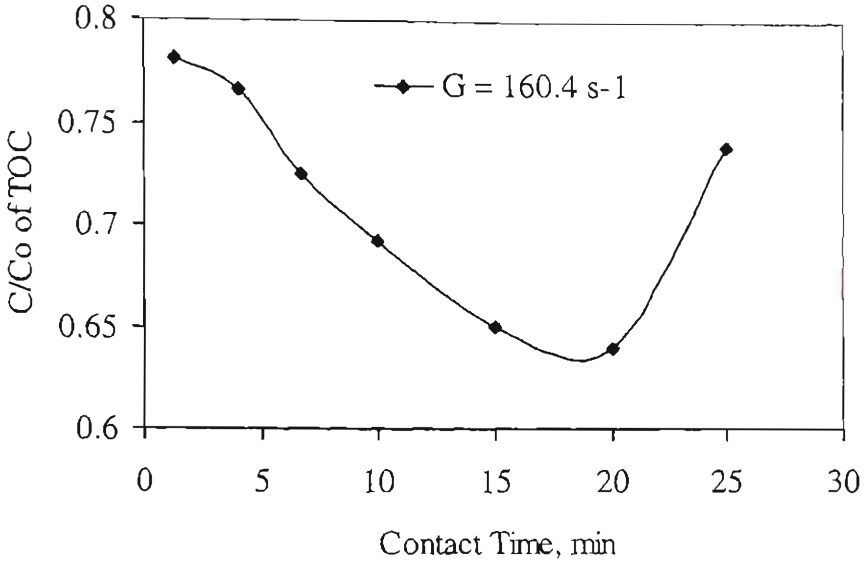

Figure B1.2 Effect of contact time on adsorption of organics
(Initial TOC = 3.5 mg/L, mixing intensity = 160.4 s^{-1}, PAC dose = 100 mg/L)

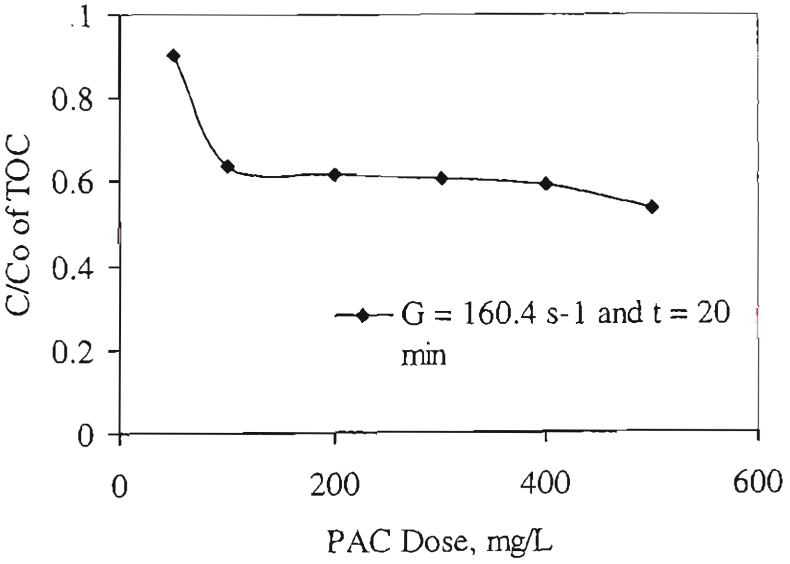

Figure B1.3 Effect of PAC dose on adsorption of organics
(Initial TOC = 3.5 mg/L, mixing intensity = 160.4 s^{-1}, contact time = 20 mins.)

Appendix -2

Relationship between Index parameters

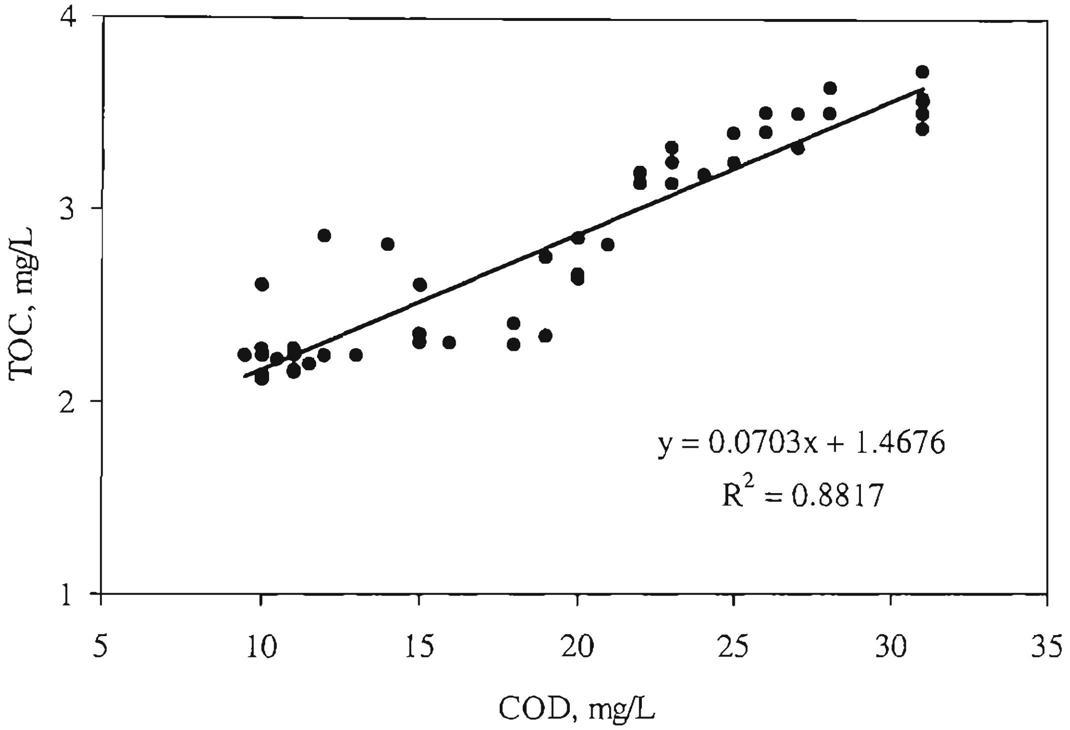

Figure A1. Relationship between total organic carbon (TOC) and chemical oxygen demand (COD) of the secondary sewage from St Marys sewage treatment plant

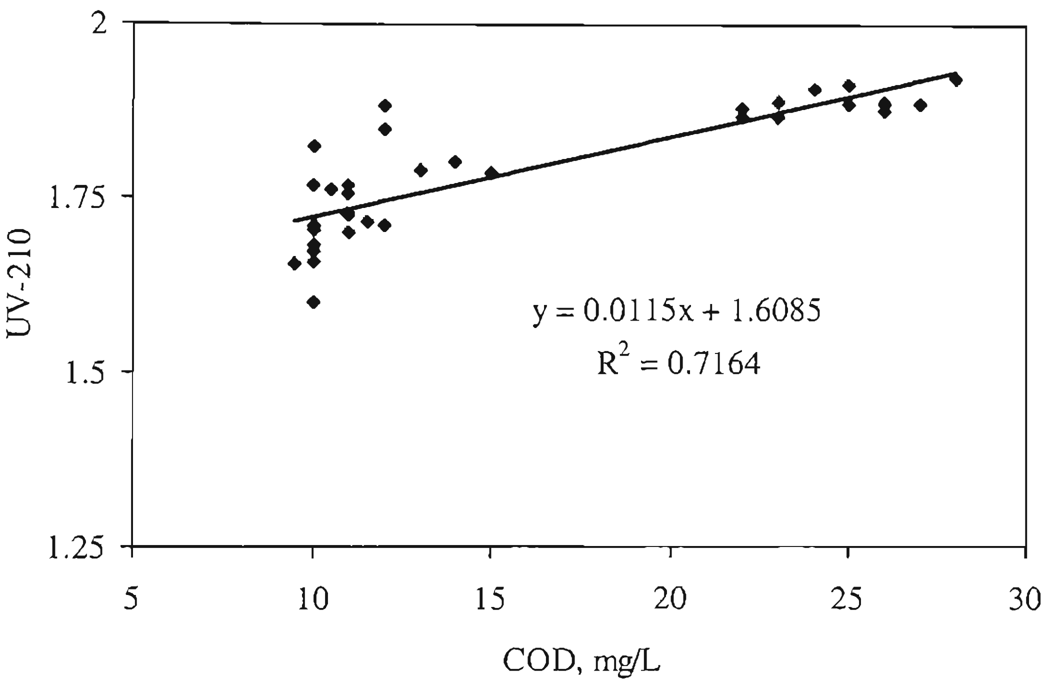

Figure A2. Relationship between UV absorbance (UV-210) and chemical oxygen demand (COD) of the secondary sewage from St Marys sewage treatment plant

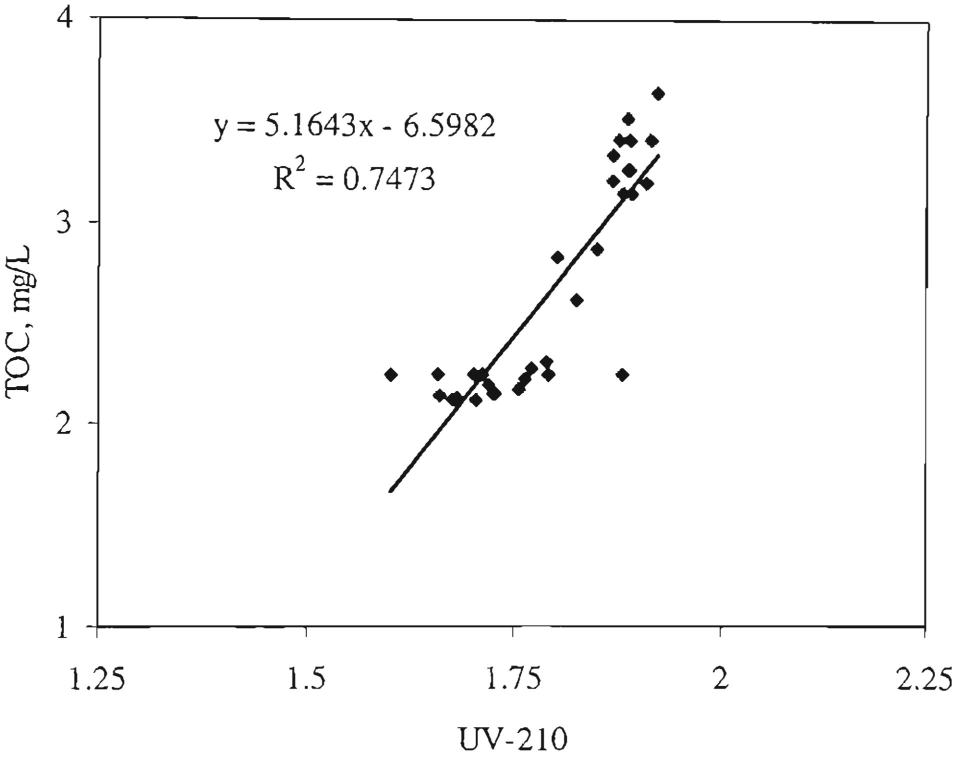

Figure A3. Relationship between total organic carbon (TOC) and UV absorbance (UV-210) of the secondary sewage from St Marys sewage treatment plant

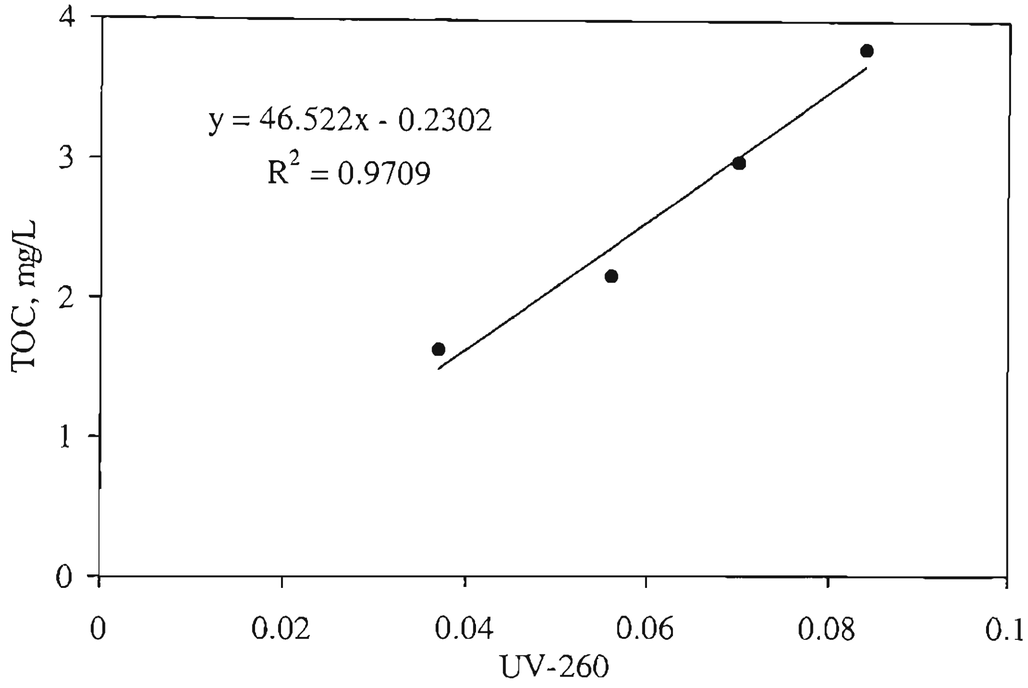

Figure A4. Relationship between total organic carbon (TOC) and UV absorbance (UV-260) of the component glucose with inorganic compounds of the synthetic wastewater

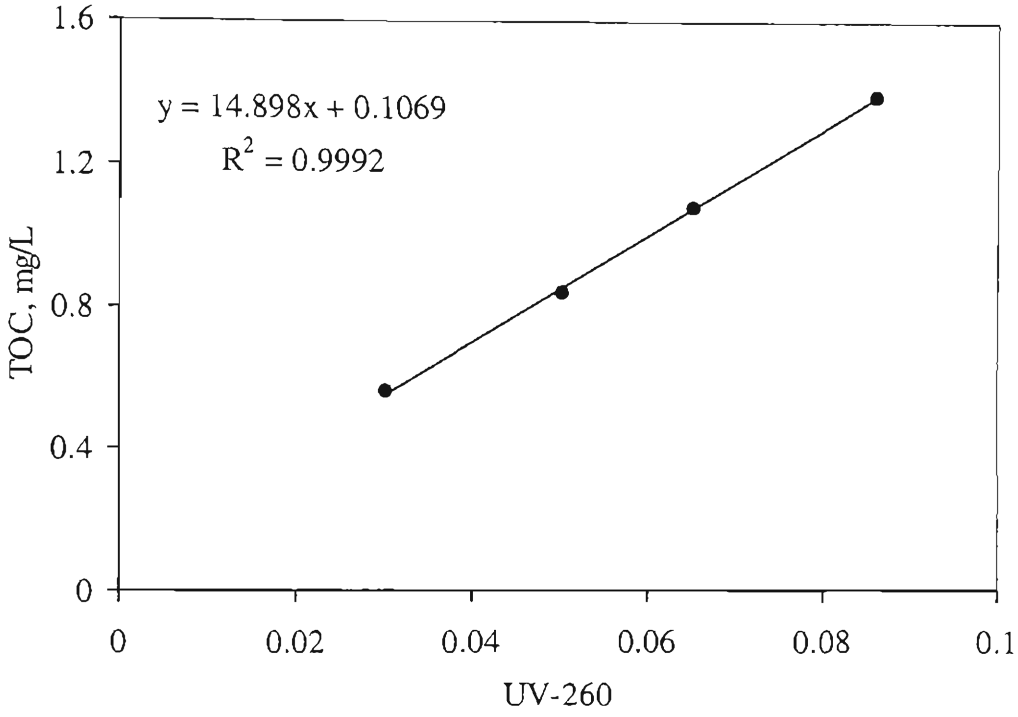

Figure A5. Relationship between total organic carbon (TOC) and UV absorbance (UV-260) of the component yeast extract with the inorganic compounds of the synthetic wastewater

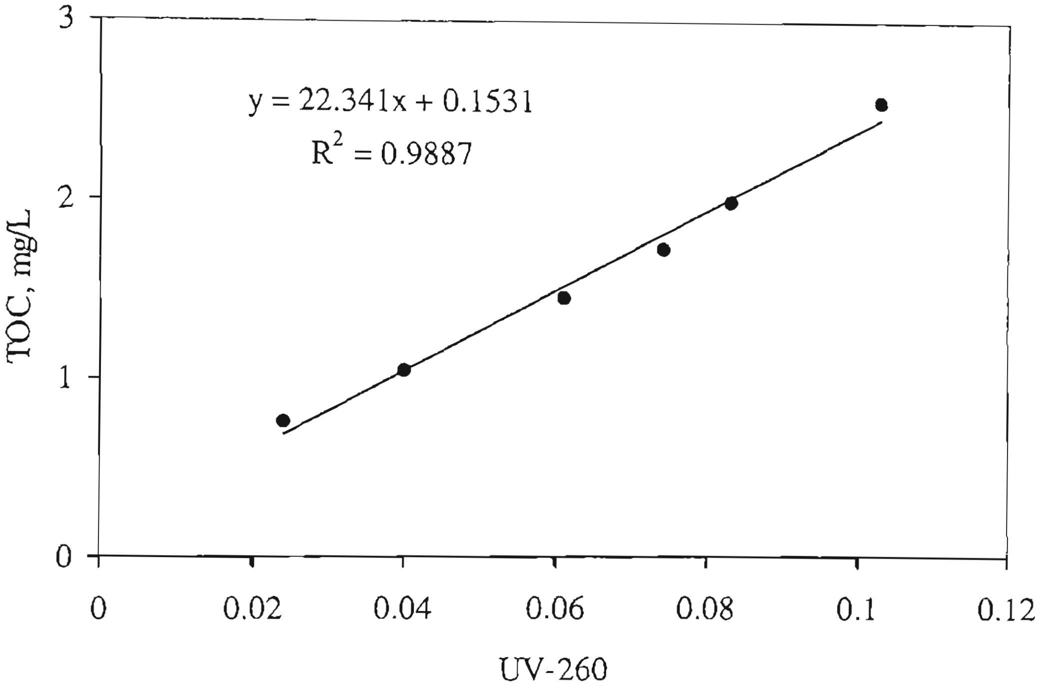

Figure A6. Relationship between total organic carbon (TOC) and UV absorbance (UV-260) of the component peptone with inorganic compounds of the synthetic wastewater

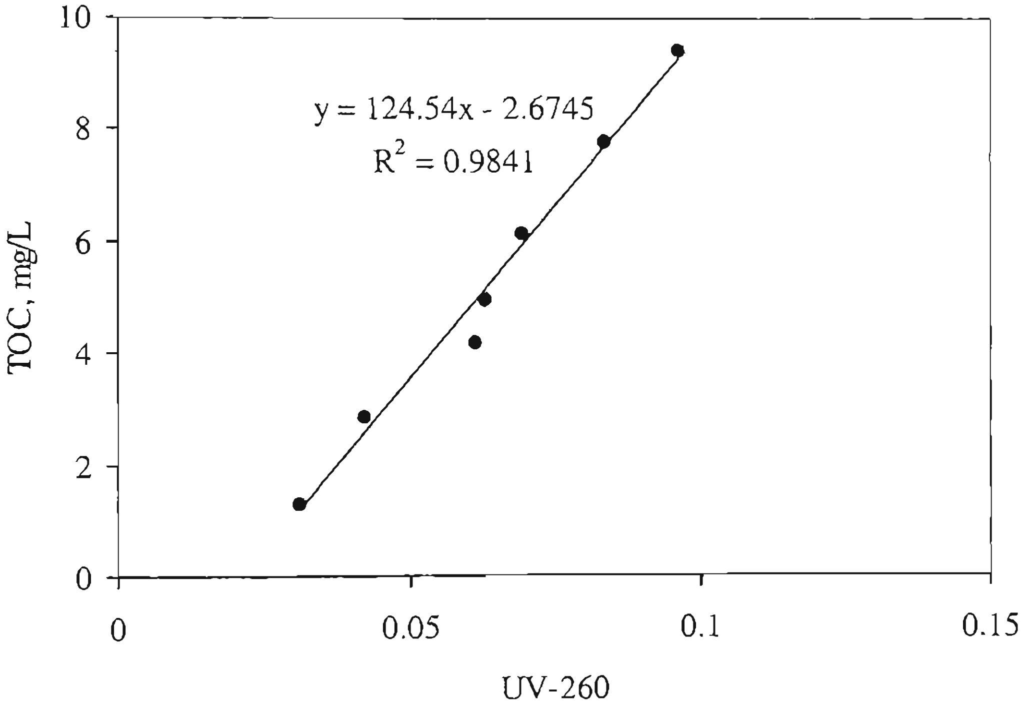

Figure A7. Relationship between total organic carbon (TOC) and UV absorbance (UV-260) of the synthetic wastewater

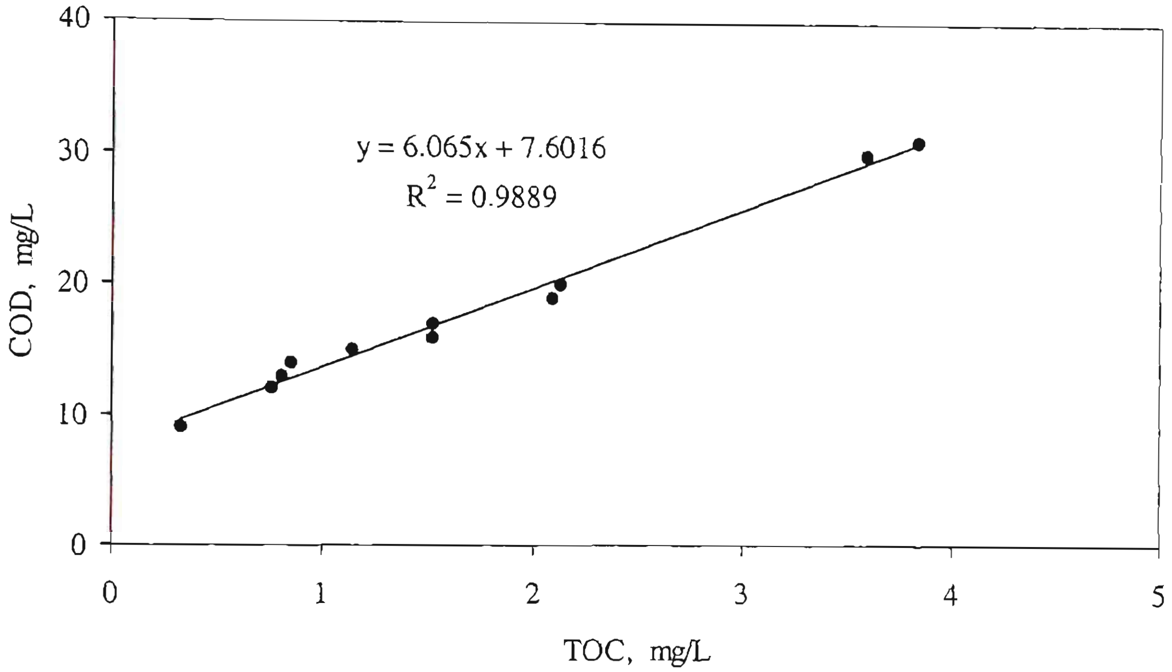

Figure A8. Relationship between chemical oxygen demand (COD) and total organic carbon (TOC) of the synthetic wastewater

Appendix -3

Publications Made from this Study

PUBLICATIONS

1. Chaudhary, D. S., Vigneswaran, S., Jegatheesan, V., Ngo, H. H., Moon, H., Shim, W.G. and Kim, S. H. (2003). Granular activated carbon (GAC) for wastewater treatment and reuse: experiments and models. *Water Science and Technology, vol.47, no. 1, pp. 113-120.*
2. Chaudhary, D. S., Vigneswaran, S., Ngo, H. H., Kim, S. H. and Moon, H. (2002). Comparison of association theory and Freundlich isotherm for describing GAC adsorption of secondary sewage effluent. *Journal of Environmental Engineering and Science* – (accepted for publication, 2003).
3. Chaudhary, D. S., Vigneswaran, S., Ngo, H. H., Kim, S. H. and Moon, H. (2002). Effects of biodegradation and background inorganic substances on granular activated carbon adsorption of wastewater. *Separation Science and Technology* – (accepted for publication, 2003).
4. Vigneswaran, S., Chaudhary, D. S., Ngo, H. H., Shim, W. G. and Moon, H. (2002). Application of PAC-Membrane Hybrid System in Removing Organics from Secondary Wastewater: Experiments and Model. *Separation Science and Technology* – (accepted for publication, 2003).
5. Chaudhary, D. S., Vigneswaran, S., Ngo, H. H., Shim, W. G. and Moon, H. (2002). Granular Activated Carbon Biofilter in low strength wastewater treatment: Experiments and mathematical modelling. *Environmental Engineering Science* – (submitted for publication, 2002).
6. Kim, S. H., Ngo, H. H., Chaudhary, D. S., Kim, J. C., Vigneswaran, S., and Moon, H. (2002). Characterization procedure for adsorption of DOC (dissolved organic carbon) from synthetic wastewater, Korean Journal of Chemical Engineering, 19, 5, 888-894.
7. Chaudhary, D. S., Vigneswaran, S., Ngo, H. H. and Jegatheesan, V. (2001). Applicability of granular activated carbon (GAC) biofilter in wastewater treatment and reuse. Proceedings of ASIAN WATERQUAL 2001, *Proceedings IWA Asia-Pacific Regional Conference*, Fukuoka, Japan, vol. 2, pp. 685-690
8. Chaudhary, D. S., Ngo, H. H. and Vigneswaran, S. (2001). Performance of a granular activated carbon biofilter in low strength wastewater treatment. *Proceedings of Scientific Conference*, Hanoi, Vietnam (2001).

9. Kim, S. H., Chaudhary, D. S., Ngo, H. H., Vigneswaran, S. and Moon, H. (2001) Characterization procedure for a synthetic wastewater. *Theories and Application of Chemical Engineering*, vol. 7, no. 1, pp. 809.
10. Kim, S. H., Chaudhary, D. S., Ngo, H. H., Vigneswaran, S. and Moon, H. (2001). Use of powdered activated carbon in removing dissolved organic carbon from wastewater. *Theories and Application of Chemical Engineering*, vol. 7, no. 2, pp. 3247-3250.
11. Kim, S. H., Ngo, H. H., Chaudhary, D. S., Vigneswaran, S., Kim, M. H., Yank, J. H. and Moon, H. (2001). Further work on characterizing a synthetic wastewater solution. *Journal of Research Institute for Catalysis*, vol. 22, pp. 75-84.
12. Kim, S. H., Moon, H., Ngo, H. H., Vigneswaran, S. and Chaudhary, D. S. (2001). Adsorption and biodegradation mechanisms in the removal of dissolved organic carbon in wastewater by powdered activated carbon. *Proceedings IWA Asia Environmental Technology 2001, Singapore, pp. 329-336.*
13. Kim, S. H., Moon, H., Ngo, H. H., Vigneswaran, S. and Chaudhary, D. S. (2001). Behaviour of Membrane Hybrid System on Permeate Flux. Proceedings of ASIAN WATERQUAL 2001, *Proceedings IWA Asia-Pacific Regional Conference*, Fukuoka, Japan, vol. 2, pp. 593-598.