# 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.

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Relationship between TOC, COD, and UV-210 & 260 of the wastewater

#### Appendix 3

Publications made from the study

### NOMENCLATURE

а	=	Specific surface area (area per unit mass of adsorbent) $(L^2M^{-1})$
А	=	Surface area normal to the filter media $(L^2)$
a' <sub>f</sub>	=	Specific surface area of the pellet with biomass $(L^2M^{-1})$
$A_{\mathrm{f}}$	=	Biofilm surface area $(L^2)$
Am	=	Membrane surface area perpendicular to the flow $(L^2)$
As	=	Surface area of the adsorbent $(L^2)$
b	=	Biofilm decay coefficient $(T^{-1})$
Βı	=	Biologically attached bacterial biomass (ML-3)
$B_2$	=	Reversibly adsorbed bacterial biomass (ML-3)
B <sub>3</sub>	=	Free bacterial biomass in the liquid phase (ML <sup>-3</sup> )
BIO	=	Biodegradation by the microbial community
b <sub>max</sub>	=	Maximum uptake rate of S $(T^{-1})$
bs	=	Biofilm shear loss coefficient $(T^{-1})$
b <sub>tot</sub>	Ξ	First order biofilm detachment coefficient for decay and shear $(T^{-1})$ .
<b>b</b> <sub>tot</sub>	=	First order biofilm detachment coefficient for decay and shear $(T^{-1})$ .
b <sub>tot</sub>	=	Overall loss rate of biomass due to both decay and fluid shear $(T^{-1})$
<b>b</b> <sub>tot</sub>	=	Total shear and decay loss $(T^{-1})$
С	=	Concentration of the adsorbate in solution phase (ML <sup>-3</sup> )
C <sub>0</sub>	=	Initial Organic concentration in the feed tank (ML <sup>-3</sup> )
$C_{b}$	Ξ	Organic concentration in the bulk phase in the reactor $(ML^{-3})$
Ce	=	Effluent concentration (ML <sup>-3</sup> )
Ci	=	Influent concentration (ML <sup>-3</sup> )
C <sub>i</sub>	=	Liquid phase organic concentration of $i^{th}$ species in the mixture (ML <sup>-3</sup> )
$C_i^0$	=	Single solute liquid phase concentration in equilibrium $(ML^{-3})$
$C_{io}$	=	Initial liquid phase organic concentration of i <sup>th</sup> component (ML <sup>-3</sup> )
$C_p$	=	Permeate organic concentration (MIL <sup>-3</sup> )
Cr	=	Q $\beta$ concentration in the bulk phase (ML <sup>-3</sup> )

Cs	=	Concentration of the adsorbate in the liquid phase at the liquid-
		particle interface, (MIL <sup>-3</sup> )
$\overline{C}$	=	Concentration density function of the solution phase
$C_r^{\infty}$	=	Equilibrium concentration of $Q\beta$ in the bulk phase (ML <sup>-3</sup> )
$C_{T}$	=	Total liquid phase concentration (ML <sup>-3</sup> )
$C_{Tcal}$	=	Calculated liquid phase concentration (ML <sup>-3</sup> )
$C_{Texp}$	=	Experimental liquid phase concentration (ML <sup>-3</sup> )
$C_{to}$	=	Initial total liquid phase concentration (ML <sup>-3</sup> )
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 $(L^2T^{-1})$
$D_{m}$	Ξ	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 <sup>th</sup> component $(L^2T^{-1})$
e <sub>i(max)</sub>	=	Maximum rate of $H_i$ hydrolysis (T <sup>-1</sup> )
F	=	Object function (%)
gc	=	Gravity conversion coefficient $(LT^{-2})$
Η	÷	Adsorption constant (Henry's Law constant)
$H_i$	=	Macromolecular organic matter of utilization class i (ML <sup>-3</sup> )
$\mathbf{J}_0$	=	Initial flux rate $(L^{3}L^{-2}T^{-1})$
$J_{f}$	=	Flux of substrate into the biofilm $(ML^{-2}T^{-1})$
Jp	=	Permeate flux $(L^{3}L^{-2}T^{-1})$
K	=	Reaction constant
k	=	Maximum specific rate of substrate utilization ( $MM^{-1}T^{-1}$ )
	=	First order reaction coefficient (T <sup>-1</sup> )
k″ <sub>d</sub>	=	Detachment rate coefficient (ML <sup>-3</sup> )
k′ <sub>d</sub>	=	Detachment rate coefficient $(ML^{-3}T^{-1})$

k <sub>a,</sub>	=	Coefficient for adsorption onto PAC
k <sub>ads</sub>	=	Adsorption constant for bacteria $(M^{-1}L^{3}T)$
k <sub>c</sub>	=	Cake formation filtration constant
k <sub>ct</sub>	Ξ	Complete blocking filtration constant
k <sub>d</sub>	=	Coefficient for the bacterial decay (T <sup>-1</sup> )
k <sub>des</sub>	=	Desorption constant for bacteria (T <sup>-1</sup> )
ke	=	Coefficient for inactivation due to the desorption of $Q\beta$ from PAC
$K_{F}$	=	Freundlich adsorption coefficient
$\mathbf{k}_{\mathbf{f}}$	Ξ	Liquid-film mass transfer coefficient, (LT <sup>-1</sup> )
$\mathrm{K}_{\mathrm{Hi}}$	Ξ	Half saturation constant for $H_i$ hydrolysis, (ML <sup>-3</sup> )
k <sub>i</sub>	Ξ	Freundlich constant for i <sup>th</sup> component
	=	Intermediate blocking filtration constant
k <sub>m</sub>	Ξ	Coefficient for attachment to the membrane
k <sub>max</sub>	=	Maximum rate of substrate utilization, mg/mg/s
k <sub>p</sub>	=	Particle phase mass transfer coefficient, (LT <sup>-1</sup> )
Ks	=	Monod half saturation coefficient (ML-3)
k <sub>s</sub>	=	Solid phase mass transfer coefficient (LT <sup>-1</sup> )
	Ξ	Standard blocking filtration constant
	Ξ	Scale factor
L	=	Bed depth (L)
$L_d$	=	Diffusion layer thickness (L)
$L_{f}$	=	Biofilm thickness (L),
Lo	=	Initial bed depth (L)
М	=	Weight of the adsorbent (M)
$M_{b}$	Ξ	Molecular weight of the solvent (M)
MCC	=	Membrane correlation coefficient,
$M_{p}$	=	Weight of the adsorbent (M)
n	=	Freundlich exponential coefficient
	=	Rotation speed $(T^{-1})$
Ν	=	Substrate uptake rate of the biofilm $(ML^{-2}T^{-1})$
	=	Number of data points
$\mathbf{N}_{\mathbf{p}}$	=	Power number

Р	=	Input power to the fluid (MLT <sup>-1</sup> )
$P_{C}$	=	Average concentrate pressure (Pa)
$P_{\rm F}$	=	Average feed pressure (Pa)
$\mathbf{P}_{\mathbf{p}}$	=	Average permeate pressure (Pa)
$\overline{q}$	Ξ	Average adsorbed phase concentration (MM <sup>-1</sup> )
Q	=	Flow rate $(L^{3}T^{-1})$
q	=	Surface concentration of adsorbed substrate (MM <sup>-1</sup> )
$q_i^0$	=	Adsorbed phase concentration in single solute state (MM <sup>-1</sup> )
$q_{m}$	=	Maximum specific rate of substrate utilization $(MM^{-1}T^{-1})$
	Ξ	Saturation amount of organic adsorbed (MM <sup>-1</sup> )
qo	=	Initial adsorbed phase concentration (MM <sup>-1</sup> )
$Q_p$	=	Permeate flow $(L^{3}T^{1})$
$q_s$	=	Equilibrium adsorbed phase organic concentration (MM <sup>-1</sup> )
$q_t$	=	Total solid phase organic concentration (MM <sup>-1</sup> )
qw	=	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 <sub>diff</sub>	=	Rate for substrate accumulation due to diffusion (ML <sup>-3</sup> T <sup>-1</sup> )
R <sub>e</sub>	=	Total external resistance $(= R_p + R_f)$
REM	=	Fraction of biomass removed by backwashing
$R_{\rm f}$	=	External fouling resistance formed by deposited cake layer
r <sub>f</sub>	=	Radial coordinate in the biofilm (L)
r <sub>gr</sub>	=	Rate of biomass growth within the biofilm (MT <sup>-1</sup> )
$R_i$	=	Internal resistance due to adsorbed substances into the pores
r <sub>loss</sub>	=	Rate of loss of biomass (MT <sup>-1</sup> )
R <sub>m</sub>	=	Intrinsic membrane resistance
$R_p$	=	Adsorbent particle radius (L)
	=	Polarization layer resistance caused by the concentration gradient
r <sub>s</sub>	=	Radial coordinate in activated carbon (L)
R <sub>T</sub>	=	Total resistance to the filtration,

r <sub>utl</sub>	=	Rate of substrate utilization in the biofilm $(ML^{-3}T^{-1})$
S	=	Substrate concentration (ML <sup>-3</sup> )
SB	=	Maximum adsorption capacity for bacteria (ML <sup>-3</sup> )
$S_b$	=	Substrate concentration in the bulk liquid (ML <sup>-3</sup> )
$S_{f}$	=	Substrate concentration in the biofilm (ML <sup>-3</sup> ),
$S_{min}$	=	Minimum substrate concentration (MIL <sup>-3</sup> )
SP	=	Maximum capacity for biological bacterial fixation (ML <sup>-3</sup> )
Ss	=	Substrate concentration at liquid/biofilm interface (ML <sup>-3</sup> )
Т	=	Temperature, °C
t	=	Time (T)
TOC	=	Total organic carbon (ML <sup>-3</sup> )
v	11	Fluid filtration velocity (LT <sup>-1</sup> )
V	=	Volume of the solute, fluid, or reactor $(L^3)$
$V_{M}$	Ξ	Volume of the membrane $(L^3)$
W	=	Weight of adsorbent (M)
Х	=	Distance along the biofilter length (L)
$\mathbf{X}_{\mathbf{f}}$	=	Cell density of biofilm (ML <sup>-3</sup> )
$X_s$	=	Suspended biomass concentration (MIL <sup>-3</sup> )
$X_{susp}$	=	Suspended cell concentration (ML <sup>-3</sup> )
Y	=	Biomass growth yield factor
Z	=	Distance normal to the biofilm surface (L)
Zi	=	Mole fraction of the i <sup>th</sup> species in the adsorbed phase

ε.	=	Bed porosity
ε′	=	Bed porosity with biofilm
εο	=	Initial bed porosity
σ	=	Biofilm shear loss coefficient (T <sup>-1</sup> )
ψ	=	Organic concentration spreading parameter
ξ	Ŧ	Void fraction

μ	=	Viscosity of the fluid ( $ML^{-1} T^{-1}$ )
$\mu_{g}$ .	=	Specific biomass growth rate (T <sup>-1</sup> )
$\mu_{gave}$	-	Average specific biomass growth rate (T <sup>-1</sup> )
φ	=	Association factor of the solvent
θ	=	Empty bed contact time (T)
β	=	Filtration efficiency
$\Delta P$	=	Transmembrane pressure (Pa)
$\rho_{p}$	=	Particle density of adsorbent (ML <sup>-3</sup> )
ρ	=	Density of the fluid (ML <sup>-3</sup> )

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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<sub>4</sub>, CaCl<sub>2</sub>, NaHCO<sub>3</sub>, NaCl, MgSO<sub>4</sub>·7H<sub>2</sub>O, KH<sub>2</sub>PO<sub>4</sub>, and NH<sub>2</sub>·NH<sub>2</sub>·H<sub>2</sub>SO<sub>4</sub>). 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 commonlyused 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<sub>f</sub>) was obtained by fitting the fixed bed experimental data. The k<sub>f</sub> 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  $\mu$ m), 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 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.