REMOVAL OF PERSISTENT ORGANIC POLLUTANTS BY ADSORPTION AND ADVANCED OXIDATION PROCESSES

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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(Javeed Mohammed Abdul)

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NOMENCLATURE

a_f = specific surface area

α_L = longitudinal dispersivity (cm)

b = constant (L/mg)

b_{tot} = total bio-film loss coefficient

c_i = fluid phase concentration (mg/L)

c_s = equilibrium concentration (mg/L)

c_{pi} = concentration inside particle (mg/L)

C = concentration of adsorbate in the bulk solution (mg/L)

C_e = equilibrium concentration of solute in the bulk of the solution

D_s = effective surface diffusion coefficient of organic (m^2/s)

D_f = diffusion coefficient (m^2/s)

D_h = hydrodynamic dispersion coefficient (cm^2/min)

D_m = molecular diffusivity (cm^2/min)

D_{ax} = axial dispersion coefficients, (m^{2}s^{-1})

eV = electron volts

F = concentration of H_2O_2 in the Fenton's reagent (mg/cm^3)

KF = Freundlich constant

KW = kilo watt

k_d = adsorption distribution coefficient

k_r = desorption rate (min^{-1})

k_f = overall mass transfer coefficient (m/s)

K_f = film mass transfer coefficient (m/s)

k_m = mass transfer coefficient (1/s)

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

K_S	=	Monod half velocity coefficient
k_s	=	solid mass transfer coefficient (1/s)
K_{max}	=	maximum rate of substrate utilization (s^{-1})
k_P	=	particle phase mass transfer coefficient
K_n	=	limiting rate constants of reaction
K	=	reaction rate constant (h^{-1})
k_{YN}	=	Yoon–Nelson rate constant (min^{-1})
K_{obs}	=	observed first order rate constant
k	=	adsorption rate constant for the column (l/min mg)
k_T	=	Thomas rate constant (l/min mg), is, is and
K_r	=	the reaction rate constant (h^{-1})
K_{ad}	=	the adsorption distribution coefficient
k_1	=	faster initial rate
k_2	=	slower final rate
k_3	=	Constant
k_4	=	Constant
k_5	=	Constant
k_6	=	Constant
k_7	=	Constant
k_8	=	Constant
L_f	=	bio-film thickness (m)
L	=	height of the column bed (cm)
m_C	=	mass of adsorbent in the column (g)
n	=	Constant
n	=	Freundlich,Sips exponent
N	=	adsorbate uptake rate per pellet

N_0	=	adsorptive capacity of adsorbent (mg/l)
P_n	=	number of characteristic packing spheres
q	=	amount of adsorbate absorbed on adsorbent (mg/g)
q_s	=	adsorbed phase concentration at the external surface of adsorbent particle (mg/g)
q_e	=	amount of solute adsorbed per gram of adsorbent,
q_m	=	saturation amount of organic adsorbed (mg/g)
q_0	=	the maximum solid-phase concentration of the solute (mg/g)
Q	=	volumetric flow rate (l/min)
R	=	radius of adsorbent (m)
R_P	=	pellet radius (m)
S	=	sorbed phased concentration (mg/cm^3 of soil)
T	=	temperature (^{0}C)
u	=	velocity of the fluid, (ms^{-1})
U	=	linear flow velocity of the feed to the bed (m/min)
V	=	pore water velocity (cm/min)
X_S	=	suspended cell concentration
X_f	=	biomass density (mg/L)
Y	=	yield coefficient (mg/mg)
z	=	bed depth, (m)
ρ_p	=	density of particle (kg/m^3)
ε_b	=	bed porosity
β	=	filtration efficiency
θ	=	empty bed contact time
σ	=	bio-film shear loss coefficient
$\bar{q}$	=	average concentration of q
σ	=	shear Loss (s^{-1})

ρ_p = the density of particle (kg/m^3)

ε_b = bed porosity

t_0 approximate transition time from fast to slow

TEq = Toxicity Equivalents (μg/L)

λ_F = self degradation rate of Fenton's reagent (min^{-1})

λ_c self degradation rate of contaminant (min^{-1})

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process at concentrations from 5 mg/L MeS to 70 or 80 mg/L MeS. Samples were oxidized for 4 hours with FR at concentrations of 0.18 mM Fe^{2+} and 6.6 mM H_2O_2.

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ABSTRACT

Water scarcity due to persistent drought is forcing the countries around the world to explore alternative fresh water resources. Groundwater is one of the natural freshwater resources that can be used for human and agricultural use. But, contamination due to improper disposal of untreated human and industrial wastes affects the groundwater quality and renders it unsuitable for human and agricultural purpose unless the water is treated for contamination removal. Some of the common contaminants that contaminate groundwater are: landfill leachate from domestic landfills, Persistent Organic Pollutants (POPs) such as pesticides (Metsulfuron methyl-MeS), Pharmaceutically Active Substances (PhAcS-Trimethoprim (TMP) and pentachlorophenol (PCP). These contaminants cannot be removed effectively by conventional treatment processes such as coagulation, adsorption and are not easily bio-degradable. Therefore, Advanced Oxidation Processes (AOPs) are preferably being used to remove these contaminants of concern because of their effectiveness against bio-refractory contaminants, faster degradation kinetics and economic viability. Common AOPs include: Photocatalysis; Fenton's oxidation; Ozonation and their combinations. Our study used Adsorption/bio-sorption (conventional treatment process) and Photocatalysis and Fenton's oxidation (AOPs) for the degradation of above mentioned contaminants.

Synthetic Landfill Leachate (SLL)

The adsorption/bio-degradation of diluted Landfill Leachate representing contaminated ground water on granular activated carbon was investigated both in batch and column (fixed bed studies) modes. The total organic carbon (TOC) (64 mg/l) removed due to adsorption by 20, 40, 60 g/l GAC was 44, 48 and 63%, whereas bio-degradation removed 85, 92 and 97% TOC respectively. The biodegradation of TOC was supported by consistent increase in microbial count on GAC particles. The Langmuir and Sips adsorption isotherms were found to fit well with the batch equilibrium. A mathematical model was developed to simulate the organics removal efficiency of the GAC bio-filtration system. In the combined process, a pre-treatment of SLL by Fenton's oxidation followed by bio-filtration led to an organic removal of 75% (an improvement of 15% over only biodegradation) even with a small oxidant (H_2O_2) dose of as low as 200-800 milli mole/L and Fe^{2+} of 15 milli moles. Photocatalysis with TiO_2 as catalyst degraded SLL by only 30%.

Metsulfuron methyl (MeS) - an Herbicide

The GAC adsorption removed more than 90% of MeS for an initial MeS concentration $[MeS]_0$ of 50 mg/L. The adsorption and kinetics of MeS on GAC were a function of the solution pH. The linear driving force approximation (LDFA) kinetic equation with Langmuir and Freundlich adsorption isotherm models were successfully applied to predict the batch adsorption kinetics data in various concentrations of MeS. The Bohart-Adams and Thomas models were found to best simulate the fixed bed adsorption of MeS.

The Fenton's process was very effective in the degradation of MeS. The MeS was degraded by more than 99% at a reaction time of 2 h and more at the optimum Fenton's reagent concentration. The results suggested that as long as a minimum threshold level of H_2O_2 (i.e., 60 mg/L) is applied, the long term (more than 1 hour) removal of MeS is primarily affected by the initial Fe^{2+} and MeS concentrations. The Fenton's process was successfully modeled using an 8-reaction, 2nd order kinetic model.

The removal of MeS by photocatalysis with TiO_2 was not effective as Fenton's oxidation. This study also investigated the toxicity of degradation by-products due to Fenton's oxidation of MeS. The herbicide toxicity of the parent and degradation by-products of MeS after Fenton's oxidation was determined by toxicological bioassay. The plant selected for this bioassay was the small aquatic flowering plant *Lemna disperma*, commonly known as duckweed, which is sensitive to MeS. The measured toxicity to *Lemna* in these treated samples was comparable to the concentrations of MeS measured by chemical method (HPLC/UV) detection.

Pentachlorphenol (PCP)

The removal of PCP from contaminated aqueous solution was investigated by GAC adsorption, photocatalysis and Fenton's oxidation processes. Adsorption by GAC was very successful in removing PCP from aqueous solution even with very small quantities of GAC. The adsorption efficiency was highest at lower pH. The adsorption of PCP on GAC occurred in two phases; a faster and a slower phase. This was modeled.

The combination of UV/ TiO_2 photocatalysis removed PCP completely within 30 minutes of reaction. Significant degradation of PCP was achieved even with a very low

dose of TiO_2 of $0.05 g.L^{-1}$ (for $[PCP]_0$ range of 10-40 $mg.L^{-1}$) and 0.1 $g.L^{-1}$ (for $[PCP]_0$ of 60-80 $mg.L^{-1}$). The first order and Sips kinetics were successfully used to predict the degradation rate of organic contaminants. The chemical analysis of Cl^- and PCP and calculation from chemical formula showed that only 44.8% PCP was completely mineralized although all 100% pure PCP underwent degradation to lower chlorinated phenol and other compounds.

Fenton's process was very effective in PCP degradation. The PCP degradation by Fenton oxidation was a function of initial concentration of FR and their ratio (H_2O_2 and Fe^{2+}), PCP (organic loading) and initial solution pH. The Sips Kinetic equation gave the best fit with the experimental data among different kinetic models tried.

Trimethoprim (TMP)

The removal of TMP by GAC adsorption was investigated at alkaline and acidic conditions. The percent TMP removed by 500 mg/L GAC at pH 3, 7 and 10 was 62.5, 82.5 and 99% respectively. Sips isotherm and dual first order kinetics explained the equilibrium and kinetic adsorption results. The removal of TMP in a GAC column (fixed bed) was also studied using 3 different shallow GAC bed heights of 2.5, 5 and 10 cm. Overall, the fit of the Thomas model was the best for fixed bed adsorption of TMP as indicated by the higher r^2 values.

In Fenton's oxidation the percent TMP removed was a function of initial FR dose. The $[Fe^{2+}]_0$ concentration for maximum TMP removal of 60% at an optimum $[H_2O_2]_0$ concentrations of 1.2 g/L was 100 mg/L. The effect of catalyst concentration on the removal of TMP was more pronounced than the oxidant concentration.

Photocatalysis (TiO$_2$/UV) decomposed 80% of TMP concentration within 180 minutes of irradiation. The optimum TiO$_2$ dose was 0.5 g/L which degraded TMP by 82% for an initial TMP concentration of 10 mg/L. In the continuous system, the feed flow rate through the photoreactor or detention time was an important factor in enhancing the TMP removal. A detention time of 50 minutes achieved 55% TMP removal.

In-situ Fenton's oxidation (ISFO) of MeS and PCP

In-situ contaminant reduction was investigated in sand columns (fixed beds). Both adsorption and Fenton's oxidation mechanisms were taken into account in ISFO to calculate the MeS removed. The In-situ Fenton's oxidation of MeS showed that for the transport and degradation of MeS in the column the residence time was the primary factor in determining the amount of MeS removal. The transport and degradation of MeS was modeled using the advection diffusion equation with reactions and rate limited sorption. The steady state adsorption of PCP in the sand filter was higher compared to that observed for MeS. The PCP removed by in-situ Fenton's oxidation was in the range of 80-90%. The in-situ Fenton's oxidation of PCP also showed that the residence time was the primary factor responsible in determining the amount of contaminant removal. Adsorption and Fenton's oxidation of PCP in the sand column was satisfactorily modeled in the same manner as MeS.