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VERIFICATION OF THE MATHEMATICAL MODELING OF BIO-PHYSICO CHEMICAL PROCESSES IN ACTIVATED CARBON COLUMNS

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Abstract—Plug-flow stationary solid phase upflow and completely mixed recycle fluidized adsorber experiments were conducted to test the predictive models developed earlier. Model parameters were determined independently from adsorption equilibrium, kinetic investigations, biokinetic experiments and correlation techniques. Two ideally adsorbable and biodegradable compounds, glucose and sucrose, as well as two actual wastewaters, a dairy waste and a landfill leachate, were used to compare the model profiles and experimental data of non-bioactive and bioactive adsorber systems. The performance prediction by the models satisfactorily described the experimental data.

INTRODUCTION

In a companion paper, Kim and Min [1] presented predictive models for integrated biodegradation and adsorption process in a plug-flow stationary solid phase column (PSSPC) and a completely mixed recycle fluidized bed (CMRFB) carbon adsorbers. The phenomenological aspects essential for model formation were the following : (1) transport of substrate in the liquid phase, (2) transport and biodegradation within the biofilm, (3) adsorption onto activated carbon, and (4) growth of the biofilm. Predictive mathematical modeling equations of PSSPC and CMRFB were presented in an appendix. PSSPC and CMRFB models are the same in describing the liquid phase material balance, solid phase diffusion in the adsorbent, diffusion and reaction in the biofilm, growth of biofilm and adsorption isotherm. However, the boundary conditions of Eqs. (18) and (24) of PSSPC model in the appendix are different from those of CMRFB model. Numerical solutions to the equations governing the models were obtained using a combination of orthogonal collocation and finite difference techniques.

In the study described here, experimental systems were designed to provide operational data for the test and verification of the predictive capabilities of these models. Two actual wastewaters as well as two ideally biodegradable adsorbates were used in these experiments.

MATERIALS AND METHODS

1. Synthetic Organic Compounds

The selection of model organic compounds to be investigated in this research is based on the following criteria; (1) Wide ranges of adsorbability on activated carbon and biodegradability by sewage bacteria. (2) Constituents present in domestic and/or industrial wastewater. (3) Established analytical methods for concentration determination. (4) Reasonable cost. Glucose and sucrose were selected as model organic compounds for these investigations. Although both these compounds are readily biodegradable, their adsorbability characteristics are different. Glucose is poorly adsorbable, while sucrose is highly adsorbable. Furthermore, these compounds are commonly used as substrates in biological research, and there is a substantial amount of published data available regarding their behavior [2]. Deionized distilled water (DDW) was used for glucose and sucrose. Potassium phosphate (KH_2PO_4) was used to provide a moderate buffer capacity (2.0×10^{-3} M phosphate) as well as to satisfy nutrient requirement for biodegradation. Ammonium hydroxide (NH_4OH) was also added to meet nitrogen requirements for biological growth. For this study, the BOD_5: N ratio was maintained at approximately 20 : 1 for all experiments.

2. Real Wastewaters

Industrial wastewater is usually comprised of a com-

plex variable mixture of dissolved colloidal and suspended matters. An eventual purpose of any modeling is to apply the modeling concept to the design of real wastewater treatment systems. However, most biologically active carbon modeling efforts reported in the literature [2-5] used synthetic solutions of organic compounds for model verification. In this research, both organic compounds and real wastewaters are used to test the general applicability of the developed models.

Criteria for the selection of real wastewaters to be investigated are; (1) Industrial wastewaters which are treated by a combined process of conventional physical and biological treatment methods. (2) Industrial wastewater which contain biodegradable, nonbiodegradable, and low as well as high adsorbable organic compounds. (3) Wastewaters that are available on a regular basis for the period of research activity. (4) Industrial wastewater which has high correlation to other industrial wastewaters.

Effluents from a dairy plant (Alta-Dena; City of Industry, L.A., CA) and leachate from a Class 1 landfill (BKK Corp; West Covina, L.A., CA) representing wastewaters with substantially different adsorbabilities and biodegradabilities were used for these studies. The leachate and dairy wastewater characteristics are depicted in Tables 1 and' 2, respectively. Since these wastewaters contained high concentrations of organic particulates and suspended solids, they were subjected to chemical pretreatment with the application of lime-alum for the dairy wastewater, and alum for the landfill leachate [6]. Adsorption equilibrium, kinetic, biokinetic and adsorber-bed studies were conducted using these settled wastewaters (SWW).

Table 1. Characteristics of BKK landfill leachate

Leachate constituent	Average concentration (mg/L)
General parameters	
COD	3,237
BOD	1,603
TSS	527
TDS	6,010
Oil and grease	71.6
Inorganic compounds	
Alkalinity	1,433
Cadmium	0.018
Copper	0.05
Cyanide	<0.02
Lead	<0.05
Nickel	0.15
Silver	0.02
Zinc	0.11
Total Kjeldahl Nitrogen (TKN)	77.4
Orthophosphate	1.1
Organic compounds	
Acetone	13.4
Methyl ethyl ketone	10.9
Tetrahydrofuran	2.9
1,2-Dichloroethane	2.3
Benzene	0.16
1,1-Dichloroethane	0.16
Methyl chloride	1.1
Toluene	0.51
1,2-Dichloropropane	1.3
1,1,2-Trichloroethane	0.23
Isophorane	0.063
Bis(2-Ethylhexyl) phthalate	0.14
Naphthalene	0.14
2,4-Dimethylphenol	0.42
Phenol	0.98

3. Activated Carbon

A bituminous coal activated carbon, (Filtrasorb 400; Calgon Corp., Pittsburgh, PA) was selected for this research based on its high adsorption efficiency and resistance to attrition. The carbon was grinded, sieved and selected size fractions were washed with DDW to remove fine particles and oven-dried for 12 hr at 105℃. After reaching room temperature in a desiccator, the carbon was stored in air tight glass containers until use.

4. Bacterial Culture

Primary effluent from a municipal wastewater treatment plant was used for seeding the solution of glucose, sucrose, and dairy SWW. The seed for leachate SWW was obtained from an activated sludge tank of

Table 2. Characteristics of the dairy wastewater

Dairy wastewater	COD (mg/L)	BOD (mg/L)	TOC (mg/L)	BOD: COD ratio	TOC: BOD ratio	Total suspended solids(mg/L)	Total nitrogen (N-mg/L)	Total phosphorus (P-mg/L)
Raw* wastewater 1	4620	2680	1160	0.58	0.43	3520	26	10.6
Settled wastewater 1	2615	1360	680	0.52	0.50	35	ND	0.7
Raw* wastewater 2	4020	2410	1110	0.6	0.46	2950	25	9.8
Settled wastewater 2	3280	1285	630	0.54	0.52	40	ND	0.72

a leachate treatment pilot plant at the BKK landfill site. Effluents from continuous biokinetic experiments were used as alternate seeding sources in biologically active granular carbon (BAGC) fluidized bed investigations.

5. Non-Bioactive Columns

Non-bioactive PSSPC and CMRFB investigations were carried out in either 1-cm or 1.85-cm ID plexiglass columns to test the models under conditions when adsorption was the only removal mechanism. Various hydraulic loadings were used ranging from 2 to 4 gpm/ft^2, which cover the expected range for practical applications. Appropriate quantites of activated carbon of 25/35 US standard mesh size were charged to each bed. Organic free water, after pH adjustment to a value of 7.0± 0.1, was pumped through the bed for approximately 2 hours to eliminate carbon fines, and also to stabilize the effect of pH on activated carbon. Silver sulfate (Ag_2SO_4) at a concentration of 3 mg/L was added to inhibit biological growth. A series of four PSSPC and CMRFB experiments were conducted. The experiments were concluded when effluent concentrations approached the influent concentrations. The schematic flow diagrams of non-bioactive mini-column and fluidized-bed experimental units are shown in Figs. 1 and 2, respectively.

6. Bioactive Columns

The bioactive phase of the experiments was designed to test the PSSPC and CMFRB models under conditions when adsorption and biodegradation were

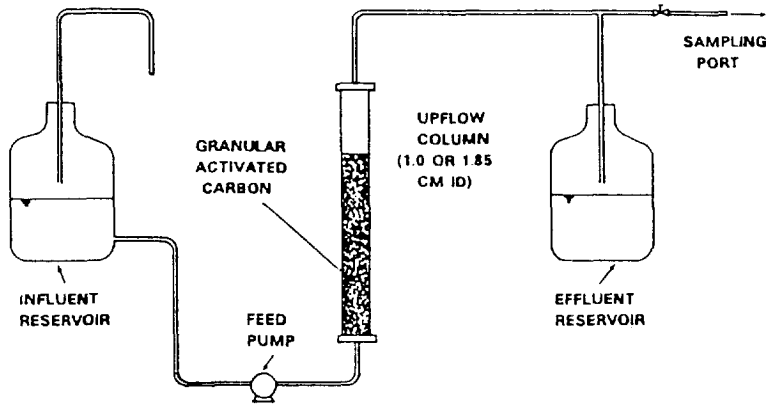

Fig. 1. Schematic experimental set-up for PSSPC studies.

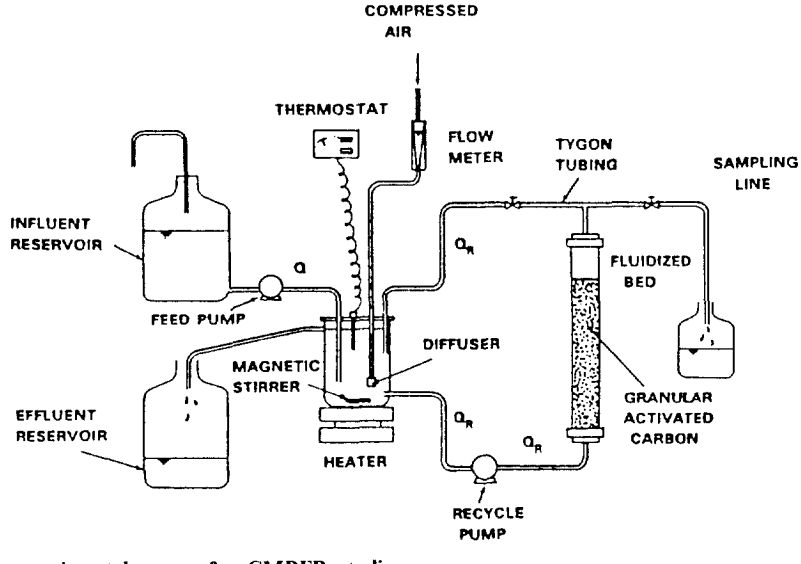

Fig. 2. Schematic experimental set-up for CMRFB studies.

both operative. Appropriate quantities of activated carbon of 25/35 mesh size were charged to each bed supported on a stainless steel screen. Carbon particles were then seeded with active mixed bacterial culture by recirculating the culture through the bed for a duration of 4 to 5 hours. Solutions of glucose, sucrose, dairy and leachate SWW were pumped from the feed tank, and oxygen supply was provided through diffusers. The dissolved oxygen concentration in the effluent was maintained above 3.5 mg/L at all times. Temperature was controlled at 19.5± 0.5℃. The effluent samples were taken at constant time intervals and acidified with concentrated H_2SO_4 to prevent biological activity. A recycle ratio of 13 to 33 was used for fluidized-bed experiments.

7. Model Parameter Determination

7-1. Choice of Concentration Parameters

Typical wastewaters contain a variety of organic compounds that cannot be easily identified or characterized. One must therefore resort to the use of certain arbitrary gross or lumped concentration parameters such as chemical oxygen demand (COD), biochemical oxygen demand (BOD) or total organic carbon (TOC), to describe characteristics of such wastewaters. TOC is one of the most frequently used gross concentration parameters because of good reproducibility as well as a relatively simple analytical procedure compared to COD or BOD. A Beckmann Model 915 TOC analyzer was used to measure the total concentration of organics present in the wastewater.

7-2. Adsorption Isotherm Parameters

Adsorption equilibrium studies were conducted to estimate the Freundlich isotherm adsorption parameters K_F and n, using a bottle point technique [7]. The pH for the solution was maintained at 7.0± 0.2, and silver sulfate (Ag_2SO_4) at 3 mg/L concentration was added to inhibit biodegradation. 200 ml of substrate solutions were transferred to tightly sealed 250-mL glass bottles, followed by the addition of carefully weighed amounts of washed/dried carbon (200-300 US mesh size). The bottles were subsequently placed on a specially designed rotary tumbler operating at approximately 27 rpm, and agitated for a few days until equilibrium between the liquid phase and activated carbon was established. Duplicate control bottles without activated carbon were used as blanks. After equilibrium was reached, the carbon was allowed to settle, and the supernatant was filtered through a 0.2 micron membrane filter to remove the remaining powdered carbon. Parameter determination of K_F and n was accomplished through least-square regression analyses of the linearized Freundlich equation.

$$\log q_e = \log K_F + n \log C_e \quad (1)$$

7-3. Diffusion Coefficients

Completely mixed batch experiments were conducted to determine surface diffusion coefficient, D_s, for adsorbates in 3.5-L Carberry reactors, specially designed to eliminate the possibility of carbon pulverization at high mixing intensities. The Carberry reactor has a cage made of 100-mesh stainless steel screen which serves the dual purpose of a mixing agitator and a carbon contactor. A mixing speed of 250-300 rpm was maintained. A measured quantity of 25/35 mesh size carbon was introduced into the stainless steel cage and agitated. Sample solutions were withdrawn periodically and analyzed for adsorbate concentration. For all the experiments, a total solution withdrawal of less than 4% was maintained. The homogeneous surface diffusion model (HSDM) [8, 9] was utilized to estimate the liquid film transfer coefficient, k_f, and surface diffusion coefficient, D_s for the adsorbates of interest using the rate parameter search program. The values of k_f and D_s corresponding to the best fit of experimental data were obtained by the generalized reduced gradient method which minimized the sum of squared differences between predicted and experimental results. The initial slope method [10] was used to obtain an *a priori* estimate of k_f to minimize the parameter search procedures.

7-4. Biological Parameters

Continuous flow biokinetic experiments were conducted to determine the biological parameters which are maximum specific substrate utilization (k), Monod half saturation coefficient (K_s), microbial yield coefficient (Y), and overall biofilm loss coefficient (K_d). A stock solution of dairy or leachate SWW was constantly fed to an aerated one-gallon completely mixed flow reactor (CMFR), which was initially seeded with sewage microorganisms. Substrate was delivered to the CMFR by a metering pump (Minipulse 2, Gilson; Middleton, WI). The flowrate was varied after the steady-state condition prevailed, giving a series of hydraulic detention times ranging from 4 to 15 hours. Temperature was maintained at 19.5± 0.5℃, and the pH was adjusted to 7.0± 0.1 by the addition of dilute NaOH or H_2SO_4. Biomass concentration was determined by a membrane technique [11]. TOC analysis was performed on the filtered sample. Aliquots were withdrawn regularly to measure pH, TOC and bacterial concentration. The following two equations were used to estimate the four biological parameters.

$$\frac{X\theta}{C_o - C} = \frac{K_s}{k}\frac{1}{C} + \frac{1}{k} \quad (2)$$

$$\frac{1}{\theta_t} = Y\frac{C_o - C}{X\theta} - K_d \quad (3)$$

The values of k and K_s were determined by plotting the term $X\theta/(C_o - C)$ as a function of (1/C), and Y and K_d, by plottings $(1/\theta_t)$ as a function of $(C_o - C)/X\theta$. The initial biofilm thickness, L_{fo}, was estimated from the ratio of initial and terminal bacterial concentrations for the circulating culture and adjusted to fit the experimental data. The maximum biofilm thickness, L_{fmax}, was estimated by two different methods. One is to estimate the film thickness based on the assumption of increase in adsorber depth as a consequence of particle enlargement due to attached biological growth, using Eq. (4).

$$L_{fmax} = \frac{\Delta V}{N_p 4\pi R^2} \quad (4)$$

The other method is that proposed by Law et al. [12], whereby an average value of L_{fmax} can be estimated using the following equation:

$$L_{fmax} = \frac{W_t}{\rho_f Na(0.99)} \quad (5)$$

, where W_t is weight of evaporated water which can be determined using a procedure suggested by Namkung [13]. The bacterial density, X_f, is then calculated from the equation

$$X_f = \frac{B_w}{NaL_{fmax}} \quad (6)$$

, where B_w is cell weight. B_w = (total weight of dry cell and activated carbon particles) − (dry activated carbon particles). In this study, both methods yielded similar results.

7-5. External Film Transfer Coefficient, k_f, and Intraparticle Surface Diffusion Coefficient, D_s

Intraparticle surface diffusion coefficient, D_s, was determined from completely mixed batch adsorption rate studies using the HSDM predictive model [8, 9] and column film transfer coefficient, k_f, from short adsorber bed (SAB) technique proposed by Liu and Weber [14].

7-6. Biofilm Diffusion Coefficient, D_f

Since wastewaters are generally composed of mixtures of several unknown compounds, it is difficult, if not impossible, to evaluate their molecular diffusivities from empirical relations. In this investigation, a representative molecular diffusivity, D_l, for the two wastewaters was determined from a correlation method suggested by Wakao and Funazkri [15]:

$$\frac{2k_f R}{D_l} = 2 + 1.1R_e^{0.6}\ Sc^{1/3} \quad (7)$$

where

$$R_e = \frac{2\rho_l R v_s \varepsilon}{\mu} \quad (8)$$

$$S_c = \frac{\mu}{\rho_l D_l} \quad (9)$$

The biofilm diffusion coefficient was then estimated using the ratio $D_f/D_l = 0.8$, as suggested by Williamson and McCarty [16].

7-7. Axial Dispersion Coefficient, D_d

Axial dispersion coefficients, D_d, were determined using a correlation technique developed by Chung and Wen [17]:

$$\frac{D_d \rho_l x}{\mu} = \frac{R_e}{0.20 + 0.011R_e^{0.48}} \quad (10)$$

where

$$x = 1, \text{ for fixed bed} \quad (11)$$

$$x = \frac{(R_e)_{mf}}{R_e} \quad (12)$$

$$R_e = \frac{2\rho_l v_s R\varepsilon}{\mu} \quad (13)$$

$$(R_e)_{mf} = (33.7^2 + 0.0408\ NG_a)^{1/2} - 33.7 \quad (14)$$

$$NG_a = \frac{d_p^3 \rho_l (\rho_s - \rho_l) g}{\mu^2} \quad (15)$$

, where $(R_e)_{mf}$ is the modified Reynolds number, and NG_a is the Galileo number. In Eq. (15), ρ_s becomes nonuniform because of the variation of bacterial growth. The bacterial effect attached on the surface of activated carbon was neglected in case of ρ_s calculation, because the thickness and weight of bacteria are much smaller than those of activated carbon particle.

RESULTS AND DISCUSSIONS

Experimental systems of non-bioactive and bioactive activated carbon beds were designed to provide operational data with which to test and verify the predictive capabilities of the PSSPC and CMRFB models, and to investigate interactions among adsorption, biological activity and substrate utilization in bioactive adsorbers. Results from fourteen PSSPC and CMRFB runs are presented herein to illustrate application of the modeling techniques described in the previous pa-

Table 3. Parameters for non-bioactive PSSPC experiments

Adsorbate	C_o (mg/L)	Q (mL/min)	K_F	n	D_s (cm^2/sec)	k_f (cm/sec)	Figure no.
Glucose	100	6.50	0.32	0.62	1.50×10^{-8}	1.95×10^{-3}	3
Sucrose	100	6.50	14.93	0.31	6.17×10^{-9}	1.74×10^{-3}	3
Dairy SWW	120	6.45	0.33	0.81	3.63×10^{-8}	1.86×10^{-3}	4
Leachate SWW	105	6.53	1.47×10^{-4}	2.00	9.13×10^{-9}	2.02×10^{-3}	4

Common parameters: W=5.96 gm, DIA=1 cm, R=0.018 cm, L=17.5 cm

Table 4. Parameters for non-bioactive CMRFB experiments

Adsorbate	C_o (mg/L)	Q (mL/min)	K_F	n	D_s (cm^2/sec)	k_f (cm/sec)	Figure no.
Glucose	105	5.8	0.32	0.62	1.50×10^{-8}	4.84×10^{-3}	5
Sucrose	100	8.0	14.93	0.31	6.17×10^{-9}	4.20×10^{-3}	5
Dairy SWW	115	5.8	0.33	0.81	3.63×10^{-8}	4.57×10^{-3}	6
Leachate SWW	140	5.8	1.47×10^{-4}	2.00	9.13×10^{-9}	5.05×10^{-3}	6

Common parameters: W=20.0 gm, DIA=1.85 cm, R=0.039 cm, L=17.5 cm, D_H=5.61 cm^2/sec, Q_r=190 mL/min

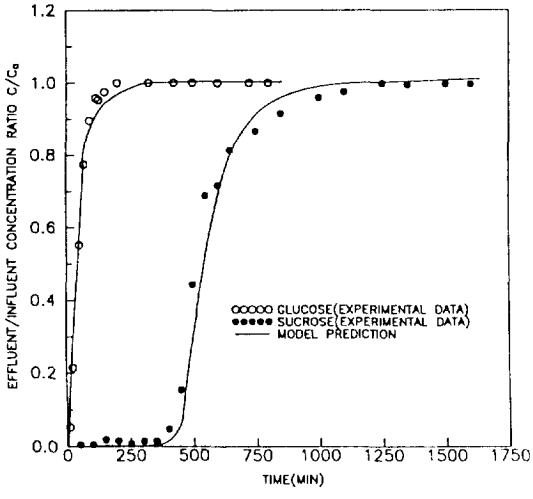

Fig. 3. Experimental breakthrough data and model simulations for glucose and sucrose in a non-bioactive PSSPC.

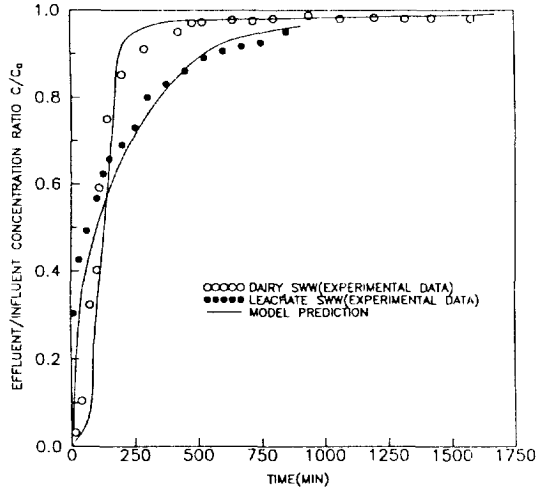

Fig. 4. Experimental breakthrough data and model simulations for dairy SWW and leachate SWW in a non-bioactive PSSPC.

per [1].

1. Non-Bioactive PSSPC and CMRFB Studies

PSSPC and CMRFB adsorber bed experiments were conducted to test the models under conditions when adsorption constitutes the only removal mechanism. The adsorption parameters required as input to the model were determined as described previously. The values of these parameters as well as detailed information pertaining to these runs are listed in Tables 3 and 4. Figs. 3 and 4 present experimental breakthrough curves and corresponding model profiles for glucose, sucrose, dairy and leachate SWW in non-bioactive PSSPC. Similarly, Figs. 5 and 6 illustrate experimental CMRFB breakthrough data and model profiles. In CMRFB of Fig. 5 and 6, complete solid phase mixing is accomplished through high rates of effluent recirculation. One of main effects of effluent recycle is to reduce the substrate concentration that is applied to the inlet of the fluidized bed. Premature breakthrough of Fig. 5 and 6 of CMRFB compared with Fig. 3 and 4 of PSSPC can be caused by the difference of solid phase mixing and liquid phase dispersion between these beds.

The comparison of the non-bioactive experimental

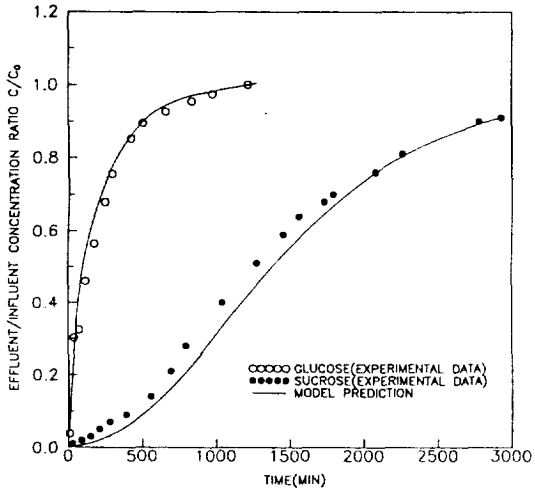

Fig. 5. Experimental breakthrough data and model simulations for glucose and sucrose in a non-bioactive CMRFB.

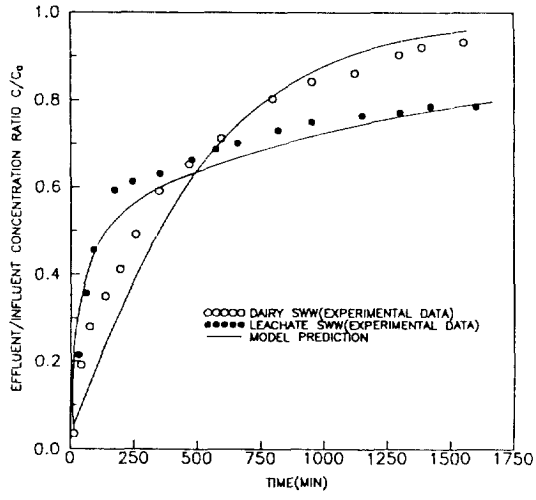

Fig. 6. Experimental breakthrough data and model simulations for dairy SWW and leachate SWW in a non-bioactive CMRFB.

data and the model predictions shows that the performance predictions of PSSPC and CMRFB models are in good agreement with experimental data for the entire run. In addition, the breakthrough data indicate that sucrose is highly adsorbable, while glucose, dairy and leachate SWWs are slightly adsorbable. These observations are in accord with the results of adsorption equilibrium studies.

2. Bioactive PSSPC and CMRFB Studies

As for the non-bioactive case, experimental systems were designed to test and verify the predictive capabilities of PSSPC and CMRFB models in biofilm adsorbers. Operational problems were encountered with PSSPC runs due to excessive biogrowth. It was found that while operating the bioactive upflow column, it was difficult to maintain constant flow rate more than a few hours once the biological growth became established. This was because the GAC particles were stuck together, causing frequent short-circuiting. Vigorous shaking of the column partially solved this problem. The oxygen limitation problems in CMRFB were not detected. This was possible, because influent dissolved oxygen concentration was as high as 8.5 to 9.0 mg/L and carbonaceous removal efficiency of CMRFB was as low as 40 to 70% compared with typical biological fluidized bed [18]. In addition, recycle flow rate was set at 190 ml/min to supply the biological carbon particles in the fluidized bed with enough dissolved oxygen.

It has been observed that as biological growth occurs on the activated carbon particles, their overall density reduces and results in a bed expansion. The carbon particles, even if they are of uniform size initially, became nonuniform because of the variation of bacterial growth along the axial distance of the bed. It was necessary to put a wire screen of 40 mesh on the top of fluidized bed to prevent the bed from expanding and causing the biological carbon particles

Table 5. Parameters for bioactive PSSPC experiments

Input parameters	Glucose (Fig. 7)	Sucrose (Fig. 7)
DIA (cm)	1.85	1.85
C_0 (mg/L)	100	105
Q (mL/min)	17.5	17.0
Q_r (mL/min)	0	0
X_L (cm)	21	21
K_F	0.32	14.93
n	0.62	0.31
W (gm)	25	25
D_s (cm^2/sec)	1.50×10^{-8}	6.17×10^{-9}
D_l (cm^2/sec)	6.9×10^{-6}	5.6×10^{-6}
k_{fi} (cm/sec)	1.18×10^{-3}	1.01×10^{-3}
D_f (cm^2/sec)	5.52×10^{-6}	4.48×10^{-6}
k (min^{-1})	5.20×10^{-3}	6.17×10^{-3}
Y (mg/mg)	1.38	1.44
K_s (mg/L)	108.2	164.6
K_d (min^{-1})	5.0×10^{-5}	6.7×10^{-5}
L_{fo} (μm)	1.0	1.0
L_{fmax} (μm)	40	65
D_d (cm^2/sec)	0	0

Table 6. Parameters for bioactive CMRFB experiments

Input parameters	Glucose (Fig. 8)	Sucrose (Fig. 8)	Dairy SWW (Fig. 9)	Leachate SWW (Fig. 9)
C_o (mg/L)	110	105	100	110
Q (mL/Min)	15	15	6.5	6.5
K_F	0.32	14.93	0.33	1.47×10^{-3}
n	0.62	0.31	0.81	2.00
D_s (cm^2/sec)	1.50×10^{-8}	6.17×10^{-9}	3.63×10^{-8}	9.13×10^{-9}
D_l (cm^2/sec)	6.90×10^{-6}	5.60×10^{-6}	6.34×10^{-6}	7.34×10^{-6}
D_f (cm^2/sec)	5.52×10^{-6}	4.48×10^{-6}	5.07×10^{-6}	5.87×10^{-6}
k (min^{-1})	5.20×10^{-3}	6.17×10^{-3}	7.14×10^{-3}	1.12×10^{-2}
Y (mg/mg)	1.38	1.44	1.05	0.85
K_s (mg/L)	108.2	164.6	135.0	145.0
X_f (mg/cm^3)	31	40	36	30
L_{fo} (μm)	1.0	1.5	1.5	1.0
L_{fmax} (μm)	20	55	50	35
k_f (cm/sec)	4.84×10^{-3}	4.20×10^{-3}	4.57×10^{-3}	5.50×10^{-3}

Common parameters: W=25 gm, DIA=1.85 cm, Q_r=190 mL/min, L=40 cm, R=0.039 cm, D_d=5.61 cm^2/sec

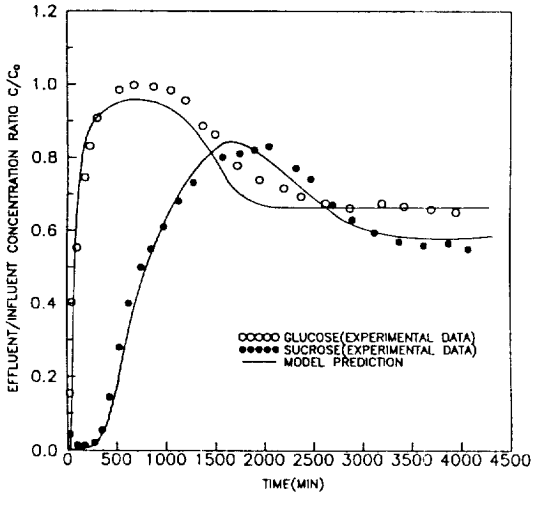

Fig. 7. Experimental breakthrough data and model simulations for glucose and sucrose in a bioactive PS-SPC.

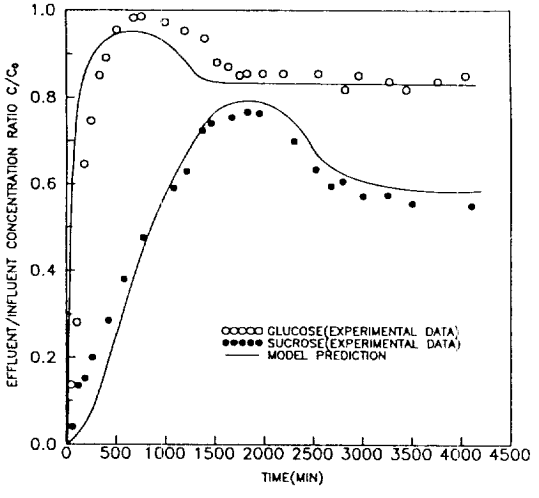

Fig. 8. Experimental breakthrough data and model simulations for glucose and sucrose in a bioactive CM-RFB.

to flow out of the reactor with the effluent. In the development of the mathematical model of fluidized bed, the biofilm thickness (L_f) and biomass concentration (X_f) on the surface of activated carbon was regarded as pseudo steady-state quantities. This means that the biofilm thickness and biomass concentration can be maintained at relatively constant values by taking the average value for nonuniform biological carbon particles.

Table 5 presents the input parameters for bioactive PSSPC model predictions for glucose and sucrose, while Table 6 lists the bioactive CMRFB model input parameters for the above two compounds as well as the dairy and leachate SWWs. The parameters for the models were determined as described previously. Fig. 7 demonstrates the experimental data and the corresponding model profiles for glucose and sucrose, respectively. Figs. 8 and 9 depict the experimental data and the corresponding model profiles for glucose, sucrose, dairy SWW, and leachate SWW, respectively. The results of model simulations and experimental data of Figs. 7 through 9 conducted for PSSPC and CMRFB

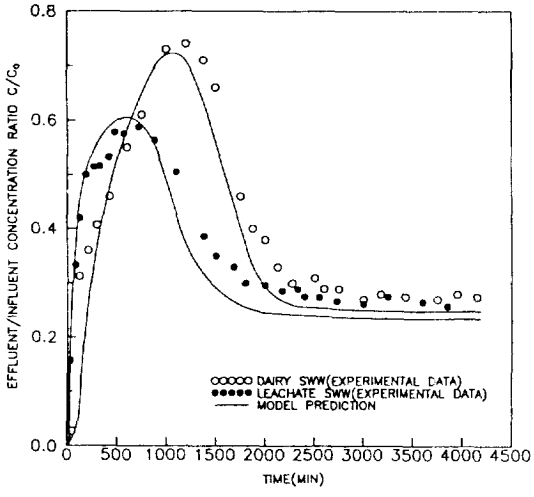

Fig. 9. Experimental breakthrough data and model simulations for dairy SWW and leachate SWW in a bioactive CMRFB.

beds show that the models satisfactorily predict the performance of bioactive adsorbers and the adsorption phenomenon controls substrate removal at the initial stages of adsorber run, while biological biodegradation controls the steady-state performance. The models in general give better predictions for readily biodegradable organic compounds such as glucose and sucrose.

CONCLUSIONS

Predictive models were developed and verified for the BAGC plug-flow stationary solid phase and completely mixed fluidized bed reactors using two biodegradable compounds, and two industrial wastewaters. The major findings and conclusions of the study are the following:

1. It was demonstrated that a numerical technique combining orthogonal collocation and finite difference methods was effective in prediction of adsorber performance.

2. The models developed in the previous study were successfully tested for the prediction of non-bioactive and bioactive adsorbers.

3. Both the non-bioactive and bioactive versions of plug-flow stationary solid phase model predicted faster rate of approach to steady-state performance than those of completely mixed fluidized-bed.

4. The premature breakthrough of CMRFB compared with PSSPC can be caused by the solid phase mixing and liquid phase dispersion due to a recycle effect of fluidized-bed.

APPENDIX

The detailed information for mathematical model development of PSSPC and CMRFB is given in the previous paper [1]. Main mathematical equations obtained from the material balances are introduced in this appendix.

1. PSSPC Model

1-1. Liquid Phase Material Balance

The material balance of the dissolved substrates to be removed for any differential segment of the bed is represented by the equation

$$\frac{\partial C(x,t)}{\partial t} = D_d \frac{\partial^2 C(x,t)}{\partial x^2} - v_x \frac{\partial C(x,t)}{\partial x} - \frac{3k_{fs}(1-\varepsilon)}{\varepsilon} \frac{(R+L_f)^2}{R^3} [C(x,t) - C_{fs}(x,t)] \tag{16}$$

whose initial and boundary conditions are

$$C(x, t=0) = 0 \tag{17}$$

$$C(x=0, t) = C_o \tag{18}$$

$$\frac{\partial C(x,t)}{\partial x}\Big|_{x=L} = 0 \tag{19}$$

1-2. Solid Phase Material Balance in the Adsorbent

The homogeneous surface diffusion model used for intraparticle diffusion of adsorbed substrate can be represented by

$$\frac{\partial q(r,t)}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial q(r,t)}{\partial r}\right] \tag{20}$$

whose initial and boundary conditions are

$$q(0 \le r \le R, t=0) = 0 \tag{21}$$

$$q(r=R, t) = q_s(t) \tag{22}$$

$$\frac{\partial q(r=0, t \ge t_o)}{\partial r} = 0 \tag{23}$$

Another boundary condition can be introduced by performing mass balance on an adsorbent particle as shown below

$$\frac{3}{R^3} \frac{\partial}{\partial t} \int_0^R q(r,t) r^2 \, dr = \frac{k_{fc} A_p}{V_t \rho_a} [C(x,t) - C_{fs}(x,t)] - \frac{3k X_f L_f}{Y \rho_a R} \frac{C_{favg}(x,t)}{K_s + C_{favg}(x,t)} \tag{24}$$

1-3. Diffusion and Reaction in the Biofilm

Assuming that substrate concentration within the

biofilm changes only in the z direction, normal to the surface of the biofilm, and that substrate concentration profile across the biofilm at pseudo steady state, the following relation can be written

$$D_f\frac{\partial^2 C_f(x, z, t)}{\partial z^2} = \frac{k X_f C_f(x, z, t)}{K_s + C_f(x, z, t)} \quad (25)$$

the boundary conditions are the following

$$C_f(x, z=0, t) = C_s(x, t) \quad (26)$$

$$C_f(x, z=L_f, t) = C_{fs}(x, t) \quad (27)$$

1-4. Growth of Biofilm

If the Monod growth model is used, the variation of biofilm thickness with time can be adequately represented by

$$\frac{\partial L_f(x, t)}{\partial t} = \frac{k C_{favg}(x, t) L_f(x, t)}{K_s + C_{favg}(x, t)} - K_d L_f(x, t) \quad (28)$$

The initial and boundary conditions are

$$L_f(x, t=0) = L_{f0} \quad (29)$$

$$L_f(x, t=t_{max}) = L_{fmax} \quad (30)$$

1-5. Adsorption Equilibrium Relationship

The Freundlich adsorption model used to relate the equilibrium solid phase concentration to liquid phase concentration near the exterior particle surface can be written as

$$q(r=R, x, t) = K_F C_s(x, t)^n \quad (31)$$

2. CMRFB Model

Eqs. (16) through (31) remain as the same in PSSPC model which describes the liquid phase material balance, solid phase diffusion in the adsorbent, diffusion and reaction in the biofilm, growth of biofilm and adsorption isotherm model respectively. However, the boundary conditions of Eqs. (18) and (24) are different from those of the PSSPC model. Eqs. (18) and (24) are replaced by (32) and (33).

$$C(x, t)|_{x=0} = \frac{QC_o + Q_r C(x, t)|_{x=L}}{Q + Q_r} \quad (32)$$

$$\frac{3}{R^3}\frac{\partial}{\partial t}\int_0^R q(r, t)\, r^2\, dr = \frac{Q}{V_r\rho_a}[C_o - C(x, t)|_{x=L}] - \frac{3k X_f L_f}{YR\rho_a}\frac{C_{favg}(x, t)}{K_s + C_{favg}(x, t)} \quad (33)$$

NOMENCLATURE

A_p : total surface area available for mass transfer [L^2]
a : surface area per particle [L^2]
B_w : cell weight [M_x]
C : effluent substrate concentration [M_s/L^3]
C_e : equilibrium substrate concentration in liquid phase [M_s/L^3]
C_f : substrate concentration in biofilm [M_s/L^3]
C_{favg} : average substrate concentration in biofilm [M_s/L^3]
C_{fs} : substrate concentration at biofilm/liquid interface [M_s/L^3]
C_o : influent substrate concentration [M_s/L^3]
C_s : substrate concentration near activated carbon surface [M_s/L^3]
D_d : axial dispersion coefficient [L^2/T]
C_o : influent substrate concentration [M_s/L^3]
C_s : substrate concentration near activated carbon surface [M_s/L^3]
D_d : axial dispersion coefficient [L^2/T]
D_l : molecular diffusivity [L^2/T]
D_f : substrate diffusion coefficient in biofilm [L^2/T]
D_s : substrate diffusion coefficient in activated carbon [L^2/T]
g : acceleration due to gravity [L^2/T]
k : maximum specific substrate utilization rate [$M_s/M_x/T$]
k_{fb} : liquid film transfer coefficient in adsorption rate study [L/T]
k_{fc} : liquid film transfer coefficient in column study [L/T]
K_d : overall biofilm loss coefficient [1/T]
K_F : Freundlich isotherm constant [$(M_s/M_q)(L^3/M_s)^n$]
K_s : Monod half saturation coefficient [M_s/L^3]
L : length of activated carbon fluidized bed [L]
L_f : biofilm thickness [L]
L_{f0} : initial biofilm thickness [L]
L_{fmax} : maximum biofilm thickness [L]
n : Freundlich isotherm constant
N : number of particles taken up for biofilm analysis
N_p : total number of particles in the GAC bed
q : sorbed phase substrate concentration [M_s/M_q]
q_e : equilibrium sorbed phase concentration [M_s/M_q]
q_s : sorbed phase substrate concentration at carbon surface [M_s/M_q]
Q : influent flow rate [L^3/T]
Q_r : recirculation flow rate [L^3/T]
r : radial coordinate in activated carbon particle [L]
R : radius of activated carbon particle [L]
R_c : recycle ratio (dimensionless)

Sc : Schmidt number (dimensionless)
t : time [T]
ΔV : bed expansion volume [L^3]
V_b : molar volume of the solute at its boiling point [L^3/M_s]
V_t : total activated carbon volume in the bed [L^3]
v_x : axial interstitial fluid velocity [L/T]
W_e : weight of evaporated water [M]
x : coordinate for axial position in activated carbon bed [L]
X : bacterial concentration in solution [M_x/L^3]
X_f : biomass density in biofilm [M_x/L^3]
Y : microbial yield coefficient [M_x/M_s]
z : coordinate for position in biofilm [L]

Greek Letters

ε : fraction of volumetric space unoccupied by activated carbon
μ : viscosity of the fluid [$M_s/(TL)$]
ρ_a : apparent density of activated carbon [M_a/L^3]
ρ_l : density of the fluid [M/L^3]
ρ_s : density of particle [M_a/L^3]
θ : hydraulic detention time [T]
θ_c : mean cell resistence time [T]

Symbols

L : length
M_a : mass of activated carbon
M_s : mass of substrate
M_x : mass of microorganisms
T : time

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