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Enhanced mitigation of para-chlorophenol using stratified activated carbon adsorption columns

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ABSTRACT

The adsorptive removal of toxic para-chlorophenol using activated carbon adsorption columns is a proven effective engineering process. This paper examined the possibility to stratify an adsorbent bed into layers, in order to enhance the adsorption process performance in terms of increased column service time and adsorbent bed saturation. Four different types of fixed-bed adsorption columns are used and compared under the same operating conditions, but with the variation of column geometry and activated carbon particle size stratification. The Type 3 column – a cylindrical column with particle stratification packing, is found to be the most efficient choice, as the extent of column service time and adsorbent bed saturation are the largest. This could eventually decrease the frequency of adsorbent replacement/regeneration and hence reduce the operating cost of the fixed-bed adsorption process. The Homogeneous Surface Diffusion Model (HSDM) was applied successfully to describe the dynamic adsorption of para-chlorophenol onto Filtrasorb 400 (F400) activated carbon in different types of columns. The Redlich-Peterson isotherm model equation, an experimentally derived external mass transfer correlation and a constant surface diffusivity are used in the HSDM. The optimised surface diffusivity of para-chlorophenol is found to be 1.20E-8 cm^2/s, which is in good agreement with other phenolics/F400 carbon diffusing systems in literature.

1. Introduction

Chlorophenols are a large group of chemicals with chlorine atoms (between one and five) attached to the phenolic structure, and there are 19 congeners exist in total. They are normally used in herbicides (Tsyganok et al., 1999), insecticides, wood preservatives and industries as synthesis intermediates or as raw materials in the manufacturing of pharmaceuticals and dyes (Pera-Titus et al., 2004). According to Pera-Titus et al. (2004), the world market of chlorophenols is fairly stable and is ca. 100 kilo-tones per year, in which the production of heavy and light chlorophenols is ca. 25–30 and 60 kilo-tones per year respectively.

Due to their poor bio-degradability (Dorn et al., 1974), the environment has little assimilative capacity towards chlorophenols. Some recent researches have demonstrated the potential to degrade recalcitrant chlorinated hydrocarbons using fungus (Marco-Urrea et al., 2009) and bacteria (Adebusoye et al., 2007). Chlorophenols' half life in aerobic waters can exceed 3 months and exceed several years in organic sediments (Keane, 2005). Chlorophenols do not just cause severe adverse effects such as toxicity and

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Nomenclature

Alphabet

C	adsorbate concentration in liquid phase (mg dm^{-3})
C_o	initial adsorbate concentration in liquid phase (mg dm^{-3})
C_s	liquid phase adsorbate concentration at adsorbent external surface (mg dm^{-3})
d_p	particle diameter (m)
D	mass transfer coefficient (cm^2 s^{-1})
D_{mol}	molecular diffusivity (cm^2 s^{-1})
D_p	average pore diameter (nm)
D_s	surface diffusivity (m^2 s^{-1})
J_d	mass transfer coefficient factor (dimensionless)
k_f	external film mass transfer coefficient (m s^{-1})
L	bed length or characteristic length (cm)
Pe	Peclet number (dimensionless)
q	solid phase pollutant concentration at time t (mg g^{-1})
Q	pollutant volumetric flowrate (dm^3 h^{-1})
r	radial position within adsorbent particle (m)
R_p	radius of adsorbent particle (m)
Re	Reynolds number (dimensionless)
R^2	R-squared value of trendline plot (dimensionless)
S_{BET}	BET surface area (m^2 g^{-1})
S_{meso}	mesopore surface area (m^2 g^{-1})
S_{micro}	micropore surface area (m^2 g^{-1})
Sc	Schmidt number (dimensionless)
Sh	Sherwood number (dimensionless)
t	service time/operating time of the column (hr)
v	interstitial adsorbate velocity (m s^{-1})
V_{total}	total pore volume (cm^3 g^{-1})
V_{meso}	mesopore volume (cm^3 g^{-1})
V_{micro}	micropore volume (cm^3 g^{-1})
Z	bed height (m)

Greek alphabet

λ_{max}	maximum absorbance wavelength (nm)
ρ	density of adsorbate solution (kg m^{-3})
ρ_p	density of adsorbent particle (kg m^{-3})
ρ_s	skeleton density (kg m^{-3})
μ	viscosity of adsorbate solution (kg m^{-1} s^{-1})
ε	bed porosity (dimensionless)

carcinogenicity (Jorens and Schepens, 1993; Huff, 2001), but also degradation of the water quality for consumptive use in terms of taste and odour problems even at concentrations below 0.1 μg/L (Verschueren, 2001). Therefore, several phenolic compounds have been listed as a group of toxic pollutants by the US Environmental Protection Agency and by the European Decision 2455/2001/EC.

According to the Agency for Toxic Substances and Disease Registry, chlorophenols can bio-accumulate in organisms in different extents, and pentachlorophenol has a higher tendency to bio-accumulate in aquatic organisms, with a bio-concentration factor (an indicator for the extent of bio-accumulation) 1000 for goldfish, 324 for mussels and 78 for oysters (ATSDR, 2001). The high bio-concentration factor implies that chlorophenols could be bio-concentrated from one species to another, and hence posing the greatest risk to human beings through food chain transport. Chronic exposure to low molecular weight chlorophenols results in liver and kidney damage, loss in weight, general fatigue and low appetite (Savant et al., 2006).

Numerous researches study the oxidation of chlorophenols with reagents, for example, potassium permanganate (Zhang et al., 2003; Bruchet and Duguet, 2004), hydrogen peroxide and ozone (Ormad et al., 1997; Pi et al., 2007), electrochemical oxidation (Gherardini et al., 2001) and hydrodechlorination (Molina et al., 2010; Sun et al., 2011). For complete mineralisation of chlorophenols into carbon dioxide, water and chloride anions or less harmful intermediates, the techniques of advanced oxidation processes, such as with Fenton's reagent (H_2O_2/Fe^{2+}) (Chamarro et al., 2001; Zimbron and Reardon, 2009), photo-Fenton's reagent (H_2O_2/Fe^{2+}/UV) (Bauer et al., 1999) and photocatalysis (Chu, 1999) have been employed to chlorophenols.

Activated carbon adsorption column operation has been studied extensively (Garcia-Mendieta et al., 2003; Sulaymon and Ahmed, 2008; Sze et al., 2008) for remediating moderately bio-degradable chlorophenols. Basmadjian (1983) proposed a reverse stratified tapered adsorber with varying cross-sectional area and different adsorbent particles arranged in a reverse layering of adsorbent size. This bed geometry provides a unique superficial velocity profile for the adsorbate solution, which influences the residence time of adsorbate and the extent of the external mass transfer film thickness around the adsorbent particles. Pota and Mathews (2000) and Mathews (2005) demonstrated that adsorption columns with particle layering/stratification perform better than columns using uniform particle size. This research is particularly designed to verify the possibility of enhancing the efficiency of an adsorption column under the effects of bed geometry and adsorbent particle stratification packing, which is advantageous in terms of reduced frequency of adsorbent regeneration/replacement and lower operating cost of the wastewater treatment plant.

2. Theoretical section

2.1. *Equilibrium adsorption isotherm*

The experimental procedure and results of the single component equilibrium adsorption isotherm study of para-chlorophenol adsorption onto F400 activated carbon were discussed in previous work (Sze and McKay, 2010). The Redlich-Peterson isotherm model was found to be the best fit model for the experimental equilibrium adsorption isotherm data obtained (Sze and McKay, 2010).

2.2. External mass transfer correlation

The method used for contacting an adsorbent with a solution, such as plug flow column operations or completely mixed batch reactors, together with the hydrodynamic and operational details of a particular system, control the magnitude of the external mass transfer coefficient (Slejko, 1985), which is evaluated from a number of different external mass transfer correlations.

2.3. Homogeneous surface diffusion model

The Homogeneous Surface Diffusion Model (HSDM) initiated by Rosen (1952), has hitherto been applied to fixed-bed adsorption column using activated carbon (Pota and Mathews, 2000; Lee and McKay, 2004; Ahmad et al., 2006). In the HSDM, there are resistances to retard the migration of adsorbate molecules to adsorb onto adsorbent particles, namely, the external stagnant film surrounding the adsorbent particle (indicating by the external mass transfer coefficient) and the intraparticle surface diffusion within the particle surface (represented by the surface diffusivity). On reaching the adsorbent surface, instantaneous equilibrium between the adsorbate fluid and adsorbent surface is established at the outer adsorbent surface, and adsorbed molecules 'hop' to vacant sites along the surface of pore walls by surface diffusion.

Assumptions to the homogeneous surface diffusion model:

1. No axial dispersion, liquid solution flows with a constant linear velocity, i.e. plug flow conditions
2. External mass transfer governed by a linear driving force
3. Adsorbent particle is spherical and homogeneous
4. Adsorbate molecules diffuse along the particle's pore surfaces by surface diffusion
5. Local adsorption equilibrium between the adsorbate in the intra-stationary phase and the adsorbate onto the carbon surface

The overall mass balance around the fixed-bed (neglecting the axial dispersion):

$$v\left[\frac{\partial C}{\partial Z}\right]_t + \left[\frac{\partial C}{\partial t}\right]_z + \rho_p\left(\frac{1-\varepsilon}{\varepsilon}\right)\left[\frac{\partial q}{\partial t}\right]_z = 0 \quad (1)$$

The corresponding initial and boundary conditions are:

$t = 0,\ 0 \le Z < L,\ C = 0$
$t > 0,\ Z = 0,\ C = C_0$

The last term on the left hand side of Eq. (1) represents the rate of accumulation of solute in the solid phase, and hence could be described by the rate of solute transfer across the stagnant liquid film. A linear driving force model is used to describe the external mass transfer, and characterised by the external mass transfer coefficient, k_f.

$$\rho_p\left[\frac{\partial q}{\partial t}\right]_z = \frac{3k_f}{R_p}(C - C_s) \quad (2)$$

The adsorption rate of solute by spherical particle is governed by surface diffusion and hence can be represented as:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[D_s r^2 \frac{\partial q}{\partial r}\right] \quad (3)$$

In Eq. (3), the surface diffusivity (D_s) is assumed to be constant and independent of the surface loading.

$$\frac{\partial q}{\partial t} = D_s\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \quad (4)$$

The initial and boundary conditions of Eq. (4) are:

$t = 0,\ 0 \le Z \le L,\ 0 \le r \le R_p,\ q = 0$
$t > 0,\ r = 0,\ \left.\frac{\partial q}{\partial t}\right|_{r=0} = 0$
$t > 0,\ r = Rp,\ \frac{k_f}{\rho_p}(C - C_s) = D_s\left.\frac{\partial q}{\partial r}\right|_{r=R}$

In order to predict the breakthrough curve, the numerical solutions for the fluid and solid phase partial differential equations (PDEs) are coupled and solved by using a finite difference method. By implementing the Crank-Nicolson method to Eq. (4), the solutions to the solid phase PDE could provide an estimate of solid phase concentration for the fluid phase PDE solution. With the respective boundary conditions associated with the solid phase PDEs, the solid phase PDE could be transformed into a matrix and solved at each time step. With a selected equilibrium isotherm equation and solid phase concentration, the fluid phase concentration can be solved at the current time level and the whole breakthrough curve could be obtained by increasing the time step.

3. Material and methods

3.1. Adsorbent

The Filtrasorb 400 (F400) activated carbon was purchased from the Calgon Carbon Corporation. The virgin F400 carbons were crushed by a hammer mill and sieved into different portions with specific particle size range, namely 150–250, 250–355, 355–500, 500–710 and 710–1000 μm. Each sieved portion was washed using deionised water, and was then dried thoroughly in an oven at 105 °C and stored individually in airtight containers to minimise the adsorption of volatile organic compounds and moisture.

The characterisation of the F400 activated carbon was worked out by conducting the nitrogen adsorption–desorption isotherms at 77 K using a pore and surface analyser (model: Quantachrome Instruments AutoSorb 1). The total pore volume (V_{total}) was determined from the amount of nitrogen adsorbed at the relative pressure of $P/P_0 = 0.96$, then the average pore diameter (D_p) was found by $D_p = 4\ V_{total}/S_{BET}$. The mesopore volume was calculated as the difference between the total pore volume and the micropore volume ($V_{meso} = V_{total} - V_{micro}$).

The t-plot method was used for the micropore analysis, with the P/P_0 range from 0.46 to 0.71. The mesopore area (S_{meso}) is the difference between the BET surface area and micropore area, that is $S_{meso} = S_{BET} - S_{micro}$. The textural properties of F400 activated carbon are summarised in Table 1. The results calculated using the t-plot method proved that the F400 carbon possesses vast majority of micropore volume

Table 1 – Textural properties of F400 activated carbon.

Skeleton density, ρ_s (kg m^{-3})[a]	2115
Particle density – wetted in water (kg m^{-3})[b]	1300
Iodine number (mg g^{-1})[b]	1000 (Min.)
Uniformity coefficient[b]	1.9 (Max.)
Ash by weight	5.3%
Abrasion number[b]	75 (Min.)
BET surface area, S_{BET} (m^2 g^{-1})[c]	825
Total pore volume, V_{total} (cc g^{-1}) at $P/P_0 = 0.96$[c]	0.491
Average pore diameter, D_p (nm)[c]	2.32
Point of zero charge, pH_{PZC}	7.20
By t-plot method,[c]	
Micropore area, S_{micro} (m^2 g^{-1})	768
Mesopore area, S_{meso} (m^2 g^{-1})	57
Micropore volume, V_{micro} (cc g^{-1})	0.387
Mesopore volume, V_{meso} (cc g^{-1})	0.104
By elemental analysis, [d]	
Carbon (%)	87.1
Hydrogen (%)	1.4
Nitrogen (%)	0.4
Sulphur (%)	0.7
Oxygen (%)	5.1

a Measured using the Quantachrome UltraPycnometer.
b Provided from the product bulletin of Filtrasorb 400 Activated Carbon (Calgon, 2009).
c Measured using the Quantachrome AutoSorb 1.
d Measured using the CHNS Vario EL III, Varian.

(about 80% of total pore volume) and micropore area contributed 93.4% to the total surface area.

3.2. *Adsorbate*

Para-chlorophenol (p-CP) with purity greater than 99% was purchased from the Aldrich Chemical Company. Table 2 shows some physical properties of the p-CP.

3.3. *Fixed-bed adsorption column studies*

A pilot-scale adsorption column rig was constructed to carry out fixed-bed adsorption column studies. The schematic diagram for the adsorption column rig is shown in Fig. 1.

The deionised water used was from the main supply and it was fed into a 50 dm^3 plastic container (T1). The deionised water then flowed into a similar tank (T2) by gravity feed. A known amount of adsorbate was added to this batch of 50 dm^3 of water and the solution was pumped into another bigger tank (T3). The pumps used (P1 and P2) and all the components which came into contact with process solution were made of inert plastic materials. The overflow solution was fed back into (T2) and this served to maintain constant agitation of the solutions.

Samples were taken from a sampling point (S1) as well as from sampling point (S2) to record the initial value of pollutant concentration used in each experimental run. Influent to the adsorber columns was pumped via (P2) and a three-way valve (V6) served to control the recycle feedback to the tank (T3). Calibrated rotameters (F1) were used to control the adsorbate flowrate through the columns (C1). Finally, the effluent was collected in a waste disposal container which is designated for handling all kinds of final effluents.

Sample points were located at various heights (S1) 5 cm apart, on the adsorbent column (C1), and 10 cm^3 syringes and stainless steel needles were used to collect sample solutions from the columns. An adsorbent retaining sieve of 65 mesh size was fixed at the lower part of the column, and then a Perspex disc with 0.5 cm Perspex tube provided the inlet line to the column. The inlet pipe was adhered to the column using the adhesive material. Sampling points were provided at 5 cm heights and each point was sealed using septa and stainless steel caps. A series of 10 cm^3 syringes was used to collect samples for analysis. Each column was associated with five sampling points.

A weighed amount of dried F400 carbon was boiled in distilled water and dried at 105 °C in an oven before being packed into the column. It was tapped well to ensure that the adsorbent settles down during packing, and then an upper retaining sieve of 140 mesh size is inserted on top of the bed and firmly secured by placing stainless steel balls on top of the retaining screen. After packing the F400 activated carbon into the columns, the columns were flushed with deionised water for 24 h to 'wet' the carbons. This is important to ensure that all air is expelled from the adsorbent particles. If air pockets exist in the packing, column operation will become unstable as channelling and air entrapment take place. Channelling is the preferential flow of fluids through passages of lower resistance which can occur in fixed-beds or columns of particle owing to non-uniform packing, gas pockets and wall effects (ASTM, 2009).

Rotameters (F1) were calibrated to give the correct flowrate and were maintained constant throughout each experimental run. At time zero, a step input in the adsorbate concentration was introduced to the flowing stream. Samples were taken at selected time interval until the adsorbate concentration was at the breakthrough point at the top of the bed. The samples were taken at various bed heights and were measured using the Varian Cary 1E UV/Vis-spectrophotometer.

In this research, portions of the fixed-bed adsorption studies were studied using uniform particle size range. Furthermore, the effect of particle size layering (or so-called the effect of stratification) in tapered and cylindrical columns was also investigated. For uniform particle size range studies, F400 activated carbon with the size in the range of 500–710 μm is chosen. On the other hand, 5 different F400 particle size ranges, namely 710–1000, 500–710, 355–500, 250–355 and 150–250 μm, were used to investigate the effect of stratification. The coarsest F400 activated carbon was packed at the bottom part of the tapered column, while the finest was put on the top.

Table 2 – Physical properties of Para-chlorophenol.

Chemical formula	C_6H_5OCl
Molecular dimension (nm)	0.46 (*w*) × 0.68 (l) × 0.1 (*t*)
Molecular weight (g mol^{-1})	129
Molecular volume (cm^3 mol^{-1})	124.3
Molecular diffusivity, D_{mol} (cm^2 s^{-1})	8.20×10^{-6}
Maximum wavelength, λ_{max} (nm)	280
Acid dissociation constant, pK_a	9.40
Octanol-water partition coefficient, K_{ow}	2.35

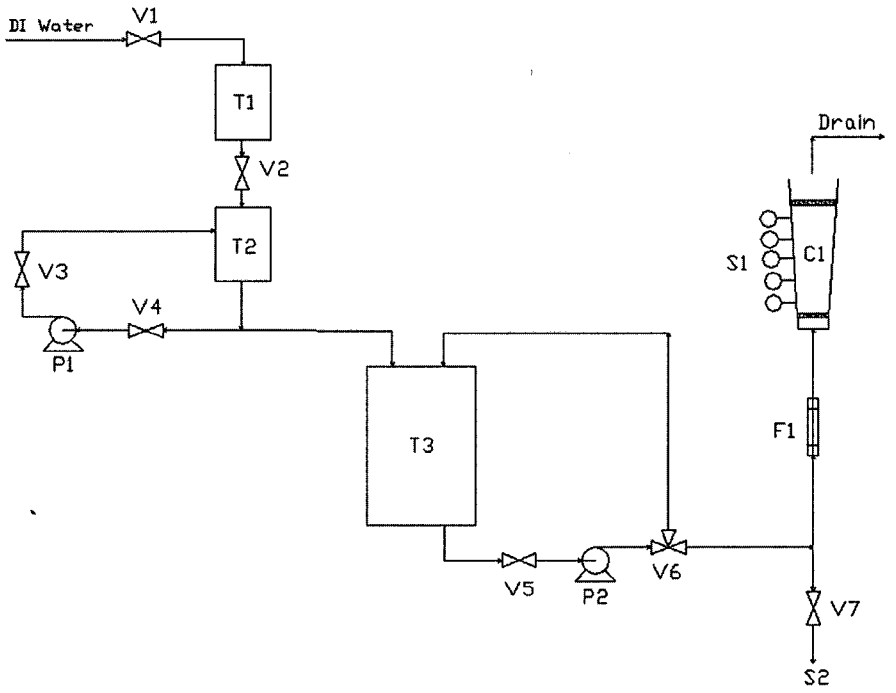

Fig. 1 – Schematic diagram of pilot plant adsorption column rig.

The adsorption column is assumed to be operated as plug flow if the axial Peclet number of the bed (Pe_L) is greater than about 100 (Levenspiel, 1972). The Peclet number is a dimensionless number relating the rate of advection of a flow to its rate of diffusion, and it is equivalent to the product of Reynolds number with the Schmidt number in the case of mass diffusion, and is defined as:

$$Pe_L = \frac{LV}{D} = Re_L * Sc \quad (5)$$

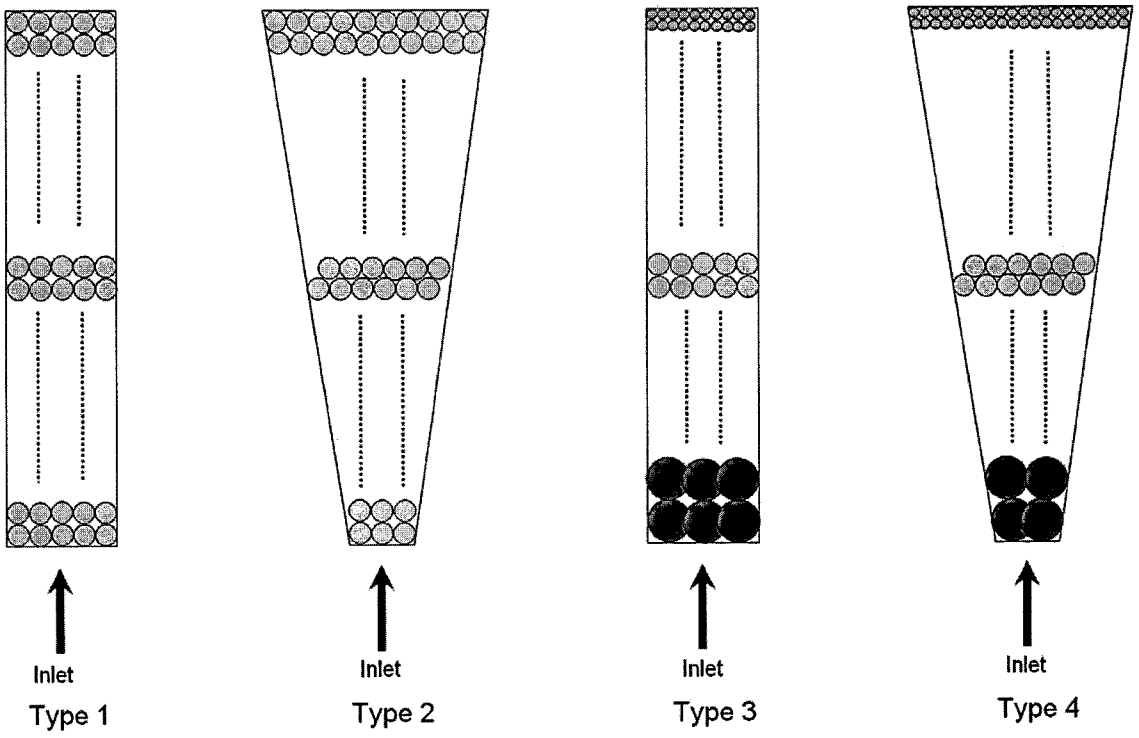

Fig. 2 – Classifications of adsorption columns investigated.

The Peclet numbers in all adsorption columns used for the dynamic adsorption of para-chlorophenol onto F400 carbons under different operating condition were calculated, and the Peclet numbers ranged from 2.35×10^4 to 2.30×10^5, which indicate that the adsorption columns are conducted as plug flow operation without significant axial dispersion.

Four types of fixed-bed adsorption columns with different column geometries and carbon particle size packings are used to study the dynamic adsorption of para-chlorophenol onto F400 activated carbons under various operating conditions. Fig. 2 illustrates these four types of fixed-bed adsorption columns, namely,

Type 1 – Cylindrical column with uniform particle size packing,

Type 2 – 5° tapered column with uniform particle size packing,

Type 3 – Cylindrical column with particle stratification packing, and.

Type 4 – 5° tapered column with particle stratification packing.

Table 3 summarizes the column conditions employed in this research. The basis of same F400 carbon mass (215 g) is kept for all four types of column. F400 carbon with a uniform particle size of 500–710 μm is used for Type 1 and 2 columns, while 5 stratified layers of F400 carbons are packed in Type 3 and 4 columns for investigating the adsorption column operation to remove para-chlorophenol. Due to the variation of packing density of different carbon particle sizes, the overall bed heights of the stratified columns used are slightly different. According to Table 3, the total bed heights of both Type 3 and 4 columns are shorter than 25 cm, so the last sampling point at 25 cm is still valid to represent the whole carbon bed in each column with a total mass of 215 g. In the end, the corresponding bed heights of each particle size in stratified columns are following. In Type 3, the heights of each particle size from the bottom of the column (Z = 0 cm) are 4.9, 9.9, 14.8, 19.8 ad 24.7 cm. In Type 4, the heights of each particle size from the bottom of the column (Z = 0 cm) are 8.9, 14.2, 18.4, 21.7 and 24.5 cm.

Table 3 – Summary of column condition, saturation percentage and average external mass transfer coefficient for four different adsorption columns removing Para-chlorophenol (operating condition: Q = 200 ml/min, Co = 200 ppm).

Type	Tapered angle (degree)	Particle size (μm)	Stratified (layers)	Inlet diameter (cm)	Outlet diameter (cm)	Total bed height (cm)	Extent of adsorbent bed saturation at			Average external mass transfer coefficient (cm/s)
							$C/C_0 = 0.1$ (%)	$C/C_0 = 0.2$ (%)	$C/C_0 = 0.3$ (%)	
1	0	500–710	No	4.50	4.50	25.0	69.6 ± 1.4	72.2 ± 0.9	73.0 ± 0.6	3.28E-03
2	5	500–710	No	2.13	6.51	25.0	68.9 ± 1.9	71.0 ± 1.7	72.9 ± 1.6	3.54E-03
3	0	150–1000	Yes (5)	4.50	4.50	24.7	82.2 ± 0.7	83.0 ± 0.4	83.5 ± 0.4	4.50E-03
4	5	150–1000	Yes (5)	2.13	6.41	24.5	78.9 ± 0.4	79.4 ± 0.5	80.0 ± 0.5	3.86E-03

4. Results and discussion

4.1. *Reproducibility of adsorption column results*

A number of column runs (ca. 20% of all columns works) have been duplicated to check whether the experimental data are reproducible. Fig. 3 shows the duplication plot of the para-chlorophenol cylindrical column adsorption onto F400 carbon at a flowrate of 150 ml/min with initial concentration of 200 ppm. The plot reveals that the experimental data obtained from two individual runs are quite similar, the hollow and solid labels are representing the experimental data obtained from the first and the second column run respectively. Other duplication tests proved experimental data are reproducible with different operating conditions and for two separate runs.

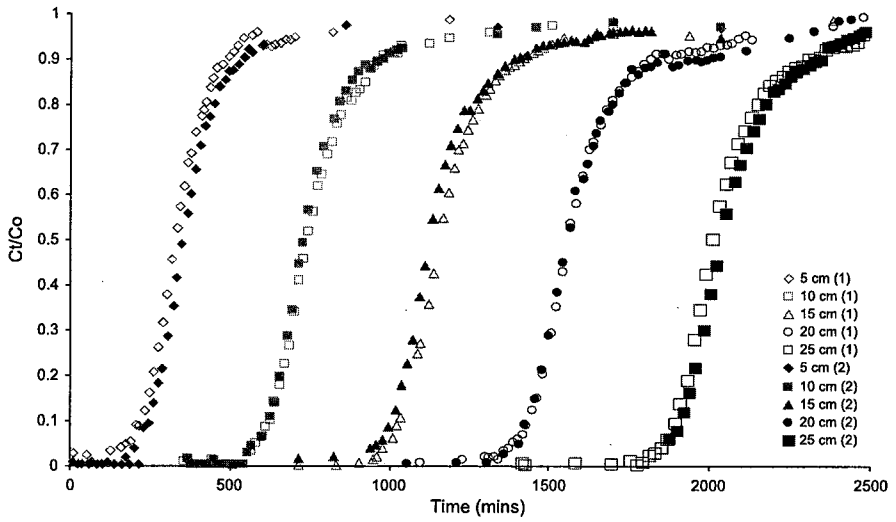

Fig. 3 – Duplication of dynamic column adsorption of para-chlorophenol onto F400 carbon in Type 1 column (cylindrical column, Q = 150 ml/min, C_0 = 200 ppm, d_p = 500–710 μm).

4.2. *Determination of the external mass transfer correlation*

The effects of volumetric flowrate, initial para-chlorophenol concentration, carbon particle size stratification and tapered angle were studied for the para-chlorophenol adsorption column system. The particle Reynolds numbers of para-chlorophenol column runs ranged from 0.147 to 18.60. The external mass transfer coefficients of fixed-bed adsorption column operation are usually estimated by the empirical correlations. Each correlation expression is a function of Sherwood number (Sh), Reynolds number (Re) and Schmidt number (Sc), sometimes it is bed porosity (ε) dependent as well. There are three possible correlations which can be used, viz. Coeuret (1976), Wilson and Geankoplis (1966) and Williamson et al. (1963), for estimating the external mass transfer coefficients of the para-chlorophenol system.

$$\text{Coeuret (for } 0.04 < Re < 30): \quad Sh = 5.4Re^{1/3}Sc^{1/4} \tag{6}$$

$$\text{Wilson and Geankoplis (for } 0.0016 < Re < 55): \quad Sh = \frac{1.09}{\varepsilon}Re^{1/3}Sc^{1/3} \tag{7}$$

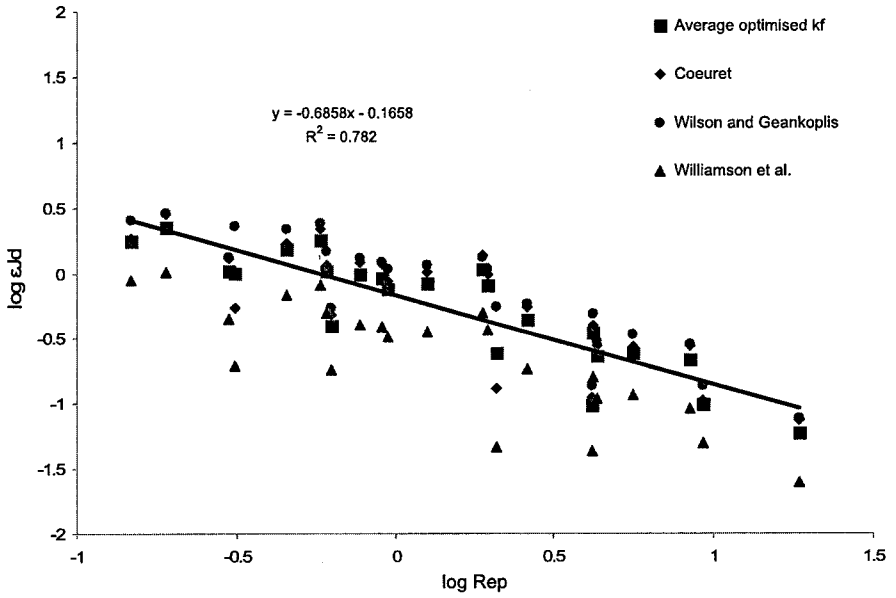

Fig. 4 – Representation of the external mass transfer correlation for para-chlorophenol fixed-bed columns by plotting log εJ_d vs. log *Re*.

Williamson et al. (for $0.04 < Re < 52$) $Sh = 2.4\varepsilon^{0.66}Re^{0.34}Sc^{1/3}$ (8)

where $Sh = \frac{k_f d_p}{D_{mol}}$, $Re = \frac{\rho v d_p}{\mu}$ and $Sc = \frac{\mu}{\rho D_{mol}}$

These correlations were developed at different experimental conditions. Coeuret (1976) experimentally determined the external mass transfer correlation using the electrochemical technique which was based on the reduction of ferricyanide ions on a cathode consisting of a fixed-bed of spherical conducting grains. Wilson and Geankoplis (1966) used a dissolution method to determine the external mass transfer correlations for the benzoic acid-water system. Hence it is more appropriate to develop a unique external mass transfer correlation to describe the para-chlorophenol adsorption onto F400 carbon columns in this research.

Each correlation is incorporated into the HSDM separately, and the k_f value becomes a variable to be optimised together with the D_s values to yield the minimum SSE value between the experimental data and the simulated HSDM results. The downhill simplex method (Nelder and Mead, 1965) is employed in sub-routine *amoeba* using the FORTRAN computer program, which is able to optimise two variables by performing a multidimensional minimisation.

The optimised k_f values from Eqs. (6)–(8) for para-chlorophenol system under different operating parameters are obtained. For Type 2 to 4 columns, the optimised k_f values of each column inlet and outlet are selected and are plotted against the corresponding Reynolds numbers in Fig. 4. The rationale of these points selection is to develop a representative correlation (experimentally based) for describing the external mass transfer coefficients within a specific column and also for different column geometries operating under different conditions.

A set of average optimised k_f values from para-chlorophenol system is used to fit the generalised form of the relationship between the mass transfer factor, εJ_d, and Reynolds number.

$$\varepsilon J_d = A\,Re^{-m} \quad (9)$$

where $\varepsilon J_d = \varepsilon(k_f/v_s)Sc^{2/3}$

Taking the logarithm of both sides of Eq. (9), gives:

$$\log \varepsilon J_d = \log A - m \log Re \quad (10)$$

The slope of the trendline is equal to $-m$ and the y-intercept is log A by plotting log εJ_d vs. log Re. From Fig. 4, the relationship between the mass transfer factor and Reynolds number for para-chlorophenol adsorption columns is expressed as:

$$\varepsilon J_d = 0.683Re^{-0.686} = \varepsilon(k_f/v_s)Sc^{2/3} \quad (11)$$

Multiplying $ReSc^{1/3}$ to both sides, it yields:

$$\varepsilon(k_f/v_s)Sc^{2/3}ReSc^{1/3} = 0.683Re^{-0.686}ReSc^{1/3} \quad (12)$$

$$Sh = (k_f/v_s)ReSc = 0.683/\varepsilon Re^{0.314}Sc^{1/3} \quad (13)$$

4.3. *Comparison of Type 1 to 4 columns adsorption operation*

The adsorption column service time and adsorbent bed utilisation of the Type 1 to 4 columns under identical operating conditions are conducted and compared. The service time of the adsorber is represented by the time when the breakthrough curve reach the breakthrough point, at which effluents from adsorber no longer meet the legislation standards, and necessitating the replacement or regeneration of spent adsorbents. The bed capacity could be determined from the graphical integration of the breakthrough curves (Perry, 1984; Helfferich, 1995), and it is usually compared with the equilibrium adsorption isotherm data to figure out the extent of bed utilisation.

As a result, the incipient 10%, 20% and 30% breakthrough percentage are selected as breakthrough point, and saturation of adsorbent bed are evaluated based on these breakthrough points. The experimental dynamic adsorption column data

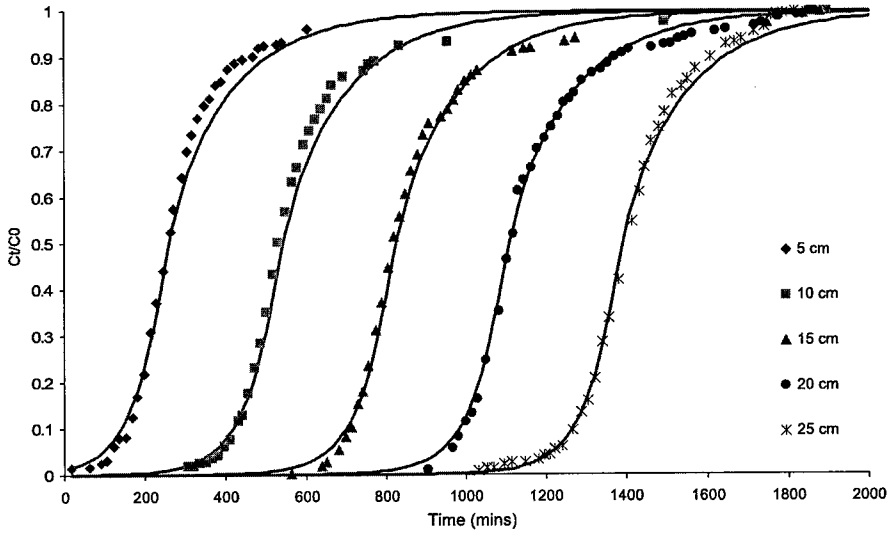

Fig. 5 – HSDM predicted breakthrough curves for para-chlorophenol removal by a Type 1 column at various bed heights (cylindrical column, Q = 200 ml/min, C_0 = 200 ppm, d_p = 500–710 μm).

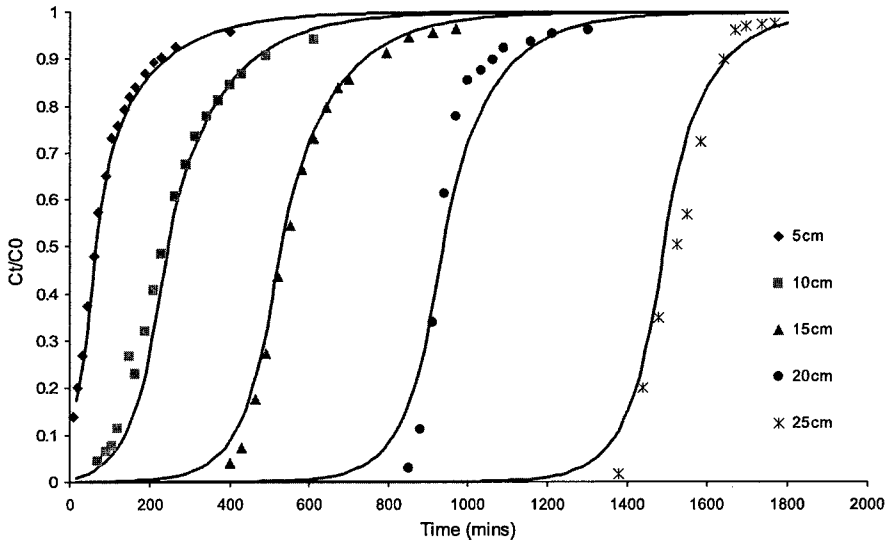

Fig. 6 – HSDM predicted breakthrough curves for para-chlorophenol removal by a Type 4 column at various bed heights (5° tapered column, 5 stratified layers, Q = 200 ml/min, C_0 = 200 ppm, d_p = 150–1000 μm).

are fitted with the HSDM using constant surface diffusivity and experimental derived external mass transfer correlation. The optimised constant D_s value obtained from the column operations for para-chlorophenol is 1.20E-8 cm^2/s. All HSDM predicted values fit very well with the experimental data for para-chlorophenol system, Figs. 5 and 6 are showing the HSDM prediction together with the experimental adsorption column data obtained in Type 1 and 4 columns.

The change of the bed geometry does not bring a pronounced effect to the bed saturation, both Type 1 and 2 columns show a similar saturation percentage (Table 3) at any breakthrough point and hence similar breakthrough curves for removing the para-chlorophenol (Fig. 7). However, when the adsorbent particle size stratification is introduced into Type 1 and 2 columns, the adsorbent bed utilisation has been greatly enhanced. The enhancement of the adsorbent bed exhibited by stratified bed is illustrated by the sharpness of the breakthrough curve; it is obvious that the mass transfer zone of Type 3 is about one half shorter than the Type 1 column. As the effect of particle size stratification and effect of column geometry are involved in the Type 2 to 4 columns, the interstitial adsorbate velocity are non-uniform and hence resulting variable external mass transfer coefficients along bed heights. According to Table 4, the averaged k_f values for Type 3 and 4 columns are larger than those in Type 1 and 2 columns, which implied the external mass transfer resistance

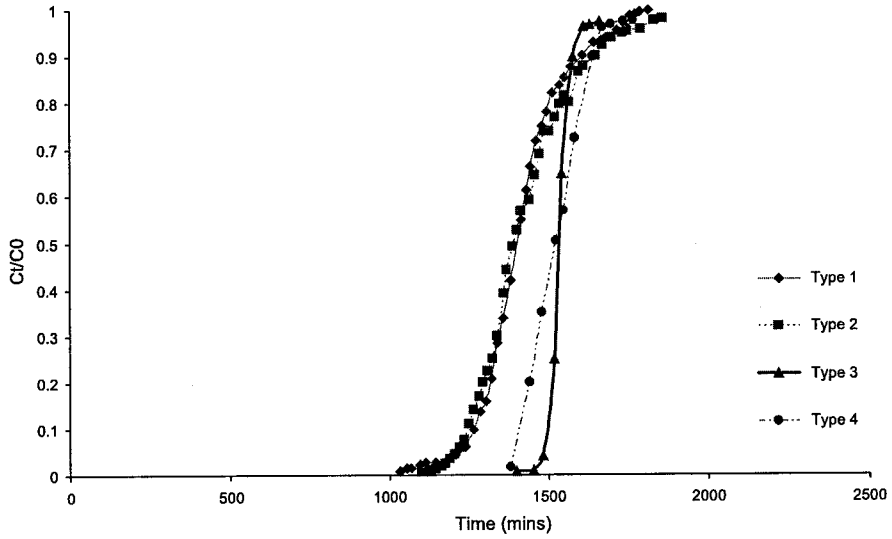

Fig. 7 – Comparison of experimental para-chlorophenol breakthrough curves for Type 1 to 4 columns (Q = 200 ml/min, C_0 = 200 ppm, Z = 25 cm).

Table 4 – Summary of surface diffusivities of different phenolics adsorption onto F400 carbon in column operation.

Adsorbate	$D_s \times 10^8$ (cm^2/s)	Reference
Phenol	3.55	(Crittenden and Weber, 1978)
p-chlorophenol	1.20	This study
p-chlorophenol	0.15	(Weber and Wang, 1987)
p-nitrophenol	0.60	(Weber and Wang, 1987)
p-bromophenol	8.56	(Crittenden and Weber, 1978)
3,5-dichlorophenol	0.0155	(Thacker et al., 1984)
3,5-dimethylphenol	0.0948	(Thacker et al., 1984)

exhibited by the carbon inside Type 3 and 4 columns are smaller. However, the enhancement of the stratified bed over the non-stratified bed is not only due to the increase in the averaged external mass transfer coefficients, but also based on the nature of fast adsorption rate exhibited by the smaller carbon particles used. Basically, the mean d_p of 575 μm could be used to represent the F400 carbon particle size in stratified columns, on the basis that the whole adsorbent bed is stratified into 5 portions with same mass. Yang and Al-Duri (2001) and Badruzzaman et al. (2004) have pointed out that small adsorbent particles possess higher adsorption rate, which agrees in accordance with the Fick's second law of diffusion (Eq. (4)); the smaller carbon particles possess a larger external surface area for adsorbate adsorption and shorter intra-particle diffusion path lengths (Chakravorti and Weber, 1975; Weber and Wang, 1987; Guibal et al., 2003). Reducing the particle size makes the inner pores more accessible, but it would not change the internal structure of carbon particles and the cumulative adsorbent capacity. Hence, the stratified F400 carbon bed with mean d_p of 575 μm is expected to possess a higher extent of saturation when compared to the Type 1 and 2 columns which are packed with a uniform mean d_p of 605 μm in the same timeframe. With both effects of increased k_f values and fast adsorption rate exhibited by the smaller carbon particles in stratified columns, there is a huge improvement in service time and bed utilisation compared to non-stratified columns.

Fig. 7 shows the breakthrough curves at the last sampling point for these four types of columns removing para-chlorophenol under same operating conditions. The order of the sharpness of the breakthrough curves (or the incipient breakthrough time) is Type 3 > Type 4 >> Type 2 ~Type 1. As a result, the Type 3 column is the best choice when considering the service time and the extent of bed utilisation to be as large as possible.

4.4. *Comparison of surface diffusivity (D_s)*

Table 4 is a summary of D_s values for phenolics adsorption onto F400 carbon in column operation. The data show D_s values (Crittenden and Weber, 1978; Thacker et al., 1984; Weber and Wang, 1987) for phenolics. Fettig and Sontheimer (1987) reported that there is a systematic decrease in surface diffusivity with increasing molecular weight of organic adsorbates. This is consistent with the surface diffusivities obtained from this research and other surface diffusing systems consulted, in which the D_s value of phenol is higher than those mono-substituted and di-substituted phenols.

5. Conclusions

Several conclusions of this research projects are listed below:

- A cylindrical column with activated carbon stratification packing (Type 3) is proven as an effective engineering process for fixed-bed adsorption operation.
- The extent of column service time and adsorbent bed saturation of Type 3 column are the largest amongst 4 types of column investigated in this study.
- Type 3 column decreases the frequency of adsorbent replacement/regeneration and reduces the operating cost of fixed-bed adsorption process.
- The Homogeneous Surface Diffusion Model (HSDM) successfully described the dynamic adsorption of para-chlorophenol onto Filtrasorb 400 (F400) activated carbon in all types of columns investigated.
- A new correlation of the external mass transfer correlation is derived and given as $Sh = 0.683/\varepsilon\, Re^{0.314} Sc^{1/3}$.
- The optimised surface diffusivity of para-chlorophenol is found to be 1.20E-8 cm^2/s.

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