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## PSEUDO KINETIC MODEL FOR SORPTION PROCESSES

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### ABSTRACT

A pseudo second order kinetic model has been applied to the adsorption of a number of components from aqueous solution. The model is based on solid phase adsorbent loadings which have been used to estimate a pseudo second order rate constant to describe the adsorption process.

The experimental systems studied in the paper are copper ions on peat, *o*-cresol on fly ash and Astrazone Blue on bagasse pith, a by-product from the sugar cane industry. The system variables include initial solute concentration, adsorbent mass and type, and temperature. Correlation coefficients have been determined for the rate constant fits with experimentally obtained data points using the pseudo second order model and the values compared with the correlation coefficients for a first order model and an intraparticle diffusion based rate parameter.

### INTRODUCTION

During the past twenty years there are references to well over five hundred different experimental sorption systems in the literature. In cases where a kinetic/mass transport study has been carried out, approximately 60% of the studies, then 80% report first order systems, 10% first order systems and 10% an intraparticle diffusion based mechanism. In most cases no correlation coefficients are reported and no comparison between different mechanisms is given.

The present work compares three sorption systems: - copper ions onto peat, Basic Blue dye onto pith (waste by product) and *o*-cresol onto fly ash using three sorption models: - pseudo first order, pseudo second order and intraparticle diffusion.

### THEORY

Several models can be used to express the mechanism of solute sorption onto a sorbent. In order to investigate the mechanism of sorption, characteristic constants of sorption were determined using a pseudo-first-order equation of Lagergren (1898), a pseudo-second-order mechanism and an intraparticle diffusion rate parameter of Weber and Morris (1963) respectively which are as follows:

For the first-order sorption rate constant:

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303} t, \quad (1)$$

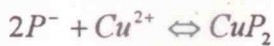
where  $q_1$  is the amount of dye sorbed at equilibrium, (mg/g);  $q_t$  is amount of dye sorbed at time  $t$ , (mg/g);  $k_1$  is the first-order sorption rate constant (1/min).

For the rate constant of intraparticle diffusion,  $k_i$ , (mg/gmin<sup>0.5</sup>):

$$q_t = k_i t^{0.5} \quad (2)$$

For rate constant for the pseudo-second-order sorption mechanism:

The peat-copper reaction may be represented in two ways (Coleman *et al.*, 1956):



and



where  $P^-$  and  $HP$  are polar sites on the peat surface.

The rate of the pseudo-second-order reaction may be dependent on the amount of divalent metal ion on the sorbent surface and the amount sorbed at equilibrium the rate expression for the second order sorption mechanism is:

$$\frac{-d[(P)_0 - (P)_t]}{dt} = k_2 [(P)_0 - (P)_t]^2 \quad (3)$$

or

$$\frac{-d[(HP)_0 - (HP)_t]}{dt} = k_2 [(HP)_0 - (HP)_t]^2 \quad (4)$$

where  $(P)_t$  and  $(HP)_t$  are the number of active sites occupied on the peat at time  $t$ ,  $(P)_0$  and  $(HP)_0$  are the number of equilibrium sites available on the peat.

The kinetic rate equation is shown, where  $k_2$  (g/mgmin) is the rate constant:

$$\frac{-d(q_e - q_t)}{dt} = k_2 (q_e - q_t)^2, \quad (5)$$

where  $q_e$  is the amount of divalent metal ion sorbed at equilibrium, (mg/g),  $q_t$  is amount of divalent metal ion on the surface of the sorbent at any time,  $t$ , (mg/g).

Separating the variables in equation (5) and integrating gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t. \quad (6)$$

The boundary conditions are  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ .

Equation (6) can be rearranged to obtain equation (7) or linearised to give equation (8)

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \quad (7)$$

and

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

If the initial sorption rate,  $h$ , is given as  $h = k_2 q_e^2$ .

The constants can be determined experimentally by plotting  $t/q_t$  against  $t$ .

## MATERIALS AND METHODS

The experimental methods and results have been reported previously by Ho *et al.* (1994) for copper on peat, by Singh and Rawent (1994) for *o*-cresol on fly ash and by McKay *et al.* (1988) for Astrazone Blue (Basic Blue 69) on bagasse pith.

## RESULTS AND DISCUSSION

### Effect of Initial Concentration

Figure 1 shows a plot of the linearised form of the pseudo-second-order model in equation (8) for the sorption of copper ions onto peat at various initial copper ion concentrations. The results in Table 1 show the correlation coefficients for the linear plots from the pseudo-second-order equation are greater than 0.995 for all systems for contact times of 120 minutes. Figure 2 shows the best fit straight line first order plots of  $\log(q_e - q_t)$  against time for the sorption of *o*-cresol/fly ash for the initial 60 minutes. The best fit first order straight lines for the sorption of copper/peat system occur in the initial 15 minutes and for BB69/pith in the initial 20 minutes as shown in the data in Table 1. However, the experimental data deviate considerably after these short periods. Figure 3 shows the amount BB69 sorbed per unit weight of pith against square root of time for the initial 20 minutes. The best fit straight lines for the intraparticle based sorption of copper/peat is the initial 15 minutes and for the sorption of OCL/fly ash is the initial 60 minutes as shown in Table 1. In the initial period of the reaction time, all the  $r_1^2$  and  $r_2^2$  are greater than 0.958. The  $q_1$  values obtained from the first-order equation are lower than experimental data and the  $q_e$  equilibrium sorption capacity calculated from pseudo-second-order model. It suggests that this sorption system is not first-order reaction. The pseudo-second-order model provides the best correlation of the data for Cu/peat and OCL/fly ash. For the BB69/pith system intraparticle diffusion and the second order model correlate the data well.

### Effect of Temperature

A series of contact time experiments has been carried out for BB69 dye/pith and OCL/fly ash with a constant initial concentration at various temperatures. Table 2 shows that the increase in

the equilibrium sorption of dye and OCL with temperature indicates that a high temperature favors dye and OCL removal by adsorption on pith and fly ash respectively. It is clear that adsorption equilibrium is temperature dependent. Again the first-order model and the intraparticle diffusion model only apply to a short initial period of reaction time.

Table 1: Comparison of Rate Parameters of Initial Solute Concentration

	$C_0$	$r_2^2$	$q_e$	$k_2$	$h$	$r_1^2$	$q_1$	$k_1$	$r_i^2$	$k_i$
Cu/Peat	25	1.000	5.75	$9.64 \times 10^{-2}$	3.19	0.973	2.80	0.102	0.958	0.702
	50	0.999	8.87	$1.68 \times 10^{-2}$	1.32	1.000	10.1	$7.05 \times 10^{-2}$	0.999	2.20
	100	0.998	12.4	$1.13 \times 10^{-2}$	1.73	0.999	6.14	$5.82 \times 10^{-2}$	0.999	1.23
	200	0.996	14.3	$8.91 \times 10^{-3}$	1.81	0.999	10.4	$5.72 \times 10^{-2}$	0.999	2.07
OCL/Fly ash	250	1.000	2.12	$7.03 \times 10^{-2}$	0.317	0.977	0.749	$2.09 \times 10^{-2}$	0.969	0.0898
	350	1.000	2.89	$3.95 \times 10^{-2}$	0.329	0.999	1.34	$2.21 \times 10^{-2}$	0.995	0.157
	500	1.000	3.55	$2.65 \times 10^{-2}$	0.333	0.992	1.78	$2.00 \times 10^{-2}$	0.986	0.207
BB69/Pith	50	0.999	44.4	$1.49 \times 10^{-3}$	2.94	1.000	40.2	$4.01 \times 10^{-2}$	1.000	6.80
	100	0.998	80.3	$4.92 \times 10^{-4}$	3.18	0.988	74.3	$2.63 \times 10^{-2}$	0.985	9.94
	150	0.998	108	$3.02 \times 10^{-4}$	3.50	0.992	98.0	$2.05 \times 10^{-2}$	0.988	11.2
	200	0.995	126	$2.44 \times 10^{-4}$	3.86	0.998	117	$2.11 \times 10^{-2}$	0.999	13.8
	300	0.998	156	$1.87 \times 10^{-4}$	4.57	1.000	147	$2.05 \times 10^{-2}$	1.000	16.9

$C_0$ : mg/dm<sup>3</sup>,  $q_e$ ,  $q_1$ : mg/g,  $k_2$ : g/mgmin,  $h$ : mg/gmin,  $k_1$ : 1/min,  $k_i$ : mg/gmin<sup>0.5</sup>

Table 2: Comparison of Rate Parameters of Temperature

	T	$r_2^2$	$q_e$	$k_2$	$h$	$r_1^2$	$q_1$	$k_1$	$r_i^2$	$k_i$
OCL/Fly ash	303	1.000	3.49	$3.10 \times 10^{-2}$	0.377	0.996	1.62	$2.06 \times 10^{-2}$	0.990	0.188
	313	1.000	3.77	$3.60 \times 10^{-2}$	0.510	0.994	1.60	$2.32 \times 10^{-2}$	0.984	0.191
	323	1.000	3.92	$4.33 \times 10^{-2}$	0.666	0.998	1.54	$2.62 \times 10^{-2}$	0.987	0.185
BB69/Pith	293	0.985	130	$1.68 \times 10^{-4}$	2.83	0.995	123	$1.68 \times 10^{-2}$	1.000	11.4
	313	0.995	141	$1.97 \times 10^{-4}$	3.93	0.999	133	$1.98 \times 10^{-2}$	0.999	13.9
	333	0.998	157	$2.17 \times 10^{-4}$	5.37	0.998	152	$2.52 \times 10^{-2}$	0.991	18.6
	353	0.999	164	$2.94 \times 10^{-4}$	7.96	0.999	159	$3.49 \times 10^{-2}$	0.999	24.5

T: °K,  $q_e$ ,  $q_1$ : mg/g,  $k_2$ : g/mgmin,  $h$ : mg/gmin,  $k_1$ : 1/min,  $k_i$ : mg/gmin<sup>0.5</sup>

The results in Table 2 also show the intraparticle coefficients,  $r_i^2$ , are high, being greater than 0.984 for the initial 60 minutes for the sorption system of OCL/fly ash and for the initial 20 minutes for the sorption system of BB69/pith. The values of the rate constants,  $k_2$ , were found to increase from  $3.10 \times 10^{-2}$  to  $4.33 \times 10^{-2}$  g/mgmin and from  $1.68 \times 10^{-4}$  to  $2.94 \times 10^{-4}$  g/mgmin, for an increase in the solution temperature from 303 to 323°K and from 293 to 353°K for the sorption of OCL and BB69 respectively. Linear plots of the pseudo rate constant  $\ln(k_2)$  against  $10^3/T$  were regressed to obtain expressions for the following relationship:

$$k_2 = k_0 \exp\left(\frac{-E}{RT}\right),$$

where  $k_2$  is the rate constant of sorption, (g/mgmin),  $k_0$  is a constant, independent factor, (g/mgmin),  $E$  is activation energy of sorption, (kJ/mol),  $R$  is the gas constant and  $T$  the solution temperature, ( $^{\circ}$ K). From this equation the activation energy of sorption,  $E$ , is 13.6 kJ/mole for the OCL /fly ash system and 7.55 kJ/mole for the BB69/pith system.

### Effect of Pith Dose

The correlation coefficients for the three models are compared for the effect of pith mass in Table 3. Overall, the data show the highest compliance for the intraparticle diffusion model.

Table 3: Comparison of Rate Parameters of Pith Dose

$m_s$	$r_2^2$	$q_e$	$k_2$	$h$	$r_1^2$	$q_1$	$k_1$	$r_i^2$	$k_i$
0.25	0.993	$1.54 \times 10^2$	$2.33 \times 10^{-4}$	5.53	0.943	$1.35 \times 10^2$	$2.11 \times 10^{-2}$	0.963	15.5
0.50	0.993	$1.48 \times 10^2$	$2.13 \times 10^{-4}$	4.67	0.989	$1.35 \times 10^2$	$2.03 \times 10^{-2}$	0.997	14.6
0.75	0.992	$1.40 \times 10^2$	$2.11 \times 10^{-4}$	4.16	0.992	$1.31 \times 10^2$	$2.08 \times 10^{-2}$	0.999	14.4
1.00	0.993	$1.40 \times 10^2$	$1.94 \times 10^{-4}$	3.80	0.998	$1.31 \times 10^2$	$1.86 \times 10^{-2}$	0.998	13.1
1.25	0.994	$1.32 \times 10^2$	$2.07 \times 10^{-4}$	3.62	0.999	$1.22 \times 10^2$	$1.75 \times 10^{-2}$	0.998	11.6
1.50	0.992	$1.27 \times 10^2$	$2.04 \times 10^{-4}$	3.28	0.993	$1.17 \times 10^2$	$1.70 \times 10^{-2}$	0.998	11.0

$m_s$ : mg/dm<sup>3</sup>,  $q_e$ ,  $q_1$ : mg/g,  $k_2$ : g/mgmin,  $h$ : mg/gmin,  $k_1$ : 1/min,  $k_i$ : mg/gmin<sup>0.5</sup>

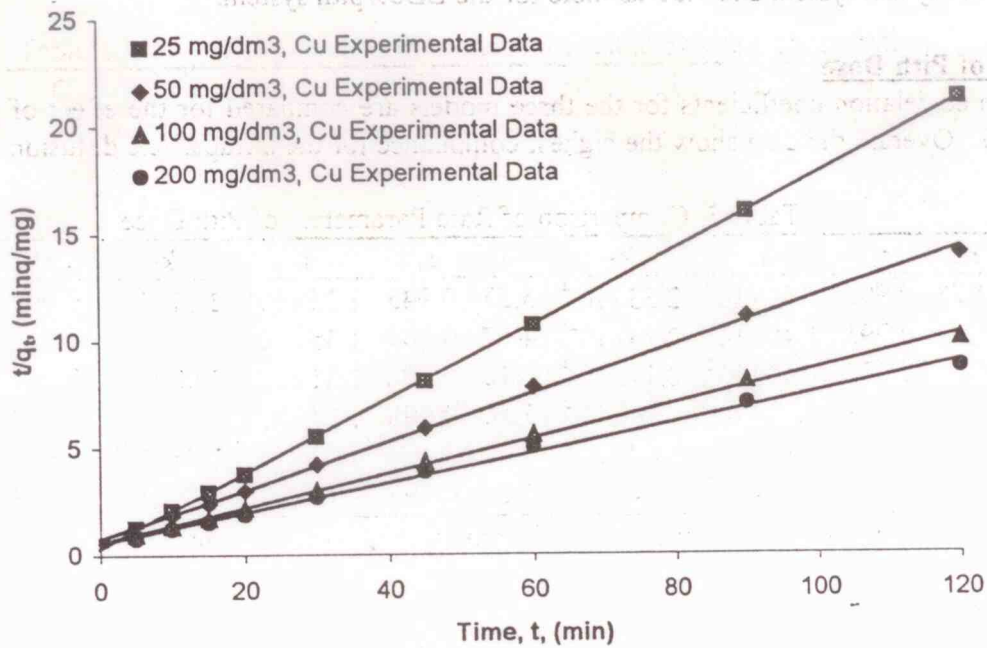
### CONCLUSION

The kinetics of sorption of copper, *o*-cresol and Basic Blue 69 on peat, fly ash and pith respectively were studied on the basis of the pseudo-second-order rate mechanism. For all of the systems studied the three models proposed fit the experimental data well for a short (30 minutes) initial period. However, over a two hour period the pseudo-second-order model provides the best correlation for Cu/peat and OCL/fly ash; whereas for the BB69 dye/pith system the second order model and the intraparticle diffusion model both correlate the data well with the diffusion model having slightly higher coefficients.

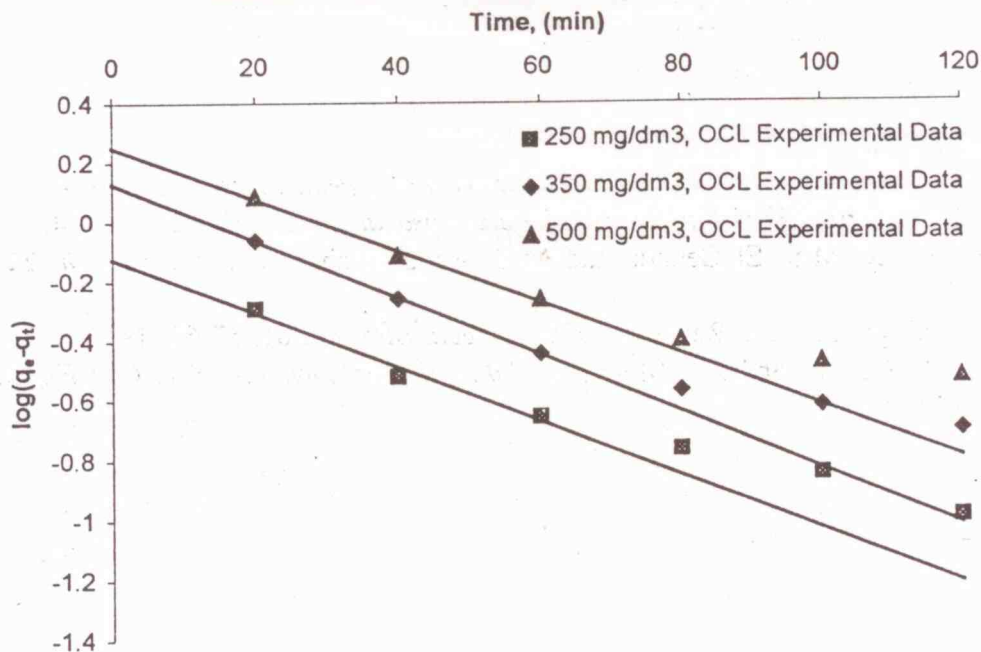
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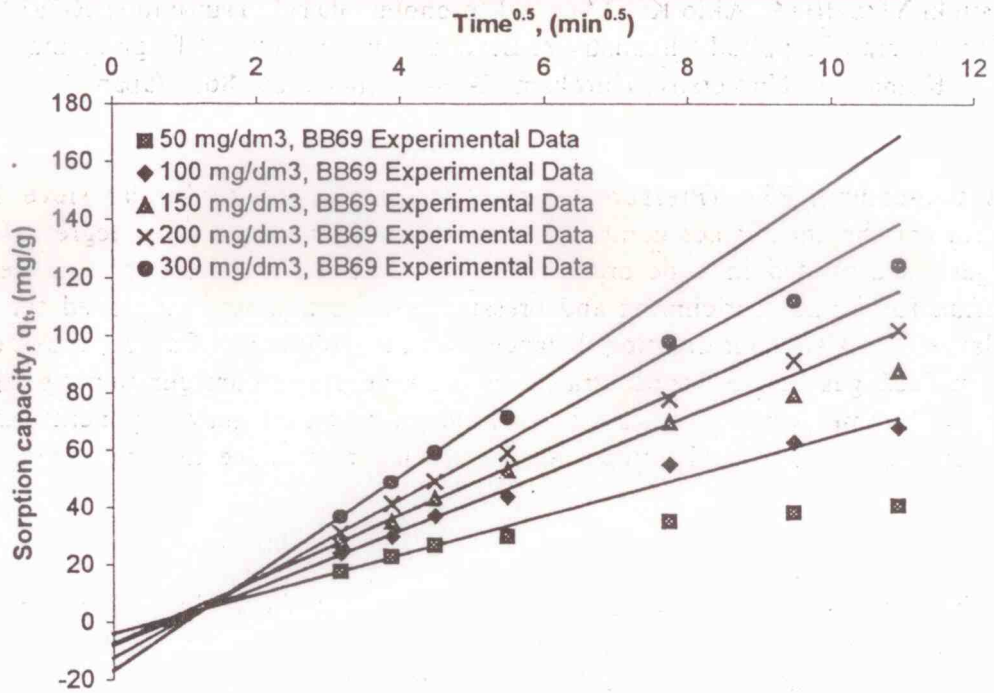
**Figure 1: Pseudo-second-order sorption kinetics of copper ions onto peat at various initial concentrations**



**Figure 2: First-order sorption kinetics of o-cresol onto fly ash at various initial concentrations**



**Figure 3: Intraparticle diffusion kinetics of BB69 on pith**



**Figure 4: Pseudo-second-order sorption kinetics of BB69 onto peat at various pith doses**

