Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Dutta, Bhaskar , Basu, Jayanta Kumar and DasGupta, Sunando(2003) 'Removal of Cresol from Aqueous Solution Using Fly Ash as Adsorbent: Experiments and Modeling', Separation Science and Technology, 38: 6, 1345 — 1360

To link to this Article: DOI: 10.1081/SS-120018813
URL: http://dx.doi.org/10.1081/SS-120018813

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 6, pp. 1345–1360, 2003

Removal of Cresol from Aqueous Solution Using Fly Ash as Adsorbent: Experiments and Modeling

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ABSTRACT

Adsorbent prepared from fly ash obtained from a thermal power plant was successfully used to remove cresol from an aqueous solution in a batch reactor. The adsorbent was characterized, and significant removal of cresol was achieved. The adsorption isotherms were evaluated and the effects of system parameters, e.g., stirrer speed and temperature on the adsorption, were studied. A theoretical model was proposed, and it was solved by using a quasi-steady-state approach. The intraparticle diffusivity was evaluated from one set of experimental data and was subsequently used to predict the change in bulk concentration with time for other experimental conditions. The predicted and the experimental results are in close agreement. The performance of the adsorbent prepared was favorably compared with that of commercially available activated carbon.

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DOI: 10.1081/SS-120018813 0149-6395 (Print); 1520-5754 (Online)

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INTRODUCTION

Phenolic compounds are common pollutants found particularly in effluents from coke ovens, pharmaceuticals, petroleum, and petrochemical plants. These compounds are toxic and corrosive and can be adsorbed through intact or abraded skin. Adsorption through skin may be very rapid, and death may result in less than an hour. One such phenolic compound is cresol, which is present in many industrial effluents. The use of activated carbon as adsorbent for removal of phenolic compounds is a common practice. Furuya et al.[1] used activated carbon for removal of phenolic compounds and developed a procedure to correlate the Freundlich coefficients with the basic properties of three components involved in adsorption (adsorbate, adsorbent, and solvent). Costa et al.[2] determined effective diffusion coefficient for adsorption of phenolic compounds on activated carbon. Abdo et al.[3] used mixed adsorbent in place of only activated carbon. But high capital and regeneration cost of activated carbon limits its use for industrial purpose. This explains the need and the current level of research activities for developing alternative, inexpensive adsorbents. People have tried to prepare low-cost adsorbent from cheap and widely available materials. Srivastava et al.[4] prepared carbonaceous adsorbent from fertilizer wastes and used it for removal of substituted phenol. Asfour et al.[5] used hardwood for adsorption of basic dyes. Srivastava et al.[6] used rice husk carbon for removal of chromium from aqueous phase. Mckay et al.[7] studied equilibrium isotherms for the adsorption of four dyestuffs onto chitin and determined the Langmuir and Freundlich constants. Effects of temperature and particle size were studied, and a composite isotherm model was used for fitting the data. Dutta et al.[8] developed adsorbent from common sawdust and used it for removal of p-nitrophenol from aqueous phase. They also studied the effect of different process parameters on the rate of adsorption and found that higher initial concentration and lower temperature are more favorable. A similar study[9] focused on the use of fly ash for the removal of copper from aqueous solution. Chatzopoulos et al.[10] studied the equilibrium dynamics of toluene adsorption and desorption in single-component aqueous solution. Adsorption rates in a batch reactor under a variety of operating conditions were also successfully fitted with the homogeneous surface diffusion model and a surface diffusion coefficient that increases exponentially with surface condition. Removal of phenols, substituted phenols, and chlorophenols by fly ash were also studied in 1987,[11] 1998,[12] 1998.[13] T. Viraraghavan and K.R. Ramakrishna[14] investigated the use of fly ash for its ability to adsorb dyes from aqueous solutions made up of four different commercial grade dyes. Their results showed that fly ash exhibited reasonably good dye removals for Basic Blue 9, Acid Blue 29, and Acid Red 91, whereas the removals by fly ash exceeded that of granular activated carbon for Disperse Red 1.

In the present work, low-cost adsorbent obtained from fly ash was used for the removal of cresol from aqueous phase. The effect of different process parameters on the kinetics of adsorption and adsorption isotherms were studied. From the experimental data, adsorption isotherms were characterized, and a kinetic model was developed. Intraparticle diffusion inside the adsorbent was studied at a very high agitation to ensure negligible mass transfer resistance in the bulk of the liquid. The kinetic data and the model were used to calculate the intraparticle diffusivity of solute inside the adsorbent. This was used for the prediction of process variables, i.e., bulk concentration for another set of experimental conditions. The model was developed by using quasi-steady-state approach for the diffusion of solute inside the adsorbent and can be used for the prediction purpose because the predicted points meet the experimental points with a very low margin of error.

EXPERIMENTAL

Fly ash obtained from a thermal power plant was washed thoroughly with water to remove all soluble parts. The adsorbent was dried at 110°C for 1 hr, and then it was calcined at 650°C for 1 hr. The physical properties of the adsorbent are tabulated in Table 1a, and the composition of the adsorbent prepared was analyzed by electron-scanning microscope and is given in Table 1b. A photograph was taken with a magnification of 1600 as shown in Fig. 1. Cresol solution was prepared by dissolving A.R. grade ortho-cresol in distilled water. The concentration of cresol in aqueous solution was measured spectrophotometrically[15,16] with 4-amino-antipyrene dye.

Table 1a. Physical properties of the adsorbent.

Bulk density:	0.774 g/cc
Solid density:	1.877 g/cc
Average total pore volume:	0.1896 cc/g of adsorbent
Surface area (BET):	7.5 m^2/g by nitrogen adsorption method

Table 1b. Characterization of adsorbents using SEM.

Element	Element (%)	Atomic	Compound	Compound (%)	No. of ions
Al	16.41	12.79	Al_2O_3	31.00	6.44
Si	26.57	19.91	SiO_2	56.85	10.02
K	0.96	0.52	K_2O	1.15	0.26
Ca	2.06	1.08	CaO	2.88	0.54
Ti	1.15	0.50	TiO_2	1.91	0.25
Fe	3.39	1.28	Fe_2O_3	4.84	0.64
Zn	0.88	0.28	ZnO	1.10	0.14
In	0.22	0.04	In_2O_3	0.27	0.02
O	48.37	63.60			32.0
Total	100.00	100.00			100.00
				Cation sum	18.31

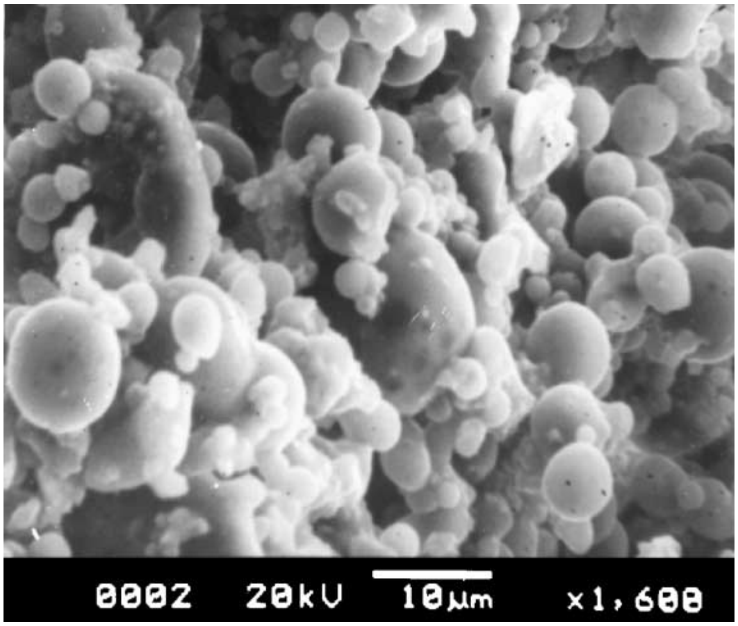

Figure 1. Electron scanning photograph of adsorbent (resolution of 1600×).

The detection limit by 4-AAP method is 0.1 mg/L. The solution is diluted for measurement to 10 mg/L so that the concentration–absorbance relation is linear.

Cresol solutions of different concentration were taken in stoppered conical flask with adsorbents in desired proportions. They were kept in an auto temperature-controlled shaker for 12 hr to attain the equilibrium. Equilibrium studies were carried out at three different temperatures of 293, 299, and 305K.

A perspex vessel (i.d., 9.9 cm; height, 25 cm; no. of baffles, 4; baffle clearance, 0.3 cm) was used for the adsorption rate studies. It was equipped with an impeller (impeller diameter, 3.0 cm). The effect of different process parameters on the rate of adsorption like stirrer speed (0, 1025, 1750, and 2500 rpm), initial concentration (50, 75,100, and 150 ppm), temperature (283, 303, and 325K) particle size (40, 56.5, and 71.5 μm) were studied.

THEORETICAL MODELING

The model was developed by assuming a low mass transfer resistance in the bulk of the liquid compared to the mass transfer resistance inside the adsorbent particle. Solid diffuses through the bulk of the liquid with experiencing practically no mass transfer resistance, and the adsorbent surface in contact with the liquid is assumed to be always at equilibrium with it. The solute diffuses from the surface of the adsorbent to the inner pores. For the diffusion inside the particles, diffusivity was assumed to be independent of adsorbent loading. Particles were assumed to be spherical and isothermal condition was maintained throughout each experiment. The diffusion of solute inside the spherical particle can be well described by the following equation:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 D_\mathrm{s}\frac{\partial q}{\partial r}\right] \tag{1}$$

Because the liquid is assumed to be perfectly homogeneous, the surface loading becomes uniform, i.e., all surfaces of same adsorbent loading are concentric spheres. Thus, concentration depends on the coordinates r and t only.

Defining a new variable, u (defined as qr), the equation is modified to

$$\frac{\partial u}{\partial t} = D_s \frac{\partial^2 u}{\partial r^2} \tag{2}$$

with the initial and boundary conditions as

$$u = 0, \quad \text{when } t = 0, \text{ for all } r \text{ between } 0 \text{ and a} \tag{3}$$

$$u = 0, \quad \text{when } r = 0, \text{ for any } t > 0 \tag{4}$$

$$u = \frac{\mathrm{K}_1 C^{\alpha}}{1 + \mathrm{K}_2 C^{\beta}}\mathrm{r} \quad \text{at } r = a, \; a \text{ being the radius of the adsorbent particle} \tag{5}$$

The last condition is essentially the Fritz-Schlünder Isotherm model that is found to be the most appropriate one for this adsorption process as will be explained in the next section.

An equation similar to Eq. (2) has been solved by Carslaw and Jager,[17] for the case of cooling of a sphere with constant surface temperature. The same solution can be used for this case also, provided zero initial loading is assumed, i.e., when fresh adsorbent is used and constant surface loading q_s is assumed. The solution of this is given by

$$q = q_s + \frac{2aq_s}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi r}{a}e^{-D_s n^2 \pi^2 t/a^2} \tag{6}$$

the average concentration of the sphere at any time is

$$q_{av} = q_s - \frac{6q_s}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-D_s n^2 \pi^2 t/a^2} \tag{7}$$

This approach cannot be used directly in the present case because the bulk concentration and hence the concentrations of the adsorbed cresol at the surface of the spherical adsorbent particles are functions of time. However, a quasi-steady-state approach may be used subject to certain conditions. In the quasi-steady-state approach it has been assumed that the surface loading remains constant over a small increment of time, whereas the boundary and initial conditions, as presented earlier, remain unchanged. It has been assumed that at

$t = 0$, the particles are brought into contact with the solution and thus $q = 0$ for all r (between 0 and a). The solution to these equations[12] are consistent provided $q = 0$ at $t = 0$ (i.e., zero initial loading). The time step taken for the quasi-steady-state assumption is large compared to the time required for the attainment of equilibrium at the surface, which is inherently a very fast process. In any time interval, q_s is taken to be the value corresponding to the changed bulk concentration [calculated from Eq. (5)] at the end of the previous time increment. For example, between the interval $t = 0$ to $t = \Delta t$, the value of q_s is obtained by using Eq. (5) taking $r = a$ in the definition of u. This value of q_s is then used to calculate q and q_{av} from Eqs. (6) and (7), respectively. Once q_{av} is obtained, a mass balance will give the new bulk concentration of cresol in liquid. For the next time interval, this changed value of the bulk cresol concentration is used to recalculate q_s by using Eq. (5), and the process is repeated till the end of the experimental time.

The time step chosen for this study was 1 sec, whereas the total operation time for the experiment was 1 hr. It was found that reducing the time step by orders of magnitude does not significantly alter the result (Table 2). This validates the quasi-steady-state approach used herein.

The diffusivity of solute inside the adsorbent was calculated from one set of experimental data for the initial concentration of 50 ppm. The value was found to be 2.3×10^{-11} cm^2/s. This diffusivity was used for the prediction of time variation of bulk concentration with different initial concentrations, i.e., initial concentration of 75, 100, and 150 ppm.

Table 2. Variation of predicted bulk concentration with changes in the time interval used in quasi-steady-state assumption.

	Predicted bulk concentration (ppm)					
Time (min)	$\Delta t = 1$ s	$\Delta t = 0.1$ s	$\Delta t = 1$ s	$\Delta t = 0.1$ s	$\Delta t = 1$ s	$\Delta t = 0.1$ s
0	150.000	150.000	100.000	100.00	75.000	75.000
10	87.972	87.976	47.136	47.143	30.164	30.172
20	68.803	68.811	34.541	34.549	21.738	21.749
30	56.945	56.939	27.891	27.897	17.627	17.632
40	48.817	48.821	23.778	23.777	15.151	15.154
50	42.922	42.920	20.971	20.971	13.477	13.481
60	38.475	38.483	18.931	18.937	12.263	12.269

$\Delta t =$ time interval taken for the calculation of adsorbent loading and hence the bulk concentration using quasi-steady-state approach.

RESULTS AND DISCUSSION

Equilibrium Studies

Equilibrium studies of cresol were carried at three different temperatures: 293, 299, and 305K. Equilibrium data were fitted to different adsorption isotherms, and the parameter values were calculated along with the standard errors and correlation coefficients by nonlinear regression analysis and were tabulated in the Table 3. All equilibrium data were fitted to three general adsorption models, and it was found that the Fritz-Schlünder Isotherm model performed the best (with minimum error and higher correlation coefficients). The model equation is as follows,

$$q_e = \frac{K_1 {C_e}^{\alpha}}{1 + K_2 {C_e}^{\beta}} \tag{8}$$

where K_1 and K_2 are constants used in Fritz-Schlünder Isotherm with dimensions $(mg/g)(mg/L)^{-\alpha}$, $(mg/L)^{-\beta}$. α and β are Fritz-Schlünder Isotherm parameters. Equilibrium data are plotted in Fig. 2. From the figure it is evident that adsorption is favorable at a lower temperature, which implies that the adsorption process used here is a physical adsorption.

Table 3. Characterization of isotherms.

		Temperature (K)		
Isotherm		293	299	305
Freundlich $q_e = K_c C_e^n$	K_c	31.05	19.34	8.29
	n	0.282	0.372	0.517
	ϵ	2.052	0.973	3.968
	σ	0.998	0.999	0.971
Langmuir $q_e = \frac{q_{max} K_L C_e}{1+K_L C_e}$	q_{max}	96.37	91.17	85.39
	K_L	0.237	0.106	0.045
	ϵ	3.191	2.681	2.379
	σ	0.996	0.995	0.989
Fritz-Schlünder $q_e = \frac{K_1 C_e^{\alpha}}{1+K_2 C_e^{\beta}}$	K_1	31.59	30.54	2.214
	K_2	0.201	1.498	0.017
	α	0.511	2.100	1.218
	β	0.532	1.743	1.362
	ϵ	1.620	0.904	1.944
	σ	0.999	0.999	0.996

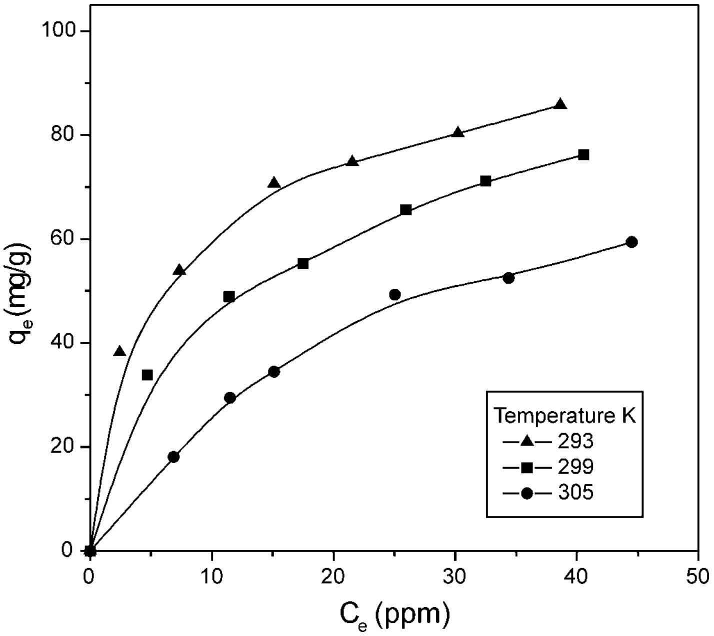

Figure 2. Equilibrium isotherms for cresol adsorption on the adsorbent at three different temperatures of 293, 299, and 305K.

Adsorption Rate Study

Concentration decay curves for the different stirrer speeds are plotted in Fig. 3. From Fig. 3, it can be seen that the reduction in concentration is more for higher speeds, implying a higher value of the mass transfer coefficient. It can also be observed that the relative reduction in concentration between two values of stirrer speed is appreciable at lower ranges of the stirrer speed (between 0 and 1025 rpm of stirrer speed). At higher speed, this reduction in concentration becomes almost independent of stirrer speed (1750 and 2500 rpm). The percentage reductions of cresol concentration after 20 min are 54% for 0 rpm, 70% for 1025 rpm, 76% for 1750 rpm, and 78% for 2500 rpm. Thus, it can be postulated that beyond 2500 rpm, the external mass transfer effect becomes insignificant. This can also be observed from Fig. 4, where average adsorbent loading after 20 min for these three stirrer speeds are plotted. Hence, all experiments were carried out for a stirrer speed of 2500 rpm.

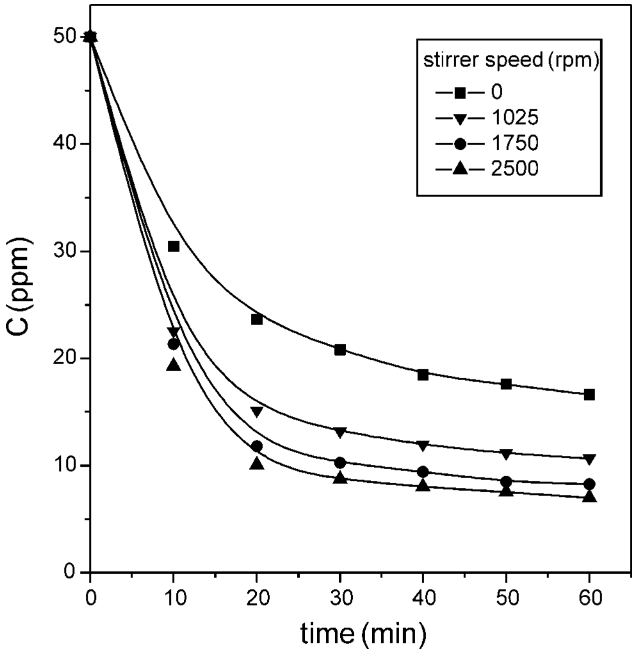

Figure 3. Effect of agitation on rate of adsorption. $C_o = 50\,\text{ppm}$, $T = 303\text{K}$, $d_p = 0.004\,\text{cm}$, $V = 1\,\text{l}$, and $m_a = 5\,\text{g}$.

Figure 5 shows temperature dependence of rate of adsorption. As is evident from the figure, adsorption of cresol is favored at lower temperature. After 20 min of adsorption at the temperatures of 283, 303, and 325K, the bulk concentration becomes 8.11, 10.4, and 12.31 ppm, respectively, signifying less adsorption. Beyond a certain time, the three curves become almost parallel to each other. Because the mass transfer resistance is negligible at a stirrer speed of 2500 rpm, the increase in the D_b with temperature [as predicted by Wilke Chang Eq.[18]] will not augment the removal of cresol from the bulk. The controlling resistance is adsorption at the adsorbent surface. As with increase in temperature, adsorption decreases; this effect more than compensates the increase in D_b. Thus, with increase in temperature, adsorption decreases, resulting in less removal of cresol from the feed.

The adsorption study was also performed with different particle sizes as well, but the particle size was found to have negligible effect on rate of adsorption because all the three curves nearly overlap with one another in

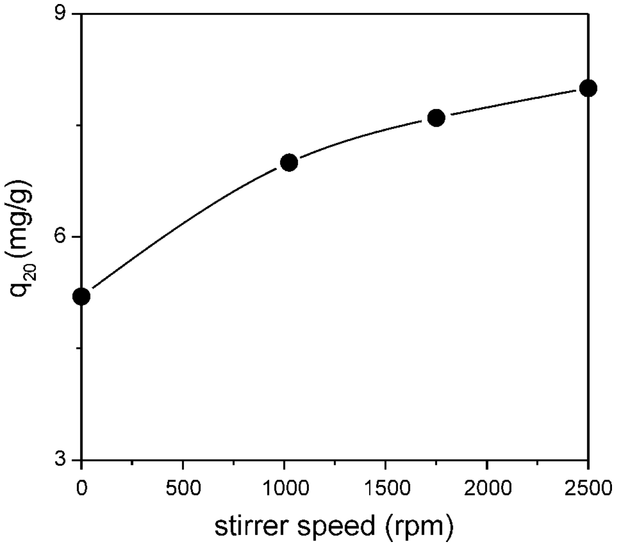

Figure 4. Variation of adsorbent loading with stirrer speed.

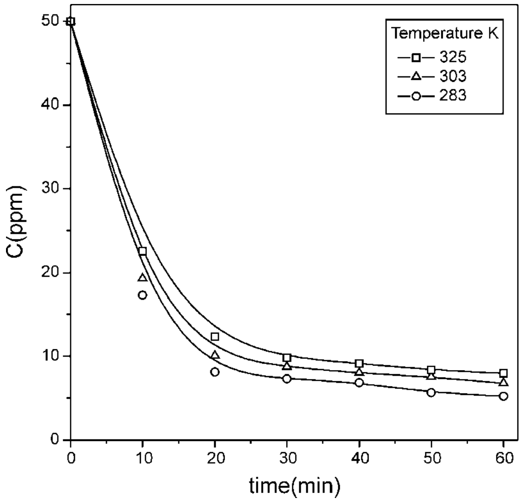

Figure 5. Effect of temperature on rate of adsorption. $C_o = 50$ ppm, rpm = 2500, $d_p = 0.004$ cm, V = 1 l, and $m_a = 5$ g.

Fig. 6. Thus, the particle size (in the range studied herein for the prepared adsorbents) will have marginal effect on adsorption.

The pore diffusivity value is estimated from the experimental results with 50 ppm initial concentration. As the other process parameters, e.g., temperature, rpm remains same; this diffusivity value was used for the prediction of the bulk concentration for the initial concentrations of 75, 100, and 150 ppm. This was done by using a quasi-steady-state approach described under the "theoretical modeling" section. The predicted time variations of the bulk concentrations are presented by the solid lines in Fig. 7. The points are the experimentally obtained values of bulk concentration. As can be seen from the figure, the match between the predictions and the experiments is quite satisfactory.

Adsorbent loading q is plotted against radius r of a spherical adsorbent at different instant of times (1.667, 10, 20, 30, 40, 50, and 60 min) in Fig. 8. Surface loading was found to decrease with time, whereas the average loading increases with time. With increase in time, the curves become less steep, and hence the adsorbent loading becomes more uniform, as can be seen from the figure (area under the curve increases for larger time).

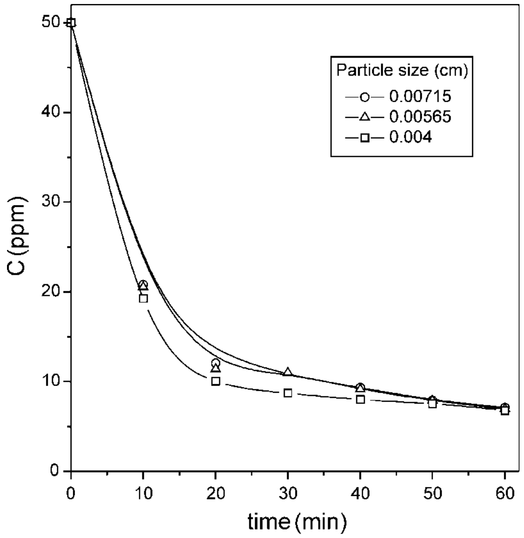

Figure 6. Effect of particle size on rate of adsorption. $C_o = 50$ ppm, rpm = 2500, $T = 303$K, $V = 1$ l, and $m_a = 5$ g.

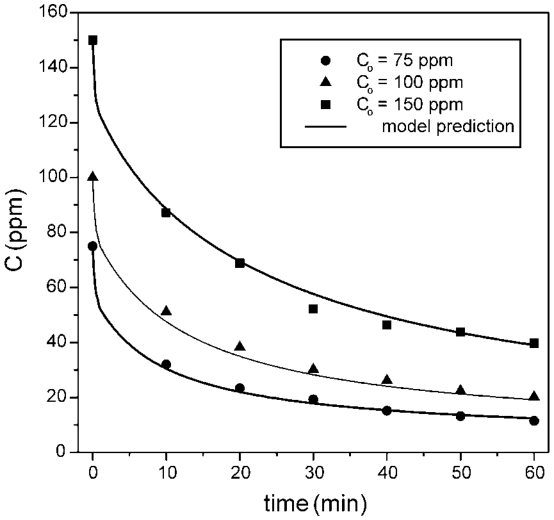

Figure 7. Comparison of predicted and experimental values for different initial concentrations of cresol. rpm = 2500, $T = 303\mathrm{K}$, $V = 1\,\mathrm{l}$, $m_a = 5\,\mathrm{g}$, and $d_p = 0.004\,\mathrm{cm}$.

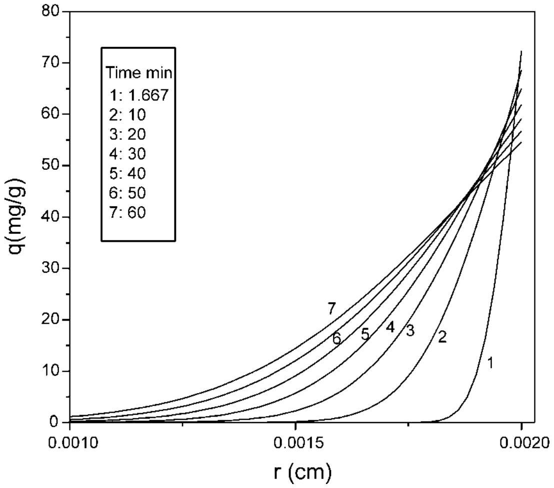

Figure 8. Variation of adsorbent loading with radius for a spherical adsorbent. $C_o = 150\,\mathrm{ppm}$, rpm = 2500, $T = 303\mathrm{K}$, $V = 1\,\mathrm{l}$, $m_a = 5\,\mathrm{g}$, $d_p = 0.004\,\mathrm{cm}$.

CONCLUSIONS

Treated fly ash from a thermal power plant was successfully used as an adsorbent for the removal of cresol from aqueous solutions in a batch reactor. The effects of stirrer speed on the external mass transfer resistance were studied. A theoretical model was proposed, and it was solved by using a quasi-steady-state approach. The intraparticle diffusivity was evaluated from one set of experimental data and was subsequently used to predict the change in bulk concentration with time for other experimental conditions. The predicted and the experimental results are in close agreement.

NOMENCLATURE

a	Radius of the particle (m)
C	Concentration in the bulk phase (mg/L or ppm)
C_e	Concentration of the adsorbate in liquid at the liquid solid interface (mg/L or ppm)
d_p	Diameter of the particle (m)
D_b	Bulk diffusivity of solute in liquid (m^2/s)
D_s	Solid diffusivity of solute in adsorbent (m^2/s)
K_c	Adsorption equilibrium constant used in Freundlich Isotherm $(mg/g)(mg/L)^{-n}$
K_L	Adsorption equilibrium constant used in Langmuir isotherm (L/mg)
K_1, K_2	Constant used in Fritz-Schlünder Isotherm with dimensions $(mg/g)(mg/L)^{-\alpha}$, $(mg/l)^{-\beta}$
n	Constant used for Freundlich Isotherm (dimensionless)
q	Solute concentration in adsorbent
q_s	Solute surface concentration at equilibrium
q_{20}	Adsorbent loading at $t = 20$ min (mg/g)
r	Radial distance (m)
t	Time (sec)
α, β	Fritz-Schlünder Isotherm parameters (dimensionless)
ϵ	Standard error
ρ	Density of the liquid phase
σ	Correlation coefficient
ν	Kinematic viscosity

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Received February 2002
Revised September 2002