Chemical Engineering Journal 129 (2007) 133–142

Chemical Engineering Journal

www.elsevier.com/locate/cej

Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal

Somnath Mukherjee [a], Sunil Kumar [b], Amal K. Misra [a], Maohong Fan [c,*]

[a] Civil Engineering Department, Jadavpur University, Kolkata 700032, India
[b] National Environmental Engineering Research Institute (NEERI), Nehru Marg, Nagpur 440020, India
[c] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

Received 26 October 2005; received in revised form 13 October 2006; accepted 23 October 2006

Abstract

Adsorption process is gaining interest as one of the effective processes of advanced wastewater treatment for treatment of industrial effluent containing toxic materials. The present work involves an investigation of the use of three carbonaceous materials, activated carbon (AC), bagasse ash (BA) and wood charcoal (WC), as adsorbents for removal of phenol from water. Batch experiments were carried out to obtain adsorption equilibrium isotherms and kinetics with phenol spiked synthetic solutions. The study was performed with two initial phenol concentrations, viz. 30 and 50 mg/L, with an equal amount of adsorbent dose (50 g/L). The effects of solution pH, concentrations of EDTA, anions, and dosages of adsorbent on removal of phenol were examined. Desorption tests were also conducted in the present study. The suitability of the different isotherm models to the equilibrium data was studied for each phenol–adsorbent system. Experimental results showed that for phenol–AC, phenol–WC and phenol–BA adsorption systems, approximately 98%, 90% and 90% removal efficiencies were achieved at given adsorption conditions. The kinetic study indicates that the phenol removal with the selected adsorbents is a first order adsorption. Freundlich isotherm model was found to fit the data for adsorption of phenol with the adsorbents. Removal efficiency of phenol slightly increased when the pH of adsorption system decreased. The effect of nitrate ion and EDTA in the solution on the adsorption of phenol was found to be insignificant; however, the chloride ion has considerable negative effects on the removal by BA. The estimation of diffusion coefficients indicated that film diffusion may control the adsorption of phenol with the studied adsorbent materials.

Keywords: Phenol; Adsorption; Batch study; Desorption; Activated carbon; Wood charcoal; Bagasse ash; Kinetics

1. Introduction

The occurrence of non-biodegradable and volatile organic compounds in streams and lakes threatens the use and reuse of our national water resources. Various treatment methods are available for removal of these materials, including adsorption, ion exchange, reverse osmosis, chemical oxidation, precipitation, distillation, gas-stripping, solvent extraction, complexation, and bio-remediation. Among these methods, adsorption has proven to be an efficient technology for separating toxic pollutant from water environment. Extensive studies have shown that activated carbon (AC) is efficient in adsorption of numerous bio-resistant organic pollutants from aqueous system [1,2]. Activated carbon adsorption has been recommended by the USEPA as one of the best available technologies (BAT) [3] in removal of organic compounds, but it is highly expensive especially for developing countries like India. In recent years, there has been a continuous search for locally available and cheaper adsorbents for the replacement of activated carbon [4–10] for removal of a variety of organic compounds such as phenol.

Phenol pollution is a serious problem in many countries. The major sources of phenolic waste are petroleum refineries, petrochemical, steel mills, coke oven plants, coal gas, synthetic resins, pharmaceuticals, paints, plywood industries and mine discharge [11]. Phenolic waste imparts a carbolic odour to river water and is also toxic to fish and human beings. Total phenol concentration in the wastewater of a typical Indian refinery processing 5.0 million tons of crude per year is around 135 mg/L and the discharge rate of wastewaters varies from 125 to 250 m^3/h with pHs being in the range of 8.8–9.4. The concentration of phonolic compounds in the wastewater from resin

---

* Corresponding author. Tel.: +1 404 385 6725; fax: +1 404 385 6725.
E-mail address: mfan3@mail.gatech.edu (M. Fan).

1385-8947/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2006.10.030

plants is typically in the range of 12–300 mg/L. The wastewater with the highest concentration of phenol (>1000 mg/L) is typically generated from coke processing. Phonolic compounds are also emanated from resin plants with a concentration range of 12–300 mg/L [11]. Environmental Protection Agency (EPA) has set a limit of 0.1 mg/L of phenol in wastewater. The World Health Organisation (WHO) is stricter on phenol regulation. It sets a 0.001 mg/L as the limit of phenol concentration in potable water [12].

People are increasingly interested in studying different approaches to removal of phenol from wastewater. Viraraghavan and Alfaro [13] investigated the adsorptive capacity of phenol by peat, flyash and bentonite with an initial phenol concentration of 1000 mg/L. They found that in comparison to AC, the adsorption capacity of these adsorbents was much lower. Kinetic study results revealed that a long equilibrium time (15 h) was needed for the adsorption of phenol by the materials. Garcia et al. [14] carried out an investigation on binary adsorption of phenol and *m*-cresol mixtures on to a polymeric adsorbent, Duolike ES 861, in a fixed bed reactor with various flow rates and feeding concentration. They developed a mathematical model considering disposed plug flow for the bulk liquid, external mass transfer resistance, and intra-particle mass transfer by pore diffusion and instantaneous equilibrium of adsorption at the pore/wall interface. Yapar and Yilmar [15] explored the adsorptive capacity of some clays and natural zeolite materials found in Turkey for removal of phenol. They found calcined hydrotalcite was the best among the studied adsorbents. It can adsorb 52% of phenol from a solution with an initial phenol concentration of 1000 mg/L at the adsorbent/phenol ratio of 1:100 while the others could adsorb only 8% of phenol for the same operation conditions. Roostari and Tezel [16] examined the adsorption of phenol from aqueous solution by silica gel, activated alumina, AC, fitrasorb 400, Hisir 1000. They found Hisir 1000 was the best among the tested materials in light of adsorption kinetics though the AC had the highest affinity and adsorption capacity of phenol. They found that both Langmuir and Freundlich isotherm equations worked for their isotherm data. Recently, Ahmaruzzaman and Sharma [17] found that pH significantly affect the adsorption capacity of coal, treated coal with phosphoric acid, coke breeze, nice husk and rice husk char. They also showed that the phenol adsorption processes with these materials are controlled by external mass transfer followed by intraparticle diffusion mass transfer. Their experimental data indicated that Langmuir isotherm fitted the phenol adsorption data better than all other models for their phenol adsorbent systems. Das and Patnaik [18] utilized blast furnace flue dust (BFD) and slag to investigate phenol adsorption through batch experiment. They observed that after 8 h of contact time, the equilibriums of phenol adsorption with BFD and slag were attained. They achieved 75% and 90% removal efficiencies for slag and BFD respectively. Both Freundlich and Langmuir isotherm models well fitted to their adsorption data.

Based on the availability of adsorbents in different places, it is obvious that more inexpensive and effective approaches need to be found for removal of phenol in water so that the strict regulation on the concentration of phenol in wastewater can be widely implemented. This research has compared carbonaceous materials, bagasse ash (BA) and wood charcoal (WC) easily available in India for their abilities in removal of phenol while AC was used as the reference material.

2. Materials and method

All chemicals and reagents used were of analytical grade. All experiments were conducted using double distilled water. Stock phenol solution of strength 1000 mg/L was prepared by diluting 0.93 mL standard phenol solution to 1 L with double distilled water. The granular AC (E-Merck, India make) was procured and pulverized to different sizes (600, 425, 212, 125 and 75 μm). The materials with varying sizes were kept in desiccators at room temperature until it was used. The geometric mean sizes of materials used in all the studies ranged from 75 to 600 μm.

The sugarcane waste was collected from the local market and then burned in the muffle furnace at a temperature of 900 °C for 8 h. The contents were then cooled and pulverized to different micron sizes (212, 125 and 75 μm). Bagasse ash was pretreated with hot distilled water, followed by using 1N HNO_3 solution. After being soaked for 24 h, BA was separated from the above solutions and thereafter thoroughly washed several times in distilled water. Then, it was dried in a hot air oven at 105–110 °C for 4 h and stored in a desiccator at room temperature.

The WC was also procured from the local market and pulverized to different sizes (600, 425, 212, 125 and 75 μm). WC was also pretreated using the same procedures used for BA adsorbent processing. The characteristics of these three test adsorbents are listed in Table 1.

3. Experimental procedure

All the experiments were conducted at room temperature. The test samples were agitated with a reciprocating type horizontal shaker (Remi, India) at 100 rpm speed. The pH, chloride ionic strength, EDTA, and initial phenol concentration were studied for their effects on phenol removal.

Table 1
Characteristics of adsorbents

Parameter	AC	BA	WC
Surface area (m^2/g)	950–1050	417–500	200–260
Bulk density (kg/m^3)	750.80	270.50	220.30
Moisture (%)	1–2	7.50	8.00
Ash (%)	0.5–8.0	30.98	33.00
Iodine number	900–1000	–	–
Chemical composition			
SiO_2 (%)	8.00	51.05	0.47
Al_2O_3 (%)	ND	10.75	0.06
CaO (%)	ND	6.04	1.54
Fe_2O_3 (%)	ND	4.26	0.07
MgO (%)	ND	1.10	0.08
K_2O (%)	–	–	0.51
Na_2O (%)	–	–	0.08
H_2O (%)	–	–	1.20

3.1. Batch sorption studies

Batch studies were conducted for evaluating the adsorption potential of phenol on AC, BA and WC and also for development of kinetics of adsorption, determination of equilibrium parameters. To start each adsorption test, phenol-spiked synthetic water samples (50 mL) with predetermined conditions including initial phenol concentration, pH, and adsorbent dosage, were loaded into a 100 ML polythene vial. Then the vial was shaken on a reciprocating type horizontal mechanical shake. The test vial were removed from the shaker at appropriate intervals of time and then filtered with filter paper (Whatman No. 42) and analysed for the residual adsorbate (phenol) concentration using a UV spectrophotometer (Shimadzu, Japan) at wavelength of 510 nm with Standard Methods [19].

3.2. Kinetic study

The adsorption kinetics study was performed by using two initial phenol concentrations, i.e., 30 and 50 mg/L, with an adsorbent (AC, BA or WC) dosage of 50 g/L. The samples were withdrawn at different pre-decided time intervals. All these samples were filtered and analysed for residual concentrations of phenol.

3.3. Adsorption equilibrium and isotherm study

Separate isotherm studies were conducted for AC, BA and WC with two initial phenol concentrations, 30 and 50 mg/L, and adsorbent dosages of 10, 20, 30, 50, 60 and 100 g/L. Equilibrium contact times determined from the kinetic studies aforementioned were used for these tests. After shaken for a certain period of time, the samples were filtered and analyzed for residual phenol concentrations.

3.4. Interruption tests

The interruption tests as proposed by Helfferich [20] and Zogorski et al. [21] were performed to determine the rate-limiting step of the studied adsorption processes. The mixtures containing 50 mL of distilled water with a phenol concentration of 50 mg/L and predetermined amount of adsorbents (AC, BA and WC) were agitated. After 30 min of agitation, one sample was withdrawn from the system and the adsorbent was separated from the solution. After an interruption time of 15 min, the same absorbent was reintroduced into the solution and put into the agitation system. The next sample was taken from the system after an adsorption time of 1 h (including interruption time) and analyzed for residual phenol concentration. But other samples were withdrawn from the system at an interval of 15 min and analyzed for residual adsorbate concentration for each adsorbent.

3.5. Batch desorption studies

Water samples with phenol concentrations of 50 mg/L and predetermined dosages of each adsorbent were agitated for an equilibrium contact time. After certain periods of adsorption, adsorbents were separated from solutions and analyzed for their residual concentrations. The amounts of phenol adsorbed onto the adsorbents were determined from the difference of initial and final concentrations of phenol in solution. The adsorbents were then dried at room temperature and used for desorption studies. Desorption studies were conducted separately using 10% acetone solution, 20% acetone solution, 10% HCl solution, 20% HCl solution, and distilled water. Two time periods, 2 and 4 h, were used during desorption tests.

3.6. Effects of initial adsorbate concentration, pH, ionic strength, chloride concentration and EDTA

The initial phenol concentrations of 20, 30, 40, 50, 60, and 100 mg/L were used for evaluation of their effects on adsorption. Different pHs, 3, 4, 7, 8 and 9 of water solutions were employed to evaluate the effect of pH on phenol removal with the three selected adsorbents. The values of pHs were determined using a digital pH meter (Systronics, India, make). The effect of ionic strength was studied by varying the concentration of $NaNO_3$ added to water solutions over the range of 10^{-4}–10^{-1} M. The effect of chloride concentration was studied by adding various amount of NaCl to the phenol-spiked solutions so that the concentrations of Cl^- are in the range of 10^{-4}–10^{-1} M. The effect of EDTA as a chelating agent was studied with its concentrations controlled in the range of 10^{-5}–10^{-2} M.

4. Results and discussion

4.1. Adsorption kinetics

Adsorption kinetics is important for understanding the uptake rates of pollutants on the surfaces of adsorbents and determining the equilibrium times of adsorptions. The changes of phenol removal efficiency with contact time for various adsorbents at two different initial phenol concentrations are shown in Fig. 1. The trends of these plots revealed that the removal rate followed the first order adsorption kinetics. Fig. 1 also shows that about 98–99% phenol removal took place within the first 1 h of contact time in case of phenol–AC systems under the given conditions (i.e., the initial phenol concentrations of phenol: 30 and 50 mg/L; adsorbent dosage: 50 g/L). The results in Fig. 1 also indicated that due to the high availability of vacant sites in the AC, and high affinity of organic compounds to AC, a high degree of concentration gradients and partitioning existed between solid and liquid phases. Once the availability of phenol diminished in the solutions, further uptakes were not observed. The removal profile of phenol by AC became flat after 1 h of adsorption. Zogorski et al. [21] observed that the adsorption of phenolic compounds by granular carbon was extremely rapid and within the first hour of contact, 60–80% of the ultimate adsorption could occur. Sachan et al. [22] also found that within 2 h of adsorption time, about 80% phenol was adsorbed by AC. No significant phenol removal was observed in the present study beyond 1 h of adsorption. Thus, 1 h was considered to be the equilibrium time for the phenol–AC adsorption system under the given test conditions.

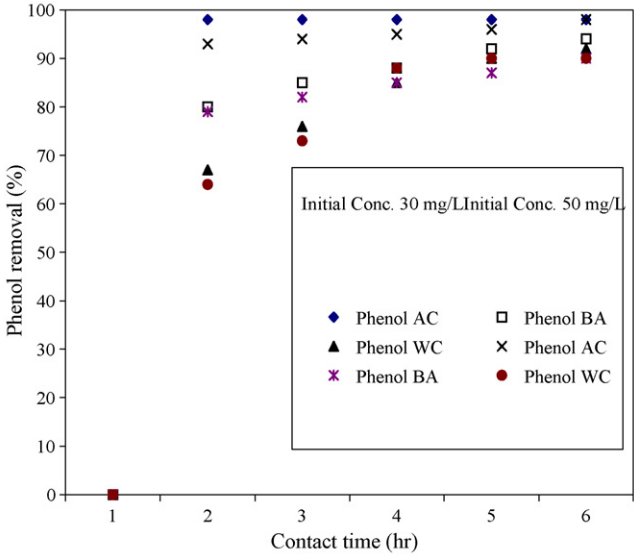

Fig. 1. Adsorption kinetics profiles for phenol removal (adsorbent dose = 50 g/L, agitation speed = 100 rpm, pH 6.8, temperature = 24 ± 1 °C).

For the BA–phenol and WC–phenol adsorption systems, it could be seen from Fig. 1 that removal patterns were almost identical. Fig. 1 also reveals that about 65% and 85% removals were achieved with WC and BA, respectively, within the first 1 h of adsorptions. The removal rates increased slightly until equilibrium states reached at about 4 h of adsorption. Both WC and BA yielded a 90% removal of phenol within a 4 h of contact period when the initial phenol concentration was 30 mg/L. The kinetic profiles in Fig. 1 exhibit two distinct zones, rapid and slow or equilibrium adsorption stages. Rapid stage zone for all the three adsorbents appeared to last for about 1 h. The equilibrium reached within 1 h for AC and 4 h for BA and WC.

The adsorption kinetics data of three adsorbents for two different initial phenol concentrations are shown in Figs. 2 and 3, respectively. It is evident from Figs. 2 and 3 that the phenol adsorption rates reasonably follow a first order kinetics. The first order adsorption rate constants estimated from Figs. 2 and 3 are listed in Table 2.

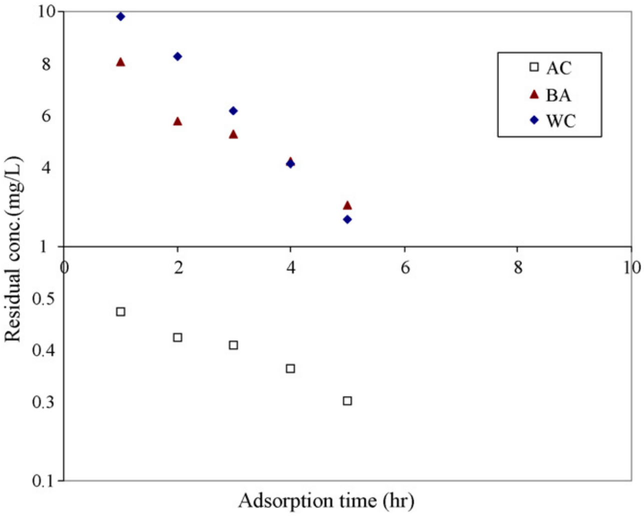

Fig. 2. First order adsorption kinetics for phenol (adsorbate–phenol, initial adsorbate concentration = 30 mg/L, adsorbent dose = 50 g/L, pH 6.8 (distilled water), agitation speed = 100 rpm, room temperature = 24 ± 1 °C).

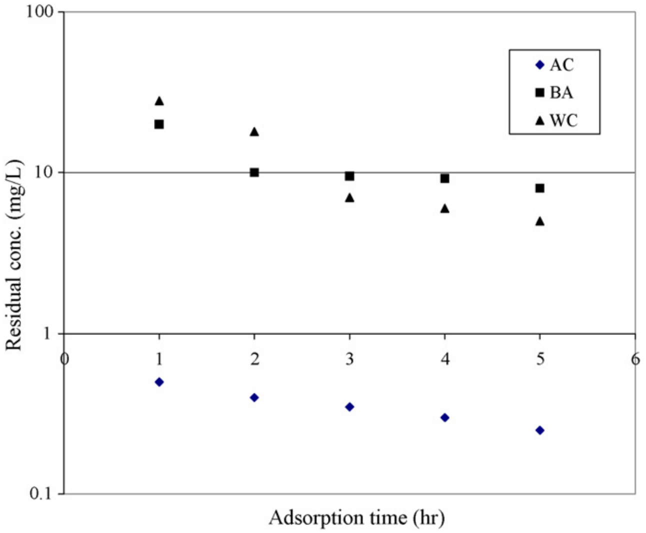

Fig. 3. First order adsorption kinetics for phenol (adsorbate–phenol, initial adsorbate concentration = 50 mg/L, room temperature = 24 ± 1 °C).

The first order reversible kinetics can be expressed as follows:

$$\frac{\mathrm{d}C_\mathrm{L}}{\mathrm{d}t}=\frac{\mathrm{d}C_\mathrm{S}}{\mathrm{d}t}=\frac{\mathrm{d}X}{\mathrm{d}t}=K_\mathrm{f}C_\mathrm{L}-K_\mathrm{r}C_\mathrm{S}$$
$$=K_\mathrm{f}(C_{\mathrm{L},0}-X)-K_\mathrm{r}(C_{\mathrm{S},0}+X) \quad (1)$$

$$=(K_\mathrm{f}+K_\mathrm{r})\left[\left\{\frac{K_\mathrm{f}C_{\mathrm{L},0}-K_\mathrm{r}C_{\mathrm{S},0}}{K_\mathrm{f}+K_\mathrm{r}}\right\}-X\right] \quad (2)$$

where C_L is the concentration of adsorbate in the liquid phase and C_S is the concentration of the adsorbate on the adsorbent at any time t, $C_{\mathrm{L},0}$ and $C_{\mathrm{S},0}$ are the initial concentrations of adsorbate in liquid and within the sorbent, respectively, X represents the amount of solute adsorbed at any instant, K_f and K_r are forward and reverse rate adsorption constants respectively. From the viewpoint of mass transfer, the equilibrium constant, K_e, is defined as the ratio of the forward rate constant (K_f) to the reverse rate constant (K_r). At the equilibrium condition, the following relations exist:

$$K_\mathrm{e}=\left(\frac{K_\mathrm{f}}{K_\mathrm{r}}\right)=\left(\frac{C_\mathrm{se}}{C_\mathrm{le}}\right) \quad (3)$$

Table 2
Estimated kinetic rate constant

Adsorbate	Adsorbent	Initial concentration of adsorbate (mg/L)	K_i (h^{-1})
Phenol	Activated carbon	30	0.3879
		50	0.7904
	Bagasse ash	30	0.4760
		50	0.4031
	Wood charcoal	30	0.7159
		50	0.7813

$$\left(\frac{\mathrm{d}C_\mathrm{L}}{\mathrm{d}t}\right) = -\left(\frac{\mathrm{d}C_\mathrm{S}}{\mathrm{d}t}\right) = \left(\frac{\mathrm{d}X}{\mathrm{d}t}\right) = 0 \tag{4}$$

The amount of adsorbate adsorbed at equilibrium state, X_e, can be derived by combing Eqs. (2) and (4):

$$X_\mathrm{e} = \frac{K_\mathrm{f}C_{\mathrm{L},0} - K_\mathrm{r}C_{\mathrm{S},0}}{K_\mathrm{f} + K_\mathrm{r}} \tag{5}$$

where C_le and C_se are the concentration of adsorbate at equilibrium, in liquid and on sorbent, respectively. From Eqs. (1), (3) and (5), the derivative of X as a function of time, t, can be reorganized as follows:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = (K_\mathrm{f} + K_\mathrm{r})(X_\mathrm{e} - X) \tag{6}$$

The integration form of Eq. (6) is expressed as:

$$\ln\left[\frac{X_\mathrm{e}}{X_\mathrm{e} - X}\right] = (K_\mathrm{f} + K_\mathrm{r})t$$

or

$$\ln[1 - U(t)] = K't \tag{7}$$

where K' is the overall rate constant, defined as:

$$K' = K_\mathrm{f} + K_\mathrm{r} = K_\mathrm{r}\left(1 + \frac{1}{K_\mathrm{e}}\right) \tag{8}$$

and $U(t)$ equals to X/X_e, called the fractional attainment. Based on Eq. (7), $\ln[1 - U(t)] \sim t$ relationships are plotted in Fig. 4. All the plots in Fig. 4 are straight lines, thus the removal of phenol with each selected adsorbent fits first order adsorption model very well [23,25].

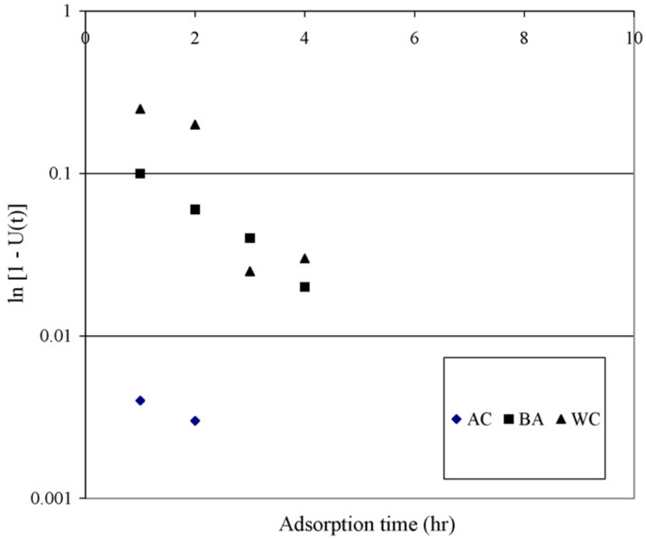

Fig. 4. First order reversible kinetics for phenol (adsorbate–phenol, initial adsorbate concentration = 50 mg/L, room temperature = 24 ± 1 °C).

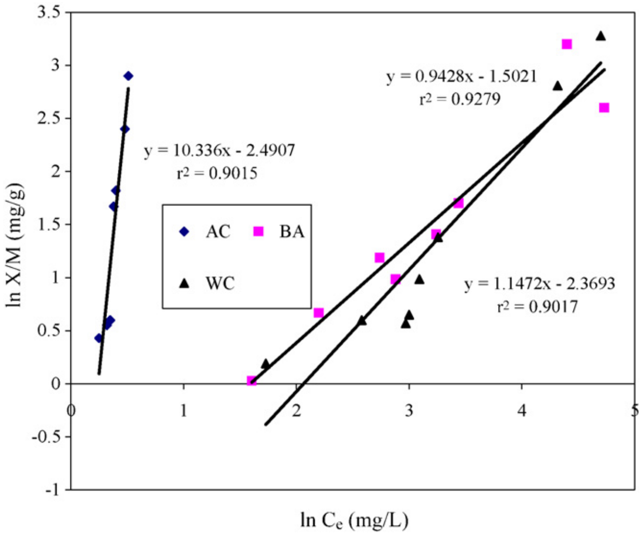

Fig. 5. Freundlich isotherm for constant phenol concentration and varying adsorbent dose (room temperature = 24 ± 1 °C; initial concentration = 30 mg/L).

4.2. Adsorption isotherms

Experimental isotherm is useful for describing the adsorption capacity of a specific adsorbent. Moreover, the isotherm places a vital role for the analysis and design of adsorption systems as well as for model prediction. Both Langmuir and Freundlich models were tried for the isotherm test data collected. However, we found that only Freundlich isotherm model fit the collected data as shown in Figs. 5 and 6. Freundlich isotherm model is typically expressed as:

$$\frac{X}{M} = KC^{1/n} \tag{9}$$

where X is the mass of solute adsorbed, M the mass of adsorbent, K a proportionality constant, C_e the equilibrium concentration, and $1/n$ is the measure of adsorption intensity. Eq. (9) is linearized as per following Eq. (10) to facilitate the calculation of 'K' and $1/n$:

$$\ln\left(\frac{X}{M}\right) = \ln K + \frac{1}{n}\ln C_\mathrm{e} \tag{10}$$

The comparison of different adsorbents can be done from their adsorption isotherm plots. Based on Eq. (10), selection

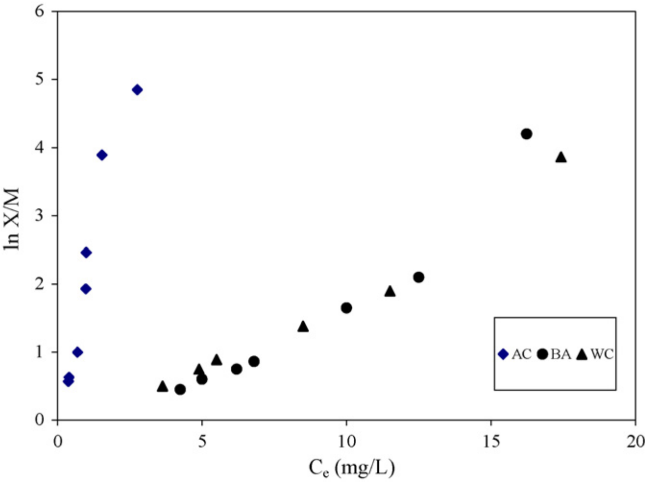

Fig. 6. Freundlich isotherm for constant phenol concentration (room temperature = 24 ± 1 °C; initial concentration = 50 mg/L).

Table 3
Isotherm constant values

Adsorbate–adsorbent	K	$1/n$	Freundlich isotherm equations
(A) For constant initial adsorbate concentration and varying adsorbent dose			
Phenol–AC			
Initial concentration = 30 mg/L	1.037	8.69	$X/M = 1037\, C_e^{8.69}$
Initial concentration = 50 mg/L	2.45	1.51	$X/M = 2.45\, C_e^{1.51}$
Phenol–BA			
Initial concentration = 30 mg/L	0.003	4.66	$X/M = 0.003\, C_e^{4.66}$
Initial concentration = 50 mg/L	0.042	1.51	$X/M = 0.042\, C_e^{1.51}$
Phenol–WC			
Initial concentration = 30 mg/L	0.002	5.12	$X/M = 0.002\, C_e^{5.12}$
Initial concentration = 50 mg/L	0.236	0.86	$X/M = 0.236\, C_e^{0.86}$
(B) For constant adsorbent dose and varying initial adsorbate concentration			
Phenol–AC	2.60	1.14	$X/M = 2.60\, C_e^{1.14}$
Phenol–BA	0.233	0.590	$X/M = 0.233\, C_e^{0.59}$
Phenol–WC	0.171	0.93	$X/M = 0.171\, C_e^{0.93}$

Table 4
Values of diffusion coefficients

Adsorbate	Adsorbent	Initial concentration of adsorbate (mg/L)	K (h^{-1})	$t_{1/2}$ (h)	D_f (cm^2/s)	D_p (cm^2/s)
Phenol	AC	30	0.1935	3.58	2.82×10^{-8}	4.81×10^{-10}
		50	0.2923	2.37	6.42×10^{-10}	7.26×10^{-10}
	BA	30	0.2825	2.45	1.80×10^{-9}	1.60×10^{-10}
		50	0.2279	3.04	1.06×10^{-9}	1.29×10^{-10}
	WC	30	0.4470	1.55	5.54×10^{-9}	1.11×10^{-9}
		50	0.5265	1.32	5.74×10^{-9}	1.30×10^{-9}

of superior adsorbent becomes simple when $\ln(X/M) \sim \ln C_e$ lines of different adsorbents are parallel; the upper lines represents better adsorption capacities and thus the better adsorbents. However, the interpretations of physical meanings of those plots become more complicated when isotherm lines cross each other, which is the case for the three studied adsorbents as shown in Fig. 6. However, the higher the K value, the more favorable the adsorbent is. The derived Freundlich isotherm models for the studied adsorption systems are listed in Table 3.

4.3. Rate limiting factors

Film and pore diffusions are the major factors that control the rate of adsorption of an adsorbate from the solution by a porous adsorbent. Two adsorption mechanisms work in series [24]. The slower one in the two processes will be the rate-limiting step [26]. Helfferich [20] used interruption tests for determination of the rate-limiting step. To improve the accuracy of Helfferich's approach, Zogorski et al. [21] successfully employed a series of artificial interruption tests to decide the rate-limiting step in their adsorption research. Furthermore, the dependences of the removal rate on adsorbate concentration, adsorbent size, and on agitation rate are some indications of either pore or film diffusion controlled adsorption.

For this research, the film diffusion coefficient (D_f) and pore diffusion coefficient (D_p) can be indirectly obtained from the slopes presented in Table 4 of the straight lines shown in Figs. 7 and 8. Assuming that the sorbent particles are spherical,

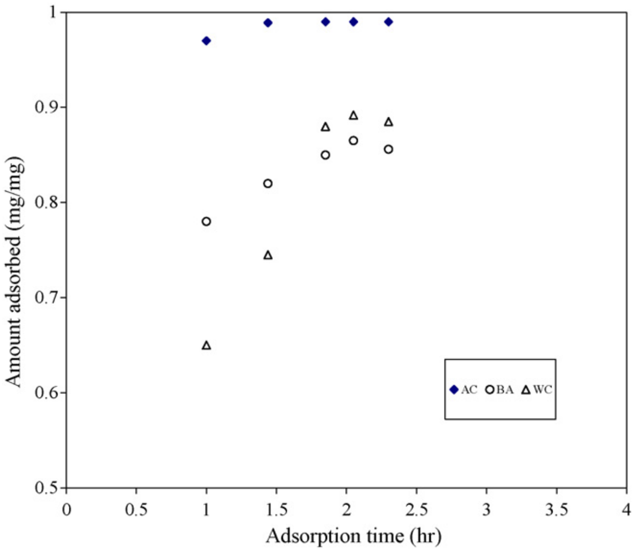

Fig. 7. Estimation of diffusion co-efficient (absorbate–phenol, initial concentration = 30 mg/L, adsorbent dose = 50 g/L, pH 6.8 (distilled water), agitation speed = 100 rpm).

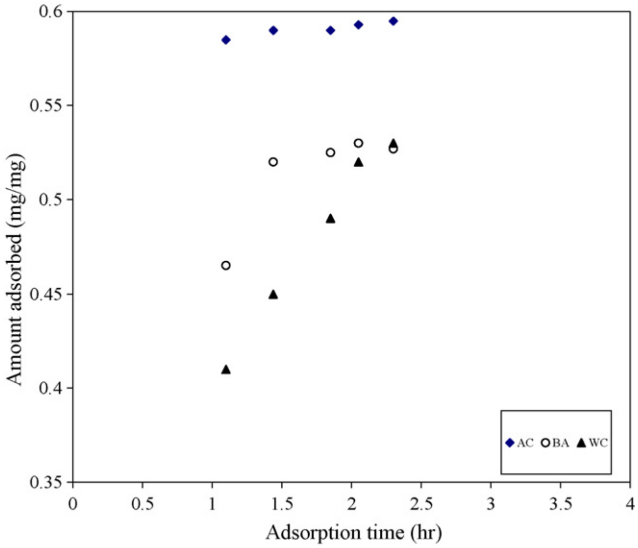

Fig. 8. Estimation of diffusion coefficient (absorbate–phenol, initial concentration = 50 mg/L).

the half time calculation equations of film and pore diffusions can be, respectively, expressed as follows:

$$t_{1/2} = \frac{0.03r^2}{D_\mathrm{f}} \tag{13}$$

$$t_{1/2} = 0.23r\left(\frac{\delta}{D_\mathrm{p}}\right)\left(\frac{C}{C_\mathrm{r}}\right) \tag{14}$$

where r (cm) is the radius of adsorbent particles; D_f and D_p are film and pore diffusion coefficients, respectively, in cm^2/s; C and C_S are the concentrations of adsorbate on the adsorbent and in solution at equilibrium state, respectively, δ (cm) is the film thickness; and $t_{1/2}$ (s) is time to obtain 50% reduction of adsorbate in the solution. The values of $t_{1/2}$ in Eqs. (13) and (14) could be estimated with the following relationship suggested by Asher et al. [27]:

$$t_{1/2} = -\ln\left(\frac{0.5r^2}{K^*}\right) \tag{15}$$

where K^* is the overall reaction rate constant, which can be obtained from the linear segment of Figs. 7 and 8 in this study. Assuming that the film thickness is 0.001 cm [20], then the values of $t_{1/2}$ were calculated from the Eq. (15) and listed in Table 4. The estimated diffusion coefficients by other investigators [28,29] are in the range of 10^{-11}–10^{-12} cm^2/s because their calculations were based on the assumption that intraparticle diffusion is the rate limiting for the sorption of organic compounds onto porous adsorbents. According to Michelson et al. [25], the film diffusion is the rate limiting step if the values of film diffusion coefficients (D_f) are in the range of 10^{-6}–10^{-8} cm^2/s. Otherwise the rate limiting step would not be pore diffusion for which the values of D_p should be in the range of 10^{-11}–10^{-12} cm^2/s. Based on the diffusion coefficients shown in Table 4 and the criteria proposed by Michelson et al., film diffusion is the controlling mechanism for the adsorption of phenol with the three adsorbents used in this research.

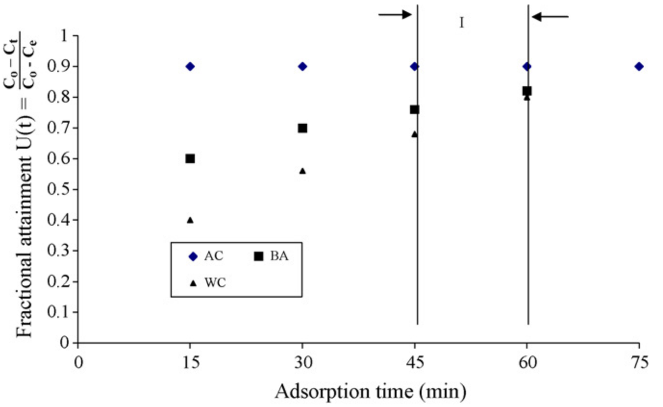

Fig. 9. Interruption test profile for phenol (adsorbate–phenol, initial concentration = 50 mg/L, optimum adsorbent dose = 50 g/L, pH 6.8 (distilled water), agitation speed = 100 rpm, room temperature = 24 ± 1 °C, ♦, ■, ▲, uninterrupted samples, interrupted sample, I interruption period = 15 min).

4.4. Interruption tests

The single point interruption test results are plotted in Fig. 9. For the film diffusion controlled process, pre-interruption and post-interruption slopes should be nearly equal whereas for pore diffusion controlled process post interruption slopes are supposed to be significantly greater than pre-interruption ones [20]. The slopes of the adsorption kinetics curves shown in Fig. 9 before and after 15 min of interruption period for adsorption of phenol with AC, BA, and WC are given in Table 5. These tabulated slope values indicate that the film diffusion is very likely to be the controlling step for all the three phenol adsorption systems involved in the present study, which corroborates the calculation results aforementioned.

4.5. Significant influencing factors

4.5.1. Effect of adsorbent dosage

The removal percentages of phenol as functions of dosages of the three adsorbents are shown in Fig. 10. Fig. 10 shows that phenol removal increased with the increase in dosages of adsorbents up to certain levels and then levelled off. From Fig. 10, it was observed that, a 98% phenol removal was achieved when AC dosage was 10 g/L and the initial phenol concentration was 30 mg/L. But for BA and WC, phenol removal increased from 86% to 90% when their dosages increased from 10 to 60 g/L under the same other conditions. The optimum dosages for different combinations of adsorbent and adsorbate systems are listed in Table 6. The results illustrated that the requirement of AC was lowest compared to the other adsorbents. However, with the market price of AC considered,

Table 5
Pre- and post-interruption slopes of kinetics curves

Adsorbate–adsorbent	Pre-interruption slope	Post-interruption slope
Phenol–AC	1.5×10^{-3}	1.5×10^{-3}
Phenol–BA	3.52×10^{-3}	3.65×10^{-3}
Phenol–WC	4.5×10^{-3}	4.5×10^{-3}

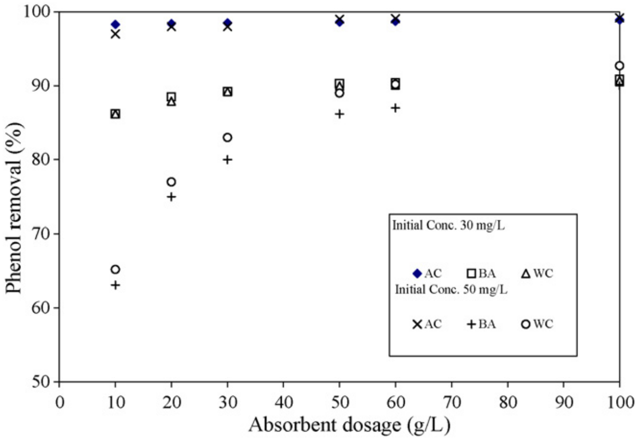

Fig. 10. Effect of adsorbent dose for phenol removal (at equilibrium condition).

Table 6
Optimum adsorbents dose for 90% removal of phenol

Phenol concentration (mg/L)	Adsorbent	Optimum dose (g/L)
30–50	AC	10
30	BA	15
50	WC	60

AC may not be the most cost-effective one for removal of phenol.

4.5.2. *Initial phenol concentration*

The test results of effect of initial phenol concentration on phenol removal are shown in Fig. 11. The adsorption efficiency of phenol by AC remained constant even though the initial concentration of phenol was up to 100 mg/L. Similar trend was also observed by Sachan et al. [22] for removal of phenol by AC. For BA and WC, the phenol removal efficiency decreased with the increase of the initial phenol concentration. Phenol removal efficiencies of BA at the initial phenol concentrations of 20 and 100 mg/L were about 92% and 80%, respectively. For WC, when the initial phenol concentration increased from 20 to 100 mg/L the phenol removal efficiency decreased from 91% to 79.5%.

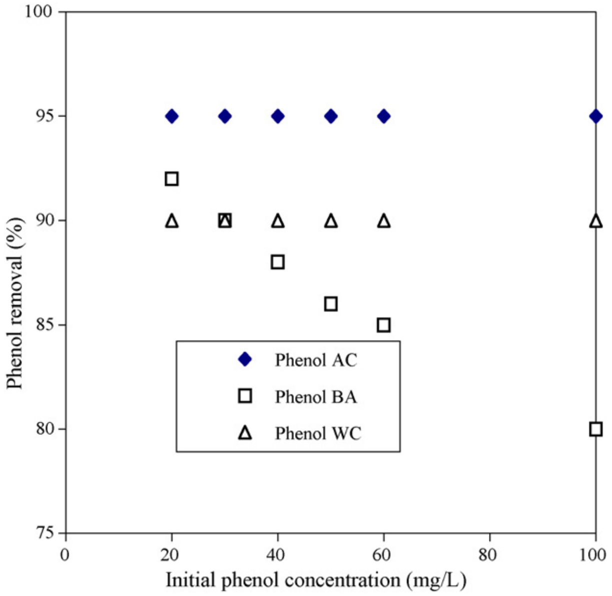

Fig. 11. Effect of initial adsorbent concentration on phenol removal (adsorbent dose = 50 mg/L, room temperature = 24 ± 1 °C, agitation speed = 100 rpm).

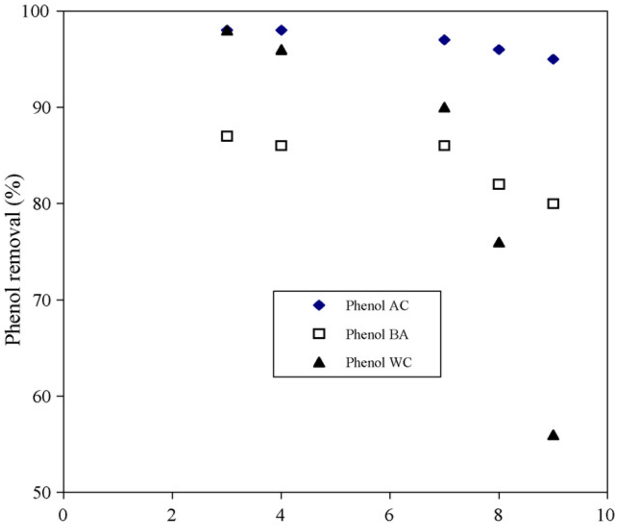

Fig. 12. Effect of pH on phenol removal (adsorbent dose = 50 mg/L, agitation speed = 100 rpm, room temperature = 25 + 1 °C).

4.5.3. *pH*

The removal of a pollutant from an aqueous medium by adsorption is highly dependent on the solution pH, which affects the surface charge of the adsorbent and the degree of ionization of the adsorbate. The effects of pH on phenol removal with the three selected adsorbents were shown in Fig. 12. It seems that the phenol removal capabilities of AC were only slightly affected by pH under the given test conditions. The adsorption of phenol with WC and BA was affected when pH was higher 7. The difference in adsorption capacity of WC and BA at different pHs may be due to the difference in the concentrations of H^+ and OH^- in the solutions. Adsorbent particles have active sites with negative charges. The H^+ ions within low pH environments can neutralize those negative particles, reduce the hindrance to diffusions of phenol ions and consequently increase the chances of their adsorption. High pH environments led to high concentration of OH^-, which can increase the hindrance to the diffusions of phenol ions and thus reduce the chances of their adsorption [6,21,22].

4.5.4. *Anions*

The overall distribution of neutral compounds onto natural materials has been shown to be affected by ionic species in aqueous phase [30]. The effects of additions of NO_3^- and Cl^- on the removal of phenol with AC, WC and BA are shown in Figs. 13 and 14, respectively. The degrees of effects of NO_3^- and Cl^- on three absorbents are in the order of BA > WC > AC. The negative effect of NO_3^- and Cl^- could be due to the fact that the NO_3^- and Cl^- may compete with OH^- ions and sup-

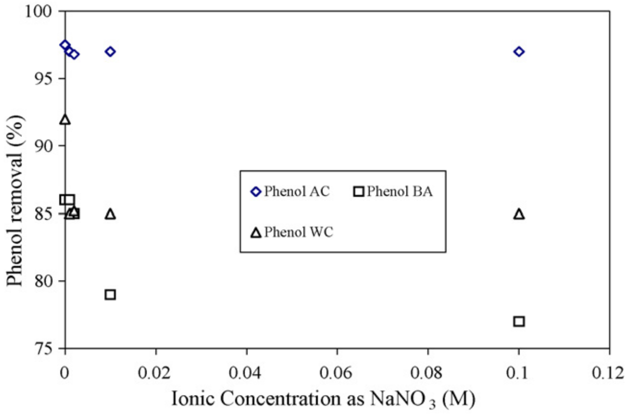

Fig. 13. Effect of ionic concentration (at equilibrium condition) (adsorbent dose = 50 mg/L, agitation speed = 100 rpm, room temperature = 24 ± 2 °C).

press the formation of the hydroxyl complexes of adsorbate ions and increase the hindrance of phenol diffusion on the surfaces of adsorbents [31]. The similar trends for removal of other contaminants by other adsorbents were observed by other researcher [32–34].

4.5.5. EDTA

Effects of with EDTA on removal of phenol by AC, WC and BA are shown in Fig. 15. Compared to AC, WC and BA are significantly affected by EDTA for their removal of phenol with the increase of the concentration of EDTA in the range of 10^{-5}–10^{-2} M. This may be attributed to the complexation of phenol by EDTA. These complexes readily influence the diffusional behaviour of the phenol and as a consequence its adsorption processes. Phenol removal efficiencies of WC and BA decreased from 90% to 57% and from 87% to 64%, respectively, when the concentration of EDTA increased from 10^{-5} to 10^{-2} M.

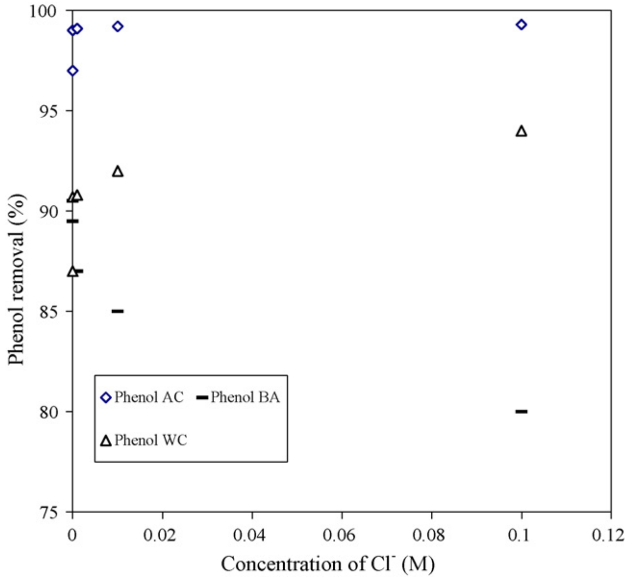

Fig. 14. Effect of chloride ion (at equilibrium condition) (adsorbent dose = 50 mg/L, agitation speed = 100 rpm, room temperature = 24 + 2 °C).

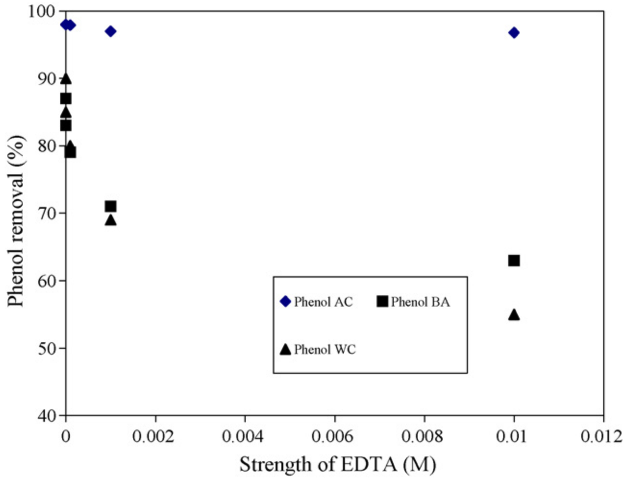

Fig. 15. Effect of EDTA (at equilibrium condition) (adsorbent dose = 50 mg/L, agitation speed = 100 rpm, room temperature = 24 + 2 °C).

5. Conclusion

The use of WC and BA as two inexpensive carbonaceous adsorbents for the removal of phenol from water environment has been found to be comparable to commercial grade AC. The phenol removals with the AC, WC and BA exhibited first order adsorption kinetics. Freundlich's isotherm model fitted the adsorption of phenol with AC, WC and BA. Film diffusion appeared to be rate-limiting step for the overall phenol removal processes of three adsorbents. Compared to AC, WC and BA are affected to higher degrees by the studied factors for their phenol removals. Future study should focus on the larger scale demonstration, comprehensive economical and environmental assessments of the proposed phenol removal technology.

References

[1] W.J. Weber Jr., J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. ASCE 18 (SA-2) (1963) 31–42.
[2] S.D. Faust, O.M. Aly, Adsorption Process for Water Treatment, Butterworths Publication, 1987.
[3] C.D. Adams, T.L. Watson, Treatability of s-altrazine herbicide metabolites using powdered activated carbon, J. Environ. Eng. ASCE 122 (4) (1996) 327–330.
[4] S. Keerthinarayan, M. Bandopadhayay, Sorption of lindane by wood charcoal, Indian J. Technol. 31 (1993) 231–238.
[5] M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Resorcinol removal from aqueous solution by bagasse fly ash and activated carbon: batch and column studies, Environ. Eng. Div. J. Inst. Eng. (India) 77 (1997) 49–52.
[6] P. Khanna, S.K. Malhotra, Kinetics and mechanism of phenol adsorption of flyash, Indian J. Environ. Health 19 (3) (1977) 224–237.
[7] S. Kumar, S.N. Upadhyay, Y.D. Upadhyay, Removal of phenol by adsorption on fly ash, J. Chem. Technol. Biotechnol. 37 (1987) 188–196.
[8] G.P. Jan, P. Mulder, L. Robert, Fly ash mediated reaction of phenol and monochloro phenols, Environ. Sci. Technol. 27 (1993) 1849–1863.
[9] D.K. Singh, A. Mishra, Removal of phenolic compound from water using chemical treated saw dust, Indian J. Environ. Health 32 (1990) 345–351.
[10] D.J. Bhat, D.S. Bhargara, P.S. Panesar, Effect of pH on phenol removal in moving media reactor, Indian J. Environ. Health 25 (1983) 261–267.
[11] J.W. Patterson, Wastewater Treatment Technology, Ann Arbor Science Inc., 1975.

[12] WHO, International Standards for Drinking Water, WHO, Geneva, 1963, pp. 40–42.

[13] T. Viraraghavan, J. Alfaro, Removal of phenol from wastewater by adsorption on peat, fly ash and bentomile, J. Environ. Eng. 5 (1992) 311–317.

[14] A. Garcia, L. Ferreira, A. Leitao, A. Rodrigues, Binary adsorption of phenol and *m*-cresol mixtures onto a polymetic adsorbent, Adsorption 5 (1999) 359–368.

[15] S. Yapar, M. Yilmar, Removal of phenol by using montmorillonite, clinoptilolite and hydrotalcite, Adsorption 10 (2004) 287–298.

[16] N. Roostari, F.H. Tezel, Removal of phenol from aqueous solution by adsorption, J. Environ. Manage. 70 (2004) 157–164.

[17] M. Ahmaruzzaman, D.K. Sharma, Adsorption of phenols from wastewater, J. Colloid Interf. Sci. 287 (2005) 14–24.

[18] C.P. Das, L.N. Patnaik, Removal of phenol by industrial solid waste, Practice Period. Hazard. Toxic Radioactive Waste Manage. ASCE 9 (2) (2005) 135–140.

[19] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 17th ed., APHA, AWWA, WPCF, 1989.

[20] F. Helfferich, Ion Exchange, Mcgraw Hill Book Co., The New York, 1962, pp. 259–264.

[21] J.S. Zogorski, S.D. Faust, J.H. Hass Jr., The kinetics of adsorption of phenols by granulas activated carbon, J. Colloid Interf. Sci. 55 (2) (1976) 329–342.

[22] V.K. Sachan, K.M. Sujatha, S. Kumar, Removal of phenol from wastewater by activated carbon, Indian J. Environ. Protect. 16 (4) (1996) 284–290.

[23] A.K. Bhattacharya, C. Venkobachar, Removal of cadmium (II) by low cost adsorbents, J. Environ. Eng. Div. ASCE 110 (1) (1984) 110–118.

[24] J. Weber Jr., Adsorption theory, concept, models and capacities for adsorption, F.O. Slejko, edition, New York, 1985.

[25] L.D. Michelson, P.G. Gidean, E.G. Pace, L.H. Kutal, Removal of soluble mercury from wastewater by complexing techniques, USDI, Office of Water Research and Technology, 1975, Bill No. 74.

[26] L.D. Benefield, J.L. Judkins, B.L. Weanal, Process Chemistry for Water and Wastewater Treatment, Prentice Hall Inc., New Jersey, USA, 1982.

[27] B.T. Asher, D.L. Sparks, J.D. Pesek, S. Feigenbaum, Analysis of adsorption kinetics using a stirred flow chamber. I. Theory and critical tests, Soil Sci. Soc. Am. J. 54 (1990) 1273–1278.

[28] S.C. Wu, P.M. Gschwend, Sorption kinetics of hydrophobic organic compounds of natural sediments and soils, Environ. Sci. Technol. 20 (1986) 717–725.

[29] J.P. Conolly, Ph.D. Dissertation, University of Texas, Austin, 1980.

[30] J. Mitra, Decontamination of quinoline from aqueous system by wood charcoal—a batch adsorption study, M.E. Thesis, Jadavpur University, 2000.

[31] C.P. Schulthess, D.L. Sparko, Competitive ion exchange behaviour on oxides, Soil Sci. Soc. Am. J. 53 (1989) 366–373.

[32] N.C. Das, M. Bandopadhyay, Removal of nickel by low coast natural medium, Indian J. Technol. 31 (1993) 312–317.

[33] S.N. Srivastava, R. Tyagi, N. Pal, D. Mohan, Process development for removal of substituted phenol by carbonaceous adsorbent obtained from fertilizer waste, J. Environ. Eng. ASCE 123 (9) (1997) 842–887.

[34] C.P. Huang, F.G. Ostovic, Removal of cadmium (II) by activated carbon, J. Environ. Eng. ASCE 104 (5) (1978) 863–873.