Use of coal fly ash for simultaneous co-adsorptive removal of phenol and cyanide from simulated coke wastewater

Bhumica Agarwal* and Chandrajit Balomajumder

Department of Chemical Engineering
Indian Institute of Technology Roorkee
Roorkee 247667, India

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ABSTRACT

The present study deals with the process parameter optimization and modeling of simultaneous adsorption of phenol and cyanide from simulated coke wastewater onto acid treated coal fly ash. At a temperature of 30 °C, pH of 9 and adsorbent dose of 40 g L^{-1}, optimum removal of phenol and cyanide was found to be 67 and 82%, respectively for initial concentration of 200 mg L^{-1} phenol and 20 mg L^{-1} cyanide. Both single-component and multi-component isotherms were applied to the experimental data in the range of initial concentration of 100-1000 mg L^{-1} of phenol and 10-100 mg L^{-1} of cyanide. Extended Langmuir and extended Freundlich isotherms were found to be best fitted model for phenol and cyanide, respectively. The monolayer capacity of fly ash as calculated by extended Langmuir isotherm was 248 mg phenol g^{-1} of fly ash and 1.2 mg cyanide g^{-1} of fly ash. Kinetic studies revealed chemisorptions to be the mechanism of adsorption of both phenol and cyanide. Thermodynamic parameters viz, ΔG^0, ΔH^0 and ΔS^0 were calculated as -1.7, -7.3 kJ mol^{-1}, -0.05 kJ mol^{-1} K^{-1} for phenol and -3.8, 24 kJ mol^{-1} and 0.09 kJ mol^{-1} K^{-1} for cyanide adsorption, respectively indicating process of phenol adsorption onto fly ash as exothermic and spontaneous while that of cyanide as endothermic in nature.

INTRODUCTION

Water pollution is one of the major concerns of the environmentalists worldwide. Ever increasing urbanization and industrialization have led to the discharge of a number of pollutants into water streams thereby leading to deterioration of their quality. Industrial discharge from coke processing industry contains large quantities of toxicants like phenol, cyanides, thiocyanides, thiosulphates, ammonium, chlorides, etc. Phenol and cyanide and their associated compounds have been listed as priority pollutants by the Central Pollution Control Board, India and Environmental Protection Agency (EPA), USA. Exposure to even low concentrations of phenol and/or cyanide can cause coma, heart pains, breathing disorders, thyroid gland enlargement, headaches, skin and eye injuries, vomiting, gastrointestinal disorders, central nervous system depression, lung, kidney, liver and heart damage ultimately leading to death [1,2]. As per the recommendation of the USEPA, the threshold concentration of phenol in effluent discharge has been set as 0.5 mg L^{-1} and cyanide as 0.2 mg L^{-1}. A number of chemical, physical and biological methods are available for treatment of such water. However the presence of multiple contaminants poses certain hindrances making no single treatment sufficient for complete remediation of wastewater. However, among available waste water treatment technologies, adsorption, particularly using granular activated carbon (GAC), has gained much popularity owing to its efficiency and ease. However high cost of GAC and difficulty in its regeneration have led to exploration of non-conventional adsorbents. In last few decades, materials which are produced as agricultural and/or industrial byproducts and require further action/treatment have attracted attention of researchers owing to their easy availability and cost effectiveness. Some of these adsorbents include saw dust [3], vegetable and fruit peels [4], peat, fly ash, bentonite [5], prawn waste [6], leaves [7], etc.

Fly ash is a fine powdery residue resulting from incomplete combustion of coal in thermal power plants. The main constituents of fly ash are silica,

*Corresponding author
Email: bhumica.agarwal@gmail.com

alumina and iron oxides. Landfill is the method of choice of disposing large amounts of fly ash generated by power industries [8]. Some alternatives for using fly ash include additive in construction material and a cheap resource for zeolite synthesis [9]. Their hydrophilic surface and hierarchical structure also make fly ash a suitable adsorbent to remove heavy metals and organic compounds from aqueous solutions [10]. The adsorptive capacity of coal fly ash is attributed to its surface properties as it is highly porous and has large surface area and pore volume owing to the presence of high amounts of SiO_2 and Al_2O_3. Therefore coal fly ash has been utilized as an adsorbent for adsorption of phenols [11,12], cyanides [13], heavy metals [14], arsenic compounds [15] and organic compounds such as dyes [16]. Another important parameter which governs the efficiency of fly ash is its carbon content; the effectiveness increases with carbon content [17]. Though fly ash has been used by many researchers for phenol and cyanide removal in single solute systems [5,11-13], no study has been carried out to study the efficiency of fly ash as an adsorbent in binary solute system to the best of our knowledge. Additionally equilibrium isotherms applicable to single solute systems viz. Langmuir, Freundlich, Redlich-Peterson, Toth, Temkin etc are not applicable to binary systems in most of the cases owing to the complexity of application of adsorption isotherms due to different solute-surface interactions [18,19]. Therefore the aim of present study is to determine the efficiency of coal fly ash as an adsorbent for phenol and cyanide from multi-component systems and to evaluate equilibrium, kinetic and thermodynamic parameters of the process. It is our belief that the above mentioned studies will help in designing continuous systems using coal fly ash for the removal of toxic compounds from coke wastewaters thereby minimizing the adverse impacts of industrial wastewaters as well as large quantities of coal fly ash.

MATERIALS AND METHODS

1. Chemicals and Adsorbent

All the chemicals used in this study were of analytical grade and obtained from Himedia Laboratories, Mumbai India. Stock solution containing 100 mg L^{-1} cyanide was prepared by dissolving 0.25 g of KCN in 1 L of Millipore water (Q-H_2O, Millipore. with resistivity of 18.2 MΩ cm) whose pH was pre-adjusted to 10 using 1 N NaOH. Stock solution containing 1000 mg L^{-1} of phenol was prepared by dissolving 1 g of pure phenol crystal in 1 L of Millipore water (pH 9 ± 0.5). Coal Fly ash, obtained from a thermal power plant in Ghaziabad region of India, was washed with Millipore water and soaked in 0.5 M H_2SO_4 for 24 h in 2:1 ratio of liquid to solid. The adsorbent was then washed several times with Millipore water and dried in hot air oven at 110 °C for 2 h to completely remove moisture, cooled to room temperature and stored in polybags until further use. Surface area, bulk density and organic carbon content of acid treated fly ash used were 67 m^2 g^{-1}, 1100 g L^{-1} and 9.5%, respectively. Fly ash of uniform particle size (30-70 µm) was selected for adsorption process. Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700, USA) was employed to determine the type of functional groups present on adsorbent's surface before and after adsorption since the extent of adsorption depends greatly on surface characteristics of adsorbent. Unloaded and loaded samples were also visualized through scanning electron microscopy, SEM (Quanta 200F, FEI, Netherlands) to observe the changes in surface morphology due to the adsorption of phenol and cyanide. For SEM analysis, sample was mounted on aluminium stub and gold coating was performed via sputtering at a pressure of 667 x 10^{-4} Pa for 50-60 s. The sample was then visualized under high electric field of 20 kV.

2. Batch Experiments

Batch experiments for optimization of process parameters and equilibrium, kinetic and thermodynamic studies were carried out in 250 mL round bottom flasks with working volume of 100 mL at 125 rpm in an incubator cum orbital shaker (Metrex, MO-250, India). To avoid photo-oxidation of phenol the incubator was properly covered with black cardboard throughout the experiment. All the experiments were carried out in triplicates and average results were used. Considering the ratio of phenol and cyanide discharged from coke wastewaters (generally 10:1), initial adsorbate concentrations were selected as 200 mg L^{-1} for phenol and 20 mg L^{-1} for cyanide. Since at industrial level narrow temperature ranges are preferred for pollution abatement temperature of 30 °C was selected for further studies [20]. The optimum pH and adsorbent dose were selected from a range of pH 4-12 and 5-40 g L^{-1} respectively on the basis of maximum percentage removal of phenol and cyanide. All the experiments were carried out for 48 h allowing sufficient time for achieving equilibrium. After every 2 h pH of the mixture was tested and readjusted to predefined value with 1 N NaOH or HCl in case of any change during operation. For study of adsorption isotherms initial concentrations of phenol and cyanide were varied from 100-1000 and 10-100 mg L^{-1} respectively. For study of adsorption kinetics an appropriate volume of sample was withdrawn at an interval of every 2 h till the equilibrium conditions were achieved, filtered with standard Whatman filter paper (Cat No 1001 125) and the filtrate was analyzed

for cyanide and phenol by colorimetric picric acid and 4-aminoantipyrene methods, respectively [21]. The amount of cyanide and phenol adsorbed per unit mass of the adsorbent was evaluated by the following mass balance Eq. 1:

$$q = \frac{(C_0 - C_t)V}{M} \tag{1}$$

RESULTS AND DISCUSSION

1. Characterization of Fly Ash

Physio-chemical characterization of acid treated fly ash was done before and after adsorption of phenol and cyanide to find the correlation between adsorption of phenol and cyanide onto acid treated fly ash and surface textural and functional properties of fly ash. Figure 1a demonstrate smooth surface of acid treated fly ash which is considerably hardened upon adsorption of phenol and cyanide (Fig. 1b). Further adsorption of phenol and cyanide onto fly ash is evident from decrease in peak area of FTIR spectrum around wave number 1089.6 cm^{-1} (Fig. 2).

2. Optimization of Process Parameters

Figure 3a indicates that the removal of phenol increases marginally (49 to 66%) on increasing the pH from 4 to 9. This phenomenon could be explained on the basis of ionization pH of phenol. As the pH of solution approaches the pKa of phenol (10.0), dissociation of phenol starts to take place which leads to increasing adsorption of phenol in its molecular form. Thereafter the adsorption of phenol decreases considerably on increasing the pH from 9 to 12. The optimum removal of cyanide was obtained in the pH range of 8-10. At pH less than 8, a sharp decrease in removal of cyanide is observed as cyanide exists mostly in HCN form at lower pH. Since HCN is highly hydrophilic its tendency to be adsorbed at low pH is markedly decreased. At pH above pK$_a$ of cyanide (9.4), removal of cyanide remains almost constant. Therefore pH of 9 was considered as optimum for adsorptive removal of phenol and cyanide.

Figure 3b depicts the effect of increasing adsorbent dose on percentage removal of phenol and cyanide. Removal of cyanide increases with increasing adsorbent dose however removal of phenol increases initially up to 40 g L^{-1} of fly ash and decreases on further increase in dose. Initial increase of percentage removal is due to the increase in surface area as well as active sites for adsorption. However at higher adsorbent doses overlapping of active sites may take place thereby decreasing the percentage removal of phenol [22]. Therefore 40 g L^{-1} of fly ash was selected as optimum adsorbent dose for further
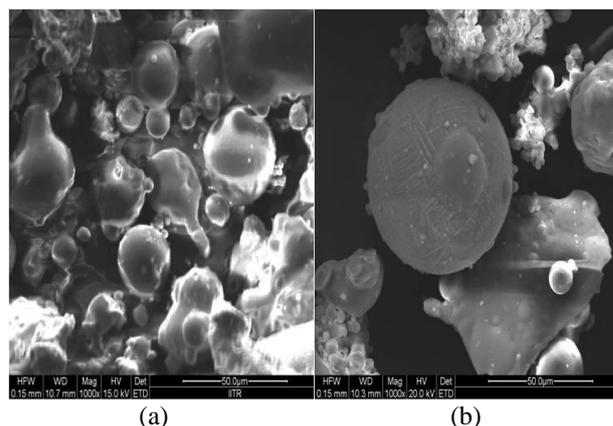

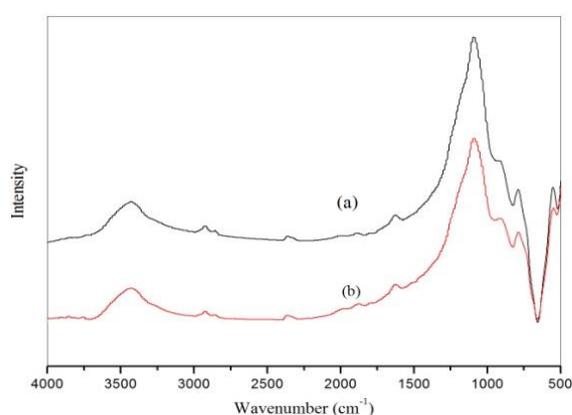Fig. 1. SEM images of acid treated Fly ash (a) before adsorption and (b) after adsorption.

Fig. 2. FTIR spectrum of (a) unadsorbed acid treated fly ash and (b) adsorbed acid treated fly ash.

studies.

Figures 3c and 3d represents the effect of increasing phenol and cyanide initial concentration on their percentage removal respectively. Removal of phenol increases on increasing its initial concentration from 100 to 200 mg L^{-1} and decreases thereafter (200-1000 mg L^{-1}). Similarly removal of cyanide increases initially and decreases later, on increasing initial concentration from 40 mg L^{-1}. The initial increase in percentage removal of both phenol and cyanide could be attributed to increased driving force due to increased concentration gradient [23]. However as active adsorption sites are occupied by the adsorbate percentage removal starts to decrease indicating less favourable sites in adsorption [24].

3. Adsorption Isotherms

The nature of interaction between adsorbate and adsorbent at the time of equilibrium could be determined by the correlation of experimental data with equilibrium isotherms. Various single component isotherms like Langmuir, Freundlich, Toth, Redlich-Peterson, Radke-Prausnitz, Temkin and Fritz-schlunder models have been described earlier and
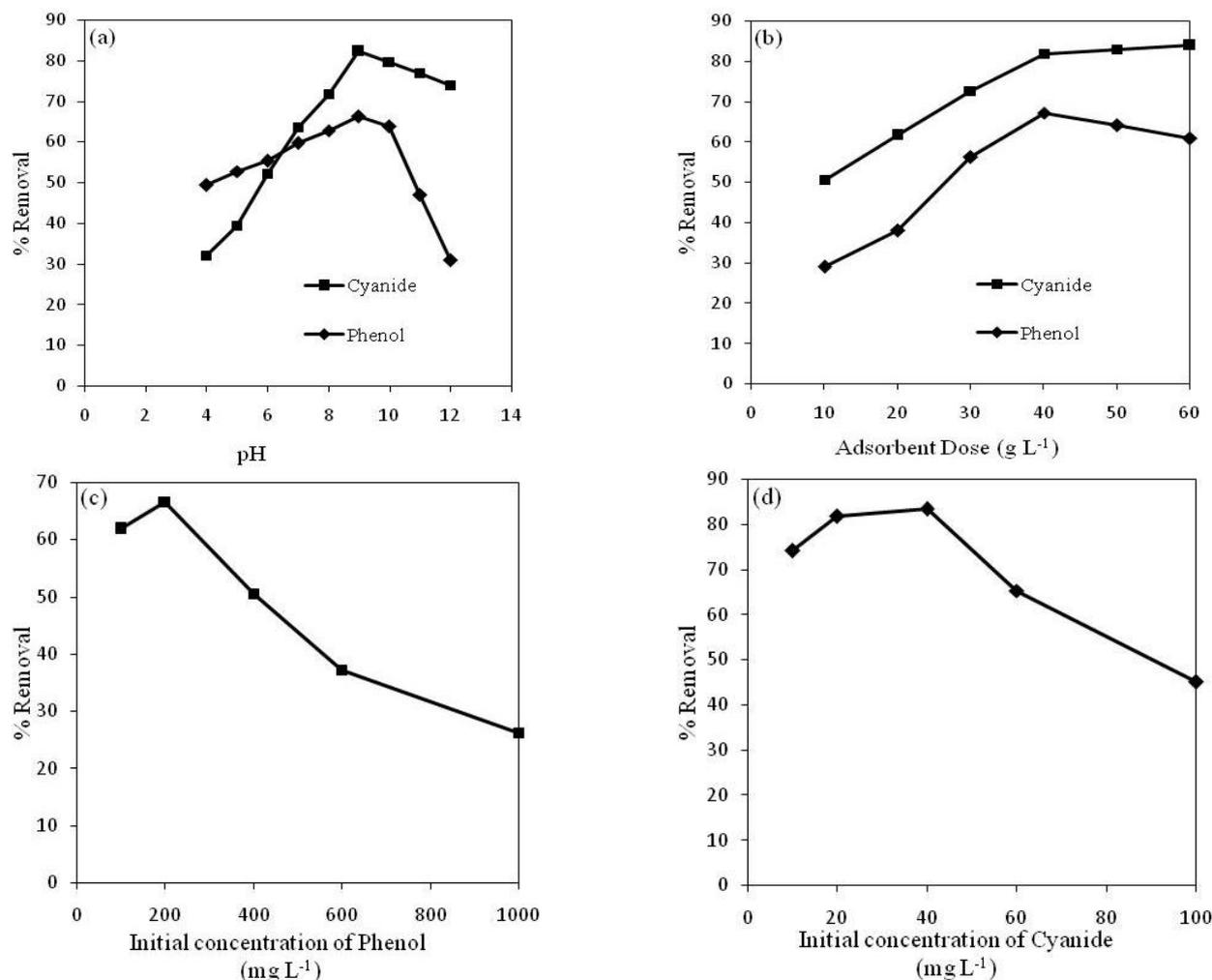
Fig. 3. Effect of parameters on percentage removal of phenol and cyanide (a) pH, (b) adsorbent dose, (c) initial phenol concentration, (d) initial cyanide concentration.

successfully applied. However multicomponent systems, like in the present study, seldom fit into these models. This deviation could be accounted by the presence of other pollutants which may either interact with adsorbate of interest or compete for same binding sites of adsorbent. Due to these limitations, amount of component adsorbed may increase, decrease or remain unaltered in the presence of other component(s). A number of variants have been proposed to correlate multicomponent adsorption. In the present study two single component and six multicomponent isotherms has been used to evaluate adsorbent-adsorbate interactions and nature of adsorption and are described below (Table 1).

The Marquardt's percent standard deviation (MPSD) was used to validate the equilibrium adsorption data along with coefficient of correlation (R^2) according to Eq. 2:

$$MPSD = 100\sqrt{\frac{\sum_{i=1}^{n}(\frac{q_{e,i}^{exp} - q_{e,i}^{cal}}{q_{e,i}^{exp}})^2}{N-P}} \qquad (2)$$

The smaller MPSD values indicate more accurate estimation of q_e value [30].

3.1. Single component isotherms

The adsorptive equilibrium data from batch studies were analyzed using Microsoft Excel 2010. Single component isotherm modeling was carried out for the estimation of parameters for multicomponent adsorption studies. Table 2 summarizes the values of parameters, coefficient of regression and MPSD obtained by the application of single component models along with data from the literature for comparison. From the table it is evident that Langmuir isotherms predict the specific uptake of phenol and cyanide better than Freundlich isotherm on the account of lower MPSD suggesting monolayer adsorption.

3.2. Multi-component modeling

Table 3 summarizes equilibrium parameters of multi-component isotherms of adsorption of phenol and cyanide onto coal fly ash. It could be clearly seen

Table 1. Equations and parameters of single- and multi-component isotherms used in present study

	Model	Equation	Parameters	Reference
Single component	Langmuir	$q_e = \dfrac{Q_0 b C_e}{1 + b C_e}$	Q_0, b	[25]
	Freundlich	$q_e = K_F C_e^{1/n}$	K_F, n	[25]
Multi component	Non- modified competitive Langmuir	$q_{e,i} = \dfrac{Q_{0,i} b_i C_{e,i}}{1 + \sum_{j=1}^{N} b_j C_{e,j}}$	$Q_{0,i}$, b_i	[26]
	Modified competitive Langmuir	$q_{e,i} = \dfrac{Q_{0,i} b_i \left(\dfrac{C_{e,i}}{n_i}\right)}{1 + \sum_{j=1}^{N} b_j \left(\dfrac{C_{e,j}}{n_j}\right)}$	$Q_{0,i}$, b_i, n_i	[27]
	Extended Langmuir	$q_{e,i} = \dfrac{Q_{0,i} b_i C_{e,i}}{1 + \sum_{j=1}^{N} b_j C_{e,j}}$	Q_0, b_i	[28]
	Extended Freundlich	$q_{e,1} = \dfrac{K_{F,1} C_{e,1}^{1/n_1 + x_1}}{C_{e,1}^{x_1} + y_1 C_{e,2}^{z_1}}$ $q_{e,2} = \dfrac{K_{F,2} C_{e,2}^{1/n_2 + x_2}}{C_{e,2}^{x_2} + y_2 C_{e,1}^{z_2}}$	$K_{F,1}$, $K_{F,2}$, n_1, n_2, x_1, x_2, y_1, y_2, z_1, z_2	[29]

Table 2. Estimated parameters of single component isotherms and data from literature for comparison

Reference	Adsorbate/ Adsorbent	Langmuir			Freundlich			Best Fit Model
		Q_0	b	MPSD	K_F	n	MPSD	
This study	Phenol/Fly ash	7.4	0.02	8	0.75	2.86	20	Langmuir
This study	Cyanide/Fly ash	2.4	0.05	35	0.15	1.5	41	Langmuir
[11]	Phenol/Fly ash	16	0.14	-	1.06	2.25	-	Langmuir
[12]	Phenol/Flyash	143	0.02	-	-	-	-	Langmuir
[5]	Phenol/Fly ash	20	0.26	-	-	-	-	-

from the table that the best fit was obtained by application of extended Langmuir for adsorption of phenol and extended Freundlich for cyanide adsorption. The adsorption of phenol followed the increasing trend of best fit models as: Non-modified Langmuir < Modified Langmuir < Extended Freundlich < Extended Langmuir whereas adsorption of cyanide followed: Non-modified Langmuir < Modified Langmuir < Extended Langmuir < Extended Freundlich trend.

From the data of Langmuir isotherm a parameter called separation factor, R_L, which describes the feasibility of adsorption process could be evaluated. R_L is calculated according to the Eq. 3:

$$R_L = \frac{1}{1 + b C_0} \qquad (3)$$

According to Hall et al. [31], if $R_L > 1$: it is unfavourable process; $R_L = 1$: linear adsorption; $0 < R_L < 1$: favourable adsorption; and $R_L = 0$: irreversible adsorption.

The values of R_L for all the concentrations of phenol and cyanide lies between 0 and 1 (data not shown) indicating adsorption of phenol and cyanide on fly ash is a favourable process. However a decrease in the value of R_L with the increase in initial concentration for both phenol and cyanide indicated favourable adsorption of phenol and cyanide at higher initial concentrations [32].

Presence of two or more than two components in aqueous systems may have three types of effects: synergism (the effect of the mixture is greater than that of each of the individual effects of the constituents in the mixture), antagonism (the effect of the mixture is less than that of each of the individual effects of the constituents in the mixture) and non-interaction (the effect of the mixture is neither more nor less than that of each of the individual effects of the constituents in the mixture) [33]. To study the effect of interaction of two adsorbates the ratio of adsorption capacity of one adsorbate (Q_{mix} or $K_{F,mix}$) in the mixture to that of the same adsorbate when present

Table 3. Calculated equilibrium parameters of multi-component isotherms

Isotherm model	Parameter	Phenol	Cyanide
Non-Modified Langmuir	MPSD	56	53
Modified Langmuir	n_j	0.78	1.02
	MPSD	49	44
Extended Langmuir	$Q_{o,i}$	248	1.2
	b_i	$9.4*10^{-4}$	0.4
	MPSD	15	26
Extended Freundlich	x_i	-3.6	0.3
	y_i	$5*10^{-7}$	4.0
	z_i	-3.1	-0.6
	MPSD	15	14

alone (Q_0 or K_F) was calculated and analysed according to following conditions [18]: $Q_{mix}/Q_0 > 1$, synergism; $Q_{mix}/Q_0 = 0$, non-interaction; and $Q_{mix}/Q_0 < 1$, antagonism.

In the present study the ratio of Q_{mix}/Q_0 for phenol and cyanide was calculated as 33 and 0.2 hence establishing the fact that phenol shows synergism, i.e., presence of phenol in the mixture containing cyanide increases the adsorption of cyanide while cyanide shows antagonism, i.e., presence of cyanide in the mixture containing phenol decreases the adsorption of phenol.

4. Kinetic Studies

Percentage removal profile of phenol and cyanide with time was assessed to evaluate the time needed to attain equilibrium and to determine the nature of sorption of phenol and cyanide onto fly ash. Table 4 summarizes linearized forms of various kinetic models used for the purpose along with associated parameters.

To evaluate the goodness of fit of kinetic experimental data, the statistical indice, Average Relative Error (ARE) between the experimental and calculated values was used [37]. The equation for evaluating ARE is given by Eq. 4:

$$ARE(\%) = \sqrt{\frac{100 \times \Sigma_{i=1}^{N}\left(\frac{q_{e,i}^{exp}-q_{e,i}^{cal}}{q_{e,i}^{exp}}\right)^2}{N}} \qquad (4)$$

Results of kinetic modeling of adsorption of phenol and cyanide onto fly ash are depicted in Figs. 4 and 5 and summarized in Table 5. Higher value of R^2 and lower value of ARE of pseudo second order model indicate that the adsorption of phenol and cyanide onto fly ash takes place through chemisorptions [38]. The results are in compliance with the data from literature [12].

Figure 6 depicts the plot of q_t vs $t^{0.5}$ and as could be seen that the graph contains two distinct linear regions. The results are indicative of initial pore diffusion, which could be a result of external mass transfer effects, followed by intraparticle diffusion of phenol and cyanide. Thus pore diffusion is not the only rate limiting factor in the adsorption of phenol and cyanide onto fly ash. The importance of intraparticle diffusion as a rate controlling agent is also reinforced from the fact that the plot does not pass through the origin [38]. Further, a better fit of data in first region ($R_1^2 > R_2^2$ from Table 5) indicates the dominance of surface diffusion in case of cyanide adsorption while rate limiting step in phenol adsorption is intraparticle diffusion ($R_1^2 < R_2^2$) [39].

5. Thermodynamic Studies

Linearized Van't Hoff equation in the following form (Eqs. 5 and 6), was used to calculate the thermodynamic parameters such as Gibbs's free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) during the process [40].

$$log\, K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \qquad (5)$$

$$\Delta G^0 = -RT\, log\, K_c \qquad (6)$$

The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept respectively from the plot of log K_c vs. 1/T for both phenol and cyanide and used for calculation of value of ΔG^0 according to Eq. 5. The results are summarized in Table 6. Negative values of ΔG^0, ΔH^0 and ΔS^0 for phenol adsorption are indicative of feasible, exothermic and spontaneous nature of the process [41] along with free diffusion of adsorbate molecules through bulk phase [42]. However cyanide adsorption onto fly ash is found to be endothermic process with increased randomness at
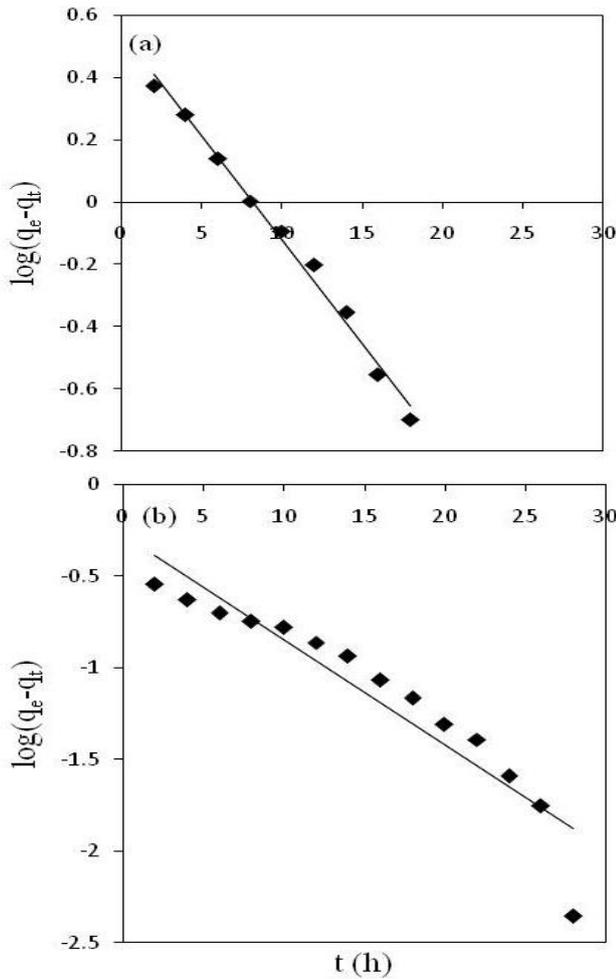
Table 4. Kinetic models used in the present study

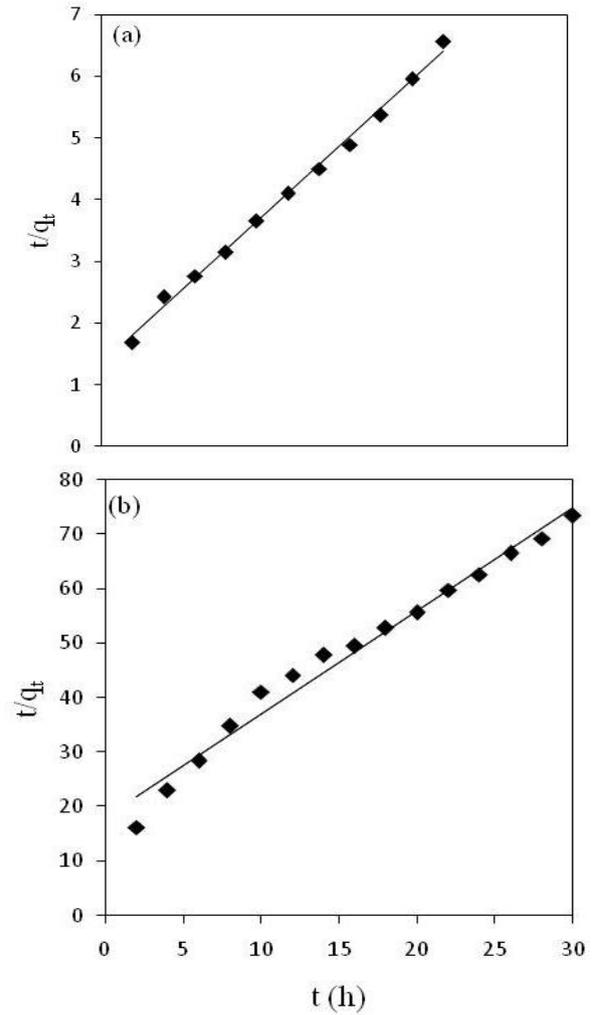| Kinetic Model	Equation	Linearized form	Parameters	References
Pseudo first order	$q_t = q_e(1 - e^{-k_1 t})$	$log\, (q_e - q_t) = log\, q_e - \frac{k_1 t}{2.303}$	q_e, k_1	[34]
Pseudo second order	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t$	q_e, k_2	[35]
Intraparticle	$q_t = k_{id} * t^{0.5}$	$q_t = k_{id} t^{0.5}$	k_{id}	[36]

Fig. 4. Pseudo first order plot of (a) Phenol adsorption onto acid treated fly ash and (b) Cyanide adsorption onto acid treated fly ash.

Table 5. Parameters of kinetic and intraparticle modeling of adsorption of phenol and cyanide on GAC

Component		Phenol	Cyanide
$q_{e,exp}$		3.6	0.4
Pseudo First	$q_{e,cal}$	3.5	0.5
Order	k_1	0.15	0.13
	R^2	0.99	0.89
	ARE	2.7	11
Pseudo Second	$q_{e,cal}$	4.4	0.5
Order	k_2	0.04	0.20
	R^2	0.99	0.98
	ARE	1.0	3.3
Intraparticle	k_{id1}	0.29	0.03
	R^2_1	0.97	0.99
	k_{id2}	3.3	0.4
	R^2_2	0.99	0.95
	ARE	2.4	1.3

Fig. 5. Pseudo second order plot of (a) Phenol adsorption onto acid treated fly ash and (b) Cyanide adsorption onto acid treated fly ash

the surface of solute-solution interface during adsorption as indicated by positive values of ΔH^0 and ΔS^0. Further the value of ΔS^0 (which is less than 1) indicates that the process is highly reversible for both phenol and cyanide [40].

CONCLUSIONS

The process of simultaneous adsorption of phenol and cyanide from simulated coke wastewater onto acid treated coal fly ash was optimized at various temperature, pH, adsorbent dose and initial concentration. Maximum removal of phenol (67%) and cyanide (82%) was achieved at a temperature of 30 ℃, pH of 9 and adsorbent dose of 40 g L^{-1} at initial concentration of 200 mg L^{-1} phenol and 20 mg L^{-1} cyanide. The process of equilibrium for phenol and cyanide was attained at 20 and 30 h respectively. Application of both single-component and multi-component isotherms to the experimental data revealed better fit of the latter as extended Langmuir
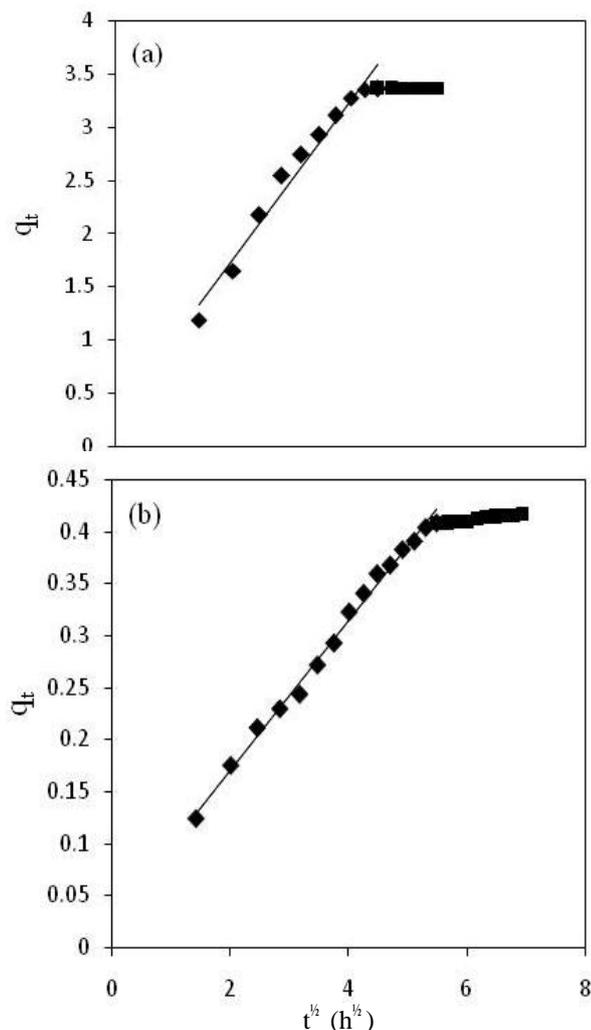
Fig. 6. Intraparticle plot of (a) Phenol adsorption onto acid treated fly ash and (b) Cyanide adsorption onto acid treated fly ash.

and extended Freundlich respectively depicted adsorption of phenol and cyanide with chemisorption to be the mechanism of adsorption. The presence of phenol showed synergism towards cyanide adsorption while presence of cyanide resulted in decrease in phenol adsorption in the mixture. Application of thermodynamics indicated exothermic adsorption of phenol and endothermic adsorption of cyanide onto fly ash. Thus simultaneous adsorption of phenol and cyanide onto fly ash is a favorable process with high capacity of fly ash as an adsorbent. The results of present study indicate that the process could be carried out in continuous mode with real waste water from coke industry for the removal of phenol and cyanide quite efficiently.

ACKNOWLEDGEMENTS

NOMENCLATURE

q: Specific uptake capacity of adsorbent (mg g^{-1} of adsorbent)

C_0: Initial pollutant concentration (mg L^{-1})

C_t: Pollutant concentration at time t (mg L^{-1})

V: Volume of the solution (L)

M: Mass of the adsorbent used (g)

K_C: Equilibrium constant (amount of adsorbate on adsorbent/ amount of adsorbate in solution)

R: Gas constant = 8.314 J mol^{-1} K^{-1}

ΔG^0: Change in Gibb's free energy (kJ mol^{-1})

T: temperature (°K)

ΔS^0: Change in entropy (kJ mol^{-1} K^{-1})

ΔH^0: Change in enthalpy (kJ mol^{-1})

$q_{e,i}^{exp}$: Experimental specific uptake (mg g^{-1})

$q_{e,i}^{cal}$: Calculated specific uptake (mg g^{-1})

N: Number of observations in the experimental isotherm

p: Number of parameters in the regression model

ARE: Average Relative Error

R_L: Separation factor

Q_{mix}: Adsorption capacity of one adsorbate in mixture

Q_0: Adsorption capacity of one adsorbate when present alone

K_F: Constant in Freundlich model (mg g^{-1} (mg^{-1} L)$^{-1/n}$)

n: Constant in Freundlich model

$Q_{0,i}$: Constant in modified Langmuir model for ith component (mg g^{-1})

$C_{e,i}$: Concentration of ith component in the binary mixture at equilibrium (mg L^{-1})

b_i: Constant of ith component in Langmuir model (L mg^{-1})

$K_{F,i}$: Constant in extended Freundlich constant for ith component (mg g^{-1})(mg^{-1} L)$^{-1/n}$

k: Rate constant of Pseudo first order Kinetic models (h^{-1})

k_2: Rate constant of Pseudo second order Kinetic model (mg g^{-1} h^{-1})

C_i: Intraparticle diffusion coefficient (mg g^{-1})

k_{id}: Intraparticle diffusion rate constant (mg g^{-1} h$^{-0.5}$)

x_i, y_i, z_i: Constant in extended Freundlich model for ith component

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