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Equilibrium, Kinetic and Thermodynamic Studies for Adsorption of Phenol on Modified Coal Fly Ash (MCFA)

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ABSTRACT

Modified coal fly ash (MCFA) is prepared from coal fly ash (CFA) by hydrothermal treatment with alkali. This MCFA is used to remove the phenol from wastewater. The effect of adsorption process variables such as adsorbent dosage, contact time, phenol concentration, pH and temperature has been investigated. The suitability of Freundlich and Langmuir adsorption models to the equilibrium data was found for phenol-MCFA system. The adsorption kinetics and thermodynamics also performed for the phenol removal. The results showed that the percentage removal of phenol increased and adsorption rate was decreased as adsorbent dosage is increased. Equilibrium time required for the adsorption of phenol on MCFA was almost 90 minutes. As initial phenol concentration increases, it resulted in increased phenol uptake. The uptake of phenol by MCFA was almost constant in the pH range of 2.0-6.0. Then the adsorption decreased with increasing pH. Adsorption capacity of MCFA increased with increasing temperature which indicates that the adsorption process was endothermic. The optimum temperature of MCFA was found to be 40 °C within the temperature range studied. Good fit was observed by both Freundlich and Langmuir models. Pseudo-second-order kinetic model gives the good correlation for the adsorption of phenol onto MCFA amongst the model studied. Gibbs free energy (ΔG) values found negative indicating the adsorption process is spontaneous and favorable for phenol-MCFA system. The positive value of ΔH (21508.318 kJ/mol) and ΔS (121.30126 kJ/mol) denotes that the process is endothermic and aided by increased randomness for phenol. The studies showed that MCFA can be used as an efficient adsorbent material for removal of phenol from wastewater.

1. Introduction

As many coal firing power plants generation started in 1920s, many millions of tons of the ash and related by-products have been created [1]. Coal fly ash (CFA) is the waste product of combustion of coal in coal-fired power plants. The global annual production of CFA is about 800 million tons and this amount is predicted to increase in the future (Williams L., 2008) as quoted by [2]. However, the global recycling rate of CFA is only 15% posing important challenges for researchers in waste management. At present, efficient disposal of CFA is a worldwide issue because of its massive production and its harmful effects on the environment [3]. Resource recovery from CFA can be one of the approaches to speed up reuse of CFA, since the major chemical compositions contained in CFA are SiO_2 and Al_2O_3 (60-70 wt% and 16-20 wt%, respectively) [1]. Other than resource recovery, modification of CFA in to MCFA which is used as an adsorbent in this study is one of the approaches to reuse CFA.

At present nearly 170 million tons of fly ash is being generated annually in India and more than 70000 acres of land is presently occupied by ash ponds as per the report of Fly Ash Association of India (faai). Several approaches have been made for proper utilization of fly ash, either to reduce the cost of disposal or to minimize the environmental impact. One of the approaches is the conversion of fly ash to zeolites, which have wide applications in ion exchange, as molecular sieves, catalysts and adsorbents.

Many researchers are worked on synthesis of zeolites and modification of different fly ash for different applications. Khadse Shaila, Dawle Nisha, Patil Pralhad and Panhekar Deepa [4] has synthesized zeolite from coal fly ash by alkali fusion method and used it for removal of Cu^{2+}, Ni^{2+} and Mn^{2+} from paper industry effluent. K.S. Hui et al. [2] also produced nano porous material zeolite-A from coal fly ash and studied their applications in environmental protection. Ashu Rani et al. [5] done the surface modification of fly ash by thermal activation and studied DR/FTIR of modified fly ash. Guyo et al. [6] synthesized and characterised zeolites made from coal fly ash. Denis Fungaro et al. [7] also synthesized and characterised zeolitic material derived from sugarcane straw ash.

Phenolic wastewater is a serious environmental problem and this water cannot release into the environment without treatment [8]. The toxic and hazardous nature of phenols and their derivatives have been well documented [9]. Phenolic compounds have been classified as high-priority pollutants by the USA, EPA, 1984 [10]. Phenolic wastewater are generated from the plastic, pharmaceutical, petrochemical, paint, paper and pulp, solvent, coal conversion industries. They are known one of the priority pollutants in wastewater, because they are harmful to organisms even at low concentrations. Many phenols have been classified as hazardous pollutants. Human consumption of phenol contaminant water can result in death. It gives bad taste and odour if it is present in the water supply [11]. Presence of chlorine in drinking water results in formation of chlorophenol, which has a medicinal taste and which is quite pronounced and objectionable. Therefore, Environmental Protection Agency regulations call for lowering phenol content in wastewater to less than 1 mg/L [11].

There are many methods, such as adsorption, microbial degradation, chemical oxidation, precipitation, ion exchange and solvent extraction to remove phenols from waste water. Adsorption is an effective separation process for treating industrial and domestic effluents. Activated carbon is the most widely used adsorbent. It has the advantage of high adsorption capacity for organic compounds, but its use is usually limited due to its high cost [11], hence there is a need for alternate adsorbents which are easily available having low cost.

The aim of this research work is to use MCFA as an adsorbent for the removal of phenol from wastewater by batch adsorption to find the effect of adsorption process variables such as adsorbent dosage, contact time, phenol concentration, pH and temperature. Freundlich and Langmuir models are studied to find which model is best fitted to experimental data.

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The adsorption kinetics and thermodynamics also performed to estimate the rate of adsorption and feasibility of phenol-MCFA adsorption system respectively.

2. Experimental Methods

2.1 Materials

The material used for this research work includes:

(i) Adsorbate: Phenol
(ii) Medium: Aqueous
(iii) Adsorbent: Modified Coal Fly Ash (MCFA)

2.1.1 Adsorbate

The composition of the synthetically prepared aqueous solutions used in this study was similar to that generated by the petrochemical and coal conversion, phenol producing industries. The stock solution was prepared by diluting the required quantities of phenol (AR grade) supplied by S.D. Fine Chemicals, in the same volume of distilled water to obtain adsorbate solutions of various initial concentrations (C_o). Fresh solutions were prepared on a daily basis with the initial concentration of the adsorbate calculated before the start of any experiment. The pH value for the aqueous solution containing the mixture of phenol was adjusted with dil. HCl and dil. NaOH solutions for the adsorption experiments. All the pH measurements were done with a pH meter.

2.1.2 Adsorbent

MCFA was synthesized by hydrothermal alkali treatment method. The fly ash used for preparation of MCFA was a low grade coal fly ash obtained from Paras Thermal Power Station at Paras village in Akola district of Maharashtra State, India. The CFA collected is washed with distilled water for three to four times to remove the contaminants present in it if any. The washed CFA then dried for two days in sunlight. This dried CFA then screened in sieve shaker having different size sieves like 75, 90, 150, 300, 600 microns and pan and separated into different screen sizes. Then the CFA of below 75 micron size has been taken for the development of MCFA. MCFA was prepared form CFA by taking 100 grams of screened CFA having 75 micron size which then treated with 1000 mL of 5 N NaOH solution in a beaker. This solution was kept for crystallization for 48 hours with continuous stirring at 80 °C. After crystallization, the product was washed with distilled water several times to remove the content of the NaOH. The washed product was dried to remove the moisture present in it. Drying is done at 300 °C for one hour. This dried product is stored in the air tight polyethylene bags for further experimentations.

2.2 Effect of Adsorbent Dosage

The effect of modified coal fly ash (MCFA) for removal of phenol was obtained by contacting 50 mL of solution having 70 mg/L phenol concentration with different amount (0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.6 g) of MCFA in stopper conical flask using Remi shaker at room temperature (30 ± 1 °C). Each sample was then agitated for four hours at a constant speed of 200 strokes/min. The sample was then filtered and the left out concentration in the filtrate solution were analyzed by UV spectrophotometer.

2.3 Effect of Contact Time

The effect of contact time study for removal of phenol is done over the time span of 0 to 240 minutes. In this study 50 mL of solution having 70 mg/L phenol concentration was taken in stopper conical flasks and numbered them from 1 to 12 and all twelve conical flasks was agitated with 1.0 g of MCFA using Remi shaker at room temperature (30 ± 1 °C). Initially after every ten minutes the sample was analyzed for phenol concentration for one hour from the conical flask number 1 to 6 and then after the sample was analyzed after every thirty minutes from the conical flask number 7 to 12 for phenol concentration by UV spectrophotometer.

2.4 Effect of Initial Phenol Concentration

The effect of initial phenol concentration on adsorption rate was studied under optimum conditions. The experiments was performed by taking 50 mL of phenol solution of varying concentration from 20 to 70 mg/L in stopper conical flask and was agitated with 1.0 g of MCFA for 240 minutes using Remi shaker at room temperature (30 ± 1 °C) . The sample was then filtered and the left out concentration in the filtrate solution were analyzed by UV spectrophotometer.

2.5 Effect of pH

The pH effect study was done in between the pH range of 2 to 9. In this study 50 mL of solution having 70 mg/L phenol concentration was taken in stopper conical flask and was agitated with 1.0 g of MCFA at room temperature (30 ± 1 °C). Agitation was made for 240 minutes at a constant speed of 200 strokes/min. The sample was then filtered and the left out concentration in the filtrate solution were analyzed using UV-spectrophotometer for the % phenol removal.

2.6 Effect of Temperature

The effect of temperature on adsorption of phenol on MCFA has been studied at different temperatures which are 30, 40 and 50 °C. In this study 50 mL of solution having 70 mg/L phenol concentration was taken in three different stopper conical flasks. Then these conical flasks were agitated with 1.0 g of MCFA at given temperature for 240 minutes. After completion of experiment the sample was analyzed for phenol concentration by UV spectrophotometer and calculation of % removal and adsorption capacity has been done.

2.7 Adsorption Equilibrium

Equilibrium studies were carried out by contacting 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6 grams of MCFA with 50 mL of solution having 70 mg/L phenol concentration in stopper conical flasks separately. The samples were then shaken at a constant speed of 200 strokes/min for 240 minutes. After equilibrium the concentrations in the samples were analyzed by UV spectrophotometer.

3. Results and Discussion

3.1 Effect of Adsorbent Dosage

Figs. 1 and 2 shows the effect of adsorbent dosage on adsorption rate (mg/g) and % removal of phenol versus adsorbent dosage. As shown in Figs. 1 and 2, adsorption rate was decreased and percentage removal of phenol increased as the amount of adsorbent dosage is increased. This is because of the increased surface area of the adsorbents and availability of more adsorption sites due to increased adsorbent dosage. A similar result was observed for the phenol adsorption on sodium zeolite [12, 13]. Hiren Patel et al. [14] also found the similar results for o-chlorophenol on surface modified microwave treated zeolite from coal fly ash (SMZCFA).

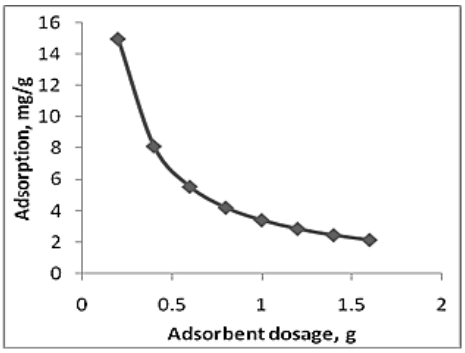

Fig. 1 Effect of adsorbent dosage on the adsorption of phenol on MCFA

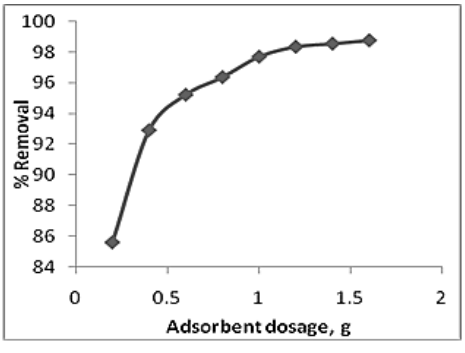

Fig. 2 Effect of adsorbent dosage on % removal of phenol on MCFA

3.2 Effect of Contact Time

The amount of phenol adsorbed versus contact time at initial concentrations of 70 mg/L is presented in Fig. 3. The results showed that the time required for reaching the equilibrium for the adsorption of phenol on MCFA was almost 90 minutes. This result also indicated that increased amount of phenol uptake was found to occur in the first rapid phase (30 min) and after that the rate of adsorption was found to slowdown. The higher adsorption rate at the initial period (first 30 min) is due to an increased number of vacant sites on the adsorbent available at the initial stage, due to which, increased concentration difference between adsorbate in solution and adsorbate on adsorbent surface has been occur. This increased in concentration difference tends to increase in phenol adsorption rate at the initial stages. As time precedes this concentration difference is reduced due to the accumulation of phenol particles in the vacant sites of the adsorbents which results in slowdown of adsorption rate at the later stages from 30 to 240 min. [13-15] also found the similar results for increased amount of phenol uptake of initial 60, 80 and 60 minutes respectively.

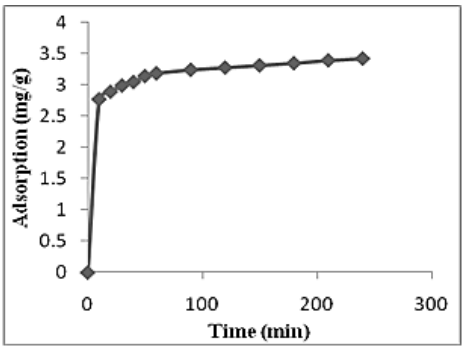

Fig. 3 Effect of contact time for the adsorption

3.3 Effect of Initial Phenol Concentration

The effect of initial phenol concentration is presented in Fig. 4. It was seen that an increase in initial phenol concentration resulted in increased phenol removal. A similar result was observed for the phenol adsorption on sodium zeolite [13-15].

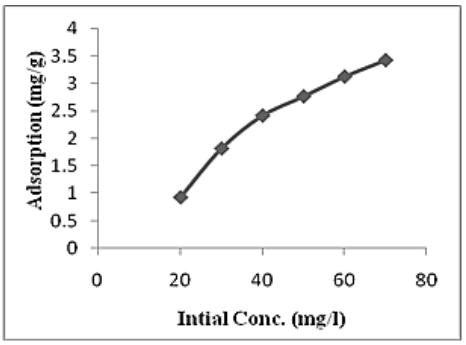

Fig. 4 Effect of initial phenol concentration

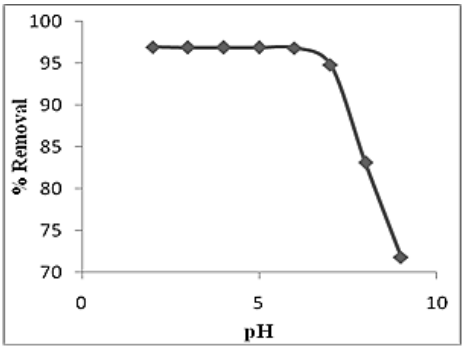

Fig. 5 Effect of pH

3.4 Effect of pH

The pH of a solution is one of the most important parameter which affects the adsorption process. Fig. 5 shows the effect of pH on the adsorption of phenol. From Fig. 5, it was observed that the removal of phenol by MCFA was almost constant in the pH range of 2.0-6.0. Then the adsorption decreased with increasing pH and it decreased from 96.86% at pH 6 to 71.82% at pH 9. A similar trend for pH effect was observed for the phenol adsorption on sodium zeolite [12, 15]. Rayalu et al. [16] found that, the rate of adsorption of phenol was maximum at neutral pH for surface altered fly ash based molecular sieves.

3.5 Effect of Temperature

The effect of temperature on adsorption of phenol onto MCFA is presented in Fig. 6. Adsorption capacity of MCFA increases with increase in temperature from 30 to 50 °C which indicates that the adsorption process was endothermic. The sorption capacity of MCFA was determined as 3.419, 3.421 and 3.424 mg/g at 30, 40 and 50 °C respectively.

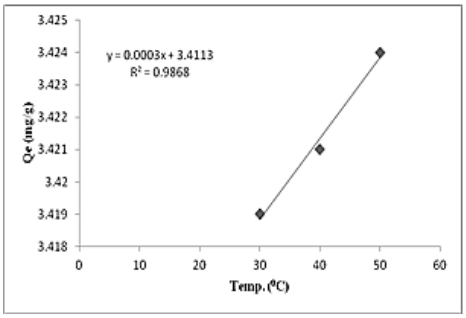

Fig. 6 Effect of temperature on the adsorption of phenol

3.6 Adsorption Equilibrium

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. Equilibrium data can be analyzed using commonly known adsorption isotherms, which provide the basis for the design of adsorption systems. The most widely used isotherm equation for modeling of the adsorption data is the Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number identical site and is given by Eq. (1),

$$q_e = q_o K_L C_e / (1 + K_L C_e) \quad (1)$$

where q_o and K_L are Langmuir parameters related to maximum adsorption capacity and free energy of adsorption, respectively. C_e is the equilibrium concentration in the aqueous solution and q_e is the equilibrium adsorption capacity of adsorbent.

The linearized form of Langmuir equation can be written as given by Eq. (2),

$$1/q_e = 1/q_o + (1/q_o K_L)(1/C_e) \quad (2)$$

The Langmuir constant q_o and K_L can be calculated by plotting $1/q_e$ versus $1/C_e$. The Langmuir adsorption isotherm is based on the concept that solid surface have finite adsorption sites. When all the adsorption sites are filled, the surface will no longer be able to adsorb solute from the solution. The maximum amount of solute (q_0) adsorbed in a particular system can be estimated from the isothermal parameters. The plot of $1/q_e$ vs. $1/C_e$ should yield a straight line. The slope is $1/q_o K_L$ and the intercept is $1/q_o$.

The influence of isotherm shape on 'favorable or unfavorable' adsorption, on the basis of feasibility criteria, has been described by [17]. For a Langmuir type adsorption model the isotherm can be classified by a term 'R_L', a dimensionless constant separation factor defined as:

$$R_L = 1/(1+K_L C_0) \quad (3)$$

where, K_L is the Langmuir constant and C_0 is the initial solute concentration. The parameter 'R_L' indicates the shape of the isotherm accordingly.

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

In present work the value of R_L is found 0.078, 0.103 and 0.130 for the temperature 30, 40 and 50 °C respectively, which shows that the favorable condition for the adsorption.

The Freundlich model is an empirical equation based on sorption on heterogeneous surface. It is given by Eq. (4),

$$q_e = K_f C_e^{1/n} \quad (4)$$

where K_f and n are the Freundlich constants that indicate adsorption capacity and adsorption intensity, respectively.

The linearized form of Freundlich isotherm can be written as Eq. (5),

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (5)$$

The value of K_f and n can be calculated by plotting $\ln q_e$ versus $\ln C_e$. The Freundlich isotherm predicts that the adsorbate concentration on the surface of an adsorbent will increase when there is an increase in the initial concentration of adsorbate in the aqueous solution. The experimental data obtained are plotted as $\ln q_e$ versus $\ln C_e$, to obtain the constant K_f and 1/n. The constant K_f is a comparative measure of the adsorption capacity of the adsorbent, while *n* is an empirical constant. The magnitude of *n* gives an indication of the favorability of adsorbent/adsorbate system. Values of $n > 1$ signify that the solute has a low affinity for the adsorbent at low concentrations. Likewise, a value of $n < 1$ is an indication of favorable adsorption and a high affinity between the solute and the solid phase.

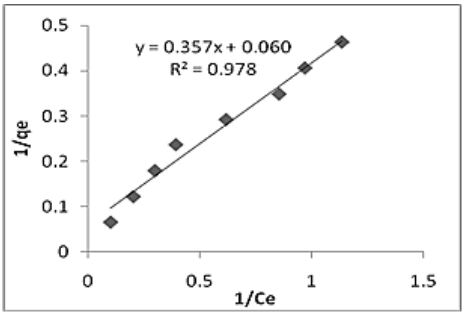

Fig. 7 Langmuir isotherm at 30 °C

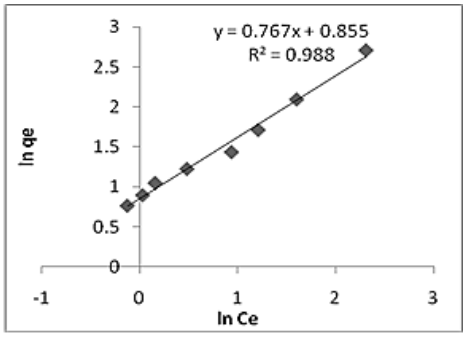

Fig. 8 Freundlich isotherm at 30 °C

Figs. 7 and 8 shows the Langmuir and Freundlich curves for phenol adsorption respectively at temperature 30 °C. From Figs. 7 and 8, it was observed that the equilibrium data are well represented by both the isotherms. The sorption equilibrium data fitted to Freundlich and Langmuir equations with correlation coefficients values of 0.988 and 0.978 respectively.

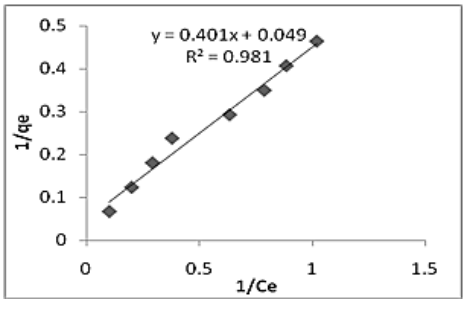

Fig. 9 Langmuir isotherm at 40 °C

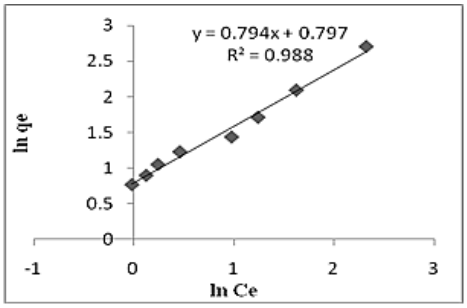

Fig. 10 Freundlich isotherm at 40 °C

Figs. 9 and 10 shows the Langmuir and Freundlich curves for phenol adsorption respectively at temperature 40 °C. From Figs. 9 and 10, it was observed that the equilibrium data were very well represented by both the equations. The sorption equilibrium data fitted to Freundlich and Langmuir equations with correlation coefficients values of 0.988 and 0.981 respectively.

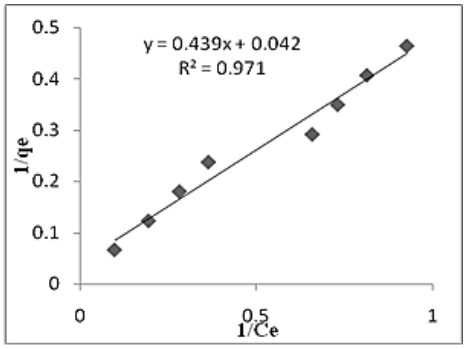

Fig. 11 Langmuir isotherm 50 °C

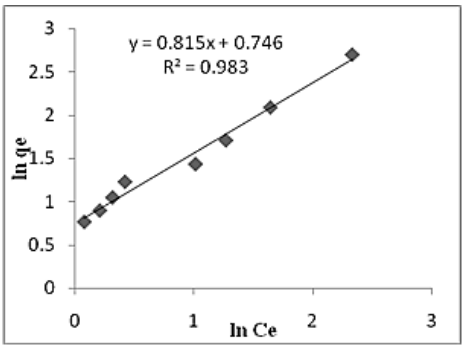

Fig. 12 Freundlich isotherm 50 °C

Figs. 11 and 12 shows the Langmuir and Freundlich curves for phenol adsorption respectively at temperature 50 °C. From Figs. 11 and 12, it was observed that the equilibrium data were very well represented by Langmuir equations. The sorption equilibrium data fitted to Freundlich and Langmuir equations with correlation coefficients values of 0.983 and 0.971 respectively.

The correlation coefficient values determined for each of the adsorption isotherms indicates that the both the models effectively fits the experimental data. The values of *n* are greater than 1 and the values of R_L are found to be in between 0 and 1 as Freundlich model signify that the solute has a low affinity for the adsorbent at low concentrations for the MCFA while Langmuir model signify the favorable conditions for the MCFA. Adsorption capacities from Langmuir isotherm models are found to be 16.667, 20.803 and 23.809 mg/g for the temperatures 30, 40 and 50 °C respectively which shows that as temperature increases, adsorption capacity also increases showing that the adsorption is an endothermic process. Hiren Patel et al. [14] found that R^2 value 0.9994 and adsorption capacity 39.92 mg/g for MZCFA for Langmuir isotherm. Saravanakumar et al. [12] found that the maximum adsorption capacity of 13.051 mg/L for natural zeolites from Langmuir isotherm. Dalang and Mohd Tuah [13] found that the adsorption of phenol on zeolite is better described by the Langmuir isotherm having R^2 value 0.993 and the adsorption capacity of 0.707 mg/g.

The Freundlich (K_f and 1/n) and Langmuir constants (q_o, K_L and R_L) determined from the adsorption isotherms for phenol shown in Figs. 7 to 12 are summarized in Table 1.

Table 1 Equilibrium constants for phenol onto MCFA

Temp. K	Freundlich isotherm parameters			Langmuir isotherm parameters			
	K_f (dm^3g^{-1})	n	R^2	q_o (mg/g)	K_L (dm^3mg^{-1})	R^2	$R_L = 1/(1+K_LC_0)$
303	2.3530	1.3024	0.988	16.666	0.1680	0.978	0.078
313	2.2190	1.2584	0.988	20.803	0.1240	0.981	0.103
323	2.1085	1.2265	0.983	23.809	0.0955	0.971	0.130

3.7 Adsorption Kinetics

In this work, kinetic models are used to examine the rate of the adsorption process and potential rate-controlling step. In the present work, the kinetic data obtained from batch studies have been analyzed by using pseudo-first-order Lagergren, pseudo-second-order rate equation, Elovich equations and intraparticle diffusion model.

The first order equation of Lagergren is generally expressed as follows [18],

$$dq / dt = k_1 (q_e - q_t) \quad (6)$$

Where q_e and q are the amounts of phenol adsorbed (mgg^{-1}) at equilibrium and at time t (min) respectively, and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}).

The integrated form of above equation becomes

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

A plot of ln (q_e –q) against t should give a linear relationship with the slop k_1 and intercept of ln q_e.

The pseudo-second-order kinetic rate equation is expressed as follows [18].

$$dq / dt = k_2 (q_e - q)^2 \quad (8)$$

where k_2 is the rate constant of pseudo-second-order sorption ($gmg^{-1}min^{-1}$).

The integrated form of above equation becomes

$$t / q = 1 / k_2 q_e^2 + (1 / q_e) t \quad (9)$$

If the second order kinetic equation is applicable, the plot of t/q against t of above equation should give a linear relationship. The q_e and k_2 can be determined from the slope and intercept of the plot.

Half adsorption time $t_{1/2}$, is defined as the time required for the adsorption to take up half as much modified coal fly ash as its equilibrium value. This time is often used as a measure of the adsorption rate.

$$t_{1/2} = 1 / k_2 q_e \quad (10)$$

The Elovich equation is given as follows [19],

$$dq_t/dt = \alpha \exp (-\beta q_t) \quad (11)$$

where α is the initial sorption rate (mg/g min) and β is the desorption constant (g/mg). To simplify the Elovich equation, it is assumed that α β t << 1 and by applying the boundary conditions $q_t = 0$ at t = 0, this equation becomes

$$q_t = \beta \ln(\alpha \beta) + \beta \ln t \quad (12)$$

Thus, the constants can be obtained from the slope and intercept of a straight line plot of q_t versus ln t.

The intraparticle diffusion equation [19], can be written by the following equation

$$q_t = k_i t^{1/2} + C \quad (13)$$

where C is the intercept and k_i is the intraparticle diffusion rate constant ($mgg^{-1}\ min^{-1/2}$) for the intraparticle diffusion model.

The plots for Lagergren-first-order kinetic is shown in Fig. 13 and Pseudo-second-order kinetic is shown in Fig. 14.

The pseudo first-order rate constant k_1, amount of phenol adsorbed at equilibrium, and correlation coefficient are shown in Table 2. The results showed that, the correlation coefficients obtained for initial concentrations C_0 was 0.964, which is comparatively low than pseudo second-order correlation coefficient and the experimental q_e did not agree with the calculated ones, obtained from the linear plots. Therefore, pseudo-first-order kinetic model did not fit the adsorption of phenol onto MCFA.

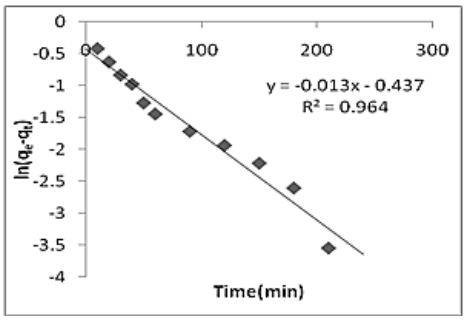

Fig. 13 Lagergren-first-order kinetic plot

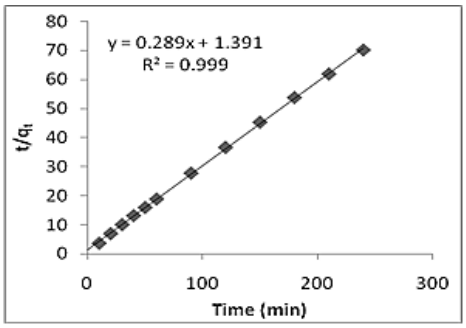

Fig. 14 Pseudo-second-order kinetic plot

Table 2 Pseudo-first order kinetic constants for the adsorption of phenol on MCFA

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	$k_1(min^{-1})$	R_1^2
70	3.419	1.5486	0.0134	0.964

The pseudo second-order rate constant k_2, amount of phenol adsorbed at equilibrium and correlation coefficient are shown in Table 3. From Table 3, it was found that the R_2^2 value is 0.9990 which is closer to 1 for initial phenol concentration. The calculated q_e is closer to the experimental value. So from these values it can be said that pseudo-second-order kinetic equation gives the good correlation for the adsorption of phenol onto MCFA. Similar results are found by [14, 15].

Table 3 Pseudo-second order kinetic constants for the adsorption of phenol on MCFA

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2(g/mg.min)	R_2^2
70	3.419	3.453	0.0603	0.999

The plots for Elovich equation is shown in Fig. 15 and Intraparticle diffusion is shown in Fig. 16.

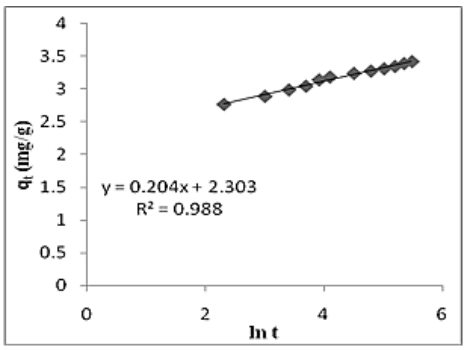

Fig. 15 Plot of Elovich equation

The Elovich equation, describes the chemisorptions on most heterogeneous adsorbents. The calculated values for Elovich equation are tabulated in Table 4. It was observed from Table 4 that Elovich equation gives a good account of adsorption of phenol with R^2 value of 0.9880.

Table 4 Elovich equation constants for the adsorption of phenol onto MCFA

C_0(mg/L)	$q_{e,exp}$ (mg/g)	α (mg/g min)	β (g/mg)	R^2
70	3.419	67.96	0.204	0.988

The plot for intra-particle diffusion (q_t versus $t^{1/2}$) was linear with R^2 value of 0.9226 as shown in Fig. 16, but the line did not pass through the origin which indicates the model did not fit the adsorption process [19]. Table 5 shows the calculated values for intraparticle diffusion equation.

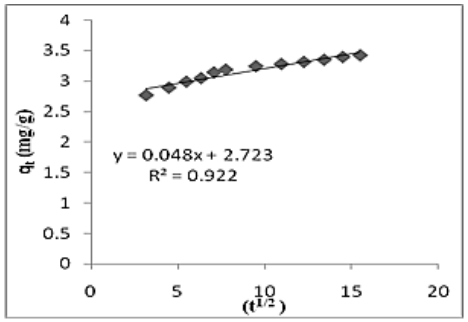

Fig. 16 Plot of Intraparticle diffusion

Table 5 Intraparticle diffusion equation constants for the adsorption of phenol on MCFA

C_0(mg/L)	$q_{e,exp}$ (mg/g)	K_i, (mgg^{-1} min$^{-1/2}$)	C	R^2
70	3.419	0.0482	2.723	0.922

3.8 Thermodynamic Study

Thermodynamics has been studied to know the feasibility of the process of adsorption of phenol on MCFA. The thermodynamic parameters like enthalpy change (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS) were determined from the adsorption data. The free energy change (ΔG) of the adsorption is calculated from equilibrium constants value (K_c) following the Eqs. (14) and (15) [20].

$$\Delta G = -RT \ln K_c \quad (14)$$

$$K_c = C_{Ae}/C_e \quad (15)$$

where C_{Ae} and C_e indicates the equilibrium solute concentration on the adsorbent and in the solution, respectively. The equilibrium constant values are calculated for the temperatures 303, 313 and 323 K. The change of enthalpy (ΔH) and entropy (ΔS) were calculated using the following Eq. (16) [20].

$$R \ln K_c = -\Delta H/T + \Delta S \quad (16)$$

By plotting R ln K_c against 1/T, it gives a straight line. ΔH and ΔS values can be obtained from the slope and intercept of the plot as shown in Fig. 17.

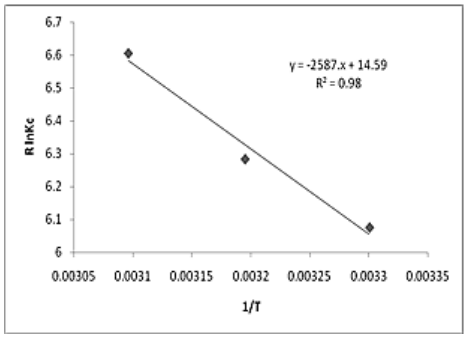

Fig. 17 Van't Hoff plot for phenol adsorption on MCFA

The calculated thermodynamics parameters are presented in Table 6.

Table 6 Thermodynamic parameters for phenol on MCFA

T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)	R^2
303	-1881			
313	-2010	21508	121	0.98
323	-2180			

As shown in Table 6, the negative value of ΔG at all temperature indicates that the adsorption process for phenol-MCFA system is favorable and spontaneous. The increased values of negative free energy change (ΔG) with increased temperature suggest that the process is favored at elevated temperature. The positive value of ΔH and ΔS denotes that the process is endothermic and aided by increased randomness for phenol. The endothermic nature of process was also indicated earlier in temperature effect study by the increased adsorption with temperature. Similar results are obtained by Sarkar et al. [20].

4. Conclusion

Hydrothermal treatment for synthesis of the MCFA found an economical as coal fly ash is available free of cost from thermal power plants. It was observed that the percentage removal of phenol increased from 85.62 at 0.2 g to 98.74 at 1.6 g and adsorption rate decreased from 14.985 mg/g at 0.2 g to 2.160 mg/g at 1.6 g. Equilibrium time required for the adsorption of phenol on MCFA was found almost 90 minutes and the maximum amount of phenol uptake was found to occur in the first rapid phase of 30 minutes and thereafter the sorption rate was found to slowdown. As initial concentration increases, it resulted in increased phenol uptake. The uptake of phenol by MCFA was almost constant in the pH range of 2.0-6.0 and it is decreased with increasing pH as from 96.86% at pH 6.0 to 71.82% at pH 9.0. The sorption capacity of MCFA was determined as 3.419, 3.421 and 3.424 mg/g at 30, 40 and 50 °C respectively. Adsorption capacity of MCFA increased with increasing temperature which indicates the adsorption process was endothermic. Equilibrium study shows that the correlation coefficient values determined for Freundlich and Langmuir isotherms as 0.988, 0.988, 0.983 and 0.978, 0.981, 0.971 at 30, 40 and 50 °C respectively, which indicates that Freundlich model, was better fitted to the experimental data. Adsorption capacities from Langmuir isotherm models are found to be 16.666, 20.803 and 23.809 mg/g for the temperatures 30, 40 and 50 °C respectively. Pseudo-second-order kinetic model gives the good correlation for the adsorption of phenol onto MCFA having R^2 value of 0.999. Gibbs free energy (ΔG) values found negative indicating the adsorption process is spontaneous and favorable for phenol-MCFA system. The positive value of ΔH (21508 kJ/mol) and ΔS (121 kJ/mol) denotes that the process is endothermic and aided by increased randomness for phenol.

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