Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20509

75 (2017) 45–57
May

Removal of pollutants of coking wastewater by adsorption

R.K. Choudhary, P.K. Chaudhari*

Department of Chemical Engineering, National Institute of Technology, Raipur, India, Tel. +91-771-2254200; Fax: +91-771-2254600, emails: pkchaudhari.che@nittr.ac.in (P.K. Chaudhari), rkchoudhary2 @sail-bhilaisteel.com (R.K. Choudhary)

Received 18 May 2016; Accepted 14 January 2017

ABSTRACT

Electrocoagulation treated coking wastewater was subjected to further treatment using adsorption in batch mode. A commercial powder activated carbon (PAC) was used as an adsorbent. Effects of pH, adsorbent dose, phenol concentration, adsorption temperature and contact time were studied on removal of phenol and chemical oxygen demand (COD). First- and second-order kinetics models were tested, conforming second-order to fitted well. Adsorption was found to decrease slightly with increase in temperature. Sorption performances were also evaluated using Freundlich, Langmuir and Temkin isotherm models. All the models were fitted well with similar accuracy (maximum deviation 5%). The thermodynamic study shows the process to be exothermic. Adsorption at best condition: pH = 6, PAC load = 3 kg/m^3 and contact time = 4 h; phenol, COD and ammonia–N removal were found to 99%, 33.5% and 91%, respectively, from 272 mg/dm^3 phenol, 793 mg/dm^3 COD and 65.9 mg/dm^3 ammonia–N. Pareto analysis of variance (ANOVA) showed a high coefficient of determination values for phenol removal (R^2 = 0.9766) between the experimental values and predicted values in a second-order regression model. Treated effluent can be recycled for quenching of hot coke of coke oven.

Keywords: Chemical oxygen demand; Phenol; Coking wastewater; Activated carbon; Adsorbent

1. Introduction

Coke is a major component to fulfil energy required in manufacturing of steel. It is produced by the pyrolysis of coal in coke oven. After pyrolysis, coke is quenched with water. The wastewater generated from coke oven consists of many pollutants such as ammonia–N, phenol, cyanide and other inorganic and organic compounds [1]. Common treatment method applied to treat coking wastewater (CWW) is coagulation followed by biological process. In biological treatment specific microorganisms are needed to reduce phenol and cyanides. To alive these microorganisms specific operating condition like pH, temperature and concentration of pollutants need, otherwise, treatment efficiency decreases. Combined processes are not able to reduce chemical oxygen demand (COD) below 1,000 mg/dm^3 and color still has dark brown. The biological treatment process opted in Bhilai Steel Plant, India, is presented in Fig. 1. Many works have been reported to treat CWW by biological process and by physical and chemical processes. In a process CWW was treated by adsorption on activated coke. COD and color removal was studied. COD and color removal was good but adsorbent dose was high [2]. In another study, coagulation and zero-valent iron process was found to be not much effective for its treatment as <50% COD removal obtained [3]. Application of heat using vacuum distillation was performed to remove COD and NH_3N of CWW, which was found to an effective process for removal of COD [4]. A two step process, nanofiltration (NF) combined with steam stripping was used to treat CWW. In this process, wastewaters were fractionated by NF into an ammonium concentrate and an ion-containing permeate stream. The concentrates were further fractionated in the steam stripping column [5]. Pulsed corona discharge to treat CWW gave good degradation of cyanide, but, degradation of phenol was poor [6]. Electrochemical oxidation was also performed to remove pollutants of CWW; this process has been approved to effective one for treatment of industrial effluents [7]. CWW exposed to UV radiation able to reduce polycyclic aromatic hydrocarbons only up to 50%

---

* Corresponding author.

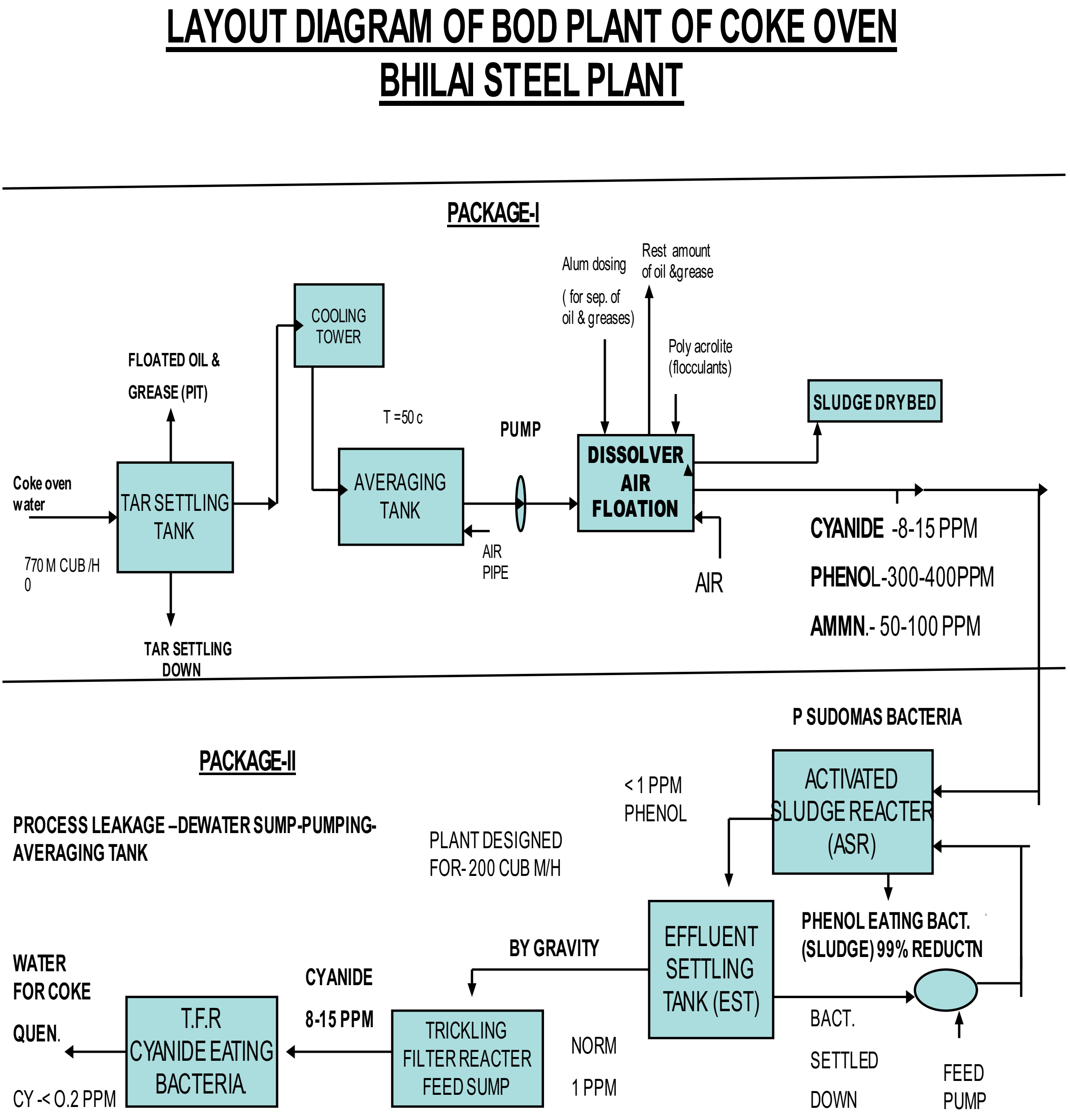

Fig. 1. Flowchart of coking wastewater treatment in Bhilai Steel Plant.

by photodegradation [8]. Integrated hybrid systems that combined coagulation, ultrafiltration and reverse osmosis gave good results in the treatment of CWW [9]. In a study ultrafiltration membranes were not found suitable to remove high level of pollutants, but pollutants were removed efficiently by reverse osmosis process [10]. Most of the physicochemical method discussed above did not remove phenol efficiently. In our laboratory CWW was first treated by electrocoagulation (EC), which was further treated by adsorption using powder activated carbon (PAC; present study). These combined methods gives significant reduction of pollutant contained in CWW.

EC treatment of CWW using stainless steel 304 electrode was already conducted in laboratory by authors. Removal efficiency of COD, cyanide, ammonia–N and phenol was 90.5%, 82.7%, 63.8% and 57.14%, respectively, from initial concentration of COD 9,000 mg/dm^3, cyanide 10.4 mg/dm^3, ammonia–N 166 mg/dm^3 and phenol 420 mg/dm^3. Since phenol is a neutral species, its removal by EC process is very less (57.14%). Therefore, further treatment was required. Treatment of phenolic wastewater using active carbon adsorbent is considered to be an effective method because of its large surface area, microporous nature, high adsorption capacity, high purity and easy availability. Several investigators have studied the adsorption of phenol and phenolic compounds on active carbons [11–15]. Therefore, in the present study removal efficiency of phenol and other pollutants from supernatant obtained from EC treated CWW was taken by using PAC. PAC has been selected in present study because it is commercially available adsorbent. Generally, other adsorbents are prepared from biomass, thus, preparation part not needed to perform. Apart from this it is widely used adsorbent in industries as its performance is found to be very good to remove various pollutants from wastewater. Fly ash of coal-based thermal power plant was also used to compare the performance of adsorbents. In present experimental study performance of PAC is found much better than fly ash. So far adsorptive treatment of EC treated CWW in second stage is not found in open literature.

2. Experimental setup

2.1. Materials and methods

The CWW was arranged from coke-oven section of Bhilai Steel Plant, Bhilai, Chhattisgarh, India. Laboratory and analytical grade chemicals made of Merck Limited, India and Germany were used in experiments and for analysis. COD, phenol, ammonia–N, cyanide, chloride and phosphate were determined by standard method prescribed by American Public Health Association (APHA) [16]. COD was determined by close reflux method. Wastewater samples were digested in COD digester (Merck, Germany) at 140°C for 2 h, after that, absorbance was determined in a UV spectrophotometer (Shimadzu, Japan) at 620 nm. Phenol was determined by direct photometric method, cyanide and ammonia–N were determined using selective electrodes (Orion, Korea). Chloride was determined by titrimetric method. Phosphate was determined by colorimetric method. Sulfate was determined by precipitation method using $BaCl_2$. The quality of CWW, supernatant after EC and after adsorption is presented in Table 1. Morphology and composition of PAC was done using scanning electron microscope (SEM; ZEISS, model EVO18, Germany) and energy-dispersive X-ray spectroscopy (EDX; X-Max, Oxford Instrument).

Adsorptive treatment of EC treated CWW (phenol = 272 mg/dm^3) was carried out in a shaker in batch mode. 50 mL of EC treated CWW (at optimum condition) was taken in 100 mL conical flask. The required amount of adsorbent was added and kept for shaking. About 5 mL samples were taken at certain time interval and phenol content was determined. Effect of pH, adsorbent dose (*m*), pollutant concentration, temperature and contact (shaking) time on phenol removal was estimated. COD, ammonia–N, cyanide and color were also determined at end of the experiment. The phenol and other parameters removal efficiency after adsorption were estimated using:

$$R\% = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

where $R\%$ is percentage removal efficiency, C_0 is the initial concentration (mg/dm^3), C_t is the concentration after time t (mg/dm^3). All measurements of samples were repeated whenever required. Optimum condition for EC treatment of CWW using SS-304 electrode was pH = 10.5, current density = 16.66 A/m^2, electrolyte NaCl concentration = 100 mg/dm^3 and electrode gap = 17.5 mm. At this operating condition removal efficiency of cyanide, ammonia–N, phenol and COD was 82.7%, 63.8%, 36.25% and 91%, respectively, from their corresponding initial values of 10.4, 166, 420 and 9,000 mg/dm^3. The data are presented in Table 1.

Table 1
Analysis of treated and untreated CWW

Parameters	CWW	pH 10.5	After adsorption
COD	9,000	793	515
Phenol	420	272	3
Cyanide	10.4	2.2	2.1
Ammonia–N	166	65.9	5.5
TDS (mg/dm^3)	642.8	347	–
TSS (mg/dm^3)	19	5	Nil
TS residue (mg/dm^3)	661.8	352	–
Chlorine (Cl^-)	4,700	2,300	2,400
Phosphate (PO_4^{2-})	25	5	3
Sulfate (SO_4^{2-})	2.5	2.1	1.5
Total hardness	210	160	150
Color	Dark brown	Light yellow	Nil
Absorbance at (475 nm)	0.185	0.06	0.035
% Color removal	–	67.56	92.53
pH	10.5	11.74	6

Note: Except pH all values are in mg/dm^3. TDS = total dissolved solid; TSS = total suspended solid; and TS= total solid.

3. Results and discussion

3.1. Characterization of PAC adsorbent

The PAC (Merck) was used as an adsorbent. It was characterized for SEM and EDX. Fig. 2 shows the SEM of PAC before the adsorption and after the adsorption experiments. After adsorption PAC was found to hazy, which is due to occupying of adsorbent surfaces by pollutants. The EDX analysis results are shown in Table 2. After adsorption of pollutants in PAC, amount of carbon decreased while nitrogen and oxygen increased. Reason for increasing nitrogen in PAC is the attachment of ammonia–N in PAC. Oxygen increased due to adsorption of phenol. Fluoride and sulfur was also found to increase. Carbon percentage decreased because increase in other components in PAC.

3.2. Effect of initial pH (pH_i) of the solution

The dependence of phenol adsorption at different solution pH (4.0, 6.0, 8.0, 10.0 and 12.0) was examined using 3 kg/m^3 PAC for 3 h. After adsorption PAC was allowed to settle and supernatant was analyzed for phenol and COD. Results are shown in Fig. 3. At various pH, i.e., 4.0, 6.0, 8.0, 10.0 and 12.0, respectively, removal efficiency of phenol was 98.35%, 98.83%, 98.54%, 97.76% and 94.17%; and COD was 36.31%, 33.50%, 14.5%, 14.09% and 13.29%. This information implies, removal efficiency by active carbon adsorption system is better at pH 6. In most cases, removal of pollutants from an aqueous media by adsorption is highly dependent on the solution pH, which affects the surface charge of the adsorbent and degree of ionization of the adsorbate. In present study, phenol removal capacities of PAC were moderately affected by pH maybe due to phenol has neutral charge. COD removal was found to highly pH dependent. Difference in adsorption capacity of PAC at different pH may be due to difference in concentration of H^+ and OH^- in the solution. Adsorbent particles (PAC) have a slight electropositive charge that helps it to attract negatively charged species [17]. The H^+ ion within low pH environment can neutralize those negative particles, reduces the hindrance of pollutants ions and consequently increase the chances of their adsorption. High pH environment led to high concentration of OH^-, which can increase the hindrance to diffusions of pollutant ion and thus reduces the chances of their adsorption [18]. It has been reported that colloidal particles and number of functional groups and ligands, especially polar molecules, and oxygen containing functional groups like hydroxyl, phenolic and carboxylic group have local negative charge [19]. These are responsible for COD of wastewater [19].

3.3. *Effect of adsorbent dose (m)*

At optimum pH 6 and temperature 30°C, *m* was varied and the results of phenol removal are presented in Fig. 4. With 1.15, 2.25, 3.0 and 4.0 kg/m^3 PAC, respectively, phenol removal was 57.72%, 66.17%, 77.20% and 79.41% in 30 min and

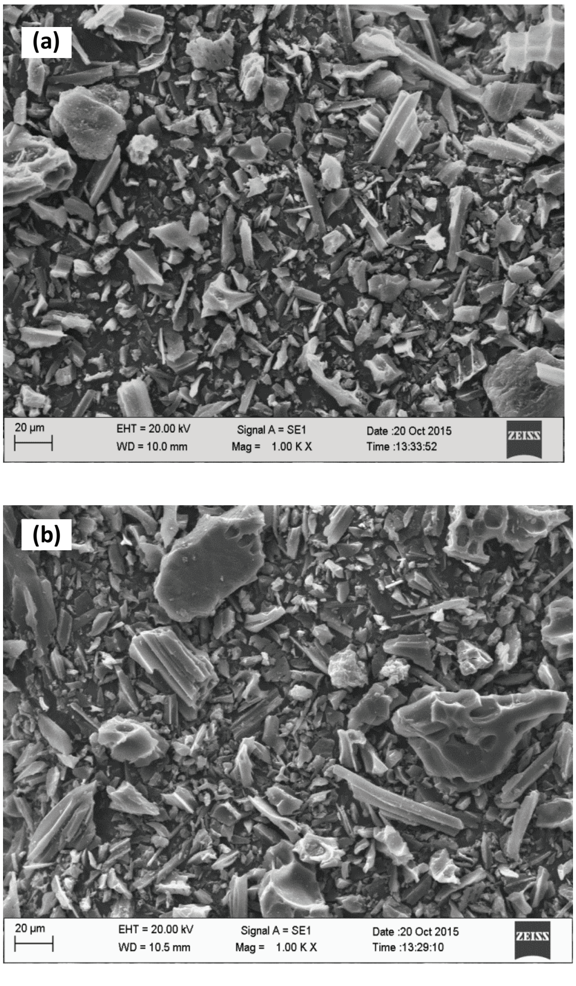

Fig. 2. SEM of powder activated carbon: (a) before adsorption and (b) after adsorption.

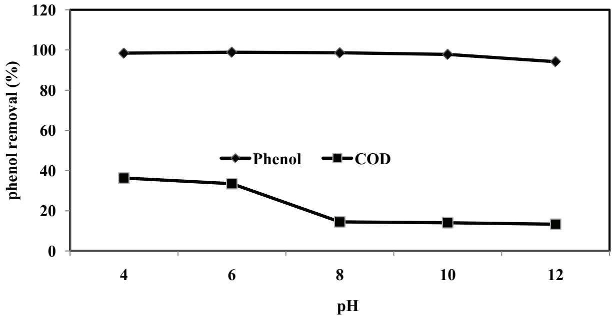

Fig. 3. Removal of phenol and COD in treatment time 4 h, COD$_i$ = 793 mg/dm^3, phenol = 272 mg/dm^3, *m* = 3 mg/dm^3.

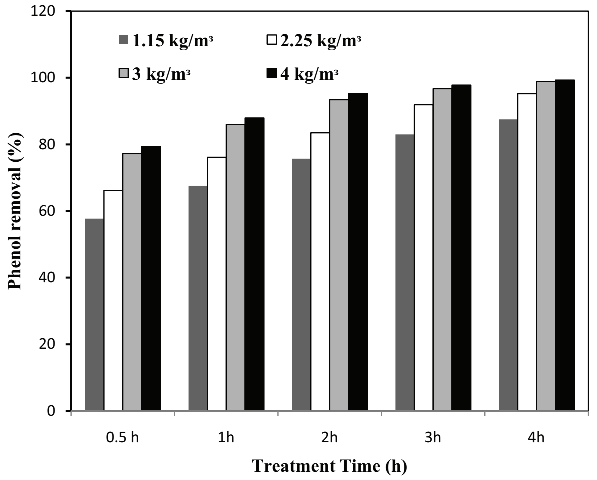

Fig. 4. Removal of phenol at different doses of PAC, COD$_i$ = 793 mg/dm^3, phenol$_i$ = 272 mg/dm^3, *m* = 3 mg/dm^3.

Table 2
Weight percentage composition of activated carbon before and after adsorption

Elements	C	N	O	F	Mg	Al	S	Cl	Ca
PAC	91.969	0.250	6.9756	0.060	0.01	0.01	0.12	0.49	0.27
PAC after adsorption	85.71	1.76	10.18	0.44	–	0.01	0.67	0.50	0.1

87.5%, 95.2%, 98.89% and 99.26% in 4 h. The phenol removal was increased rapidly with an increase in m up to 3 kg/m^3 and remained almost unaffected at $m > 3$ kg/m^3. Therefore, 3 kg/m^3 PAC can be considered as optimum dose. Increase in phenol adsorption with increase in m is due to increase in mesoporous surface area available for adsorption, and hence, the availability of more adsorption sites. However, unit adsorption per unit mass of adsorbent decreases with increase in m is because of fact that an increase in m at constant concentration and volume of adsorbate leads to the saturation of sorption sites [18,20]. Apart from this, the particle–particle interaction such as aggression at higher m causes decrease in the availability of total surface area for the sorbent [21,22].

3.4. Effect of adsorbent dose and temperature

Variation of m (1.15–4 kg/m^3) and temperature (30°C–60°C) was also studied on uptake of phenol at optimum pH 6. The results are presented in Fig. 5. Phenol removal was increased considerably with increase in adsorbent dose, while decreased moderately with increase in temperature. For all the temperature and m the phenol removal pattern with time is similar (Fig. 5). Phenol concentration in solution in 4 h reached to values 34, 13, 3 and 2 mg/dm^3 at 30°C; 32, 16, 5 and 2 mg/dm^3 at 40°C; 38, 15, 8 and 4 mg/dm^3 at 50°C; 50, 18, 12 and 8 mg/dm^3 at 60°C and at m 1.15, 2.25, 3.0 and 4.0 kg/m^3. Decrease in phenol removal with increase in temperature indicates its removal to exothermic. Increase in phenol removal with decrease in temperature was also observed by Yan et al. [14].

3.5. Effect of initial concentration and temperature

The equilibrium uptake, thus, removal of phenol by adsorbent is affected by initial concentration and temperature. Fig. 6 shows the effect of phenol initial concentration (phenol$_i$; 136, 181 and 272 mg/dm^3) and temperature 30°C and 50°C, on phenol removal at their optimum pH 6. At temperature 30°C, phenol$_i$ of 272, 181 and 136 mg/dm^3 reached to 62, 56 and 38 mg/dm^3 in 30 min and 3, 2 and 1 mg/dm^3 in 4 h. At 50°C, phenol concentration dropped to 84, 72 and 66 mg/dm^3 in 30 min and 8, 5 and 3 mg/dm^3 in 4 h. The percentage phenol removal was more at its higher initial concentration and removal decreased with decrease in initial concentration. It should be also noted that variation in concentration of phenol in solution is up to 25 mg/dm^3 in 30 min, which reached to 5 mg/dm^3 in 4 h. Increase in percentage removal of picoline with increase in its initial concentration was also observed by Lataye et al. [22] in adsorptive removal process using PAC. The increase in amount adsorbed with high initial concentration is attributed to the increase in the mass transfer driving force due to high concentration of adsorbate.

3.6. Effect of contact time

Increase in contact time increased the phenol removal at all operating conditions. Effect of contact time on removal of phenol at optimum pH 6, temperature 30°C and PAC loading (1.15–4 mg/dm^3) is presented in Fig. 7. At optimum pH 6, with PAC 1.15, 2.25, 3.0 and 4 kg/m^3, respectively, phenol removal

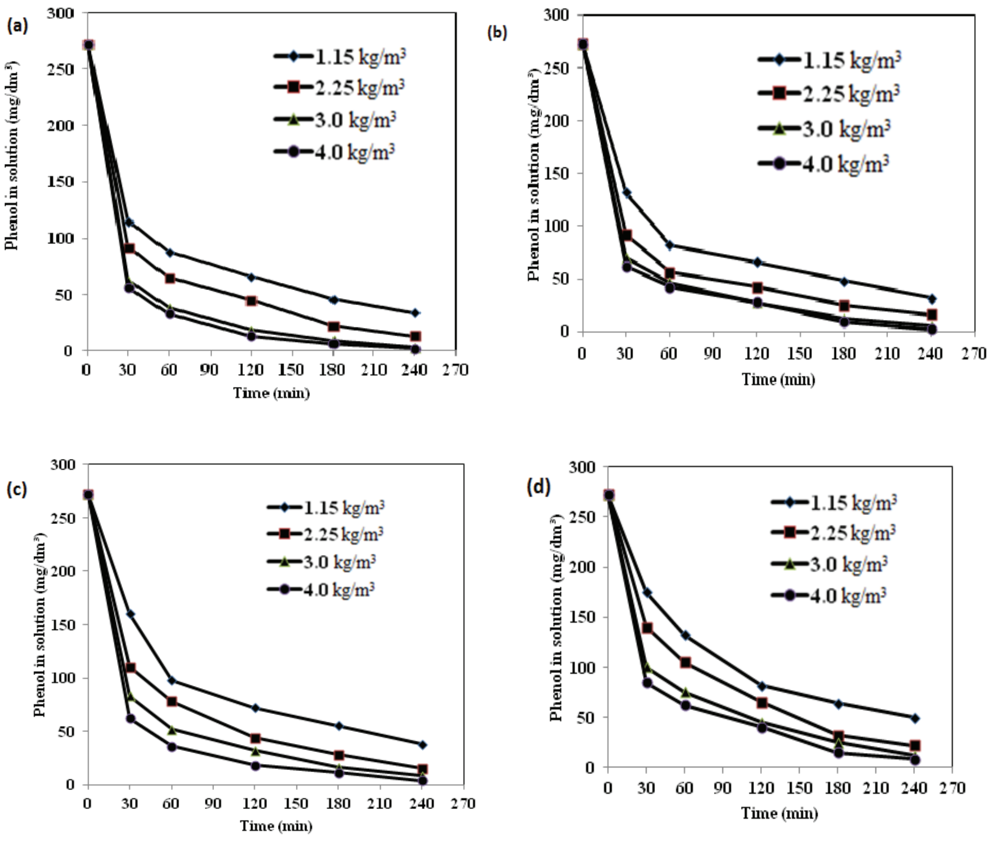

Fig. 5. Removal of phenol at different adsorbent dose: (a) 30°C, (b) 40°C, (c) 50°C and (d) 60°C.

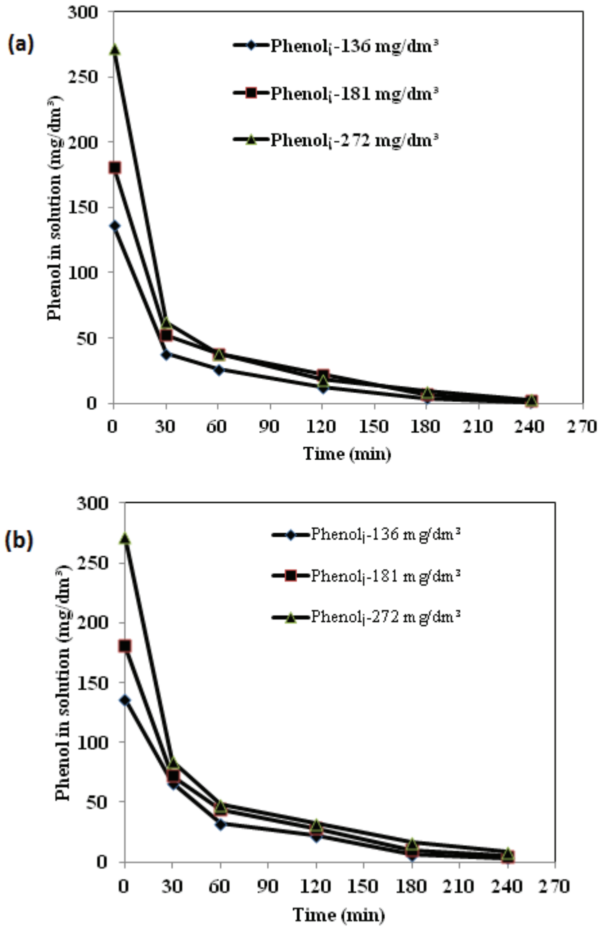

Fig. 6. Phenol removal at different phenol concentration: (a) 30°C and (b) 50°C.

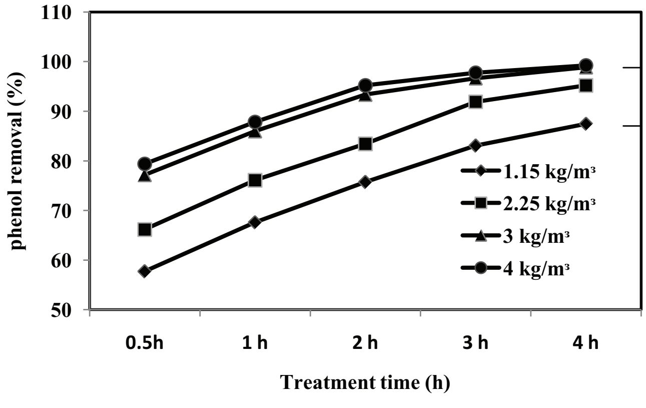

Fig. 7. Percentage removal of phenol at different doses and time.

of 57.72%, 66.10%, 77.20% and 79.41% after 0.5 h; 67%, 76%, 86% and 88.0% after 1 h; 76%, 83%, 93% and 93% after 2 h; 83%, 92%, 96.7% and 97.8% after 3 h; and 87.5%, 95.2%, 98.9% and 99.26% after 4 h were observed. Phenol removal was also tested at pH 6 and PAC loading of 3 kg/m³. Its removal of 22%, 38% and 55% was achieved in 5, 10 and 15 min, respectively. Initial adsorption was high because availability of much adsorptive sites, which decreased with time proceeds. These information implies that best condition for removing phenol by PAC adsorption system as a secondary treatment after electro chemical treatment (ECT) is pH = 6.0, m = 4 kg/m³, contact time = 3 h or pH = 6, m = 3 kg/m³, contact time 4 h. At these conditions, researchers found 99% phenol removal. Similar extent of phenol removal was found by other researchers, but, they have used synthetic phenolic wastewater [15]. In our case industrial CWW was used.

3.7. Regeneration and reuse study of spent adsorbent

Chemical process for regeneration of spent PAC was performed as per literature [23]. To regenerate the spent PAC, 3 g spent PAC was taken in 100 mL Erlenmeyer flask containing 75 mL of 0.1 N H_2SO_4 at room temperature (~27°C) for 6 h. After this, the PAC was washed with deionized water many times till its pH reached ~7 and then dried at 120°C for 12 h. With fresh PAC, phenol removal of 96.7% obtained decreased to 85.9% in first regeneration and 76.6% in second regeneration. The decrease in adsorption is because of changes in morphology of regenerated PAC.

3.8. Kinetic study

Adsorption kinetics experiments of known phenol concentrations 136, 181 and 272 mg/dm³ and known dose of PAC 1.15, 2.25, 3.0 and 4.0 kg/m³ was carried out at temperature 30°C, 40°C, 50°C and 60°C. Some data were also taken as PAC dose 1.5 kg/m³ for response surface mythology (RSM) studies. Samples were taken at interval of 0.5, 1, 2, 3 and 4 h. Pseudo-first-order and pseudo-second-order kinetics studies are given below.

3.8.1. Pseudo-first-order

Experimental data were tested for pseudo-first-order kinetics. For this, the Lagergren's rate equation [24] was tested. The equation is given as:

$$\log(q_e - q_t) = \log q_e \frac{K_F}{2.303} t \tag{2}$$

where q_e and q_t are the amount of phenol adsorbed (mg/kg) at equilibrium and at time t, respectively, and K_F is the pseudo-first-order rate constant. Fig. 8(a) shows a plot between C_e/q_e and C_e of Eq. (1) at temperature 30°C, 40°C, 50°C and 60°C. The plot was found to linear with good correlation coefficient (R^2) which varied from 0.875 to 0.963. The data evaluated are presented in Table 3.

3.8.2. Pseudo-second-order

Phenol removal data were also tested for following equation [25]:

$$\frac{t}{q_t} = \frac{1}{K_s q_e^2} + \frac{1}{q_e} t \tag{3}$$

where K_s is the pseudo-second-order rate constant. The plots between t/q_t vs. t were drawn and shown in Fig. 8(b). Correlation coefficient (R^2) for the pseudo-second-order kinetic model were 0.998, 0.999, 0.999 and 0.999 at 30°C, 40°C, 50°C and 60°C, respectively. This suggests that the present adsorption system described by pseudo-second-order process. Between the kinetic model, pseudo-second-order fitted better to pseudo-first-order.

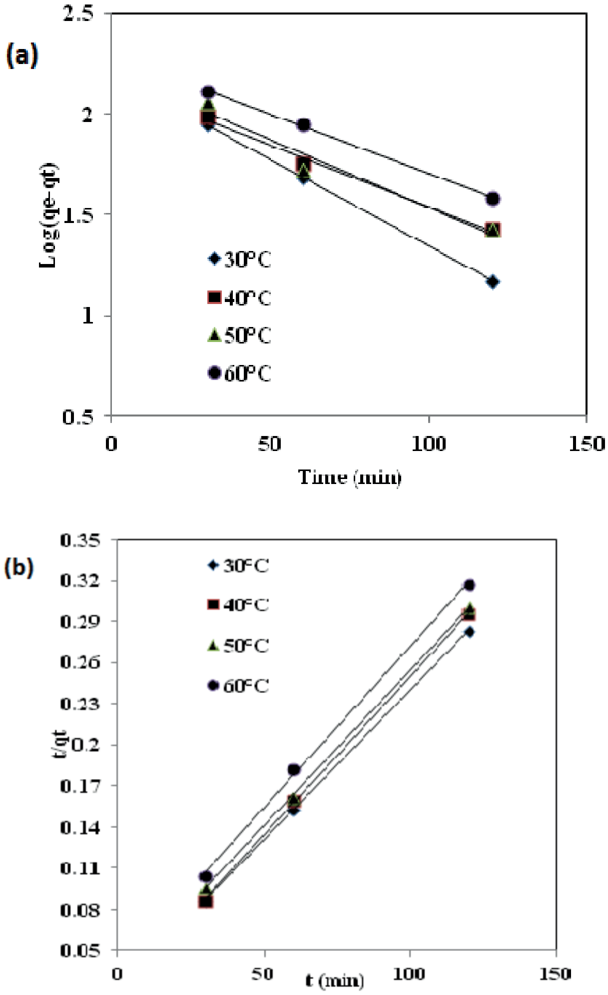

Fig. 8. Kinetic studies for removal of phenol by PAC: (a) pseudo-first-order and (b) pseudo-second-order.

Table 3
Kinetic parameters for phenol removal by PAC

Temperature (°C)	Pseudo-first-order		Pseudo-second-order	
	K_{ad1}	R^2	K_{ad2}	R^2
30	0.019	0.9999	0.00236	0.9999
40	0.014	0.9917	0.00231	0.9997
50	0.015	0.9549	0.00238	0.9997
60	0.013	0.9996	0.00239	0.9996

3.9. Adsorption isotherm

Adsorption isotherm models are used to describe the relation between adsorption capacity and equilibrium concentration. Langmuir [26], Freundlich [27] and Temkin [28] isotherm are widely used for this.

The linear Langmuir equation has the following form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{4}$$

where q_m is the monolayer adsorption capacity (mg/kg adsorbent) and K_L is the Langmuir constant related to energy of adsorption (dm^3/mg).

A plot between C_e/q_e and C_e for the adsorption of phenol is shown in Fig. 9(a). The value q_m and K_L have been evaluated from the intercept and slop of these plots, which are given in Table 4. A perusal of Table 4 shows that monolayer capacity (q_m) of the adsorbent of phenol is comparable with the maximum adsorption obtained from adsorption isotherm. The essential feature of Langmuir isotherm can be expressed in terms of R_L, a dimensionless constant referred to as separation factor or equilibrium parameters. R_L is calculated using the following equation:

$$R_L = \frac{1}{1 + K_L C_i} \tag{5}$$

The value of 'R_L' calculated as per above equation is presented in Table 4. As the R_L value lies between 0 and 1, the Langmuir adsorption isotherm is favorable. C_i is initial concentration of phenol.

The Freundlich equation is given as:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e \tag{6}$$

where K_F (mg/dm^3)$^{1/n}$ is a Freundlich constant which indicates the sorption capacity of the adsorbent (mg/kg adsorbent), and $1/n$ is a constant which gives the intensity of adsorption. These constants were evaluated by plotting between $\log q_e$ and $\log C_e$ (Fig. 9(b)). The values obtained are presented in Table 4. This model was fitted well with R^2 0.980–0.988.

The Temkin isotherm equation is given as:

$$q_e = B_1 \ln(K_T) + B_1 \ln(C_e) \tag{7}$$

where $B_1 = RT/b$ is a constant related to heat of adsorption, b is variation of adsorption energy (J/mol), K_T is Temkin constant which accounts the interaction between the adsorbate and adsorbent (dm^3/mg). To evaluate the constants, a plot between q_e and $\ln C_e$ is made (Fig. 9(c)) and values are presented in Table 4. The model fitted well with R^2 0.92–0.95.

3.10. Thermodynamics study

The thermodynamic parameters, namely, the standard Gibbs energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and

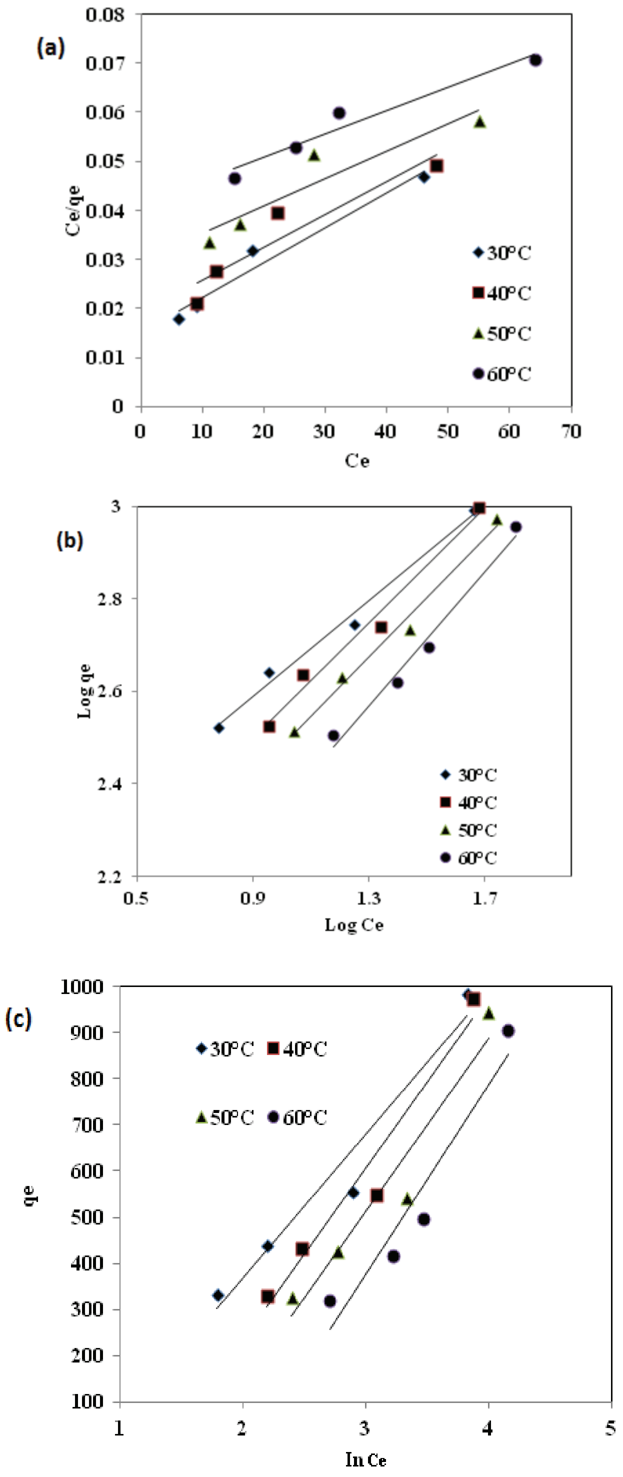

Fig. 9. Plot for adsorption isotherm for removal of phenol by: (a) Langmuir isotherm, (b) Freundlich isotherm and (c) Temkin isotherm.

entropy change ($\Delta S°$) of the adsorption of phenol on activated carbon were determined by using Eqs. (8)–(10) and the values for these parameters are presented in Table 5.

$$\Delta G° = -RT\ln K_L \tag{8}$$

$$\Delta H° = R\left(\frac{T_2 T_1}{\left(T_2 - T_1\right)}\right)\ln\left(\frac{K_{L2}}{K_{L1}}\right) \tag{9}$$

$$\Delta S° = (\Delta H° - \Delta G°)/T \tag{10}$$

where T is the temperature; R is the universal gas constant; K_{L1} and K_{L2} are Langmuir constants at 30°C, 40°C, 50°C and 60°C.

In Table 5, negative values of the Gibbs free energy change ($\Delta G°$) show the phenol adsorption on PAC is spontaneous and thermodynamically feasible in the studied temperatures range (303–333 K). The values of $\Delta G°$ increased with increase in temperature indicate that the sorption is inversely proportional to temperature [29]. In studies adsorption was found to decrease with increase in temperature. The $\Delta H°$ for phenol adsorbed onto PAC was negative (–24.033 kJ/mol), indicating that the adsorption process was exothermic [30]. According to the ranges of energy of adsorption from different forces [14,31] van der Waal forces 4–10 kJ/mol, hydrophobic bond forces about 5 kJ/mol, hydrogen bond forces 2–40 kJ/mol, coordination exchange about 40 kJ/mol, dipole bond forces 2–29 kJ/mol, chemical bond forces >60 kJ/mol, it is indicated that in present adsorption system all the mechanisms except coordination exchange and chemical bond forces are possible. The $\Delta S°$ for phenol adsorbed onto PAC was –0.0542 kJ/mol. The negative value of $\Delta S°$ suggested a decrease in degree of freedom of the adsorbed phenol [14,32]. It can be also seen that the value for $\Delta H°$ is <40 kJ/mol which suggests the physical adsorption is involved in the process [33].

3.11. Removal of pollutants using fly ash

Fly ash of coal-based thermal power plant was also used to study its comparative performance with PAC. The powder fly ash was grinded with laboratory grinder and its size (<100 μM) was selected for adsorption studies. The PAC was washed with deionized water and it was kept for drying at 220°C for a period of 6 h [34]. Effect of pH keeping constant to fly ash mass loading 3 kg/m^3 and 3 h contact period was studied to remove COD, phenol, CN$^-$ and ammonia–N from CWW. The results are presented in Table 6. Highest 24% COD and 37% phenol removal was seen at pH 8, while, maximum 7% CN$^-$ and 34% ammonia–N removal obtained at pH 4. It is well known that removal of species varies with pH. Removal of all the pollutants was quite below to that obtained with PAC.

3.12. Comparison of results

Experimental results obtained by various investigators are presented in Table 7. From the table, it can be seen that in our study, initial phenol concentration is highest (272 mg/dm^3) to that of others. Highest percentage phenol removal (~98%) and highest phenol removal per unit mass of adsorbent (PAC) obtained (q_e = 438.33 × 10^3 mg/kg adsorbent). Another importance of present study is that the effluent is industrial effluent which contains COD, ammonia–N, cyanide and other cations and anions. Other investigators used synthetic phenolic water. Further, various physicochemical methods reported to treat CWW are not such effective. Wet oxidation is also an effective process in which 100% destruction of phenol is possible, but at moderate treatment condition phenol oxidized into other

Table 4
Isotherm parameters for adsorption of phenol on PAC

Temperature (°C)	Langmuir constants				Freundlich constants			Temkin constants		
	$q_m \times 10^3$ (mg/kg)	K_L	R_L	R^2	n	K_F (m^3/kg)	R^2	K_T (m^3/kg)	B (J/mol)	R^2
30	1,428.57	0.0491	0.069	0.963	1.94	133.5	0.980	161	142.22	0.95
40	1,428.7	0.0362	0.092	0.887	1.61	87.84	0.988	32	150.36	0.95
50	1,666.67	0.0215	0.146	0.875	1.56	69.61	0.986	11	135.34	0.93
60	2,000	0.0105	0.256	0.948	1.38	42.73	0.982	1	127.38	0.92

Table 5
Thermodynamic parameters for adsorption of the phenol

ΔG (kJ/mol)				ΔH (kJ/mol)	ΔS (kJ/mol)
30°C	40°C	50°C	60°C		
–7.592	–8.636	–10.311	–12.614	–24.033	–0.0542

Table 6
Removal of COD, phenol, CN^- and ammonia–N of electrochemical treated CWW by adsorption using fly ash

pH	COD (mg/dm^3)	Phenol (mg/dm^3)	Cyanide (mg/dm^3)	Ammonia–N (mg/dm^3)
pH 2	21%	31%	5.0%	10%
pH 4	18%	29%	7%	34%
pH 6	20%	30%	5.5%	12%
pH 8	24%	37%	6.5%	19%
pH 10	17%	24%	1%	23%

Note: COD_i = 803 mg/dm^3, $phenol_i$ = 309 mg/dm^3, CN_i = 2.6 mg/dm^3, ammonia–N_i = 70 mg/dm^3.

Table 7
Comparison of results for removal of phenol

S. No.	Adsorbent material	Dose (kg/m^3)	Time (min)	Initial phenol (mg/dm^3)	% Removal	$q_{e \times 10}{}^3$ (mg/kg)	References
1	PAC	3	60	272	77.20	390	Present study
		4	60		79.41	298.75	
		3	180		96.69	438.33	
		4	180		97.79	332.5	
2	Date pit activated carbon	4	180	88	–	11.5	[11]
3	Lignite activated carbon	0.5	60	250	50	225	[12]
4	Cocoa shell-based activated carbon	4	25	–	–	167.17	[13]
5	Sheesham sawdust	1	60	25	93.95	344.83	[35]
6	Gemini surfactant modified montmorillonite	–	40	10	82	–	[36]
7	Luffa cylindrica fibers	3	90	20	70	–	[37]
8	*Bacillus* sp. immobilized onto tea waste	15	120	50	80	7.761	[38]
9	Reduced-charge montmorillonites modified by bispyridinium dibromides	–	120	47	69	0.34	[39]
10	Gondwana shale	50	24	475	74	0.34	[40]

carboxylic acids which are responsible for COD in treated water [41]. Thus, adsorptive treatment of EC treated CWW using PAC in second step is very effective and industrial applicable. The characteristics of CWW treated by EC process and by EC cum adsorption are given in Table 1, in which various pollutants removed to significant level. The treated effluent can be recycled in coke oven for quenching of coke.

3.13. Statistical analysis and modeling

In a study, it has been found that adsorption kinetics is represented by doses of adsorbent, operation temperature and time. These are the variables, which considerably affect the removal of species in adsorption process. Therefore, statistical analysis was performed taking these variables. Table 8 gives the chosen variable and its level. The encoded values along with set of data used for statistical analysis and corresponding % COD removal values are given in Table 9, which was designed as per earlier report [42].

Regression method using ANOVA was used to fit second-order polynomial to the experimental data. The relation obtained in term of uncoated factors for % COD removal is given by Eq. (10). The model gave significant of determination (R^2) = 0.9776% and adjusted R^2 = 0.9373%. These data are quite better to that obtained (R^2) = 0.9144 by Thakur et al. [43]. Predicted values mentioned in Table 9, which was determined from Eq. (11) is very close to experimental values also confers validity of model.

Table 8
Process parameters and their level for the adsorptive treatment using PAC

Variables	–1	0	1
PAC dose (*m*), A	1.5	2.25	3
Temp (°C), B	30	40	50
Time (min), C	60	120	180

$$\text{\% COD removal} = 10.8763 + 20.8233A + 1.3256B + 0.1407C - 0.5178A^2 - 0.0129B^2 - 0.0003C^2 - 0.2407AB + 0.0026AC + 0.0011BC \quad (11)$$

where A is adsorbent mass loading (kg/m^3), B is operational temperature (°C) and C is adsorption time (min).

The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using analysis of variance (ANOVA). The ANOVA for the second-order equation fitted for COD removal is presented in Table 10. ANOVA result shows F value 24.24 and p value 0.001. Value of F is large, which shows most of the variation in response can be explained by the regression. The associate p value is used to estimate F. In our case value of p is 0.001, which is less than maximum recommended value 0.05 [44]. This indicates the model is statically significant. In RSM studies for COD removal, values of F and p were 16.55 and 0.0001 [43] and 68.74 and 0.0001 [44], respectively.

The response surface plot and contour plots for COD removal is presented in Fig. 10. Figs. 10(a) and (b) show the effect of PAC loading (m) and temperature on phenol removal at constant time 120 min. From the figure, it can be seen that phenol removal is high at high values of m and low temperature. In between 30°C–37°C and m = 3 kg/m^3 PAC, >92% phenol removal can be seen. Figs. 10(c) and (d) show effect of m and adsorption time on phenol removal at constant temperature 40°C. Phenol removal was increased with increase in m and adsorption time. In between 160–180 min and m = 3.0 kg/m^3, >95% phenol removal reflected. Phenol removal at constant m = 2.25 kg/m^3 and variable temperature and adsorption time is mentioned in Figs. 10(e) and (f). The removal favored to low temperature and high adsorption time. More than 90% removal observed temperature below 45°C and contact time 180 min. Reason for variations in phenol removal is already discussed in results and discussion section.

Table 9
Design of RSM and its actual and predicted values

Standard order	Adsorbent dose (*m*; mg/dm^3)	Temperature (°C)	Adsorption time (min)	% COD removal	
				Actual	Predicted
1	3	30	120	93.08	96.96
2	3	50	120	88.23	86.71
3	3	40	180	95.58	97.12
4	1.5	30	120	74.1	75.26
5	2.25	40	120	84.55	84.37
6	2.25	30	180	91.91	89.62
7	2.25	50	60	71.32	73.07
8	2.25	40	120	84.55	88.69
9	1.5	40	180	83.2	83.11
10	2.25	50	180	89.7	88.61
11	2.25	40	120	84.55	84.37
12	3	40	60	83.08	82.65
13	2.25	30	60	76.1	79.87
14	1.5	50	120	76.47	80.76

Table 10
ANOVA for analysis of variance for % COD removal quadratic model

Source	DF	Sum of square	Mean square	*F*	*p*
Regression	9	845.006	93.88952	24.24	0.001
Linear	3	821.037	7.7962	2.01	0.231
A	1	378.675	16.3971	4.23	0.095
B	1	11.210	8.4859	2.19	0.199
C	1	431.152	6.6541	1.72	0.247
Square	3	9.233	3.0776	0.79	0.547
A^2	1	0.061	0.3132	0.08	0.788
B^2	1	5.452	6.1325	1.58	0.264
C^2	1	3.720	3.7201	0.96	0.372
Interaction	3	14.736	4.9121	1.27	0.380
AB	1	13.032	13.0321	3.36	0.126
AC	1	0.053	0.0529	0.01	0.912
BC	1	1.651	1.6512	0.43	0.543

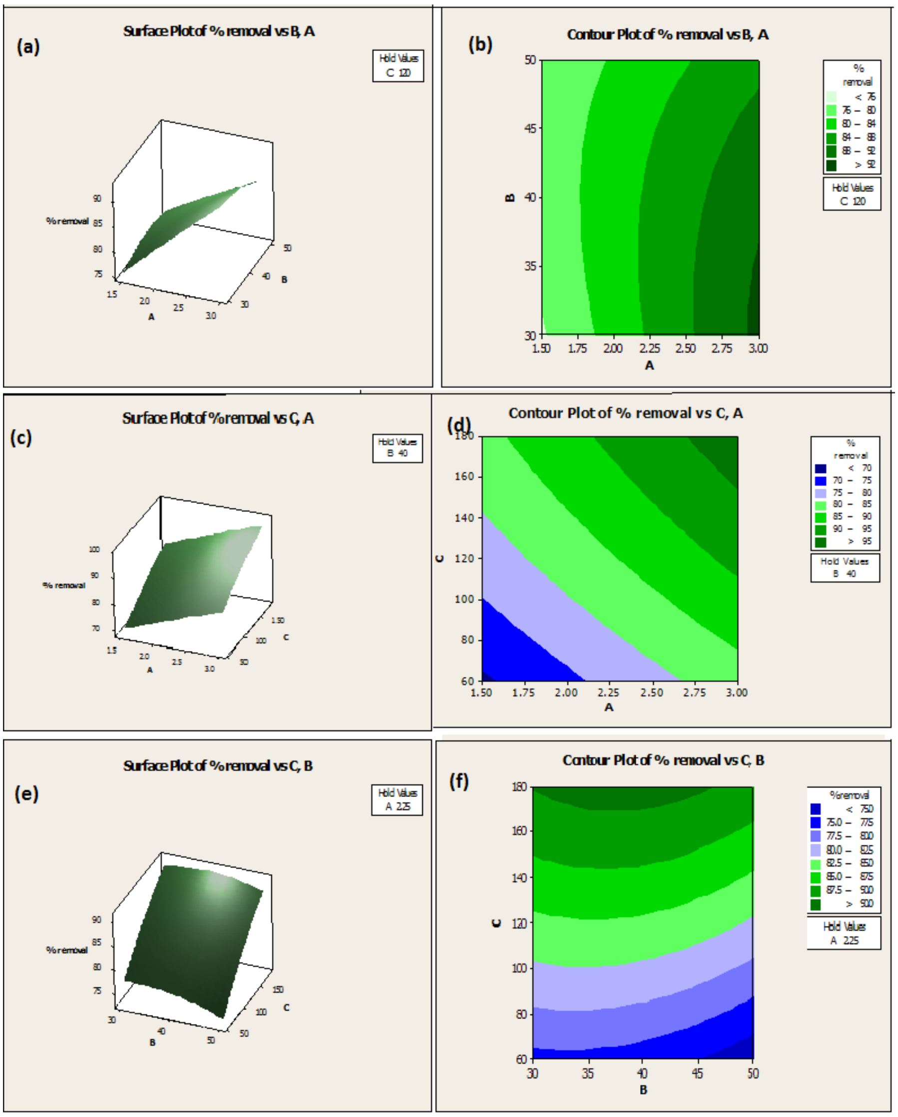

Fig. 10. Three-dimensional response surface graphs for COD removal.

4. Conclusions

Main conclusions drawn from the study are as below:

- Activated carbon is found to be good adsorbent for removal of phenol from CWW. It performed well for removal of phenol at wide range of pH, however, COD removal was pH dependent, gave better performance at acidic pH. Adsorption of phenol decreases slightly with increase in temperature indicating an exothermic process. Since pH and temperature dependence is small for phenol removal the process can be applied at wide range of pH and temperature with little decrease in sorption efficiency.
- Phenol adsorption rate fits well at pseudo-second-order kinetics model. All the models, i.e., Freundlich, Langmuir and Temkin fitted well with low deviation in regression coefficient R^2 (maximum up to 10%). For all the models R^2 lies between 0.875 and 0.988.
- Using 3 kg/m^3 PAC in 4 h and 4 kg/m^3 PAC in 3 h, >99% of phenol removal was obtained from initial value of phenol 272 mg/dm^3. Adsorption using PAC can be good prospect in second stage of treatment after EC of CWW. Combination of ECT and adsorption could be utilized in coking/steelmaking industries to bring CWW to recycle level.
- The quadratic model developed based on RSM statistical analysis showed a high coefficient of determination (R^2 = 0.9776) ensuring a good representation of experimental data by regression model.
- Among PAC and fly ash as adsorbent, the performance of PAC was found to much better.

References

[1] F. Masanon, I. Vazquez, J. Rodfiguez, L. Castrillon, Y. Fernadzed, H. Loopez, Treatment of coke wastewater in a sequential batch reactor (SBR) at pilot plant scale, Bioresour. Technol., 99 (2008) 4192–4198.

[2] M.H. Zhang, Q.L. Zhao, X. Bai, Z.F. Ye, Adsorption of organic pollutants from coking wastewater by activated coke, Colloids Surf., A, 362 (2010) 140–146.

[3] P. Lai, H. Zhangzhao, M. Zeng, J. Ni, Study on treatment of coking wastewater by biofilm reactors combined with zero-valent iron process, J. Hazard. Mater., 162 (2009) 1423–1429.

[4] W. Mao, H. Ma, B. Wang, Performance of batch vacuum distillation process with promoters on coke-plant wastewater treatment, Chem. Eng. J., 160 (2010) 232–238.

[5] M. Minhalma, M. Pinho, Development of nanofiltration/steam striping sequence for coke plant wastewater treatment, Desalination, 149 (2002) 95–100.

[6] G. Shao, J. Li, W. Wang, Z. He, S. Li, Desulfurization and simultaneous treatment of coke-oven wastewater by pulsed corona discharge, J. Electrostat., 62 (2004) 1–13.

[7] M. Rodrigo, P. Canizares, A. Carretero, C. Saez, Use of conductive-diamond electrochemical oxidation for wastewater treatment, Catal. Today, 151 (2010) 173–177.

[8] M. Włodarczyk-Makuła, E. Wiśniowska, A. Turek, A. Obstój, Removal of PAHs from coking wastewater during photo degradation process, Desal. Wat. Treat., 57 (2016) 1262–1272.

[9] K. Mielczarek, J. Bohdziewicz, M. Włodarczyk-Makuła, M. Smol, Comparison of post-process coke wastewater treatment effectiveness in integrated and hybrid systems that combine coagulation, ultrafiltration, and reverse osmosis, Desal. Wat. Treat., 52 (2014) 3879–3888.

[10] K. Mielczarek, J. Bohdziewicz, M. Włodarczyk-Makuła, M. Smol, Modeling performance of commercial membranes in the low-pressure filtration coking wastewater treatment based on mathematical filtration models, Desal. Wat. Treat., 52 (2014) 3743–3752.

[11] M. El-Naas, S. Al-Zuhair, M. Alhaija, Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated carbon, Chem. Eng. J., 162 (2010) 997–1005.

[12] L. Guocheng, H. Jiao, L. Liu, M. Hongwen, The adsorption of phenol by lignite activated carbon, Chin. J. Chem. Eng., 19 (2011) 380–385.

[13] F. Ahmad, W. Daud, M. Ahmad, R. Radzi, Using cocoa (*Theobroma cacao*) shell-based activated carbon to remove 4-nitrophenol from aqueous solution: kinetics equilibrium studies, Chem. Eng. J., 178 (2011) 461–467.

[14] M. Yan, N. Gao, W. Hu, C. Li, Removal of phenol by powdered activated carbon adsorption, Front. Environ. Sci. Eng., 7 (2013) 158–165.

[15] Q. Riaz, A. Rehan, A study of the adsorption of phenol by activated carbon from aqueous solution, Turk. J. Chem., 26 (2002) 357–361.

[16] American Public Health Association, Standard Methods for Examination of Waste and Wastewater, APHA, AWWA, WEF, Washington, D.C., USA, 2013.

[17] https://chemistry.stackexchange.com/questions/341/why-does-activated-carbon-preferentially-adsorb-anions

[18] A. Jain, S. Jain, A. Bhatnagar, Removal of 2-fluoro and 2-iodophenol from aqueous solutions using industrial wastes, Environ. Technol., 25 (2004) 15–22.

[19] P.K. Chaudhari, I.M. Mishra, S. Chand, Decolourization and removal of chemical oxygen demand (COD) with energy recovery: treatment of biodigester effluent of a molasses-based alcohol distillery using inorganic coagulants, Colloids Surf., A, 296 (2007) 238–247.

[20] B. Singh, N. Rawat, Comparative sorption equilibrium studies of toxic phenols on flyash and impregnated flyash, J. Chem. Technol. Biotechnol., 61 (1994) 307–312.

[21] Y. Yu, S. Shukla, K. Dorris, A. Shukla, J. Margrava, Adsorption of chromium from aqueous solution by maple saw dust, J. Hazard. Mater., 100 (2003) 53–63.

[22] D. Lataye, I. Mishra, I. Mall, Adsorption of α-picoline onto rice husk ash and granular activated carbon from aqueous solution: equilibrium and thermodynamic study, Chem. Eng. J., 147 (2009) 139–149.

[23] S.W. Nahm, W.G. Shim, Y.K. Park, S.C. Kim, Thermal and chemical regeneration of spent activated carbon and its adsorption property for toluene, Chem. Eng. J., 210 (2012) 500–509.

[24] S. Lagergen, About the theory of so-called adsorption of soluble substance, K. Sven. Vetensk. Akad. Handl., 24 (1898) 1–39.

[25] Y. Ho, G. Mckey, Psuedo-second order model for sorption process, Process Biochem., 34 (1999) 451–465.

[26] I. Langmuir, The adsorption of gases on plain surface of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.

[27] H. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 385–471.

[28] M. Temkin, V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalyst, Acta Physiochim. URSS, 12 (1940) 327–356.

[29] E. Tutem, R. Apak, C. Unal, Adsorptive removal of chlorophenols from water by bituminous shale, Water Res., 32 (1998) 2315–2324.

[30] D. Lataye, I. Mishra, I. Mall, Adsorption of 2-picoline onto bagasse fly ash from aqueous solution, Chem. Eng. J., 138 (2008) 35–46.

[31] V. Kordel, W. Klein, Sorption of nonpolar and polar compounds to soils: processes, measurement and experience with the applicability of the modified OECD-Guideline 106, Chemosphere, 22 (1991) 285–304.

[32] Q. Fu, Y. Deng, H. Li, J. Liu, H. Hu, S. Chen, T. Sa, Equilibrium, kinetic and thermodynamic studies on the adsorption of the toxins of *Bacillus thuringiensis* subsp. *kurstaki* by clay minerals, Appl. Surf. Sci., 255 (2009) 4551–4557.

[33] http://www.thebigger.com/chemistry/surface-chemistry/distinguish-between-physical-adsorption-and-chemisorption

[34] A.B. Soni, V. Verma, A. Keshav, Removal of glycolic acid from aqueous solution using bagasse fly ash, Int. J. Environ. Res., 6 (2012) 297–308.

[35] S. Mubarik, A. Saeed, Z. Mehmood, M. Iqbal, Phenol adsorption by charred sawdust of sheesham (Indian rosewood; *Dalbergia sissoo*) from single, binary and ternary contaminated solutions, J. Taiwan Inst. Chem. Eng., 43 (2012) 926–933.

[36] G. Xue, M. Gao, Z. Gu, Z. Hu, The removal of p-nitrophenol from aqueous solutions by adsorption using gemini surfactants modified montmorillonites, Chem. Eng. J., 218 (2013) 223–231.

[37] A. Wahab, Adsorption of phenol from aqueous solutions by *Luffa cylindrica* fibers: kinetics, isotherm and thermodynamic studies, Egypt. J. Aquat. Res., 39 (2014) 215–223.

[38] A. Gupta, B. Majumder, Simultaneous removal of Cr (VI) and phenol from binary solution using *Bacillus* sp. immobilized onto tea waste biomass, J. Water Process Eng., 6 (2015) 1–10.

[39] Z. Luo, M. Gao, S. Yang, Q. Yang, Adsorption of phenols on reduced-charge montmorillonites modified by bispyridinium dibromides: mechanism, kinetics and thermodynamics studies, Colloids Surf., A, 482 (2015) 222–230.

[40] K. Sadhu, A. Mukherjee, S.K. Shukla, K. Adhikari, S. Dutta, Adsorptive removal of phenol from coke-oven waste water using Gondwana shale, India: experiment, modeling and optimization, Desal. Wat. Treat., 52 (2014) 6492–6504.

[41] E.E. Chang, H.J. Hsing, P.C. Chiang, M.Y. Chen, J.Y. Shyng, The chemical and biological characteristics of coke-oven wastewater by ozonation, J. Hazard. Mater., 156 (2008) 560–567.

[42] P.S. Beula, T. Sai, Kinetics of esterification of palmitic acid with ethanol optimization using statistical design of experiments, Int. J. Chem. Eng. Appl., 4 (2013) 388–393.

[43] C. Thakur, V. Shrivastav, I.D. Mall, Electrochemical treatment of simulated distillary wastewater: parameter and residue disposal study, Chem. Eng. J., 148 (2009) 496–505.

[44] P. Asaithambi, M. Matheswaran, Electrochemical treatment of simulated sugar industrial effluent: optimization and modeling using response surface methodology, Arab. J. Chem., 9 (2011) S981–S987. doi:10.2016/jarabic.2011.10.004.