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Adsorptive removal of phenol from aqueous solutions and coking wastewater by coke produced from hard and soft coking coals

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ABSTRACT

A series of coke samples were prepared by carbonization of different blending of hard and soft coking coals, characterized by different physicochemical methods and a selected sample was used for adsorptive removal of phenol from its aqueous solutions as well as effluent of coke oven plant. The solution pH influenced the phenol adsorption showing highest adsorption in the pH range 4–6. Langmuir, Freundlich and Temkin isotherm models were used to express the sorption phenomena. Both Langmuir and Freundlich isotherm model fitted well to adsorption giving maximum adsorption capacity of 2.1 mg/g. The pseudo-first-order, pseudo-second-order kinetic and intraparticle diffusion models were used to analyze the kinetic data of phenol adsorption. Although pseudo-second-order equation was best fitted in terms of R^2 value, the large difference between the theoretically calculated and experimental amount of phenol adsorbed on coke (mg/g) supported the pseudo-first-order kinetics. Efficiency of the selected sample was also tested for phenol removal from coke oven plant effluent of Neelachal Ispat Nigam Limited containing phenol (307 mg/L), CN^- (13 mg/L), NH_4^+ (285 mg/L), P (20.39 mg/L), chemical oxygen demand (2,850 mg/L). Under optimized conditions, 95% of the phenol was removed along with substantial amount of other contaminants.

Keywords: Adsorption; Kinetics; Activated charcoal; Phenol; Water treatment

1. Introduction

Phenols and phenolic compounds in wastewaters pose one of the most serious environmental threats across the globe and are classified as high-priority pollutants by US Environmental Protection Agency [1]. Phenols are encountered most frequently in the effluents of high-temperature coal conversion processes, coke oven [2], petroleum refineries [3], petrochemicals [4], chemical and pharmaceutical industries, paper and pulp mills, but also present where industrial activities such as paints, resin and plastic, leather and textile manufacturing, rubber reclamation plants, etc., that utilize petroleum distillates [5,6] in the concentration range 1–7,000 mg/L [7].

The toxic and hazardous effects of phenols and their derivatives to human and other organisms as well as plants are well known [5]. Long-term exposure to phenols can lead to irregular breathing, muscle weakness, tremor, coma and even respiratory arrest at lethal doses in humans. Phenols also effect the nervous system, heart, liver and kidney and is readily absorbed through skin and mucosa. Excessive exposure to phenols causes skin/eye irritation, gastrointestinal discomfort and headaches [4,5,8]. Phenolic compounds can also cause unpleasant taste and odour, even at low concentration and can be an obstacle for the use and/or reuse of wastewaters. The permissible limits of phenols in waste and potable waters are set to 0.1 and 0.002 mg/L, respectively, and therefore, removal of phenols from industrial effluents to the permissible levels is essential before their discharge into the water streams.

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Several methods including advanced/electrochemical oxidation [3,9], biological degradation [8], photocatalytic degradation [10,11], membrane separation [12], coagulation [4], solvent extraction [13], reverse osmosis [14] and adsorption [15–21] have been developed, and some of them are currently used for the removal of phenol and its derivatives from wastewaters. Adsorptive removal of phenols using different materials continues to be the most effective technique for both laboratory and industrial scales. Among different adsorbents used, the activated carbons/charcoals (ACs) are the most widely used adsorbents due to their large surface area, micro-porous nature, high adsorption capacity, high purity and easy availability [17,18]. The adsorption capacity of ACs primarily depends on the starting materials used, methods of preparation, physical and chemical treatments of the starting materials, etc., as they significantly affect the surface area, porosity and surface active sites for adsorption in the final product [19,20]. A large variety of starting materials including coals and other naturally occurring raw materials have been used in the preparation of ACs. Coke, another carbonaceous material, is produced in huge quantities in coke oven plants from coal for industrial uses and also possesses moderate adsorption capacity. Adsorption potential of coke samples such as lignite activated coke towards removal of organic pollutants from super heavy oil wastewater [22] and coking wastewater [23], activated coke towards removal of organic compounds with widely distributed molecular size from the deposited lignite pyrolysis wastewater [24], and activated petroleum coke towards removal of colour and chlorinated organics from pulp mill wastewater [25] has been reported.

India is producing about 32 million tonnes (MT) of coke annually for its integrated iron and steel industry in public and private sectors with 23 and 9 MT/annum recovery and non-recovery type byproducts, respectively [26]. In integrated iron and steel industry, wastewater generated from coke oven byproduct plant is considered to be the most polluting stream. Neelachal Ispat Nigam Limited (NINL) is an integrated iron and steel plant in Jajpur district, Odisha, which produces on an average ~1,500 tonnes coke per day from high grade coals for its use in blast furnace. The coke oven gas is condensed to liquor which contains several inorganic and organic contaminants including phenols, cyanide, ammonia, coal tar, etc. After separation of coal tar, the liquor is stored in biological oxygen demand (BOD) plant and then subjected to biological/chemical treatment to reduce their concentrations before final discharge of the effluent. A simpler and cost-effective adsorptive method using indigenously prepared materials as adsorbent could provide a viable alternative to the use of ACs [2,23] as adsorbent or biological degradation/chemical oxidation method [27] for removal of phenol from coke wastewater.

The present study is undertaken to evaluate the efficiency of coke samples, prepared from proper blending of hard and soft coals by carbonization process, as adsorbent towards aqueous phenol under varying conditions. Adsorptive removal of phenol and other contaminants present in coking wastewater of NINL by the most efficient coke sample was also studied to assess its practical utility.

2. Materials and methods

2.1. Materials

Hard and soft graft grade coking coals, collected from coal yards of NINL, were air dried, analyzed and used for production of coke samples by carbonization technique. Altogether three samples were prepared with different blending hard and soft coking coals with weight percentage ratio 80:20, 70:30 and 60:40 and hereafter referred as C-80/20, C-70/30, C-60/40, respectively. In a typical lot, the mixture of coal samples (with 80% particles of +3 mm size) was carbonized in the absence of air in a product oven at a predetermined temperature in between 1,100°C and 1,350°C for 16 h. Carbonization was done by the combustion of fuel gas in flues built in the refractory bricks walls which separates the ovens. The products of combustion of the fuel gas and the volatile products of carbonization were kept separate all the times. The resulted dried material was grounded, sieved (+1 mm to 240 mesh ASTM) and different fractions were stored in airtight containers. Based on the adsorption efficiency of different size fractions of coke samples, the fraction 62 μ was mostly used for adsorption studies.

All other chemicals used were of analytical reagent (AR) grade and were used without further purification. Deionized distilled water was used in all experiments.

2.2. Characterizations of coal and derived coke samples

Chemical analyses of coal and coke samples were done by both conventional and instrumental (LECO proximate analyzer, atomic absorption spectrometer) methods. The components in ash content of coal and coke were analyzed by X-ray fluorescence (Phillips, Axios 4 kW). The crystalline phases in coal and coke samples were identified by recording the powder X-ray diffraction patterns on a Rigaku Miniflex II X-ray diffractometer using Ni filtered CuK$_\alpha$ radiation (30 kV, 15 mA) and at a scanning speed 2° min^{-1}. Fourier transform infra-red (FT-IR) spectra of different samples in KBr phase were recorded on a Shimadzu (IR Affinity 1) FT-IR spectrophotometer with a nominal resolution of 4 cm^{-1} and averaging at least 44 scans to improve signal to noise ratio. The Brunauer–Emmett–Teller surface area of a few samples was measured using Smart Sorb 92/93 surface area analyzer after degassing the samples under vacuum (2×10^{-4} Pa) at 100°C. The point of zero charge (pH$_{PZC}$) was determined by batch acid–base titration technique following the method of Huang and Ostavic [28].

2.3. Adsorption/desorption experiments

Stock solution of phenol (1,000 mg/L) was prepared from AR grade phenol. Working solutions at desired concentration were prepared by dilution of stock solution. Adsorption of phenol from its solution was carried by batch equilibrium adsorption method at 30.0°C ± 0.2°C and continuous shaking (100 strokes/min) using a thermostated water bath shaker (S. D. Instruments & Equipments, India). The initial pH of phenol solutions was adjusted to desired values by dropwise addition of 0.1 M NaOH and 0.1 M HCl solutions which was never exceeded 0.5 mL. At different time intervals and at equilibrium, a definite volume of the phenol solution was withdrawn, centrifuged (Research Centrifuge, REMI R24) or filtered through 0.45 μm Millipore filter to separate the solid adsorbent. The phenol content in solution was analyzed spectrophotometrically (ABBOTA V–1200) at 510 nm using 4-aminoantipyrine/potassium ferricyanide as the colouring agents. The amount of phenol adsorbed per unit mass of adsorbent (q_e in mg/g) was calculated from the difference between the initial and the final phenol concentrations as follows:

$$q_e = (C_i - C_f)V/m \quad (1)$$

where C_i and C_f are the initial and final phenol concentrations (mg/L), respectively; m is the adsorbent dosage (g/L) and V is the solution volume (L).

The effects of various parameters such as pH (2.0–11.0), adsorbent dosage (1.0–40.0 g/L), initial phenol concentration (2.0–50 mg/L), contact time (0–300 min) on adsorption of phenol onto coke samples were studied. It was observed that the adsorption process was essentially complete within 240 min irrespective of coke samples and as such, all further experiments was carried out keeping the adsorption time fixed at 240 min. All adsorption experiments were carried out at least in duplicates and the average values were reported.

The regeneration ability of spent coke samples was investigated by chemical regeneration using 0.1 M NaOH/HCl and thermal regeneration using hot water/steam. Phenol loaded coke sample under experimental conditions: initial phenol concentration, 50 mg/L; coke, 10 g/L; pH, 6.0 and contact time, 4 h was used for desorption. An amount of 2.0 g phenol loaded coke, placed in 100 mL of 0.10 M NaOH solution, was shaken mechanically for 2 h. The desorption equilibrium was attained in about 1 h in comparison to 4 h required for adsorption equilibrium. For treatment with hot water, 2.0 g of phenol loaded coke was placed in 100 mL of water and shaken in a thermostatic water bath at 85°C–90°C for 2 h. Similarly, steam was passed through 2.0 g of phenol loaded coke packed in a small column for different time intervals. The phenol desorbed at different time intervals and at the end was estimated spectrophotometrically. The regenerated coke was washed with distilled water and dried at 105°C for further use.

In order to see the practical applicability, efficiency of coke samples was also assessed for the removal of phenol from the effluent of coke oven plant under optimized set of conditions of batch equilibrium method. In such experiments, the partially treated effluent of coke oven plant of NINL containing phenol (307 mg/L), CN^- (13 mg/L), NH_4^+ (285 mg/L), P (20.39 mg/L) and COD (2,850 mg/L) was used as the adsorbate.

3. Results and discussion

3.1. Characteristics of coal and derived coke samples

The percentage of volatile matter (VM), ash and fixed carbon (FC) in hard and soft coking coals and their combination in different ratios are given in Table 1. In comparison, the VM of soft coal is more than hard one while its variation is negligible with variation of their amount in the blended samples. The general characteristics of coke samples derived from hard/soft coking coals are presented in Table 2. The high coke strength after reaction (CSR) values of coke in all samples indicates their better strength. The ash content is relatively higher than the activated charcoals generated from different raw materials [18].

Preliminary results of phenol adsorption on coke samples under identical conditions showed that C-60/40 sample exhibits highest adsorption efficiency in all size fractions (Table 3). Among C-60/40 coke samples, the 62 μ size fraction (hereafter denoted as C-60/40-62) showed the maximum phenol adsorption (Table 3). Hence all further characterizations and adsorption studies were carried out using C-60/40-62.

The powder XRD patterns and FT-IR spectra of hard/soft coals and representative coke samples (C-60/40-62 and C-70/30-62) are presented in Figs. 1 and 2, respectively. The broad peaks at 2θ values ~26.4° and 43.0° are characteristic of amorphous carbonaceous materials [29,30]. FT-IR spectra of both the coal samples showed characteristic bands for –OH and –NH stretching in between 3,500 and 3,100 cm^{-1}, C–H aromatic in between 3,100 and 3,000 cm^{-1}, C–H aliphatic in between 3,000 and 2,800 cm^{-1} besides bands in between 1,640 and 1,750 cm^{-1} due to C=O stretching vibrations of phenolic ester, carboxylic acid and conjugated ketonic structures. The absorption peak at ~1,400 cm^{-1} was assigned to the C–H stretch in $-CH_2-$ or $-CH_3$ while peaks at 1,300–900 cm^{-1} with the maximum at ~1,089 cm^{-1} was attributed to C–O stretching vibrations [30]. The bands below 900 cm^{-1} are attributed to various bands related to aromatic, out of plane C–H bending. FT-IR spectra of two representative coke samples C-60/40-62

Table 1
Proximate analysis of hard and soft coking coals

Parameters	Samples				
	Hard	Soft	Hard/soft (60/40)	Hard/soft (70/30)	Hard/soft (80/20)
VM	22.79	26.48	24.24	23.89	23.5
Ash	7.20	8.58	7.72	7.61	7.50
FC	69.51	65.01	68.04	68.50	69.0
Moisture, %	10.22	9.88	10.10	10.12	10.14
Porosity, %	11.38	12.56	11.18	11.64	9.61
Density. g/cm^3	0.72	0.78	0.74	0.73	0.74
Calorific value, kCal/kg	5,850	5,550	5,732	5,758	5,790
Carbon content, %	88.46	87.20	87.85	88.08	88.25
Crucible swelling number	6–9	0–5.5	7–9	7–9	7–9

Table 2
Characteristics of coke samples derived from hard/soft coking coals

Parameters	Coke samples prepared from				
	Hard	Soft	Hard/Soft (60/40)	Hard/Soft (70/30)	Hard/Soft (80/20)
+1 mm	32.12	31.82	36.4	35.95	35.62
–1 mm	60.48	60.68	63.6	62.82	62.42
M40	88.12		85.6	86.7	86.92
M10	4.02		5.80	4.42	4.20
CRI[a]	18.48		21.8	20.48	20.2
CSR	68		64.82	65.88	66.82
Porosity (%)	44.08		49.3	48.92	47.42
Surface area (m^2/g)[b]			18.43	17.30	16.12
True Sp. gr., g/cm^3	2.0		2.07	2.04	2.02
Approx. Sp. gr, $g.cm^3$	1.98		1.95	1.72	1.77
VM	0.52		0.68	0.60	0.58
Ash	11.02		11.47	11.32	11.17
FC	88.46		87.85	88.08	88.25
Sulphur	0.68		0.56	0.60	0.62
Ash components					
Silica	64.22		63.02	65.0	62.02
Alumina	22.42		24.90	25.12	25.62
Total iron	4.89		5.04	5.42	5.82
CaO	4.68		4.76	4.78	4.88
MgO	1.02		1.20	1.22	1.18
P_2O_5 (P)	0.02		0.018	0.016	0.017

[a] CRI, coke reactivity index.

[b] For sample size fraction 62 μ.

Table 3
Comparative phenol adsorption by different fractions of coke samples (phenol, 11.4 mg/L; coke, 10 g/L; pH, 7.05 and contact time, 4 h)

Size fraction	C-60/40	C-70/30	C-80/20
+1 mm	45.3	39.5	34.4
+0.5 mm	48.5		
+18 mesh (850 mic)	53.5	46.6	40.4
+50 mesh (300 mic)	66.2		
+71 mesh (212 mic)	69.4		
+100 mesh (150 mic)	71.0		
+240 mesh (64 mic)	77.5	67.9	58.6

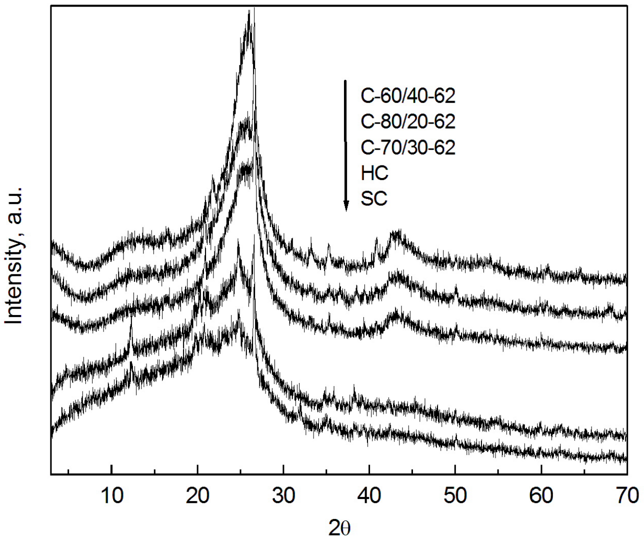

Fig. 1. Powder XRD patterns of coal and coke (C-60/40-62 and C-70/30-62) samples.

and C-70/30-62 displayed the similar peaks but with relatively lower intensities.

The surface area values of derived coke sample are found to be 18.43, 17.30 and 16.12 m^2/g for C-60/40-62, C-70/30-62 and C-80/20-62, respectively. These values are relatively low in comparison to values reported for pet coke, coal and AC samples (see later Table 4) presumably due to use of higher carbonization temperature for coke preparation. The values of pH_{pzc}, defined as pH of suspension where the surface charge is equal to zero, are found to be 5.7 and 5.9 for C-60/40-62 and C-70/30-62, respectively, which are well within the range of values reported for AC samples derived from different starting materials [31].

3.2. Adsorption of phenol on coke sample (C-60/40-62)

3.2.1. Effect of contact time

Fig. 3 depicts the effect of contact time on the removal of phenol at various initial concentrations (10–30 mg/L).

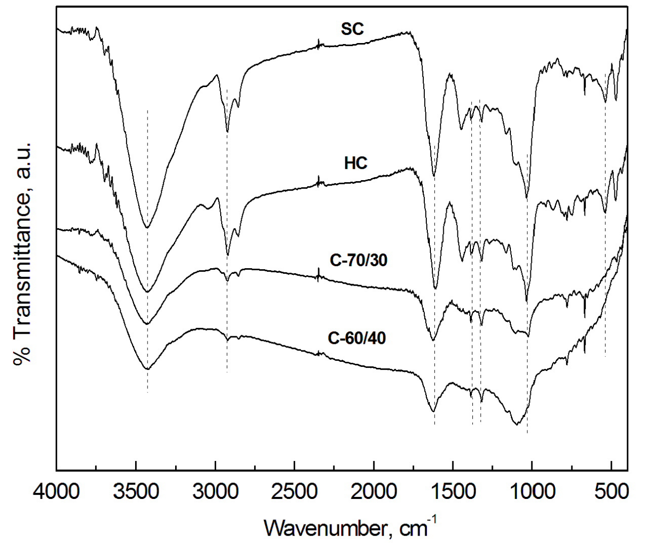

Fig. 2. FT-IR spectra of coal and coke (C-60/40-62 and C-70/30-62) samples.

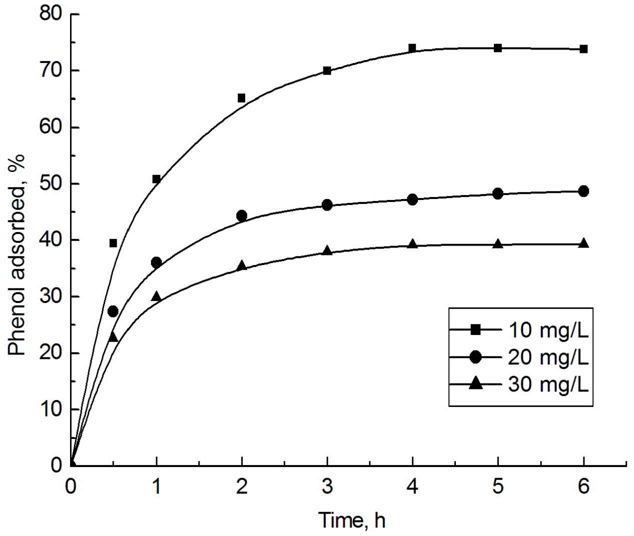

Fig. 3. Time profile adsorption of phenol on C-60/40-62 at pH ~6.4 with adsorbent dose, 10 g/L.

Table 4
Adsorption parameters derived from Langmuir and Freundlich isotherms along with maximum adsorption capacity of different materials for phenol

Sample	Surface area, m^2/g	Initial phenol conc., mg/L	pH	Adsorption parameters						
				Langmuir			Freundlich			Ref
				Q_o (mg/g)	b (L/mg)	R^2	K_F	$1/n$	R^2	
Samla coal	133.35			13.23	0.00813	0.9675	1.442	0.3176	0.9442	[34]
Residual Samla coal	165.05			45.45	0.0133	0.9347	6.357	0.2728	0.9333	[34]
Coke breeze				0.172	0.0015	0.9721	0.9171	2.855	0.9569	[34]
Petroleum coke	96.44			6.01	0.00267	0.9655	0.2591	0.4149	0.9477	[34]
Rice husk char	230.09			7.91	0.00318	0.9867	0.909	0.2799	0.9316	[34]
AC-commercial				322.5	0.0154	0.9856	53.27	0.266	0.9448	[34]
Activated carbon[a]	1,634	1–12	7.0	17.83	0.46	0.999	12.48	1.162	0.999	[35]
Activated carbon[b]	1,474	1–12	7.0	0.55	2.68	0.9273	134.64	3.325	0.991	[35]
Activated carbon[c]	490.1	46-300	8.0	262.3	0.385	0.95	118	0.17	0.92	[32]
Activated carbon[d]	–	25–250	~6.0	149.25	0.16	0.98	29.37	0.403	0.86	[36]
Activated carbon[e]	1,809	10–500		244	0.008	0.987	16	0.404	0.997	[37]
Activated carbon[f]	–	–	4.0	42.31	0.209	0.969	3.205	0.255	0.992	[38]
AC-commercial		10–200	–	49.72	0.1099	0.9947	6.193	0.616	0.984	[39]
Activated carbon[g]	632.8	94–376	6.0	112.8	0.022	0.987	0.76	0.258	0.972	[40]
Coke		20–300		90	0.08	–	–	–	–	[41]
Lignite coal	–	–	–	10.0	–	–	–	–	–	[42]
Granular activated coal		5.157	8.4	1.481	0.065	0.98	0.97	1.261	0.97	[2]
Coke	18.43	10–50	6.0	2.07	0.1625	0.989	1.815	0.3431	0.992	This work

[a] From K_2CO_3 and KOH treated tobacco residue.
[b] From date-pit.
[c] From biomass.
[d] From $ZnCl_2$ treated soybean straw.
[e] Lignite coal.
[f] Water hyacinth.
[g] Biologically treated coke wastewater containing phenol 5–15 mg/L.

More than 70% of the total phenol adsorbed in the first 1 h of adsorption indicating the adsorbent has plenty of readily accessible sites. This is followed by slow adsorption leading to an equilibrium within ~4 h which is practically same irrespective of initial phenol concentration. Continuous and smooth adsorption curves are observed in all concentrations. It is also seen that the overall phenol uptake (mg/g of coke) increased with increase of its initial concentration.

3.2.2. *Effect of solution pH*

It is well known that phenol adsorption onto ACs occurs via a complex interplay of electrostatic and dispersion interactions by three possible mechanisms [32]:

- π–π dispersion interaction between the phenol aromatic ring and the delocalized π electrons present in the aromatic structure of the graphite layers.
- Hydrogen bond formation.
- Electron donor–acceptor complex formation at the carbon surface where the oxygen of the surface carbonyl group acts as the electron donor and the phenol aromatic ring as the acceptor.

In addition, electrostatic interactions can play a significant role if phenol is predominately as phenolate ion interacts with the charged AC surface. Both aspects are determined by the solution pH. The effect of initial pH in the range 2–11 on phenol adsorption is presented in Fig. 4. It is evident that the removal of phenol remains practically unaffected with variation of pH from 4.0 to 6.0 and thereafter decreases progressively with further increase of pH. A similar trend of pH effect has been observed for the adsorption of phenol on ACs [32]. Phenol as a weak acid compound ($pK_a \approx 9.89$) undergoes dissociation leading to negative phenolate ion at higher pH, especially at pH > 8.0. The surface of coke becomes negatively charged at pH above its pH_{pzc}, that is, 6.5. Also at higher pH, the coke surface acquires negative charge due to adsorption of OH^- ion and dissociation of polar acidic functionalities such as –COOH on coke surface. The decrease of adsorption at higher pH is, therefore, partly due to ionization of adsorbate molecules, electrostatic repulsions between the negative surface charge and phenolate ion, and the greater solubility of phenolate ion at higher pH. At lower pH values ≤4.0, both the phenol molecules and the chemical groups on coke surface are mostly protonated which results in a decrease of interactions between coke sites and phenol molecules and in turn, the amount of phenol adsorbed decreases as the pH decreases. As such, all further experiments for optimization of adsorption parameters were carried out keeping the pH at ~6.0.

3.2.3. *Effect of adsorbent dose on phenol adsorption*

Fig. 5 shows the effect of adsorbent dose (1.0–40.0 g/L) on removal percentage of phenol at fixed initial concentration (10 mg/L) and pH (~6.0). It is seen that the percentage of phenol removal increases almost linearly at lower dose of coke (up to 8 g/L) but deviates from linearity at higher doses. The deviation at higher doses is primarily due to non-availability of enough phenol in solution for adsorption.

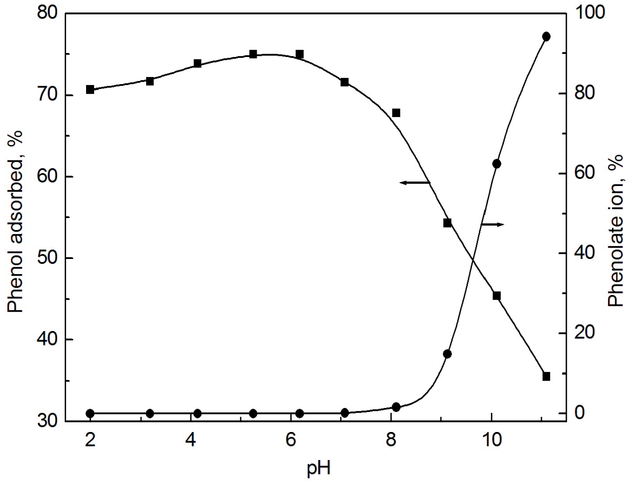

Fig. 4. Effect of pH on phenol dissociation and its adsorption on C-60/40-62 with initial phenol concentration, 10 mg/L and adsorbent dose, 10 g/L.

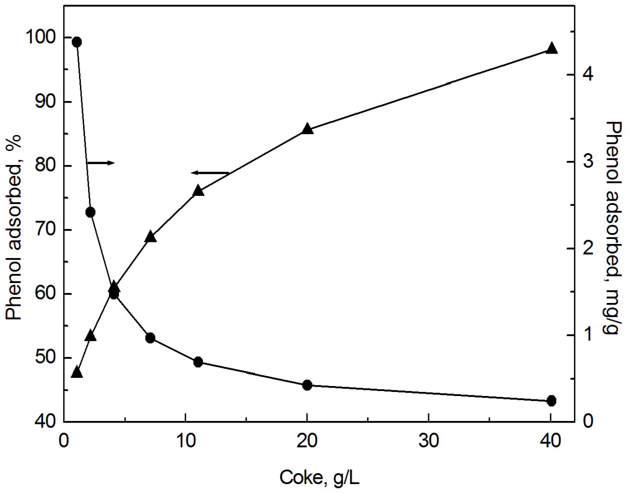

Fig. 5. Effect of adsorbent dose on adsorption of phenol by C-60/40-62 at pH 6.3 ± 0.2 with initial phenol concentration, 10 mg/L.

On the other hand, the increase of phenol adsorption with increasing adsorbent dose is mainly attributed to availability of more functional groups and active adsorption sites. It may be noted that the overall uptake of phenol is decreased with increase of adsorbent dose. For instance, the percentage of phenol removal increased from 47 to 98.9 with an increase of adsorbent dose from 1 to 40 g/L at the expense of decreased phenol uptake from 4.37 to 0.24 mg/g. Based on the above findings, a coke dose of 10 g/L was maintained in all the subsequent experiments to keep a balance between the total adsorbed amount of phenol and percentage of removal.

3.2.4. *Effect of initial phenol concentration and adsorption isotherms*

The effect of initial phenol concentration in the range (10–50 mg/L), keeping all other parameters constant, is shown in Fig. 6. As evident from the figure, the removal efficiency decreased with increase of initial phenol concentration. The adsorption data are fitted to different adsorption isotherms which are important to describe how solutes interact with adsorbents, and are critical in optimizing the use of adsorbents. In the present case, the adsorption data were fitted to linearized forms (Eqs. (2)–(4)) of three commonly used adsorption isotherms namely the Langmuir, Freundlich, and Temkin and Phyzev.

$$\text{Langmuir: } C_e/q_e = 1/Q_o b + C_e/Q_o \tag{2}$$

$$\text{Freundlich: } \ln q_e = \ln K_F + (1/n) \ln C_e \tag{3}$$

$$\text{Temkin and Pyzhev: } q_e = (RT/b) \ln K_T + (RT/b) \ln C_e \tag{4}$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate; q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent; Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively; K_F ((mg/g)(L/mg)$^{1/n}$) is roughly an indicator of the adsorption capacity; (1/n) is the indicator of the adsorption intensity, $RT/b = B$ is the Temkin constant related to adsorption heat and K_T (L/mg) = A is the Temkin parameter related to equilibrium binding energy.

The plots of C_e/q_e vs. C_e (Fig. 6) is practically linear with $R^2 = 0.98$. Values of Q_o and b, calculated from this plot using the least square method, are listed in Table 4. The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless separation factor (R_L):

$$R_L = 1/(1 + bC_o) \tag{5}$$

where b is the Langmuir constant and C_o is the highest phenol concentration (mg/L) used. The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The value of R_L is found to be 0.109 indicating the adsorption of phenol on coke under the experimental conditions used is favourable.

The plot of lnC_e vs. lnq_e is also linear (Fig. 7) with R^2 value close to unity (0.992) indicating slightly better fitting of adsorption data to Freundlich isotherm. The values of lnK_F and 1/n, obtained from the slope and intercept of the linear Freundlich plot, are also listed in Table 4. Relatively lower value of K_F in comparison to those reported for AC samples is indicative of moderate adsorption capacity of coke [33]. The value of 1/n, a measure of the surface heterogeneity, in the range 0 and 1 represents favourable adsorption, and as its value gets closer to zero, the surface becomes more heterogeneous [34]. A value of 0.3431 in the present case indicates that the adsorption condition is favourable.

The adsorption data is, however, not fitted well to Temkin isotherm model. The plot of q_e vs. lnC_e (figure not shown) yielded relatively lower R^2 value (0.93) than the values obtained from fitting of adsorption data to Langmuir and Freundlich isotherm models.

The derived adsorption parameters of Langmuir and Freundlich isotherms are listed in Table 4 along with maximum adsorption capacity (Q_o) of some relevant carbonaceous samples. Although the experimental conditions used in different materials were widely varied, it is evident that the value of Q_o in the present case (2.07 mg/g) is relatively lower than the values reported for raw coal samples such as Samla coal (13.2 mg/g), residual Samla coal (45.5 mg/g) [34] or even lignite coal (10.0 mg/g) [42], presumably due to lower surface area of coke sample. The Q_o values obtained with petroleum coke (6.0 mg/g) or rice husk char (7.9 mg/g) [34] are also higher due to much higher surface area values. The AC samples, commercial or prepared from different natural sources, with relatively high surface area also showed substantially higher Q_o values (commercial AC, 7.9 mg/g [39]; date-pit AC, 262 mg/g [32]; biomass AC, 149 mg/g [37]; chemically treated soybean AC, 244 mg/g [37]), partly due to use

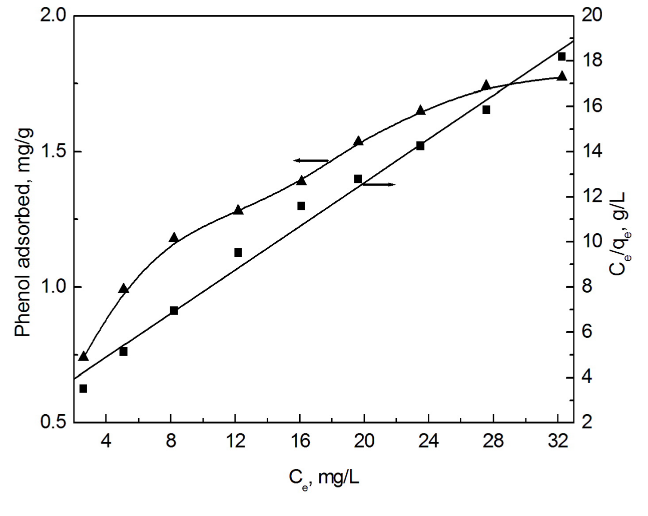

Fig. 6. Fitting of adsorbent data to Langmuir isotherm model (initial phenol concentration, 10–50 mg/L; adsorbent dose, 10 g/L and pH 6.3 ± 0.2.

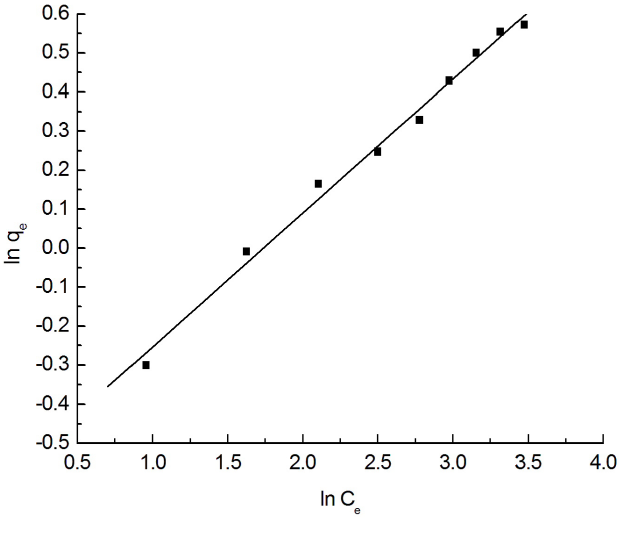

Fig. 7. Fitting of adsorbent data to Freundlich isotherm model (initial phenol concentration, 10–50 mg/L; adsorbent dose, 10 g/L and pH 6.3 ± 0.2.

of higher initial phenol concentration for adsorption experiments. Interestingly, maximum adsorption capacity value of coke sample is higher than those reported for KOH treated tobacco residue AC (0.55 mg/g) [35] and granular activated coal (1.48 mg/g) [2] presumably due to their unfavourable adsorption condition which is also evident from $1/n$ values obtained from corresponding Freundlich isotherms (Table 4).

3.2.5. Adsorption kinetics

The adsorption data were fitted to various kinetic models, namely Lagergren pseudo-first-order kinetics (Eq. (6)), the pseudo-second-order kinetics (Eq. (7)) and intraparticle diffusion model (Eq. (8)):

$$\ln(q_e - q_t) = \ln q_e - k_1.t \quad (6)$$

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t \quad (7)$$

$$q_t = k_i t^{0.5} + c \quad (8)$$

where q_e refers to the amount of phenol adsorbed (mg/g) at equilibrium; q_t refers to the amount of phenol adsorbed (mg/g) at any time, t (h); k_1 is the equilibrium rate constant of pseudo-first-order sorption (time^{-1}); k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg h); k_i is intraparticle diffusion constant (mg/g min$^{0.5}$).

The plots of $\ln(q_e - q_t)$ vs. t with varying initial phenol concentrations (Fig. 8) are linear with R^2 values in the range 0.957–0.987. The values of k_1 and q_e, calculated from the least squares slopes of such plots, are given in Table 5. As expected, the values of rate constants are gradually decreased with the increase of the initial phenol concentration. It is also seen that the difference between the calculated and experimental values of q_e is small.

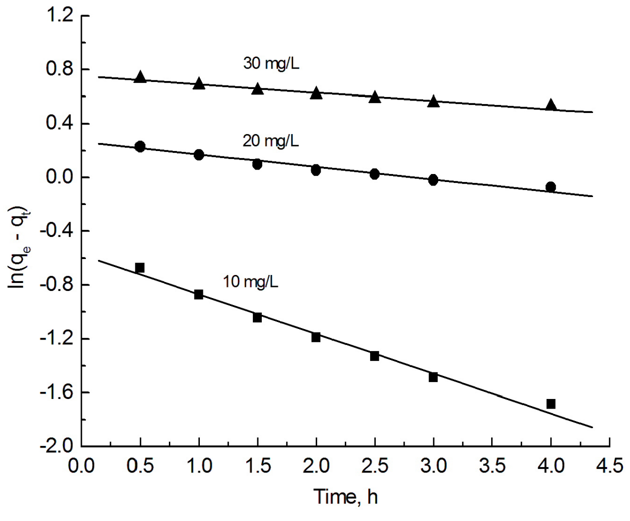

Fig. 8. Fitting of adsorbent data to pseudo-first order kinetics (initial phenol concentration, 10–30 mg/L; adsorbent dose, 10 g/L and pH 6.3 ± 0.2.

Further treatment of adsorption data to pseudo-second-order kinetic model showed that the plots of t/q_t vs. t are linear with R^2 values close to unity (0.997–0.999) at all concentrations (Fig. 9). The values of q_e and k_2, derived from slopes and intercepts of such plots, are also given in Table 5. Although the R^2 values are very close to unity, the difference between the calculated and experimental values of q_e is quite large indicating pseudo-second-order kinetics for adsorption of phenol on coke through rate-controlled chemisorption process is less likely in the present case. In contrast, pseudo-second-order adsorption mechanism has been reported predominant in the cases of phenol adsorption by ACs prepared from different sources such as biomass material [36], beet pulp [43] and plum kernels [44].

The fitting of adsorption data to intraparticle diffusion model showed that the plots q_t vs. $\ln q_e$ deviate from linearity (figure not shown) with non-zero intercept (c) and more than one linear portion. It is known that if the value of c is zero, then the rate of adsorption is controlled by intraparticle diffusion for the entire adsorption period. As the plots are nonlinear over the whole time range implying more than one process affected the phenol adsorption.

3.2.6. Desorption studies

Desorption studies help not only to elucidate the mechanism of adsorption but also to recover the valuable phenol and adsorbent for repeated use. A variety of chemical/thermal regenerating agents such as HCl, NaOH, ethanol, ethanol–NaOH–H_2O_2, ethanol–H_2O_2, hot water and steam have been used for regeneration of spent date-pit AC [32], commercial ACs [39,45]. Among chemical regenerating agents, NaOH [45] and its combination with H_2O_2 [32] were found most effective. In the present case, phenol loaded coke was treated with NaOH, HCl, hot water and steam for release of adsorbed phenol. Treatment with $[\text{NaOH}] \leq 0.10$ M for 1.0 h results not more than 65% desorption of adsorbed phenol; the desorption is mainly due to formation of sodium salt of phenol which facilitates the desorption. Under identical conditions, the HCl treatment desorbed only 6.54% phenol from the spent coke. The amount of phenol desorption form spent coke by hot water treatment (85°C–90°C) is time dependent and a maximum of 72% phenol gets desorbed in 1.0 h. Phenol desorption is found most effective with steam which reached up to 95% on passage of steam for 1.0 h. Further experiments with steam regenerated coke sample showed that both phenol adsorption and desorption progressively decreased in subsequent cycles up to fourth cycle as observed previously in the case of phenol desorption from AC [32]. The above study clearly indicates that phenol desorption from spent coke is not quantitative and more studies are required on regeneration of spent coke for repeated use.

3.2.7. Removal of phenol from effluent of coke oven plant

In order to see the practical applicability of prepared coke as adsorbent in real systems, the efficiency of coke sample was tested using coke oven plant effluent of NINL. In the present case, coke oven plant effluent after partial biological treatment (Aeration-1) with phenol (307 mg/L) and other hazardous contaminants such as CN^- (13 mg/L), NH_4^+

Table 5
Kinetic parameters for adsorption of phenol on coke sample

Samples	Initial phenol concentration, mg/L	q_e, mg/g (experimental)	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion			Reference
			q_e, mg/g	10^3 k_1 min	R^2	q_e, mg/g	k_1, g/mg min	R^2	k_i, mg/g min$^{1/2}$	c (mg/g)	R^2	
Samla coal	1,000			2.53					0.0353			[34]
Residual Samla coal	1,000			2.99					0.0307			[34]
Commercial AC	1,000			4.83					0.0268			[34]
Activated carbon[a]			1.490	83	0.819	5.19	0.082	1.00	0.06	4.95	0.771	[35]
Activated carbon[a]			0.791	192	0.802	2.92	0.52	1.00				[35]
Activated carbon[b]	46–300		12.6–39.7	33.9–19.4	0.95–0.87	26.7–76.3	0.0064–0.0013	1.0	1.129–0.225	–	–	[32]
Activated carbon[c]	25–250	23.4–140.7	5.88–43.92	4.73–8.66	0.587–0.971	23.3–142.5	0.149–0.012	0.99–1.0	0.167–0.402	7.71–82.65	0.959–0.995	[36]
Activated carbon[d]	250	22.26	1.195	70.17	0.992	22.27	0.2212	1.0		–	–	[38]
Commercial AC	10–250			23.54	0.987							[40]
Granular AC	10–40		0.169–0.264	19.5–162	0.997–0.999	-	-	-	–	–	–	[2]
Coke	10	0.74	0.55	4.82	0.87	84.74	0.0183	0.996	–	–	–	This work
	20	0.98	1.27	1.38	0.967	106.4	0.0210	0.996				
	30	1.18	2.09	0.975	0.957	128.2	0.0184	0.996				

[a] From K_2CO_3 and KOH treated tobacco residue.
[b] From date-pit.
[c] From biomass.
[d] Lignite coal.

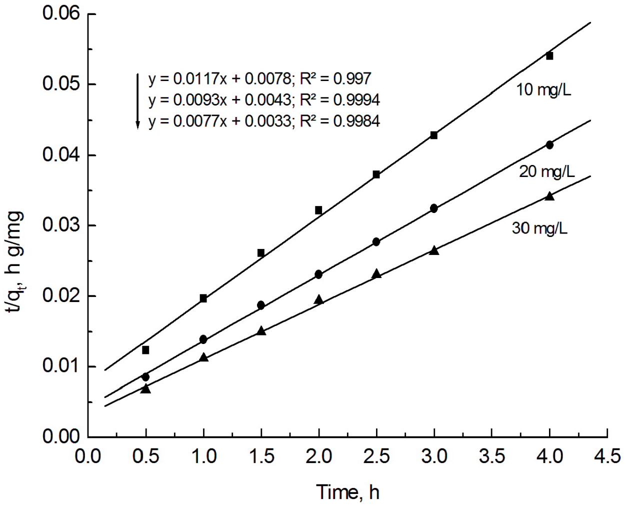

Fig. 9. Fitting of adsorbent data to pseudo-second-order kinetics (initial phenol concentration, 10–30 mg/L; adsorbent dose, 10 g/L and pH 6.3 ± 0.2.

(285 mg/L), P (20.39 mg/L), COD (2,850 mg/L) at pH 9.45 was used for treatment. Under the optimized set of conditions, weighed amounts of coke (100, 120, 140, 160, 180 and 200 g/L) was added to 100 mL of effluent and the pH was adjusted to pH ~6.0. After allowing for ~4 h under stirring condition, the remaining phenol contents in treated effluent were estimated. It is found that more than 95% of phenol gets adsorbed with a coke dose of 200 g/L. In order to optimize the pH range for best results, the pH of the coke oven plant effluent was varied in the range 2–9.45, keeping the coke dose fixed at 200 g/L. As evident from Fig. 10, the phenol adsorption from the effluent is practically unchanged in the pH range 4–6 but decreased significantly at higher pH, especially at pH ≥ 8.0. It may be noted that the other contaminants (CN^-, NH_4^+, P and COD), present in the coke oven effluent, are also removed along with phenol. Adsorption of these contaminants is also pH dependent (Fig. 10). At optimum pH (~6.0), 94.7% of phenol, 68.2% of CN^-, 90.1% of P and 83.2% of COD from coke oven effluent are removed. In comparison, using activated coke with identical dose (200 g/L) and pH ~9.0, 91.6% of COD and 90% of colour from coking wastewater were removed [23]. The above results indicate that coke samples derived from coking coals, as such or after suitable activation, can be further exploited as promising adsorbents in treatment of coking wastewater and other phenol containing industrial effluents.

4. Conclusions

The present study demonstrated the potential of coke samples, prepared by carbonization of different blending of hard and soft coking coals, for adsorption of phenol from aqueous solution/coke oven plant effluent by batch equilibrium method. Phenol adsorption on coke was strongly dependent on the pH of the solution especially at pH > 6.0. The phenol uptake was increased with increase of coke dose and decrease of initial phenol concentration. Under optimized conditions with coke dose (10 g/L), pH (~6.0) and contact time (4 h), ~74% of phenol (10 mg/L) was adsorbed. The time course adsorption data were fitted well to pseudo-first-order rate expression and the equilibrium adsorption data were better described by Freundlich isotherm model. Among different chemical/thermal agents used for regeneration of spent coke, the steam treatment was found most effective which desorbed up to 95% of adsorbed phenol on coke in 1.0 h. Under optimized conditions, the most efficient coke sample was also effective for the removal of phenol and other contaminants such as CN^-, NH_4^+, P and COD from partially treated coke oven plant effluent. Further studies are required for activation of coke samples to improve the adsorption capacity towards phenol and to optimize the regeneration process of spent coke samples for repeated use.

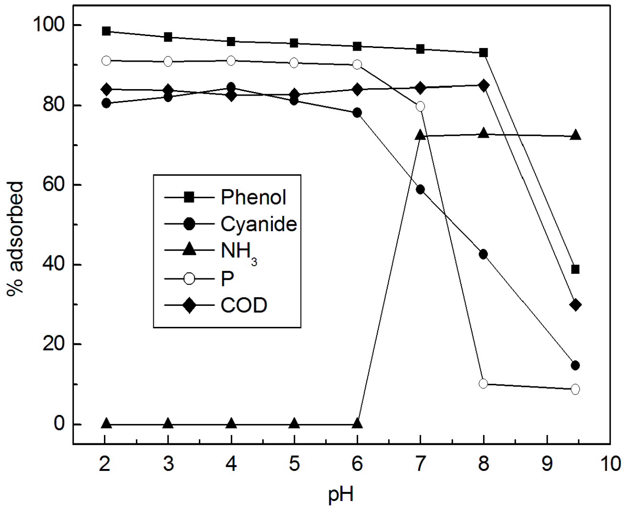

Fig. 10. pH dependent adsorption of phenol and other contaminants from coke oven plant effluent by C-60/40-62 (adsorbent dose 200 g/L).

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