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Enhancement of phenol adsorption on mesoporous carbon monolith modified by NaOH and NH_3: equilibrium and kinetic studies

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ABSTRACT

Carbon-coated monoliths (CCMs) were chemically modified by sodium hydroxide (NaOH) and ammonia aqueous solution (NH_3) in order to enhance phenol adsorption. The adsorptive performance of phenol onto CCM-NaOH and CCM-NH_3 was comparatively evaluated by batch mode. Experiments were carried out by varying pH, contact time, and initial adsorbate concentration. The optimum molarities for modification were 1.5 M NaOH and 2 M NH_3 solutions. The basicity groups of modified CCM were 0.198 and 0.339 mmol g^{-1} for CCM-NaOH and CCM-NH_3 by Boehm titration method, respectively. The presence of basic groups (O–H and NH_3) was also confirmed by FT-IR. The studies showed optimum phenol adsorption, at pH 4 for both adsorbents. As compared to unmodified CCM, the CCM-NH_3 and CCM-NaOH enhanced phenol uptake by 16.5 and 9.7%, respectively. The maximum equilibrium adsorption capacities were 51.29 ± 0.7 mg g^{-1} for CCM-NaOH and 54.45 ± 0.7 mg g^{-1} for CCM-NH_3 in the range of concentration 50–350 mg L^{-1}. The equilibrium adsorption data for CCM-NaOH and CCM-NH_3 was fitted to both Langmuir and Freundlich models. Kinetic studies of both modified CCMs showed better applicability of pseudo-second-order kinetics model. The regeneration studies showed a 26% drop in adsorption capacity after four cycles for CCM-NH_3.

Keywords: Phenol adsorption; Mesoporous carbon-coated monoliths; Surface modification; Ammonia; Sodium hydroxide

1. Introduction

In recent years, industrial processes produce a variety of pollutants that might bring negative impacts for ecosystems and humans. Phenol, a derivative of benzene, is one of the most common organic water pollutants generates toxicity even at low concentrations. Phenol pollutant may be found in waste water of many industries such as petrochemicals, oil refineries, plastics, leather, paint, pharmaceutical, steel industries, and pesticides. Phenolic compounds constitute 11th of the 126 chemicals which have been designated as priority pollutants by the United States Environmental Protection Agency. It is recommended to lower the phenol content to less than 1.0 mg L^{-1} in the industrial effluents for safe discharge into surface waters. While World Health Organization

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recommends the allowable phenolic concentration of 0.001 mg L^{-1} in potable waters [1–4]. These water pollution problems are becoming an alarming issue and there is a growing awareness about the need to curb this issue.

Various removal technologies such as oxidation [5,6], precipitation [7], adsorption [8–11], ion exchange [12], and solvent extraction [13] have been developed for the removal of phenol from wastewater [14]. Among these, adsorption is considered as an efficient and economically feasible technology for the removal of contaminants from wastewaters due to its simple design, ease of operation, and its ability to effectively remove pollutants even at low concentrations [15].

Activated carbon is commonly used as adsorbent in low volume and high strength phenolic wastewater adsorption process [14] due to its large surface area, microporous nature, and high adsorption capacity [16]. However, pore blockage and regeneration cost are the difficulties faced in the use of activated carbon as adsorbent [17,18]. Monolithic structure is recently introduced due to its favorable properties such as low pressure drop, high geometric surface area, short diffusion lengths, and less attrition by vibration and thermal shock resistance [19,20]. Previous work revealed the applicability of carbon-coated monolith (CCM) for adsorption process [8,21]. The textural characteristics and surface chemistry of carbons play a fundamental role in phenol adsorption [22]. The surface properties of carbon materials can be modified in order to enhance their affinities toward phenol adsorption [23,24]. The formation of basic, carbonyl, and surface nitrogen groups may contribute to an increase in the phenol removal capacity [25,26].

This work aims to investigate the surface modification of CCM as an adsorbent for the adsorption of phenol. In this study, cordierite carbon monolith was chemically treated with sodium hydroxide and ammonia solution. The modified CCM was termed as sodium hydroxide-modified carbon-coated monolith (CCM-NaOH) and ammonia-modified carbon-coated monolith (CCM-NH_3). The adsorption performance of phenol on the modified CCM was then evaluated.

2. Experimental

2.1. Chemical and materials

The cordierite monoliths (circular cross-section with square channel) having length of 10 cm and diameter of 2.5 cm were purchased from Beihai Huihuang Chemical Packing Co., Ltd., China. Chemical compositions of monolith are SiO_2—50.9 ± 1%, Al_2O_3—35.2 ± 1%, MgO—13.9 ± 0.5%, and others <1%. The ceramic monolith has channel width 1.02 ± 0.02 mm, channel density of 62 cell cm^{-1} (400 cpsi), and wall thickness of 0.25 ± 0.02 mm. Phenol (99%) was supplied by Sigma–Aldrich. Furfurly alcohol (99%), polyethylene glycol (PEG) (M_W = 8,000), pyrrole (99%), and nitric acid (65%) were purchased from Sigma-Aldrich. For modification of monolith, sodium hydroxide was purchased from Sigma-Aldrich while ammonia solution (25 wt.%) was purchased from System (ChemAR). The reagents and chemicals used were of analytical grade or as specified.

2.2. Preparation of modified CCM

The monolith was polymerized using dip-coating method [27]. Furfuryl alcohol as carbon source (60 mL), polyethylene glycol (PEG, M_W = 8,000) as pore former (33 g), and pyrrole as binder (10 mL) were homogeneously mixed. The partially polymerized furfuryl resin was stirred at 20 ± 1°C using HNO_3 as a catalyst. Five millilitres acid was constantly added for an hour at an interval of every 5 min. To avoid a thermal runaway condition, the reaction was carried out in an ice bath. Dried monolith was immersed in a viscous polymerized mixture for 30 min. The excess solution choking monolith channels was purged using pressurized air. A light brown monolith was dried in an oven at 100°C for 24 h. Consequently, the monolith was carbonized in a furnace at 700°C for a residence time of 4 h under N_2 atmosphere. This finally produced CCM.

The CCM was then chemically modified using sodium hydroxide or ammonia solution (250 mL). One piece of CCM (approximately 0.6 g carbon) was immersed into the solution. The sample was left in a shaker for 24 h at room temperature. The sample (modified CCM) was removed from the solution and then rinsed with de-ionized water until it attains neutral pH. The final products were then dried at 100°C for 24 h in an oven. These samples were then kept in a desiccator and known as sodium hydroxide-modified carbon-coated monolith (CCM-NaOH) and ammonia-modified carbon-coated monolith (CCM-NH_3). To determine the optimum molarities of basic solution, batch adsorption studies (see Section 2.5) were carried out using CCM modified with different concentrations (from 0.5 to 3 M).

2.3. Characterization of modified CCM

To study the functional groups present on modified CCM surface for phenol adsorption, fourier transform-infra red (FT-IR) analysis was carried out.

Surface *characteristics*, pore size distribution, and specific surface area were measured by N_2 adsorption/desorption using a Sorptomatic V1.03 micropore analyzer. The BET method is used for the calculation of the surface area. Scanning electron microscopy (SEM) was carried out using an electron microscope system (LEO 1450VP) for surface morphology analysis of CCM. The point of zero charge (pH_{PZC}) of modified CCM was determined by solid addition method [28]. Potassium nitrate (KNO_3, 50 mL) solutions with pH ranging between 2 and 10 were adjusted using 0.1 M KOH and 0.1 M HNO_3 solutions. Modified CCM (0.5 g) was added to each solution and the solutions were agitated in a shaker at 150 rpm under ambient temperature conditions. The difference between initial and final pH (ΔpH) was plotted against pH_i. The point of zero charge (ΔpH = 0) was determined from the intersection point between the resulting curve and abscissa (x-axis). Boehm's acid–base titration study was carried out to determine acid and base functional groups present of monolith sample. The surface active (acid and base) sites present on samples were determined by Boehm's acid–base titration experiments. The acidic sites present on CCM-NH_3 and CCM-NaOH (0.5 g) were neutralized by 50-mL 0.1 M solutions of Na_2CO_3, $NaHCO_3$, and NaOH. The neutralization of basic sites on CCM-NH_3 and CCM-NaOH were carried out by 50-mL 0.1 M HCl solution. The samples were equilibrated for 4 d at 150 rpm under ambient temperature conditions. Afterward, 10 mL of each sample was titrated with 0.1 M HCl and 0.1 M NaOH solutions.

2.4. Preparation and adsorbate analysis

A phenol stock solution (1,000 mg L^{-1}) was prepared by dissolving the desired amount of phenol in de-ionized water without pH adjustment. The solutions of desired concentration were obtained by successive dilutions. Phenol solution is colorless, and UV spectrophotometer shows the maximum wavelength. UV–vis spectrophotometer (HALO DB-20, Australia) at maximum wavelength (λ_{max})—270 nm was used to measure phenol concentration.

2.5. Adsorption studies

Adsorption studies were performed in batch mode. Various parameters such as NH_3 and NaOH concentrations used for modification, pH, initial concentration, and contact time were evaluated. For all experiments, one piece of monolith with approximately 0.6 g carbon was added to a 250 mL conical flask containing phenol solution. Each sample was kept in a shaker at 150 rpm under ambient temperature (30˚C) to reach solid–solution equilibrium. The uptake of adsorbate at equilibrium (q_e, mg g^{-1}) was determined by:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_o and C_e (mg L^{-1}) are the initial and equilibrium adsorbate concentrations, respectively, V (L) is the volume of the solution, and m (g) is the mass of adsorbent.

The effect of pH was studied over a pH range of 1–9 and the studies were equilibrated on a shaker at 150 rpm for 48 h. The pH was adjusted using 1.0 M HCl and 1.0 M NaOH in 200 mL adsorbate solution. The concentration of solution was fixed at 100 mg L^{-1}, with adsorbent mass of 0.6 g (carbon), and temperature of 30˚C. The equilibrium and contact time studies were carried out by varying initial adsorbate concentration from 50 to 350 mg L^{-1}. These values were within the typical concentration range of phenol effluents [14]. For equilibrium studies, 500 μL of samples were withdrawn and diluted to appropriate concentration after 48 h and analyzed using UV–vis spectrophotometer. Four replicates were run for each dilution point. Kinetic studies were carried out at the appropriate time intervals. The adsorption capacity (q_t, mg g^{-1}) at time t was determined. Each experiment was carried out three times to ensure repeatability.

2.6. Reusability of adsorbents

The adsorbent was separated from the phenol solution after adsorption process, washed several times with de-ionized water (ultrasound), and the sample was then shaken for 4 h to remove the adsorbed phenol and dried in an oven overnight. The adsorbent was used for several cycles in the adsorption process. In each cycle, the adsorbed phenol was measured after 24 h.

3. Results and discussion

3.1. Characterization of adsorbent

The FT-IR spectra of CCM, CCM-NaOH, and CCM-NH_3 before and after adsorption of phenol are presented in Fig. 1(a)–(b). For CCM-NaOH, a broad peak at 3,200–3,700 cm^{-1} is assigned to the presence of O–H group (Fig. 1(a)). A similar trend for CCM-NH_3

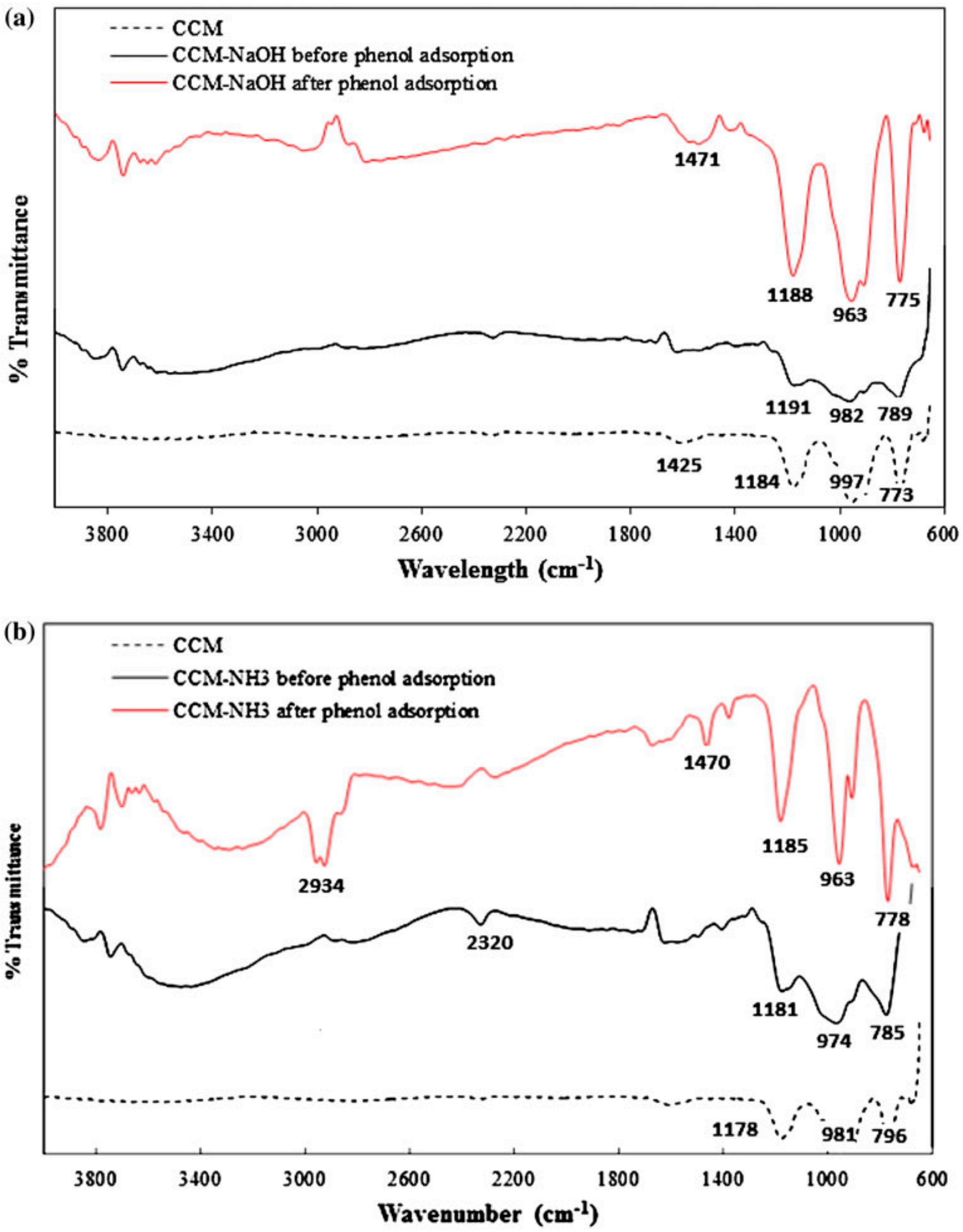

Fig. 1. FT-IR spectra of modified CCM: (a) CCM-NaOH and (b) CCM-NH_3.

is observed due to new bands related to N-containing species via the modification of ammonia solution (Fig. 1(b)) [26]. The ammonization resulted in a formation of new nitrogen-containing groups in the structure of carbon including C–N, C=N, groups and nitrile groups (C≡N). Nitrogen-containing surface groups made carbon more alkaline and so adsorption of phenol (acidic agents) is increased. A few small bands were presented between 2,900 and 2,800 cm^{-1} of spectrum CCM-NH_3; these can be assigned to aliphatic groups, *v*as(C–H) and *v*s(C–H) vibrations (s = symmetric, as = asymmetric). A significant peak at 2,327 cm^{-1} was assigned to C–N stretching vibrations in nitrile groups (CCM-NH_3). This peak was created after modification using ammonia. In case of CCM-NH_3, two bands located at 1,913 and 1,745 cm^{-1} can be related to the presence of oxygen-containing groups, namely carboxylic group (–COOH) and lactose group (C=O), respectively. In contrast, a set of wide peaks between 1,650–1,400 cm^{-1} (Fig. 1(b)) were attributed to N-containing species presented, i.e. C=N, NH, and cyclic amides [29]. Existence of C–O stretching vibrations of carboxyl and phenolic groups was confirmed by the wide band at 1,176 cm^{-1}. In the low wave length region of the spectra, a wide peak was emerged at 967 cm^{-1} representing C–H plane bending vibrations of aromatic group [30]. A strong peak at 776 cm^{-1} is a typical of out-of-plane O–H bending. After adsorption of phenol, a peak at 2,900 cm^{-1} appeared in the spectra of CCM-NH_3. In the spectra of CCM-NaOH, a band at 2,353 cm^{-1} was found to be completely disappeared after adsorption of phenol [31]. This shows that the active sites for phenol adsorption via electrostatic interaction were due to the bands. The presence of O–H group at 3,200–3,700 cm^{-1} was almost disappeared [32].

The pore volume and the surface area were determined using N_2 adsorption/desorption isotherms. BET equation and *t*-plot were used in order to calculate the total surface area and the volume of micropores in the relative pressure $P/P^0 = 0.995$. N_2 adsorption/desorption isotherm of CCM revealed a type IV isotherm at 77 K, according to the IUPAC classification. Type IV isotherm, as a mesoporous system, was defined in the IUPAC classification. The sample exhibited multimodal pore size distribution in both the mesopore and micropore domains. The mesoporous volume is calculated by taking the difference of total volume and micropore volume. The surface active sites were determined by acid–base titrations. The alkaline NaOH solution neutralized carboxyl, lactone, and phenol groups; Na_2CO_3 solution neutralized carboxyl and lactone groups; and $NaHCO_3$ solution neutralized carboxyl groups. The summation of carboxylic, phenolic, and lactonic is considered as the acidic groups. HCl solution neutralized all basic groups present. The textural parameters are summarized in Table 1. Surface morphology of mesoporous carbon-coated was demonstrated in Fig. 2. *The image* of a CCM taken at a magnification of 20.0 kX shows porous surface with highly dense and irregular surface. The decomposition of PEG as pore former in the mesoporous carbon prior to carbonization process created these irregular pores.

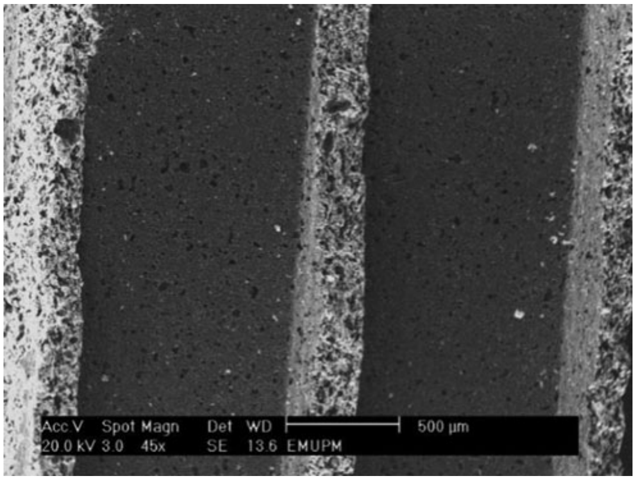

Fig. 2. SEM image of CCM inside cells.

3.2. Effect of activating agents (NaOH and NH_3)

Concentration of basic solution used is important in order to determine the most efficient adsorption capacity of phenol. The effect of NaOH and ammonia concentration used in the modification of CCM was studied by varying the concentration from 0.5 to 3.0 M. The influence of basic concentration was shown in Fig. 3. It was found that the uptake of phenol increased with increase in NaOH and NH_3 concentrations until 1.5 and 2.0 M, respectively. Further increase in NaOH and NH_3 concentrations decreased the phenol adsorption capacity. Therefore, NaOH of 1.5 M and NH_3 solution of 2.0 M were used subsequently for modification of CCM.

3.3. Effect of initial pH

The point of zero charge of CCM, CCM-NaOH, and CCM-NH_3 were found to be pH 6.5, 9.0, and 8.7, respectively (Fig. 4). Modification with NaOH and ammonia on CCM proved an increase in the basic character affecting the pH_{PZC}. The increase in surface basicity of CCM-NaOH may be a consequence of the formation of functional groups such as –OH [32],

Table 1
Physical-chemical properties of CCM and its modifications

Sample	Carboxylic (mmol g^{-1})	Phenolic (mmol g^{-1})	Lactonic (mmol g^{-1})	Total acidity	Total basicity	S_{BET} (m^2 g^{-1})	Micropore (cm^3 g^{-1})	Mesopore (cm^3 g^{-1})
CCM	0.307	0.808	0.152	1.267	0.124	486.5	0.021	0.141
CCM-NH_3	0.241	0.637	0.114	0.992	0.198	402.3	0.016	0.113
CCM-NaOH	0.161	0.501	0.080	0.742	0.339	250.8	0.008	0.071

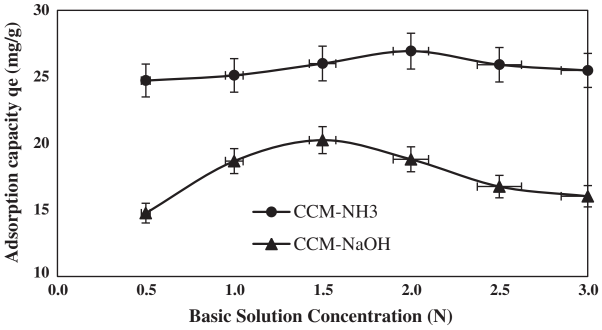

Fig. 3. Optimum concentration on modified CCM. (Conditions: initial phenol concentration—100 mg L^{-1}, agitation speed—150 rpm, temperature—30˚C, and contact time—48 h).

while CCM-NH_3 surface basicity contributed by the formation of basic nitrogen-containing surface groups that are capable of binding with protons [31]. The surface charge of adsorbent depends on the solution pH and pH_{PZC}. In relation to phenol adsorption, the pH value must be lower than the pH_{PZC} of the adsorbent under consideration in order to maximize adsorption [33].

At a pH of above 10, however, it exists in its conjugate base form, and is a very good nucleophile, because it is not an oxygen lone pair. A low uptake of phenol was obtained on both modified CCM at low pH and gradually increased up to pH 4. The maximum uptake was achieved at pH 4. However, when pH was increased from 4 to 10, there was a distinct decline in phenol adsorption capacity from the solutions. At pH around 4–6, a significant phenol uptake occurred via electrostatic attraction present between the positively charged surface of the modified CCM and adsorbate. Phenol molecules indicated weak tendencies to lose H^+ ion from the hydroxyl group and forming highly water soluble phenolate ion. At high pH, the phenol's hydroxide group loses its proton (anion) and negatively charged surface of modified CCM caused an electrostatic repulsion on phenol adsorption. Therefore, pH 4 was selected for subsequent adsorption studies (Fig. 5).

3.4. Effect of contact time at various initial concentrations

The effect of contact time is important to study the equilibration time for phenol adsorption. Both parameters were investigated at pH 4. The solution pH was maintained at optimum value (pH 4) during phenol adsorption by adding acidic or basic agents. Fig. 6(a) and (b) depicted the effect of contact time on the phenol adsorption at various concentrations. Fast phenol adsorption was observed on CCM-NaOH and CCM-NH_3 in the initial stage probably due to a large concentration gradient between the adsorbate in solution and adsorbate on the adsorbent. A large amount of empty surface sites are accessible at the initial stage. The adsorption process approached gradually to equilibrium with the decrease in active sites due to occupation of phenol with time. For most initial phenol concentrations, the adsorption curves reach a plateau after approximately 900 min. However, at high initial phenol concentrations, adsorption capacity of CCM-NH_3 was still slowly increased after 2,000 min. Therefore, equilibrium data for high initial phenol concentrations was taken after 5 d of batch adsorption.

3.5. Adsorption isotherm

The equilibrium isotherm theories describe the nature of coverage of adsorbate over an adsorbent surface and adsorbate–adsorbent interaction at uniform

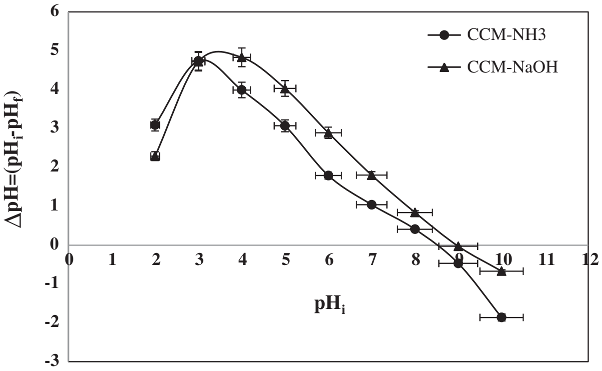

Fig. 4. Point of zero charge (pH_{PZC}) plot of modified CCM.

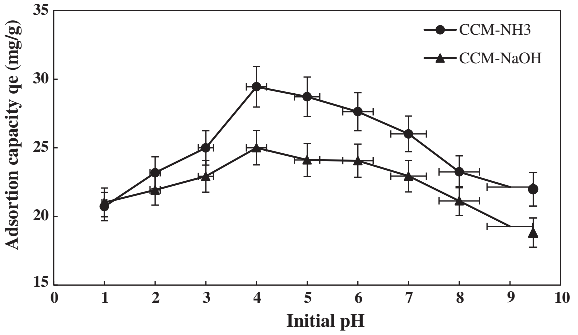

Fig. 5. Effect of pH for phenol adsorption on modified CCM. (Conditions: initial phenol concentration—100 mg L^{-1}, agitation speed—150 rpm, temperature—30˚C, and contact time—48 h).

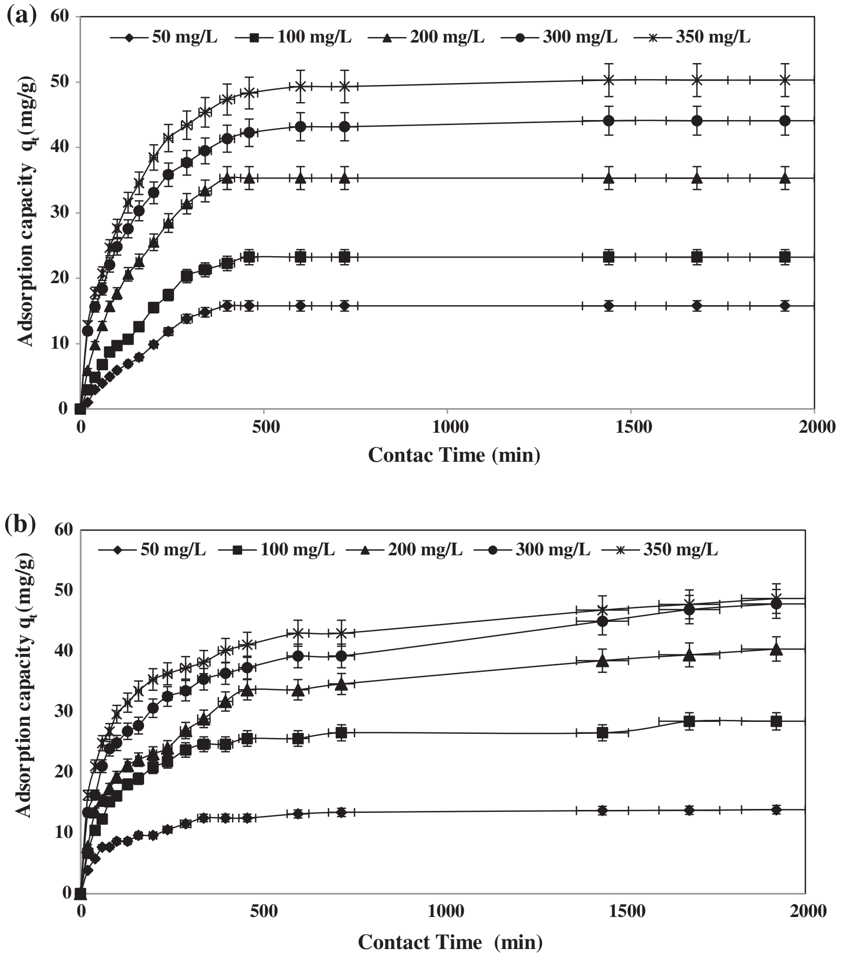

Fig. 6. Effect of contact time for the adsorption of phenol on modified CCM at various initial concentrations: (a) CCM-NaOH and (b) CCM-NH_3. (Conditions: agitation speed—150 rpm and temperature—30°C).

temperature [34]. Phenol adsorption isotherm was fitted to both Langmuir and Freundlich models. Langmuir isotherm is widely used for modeling equilibrium in either gas or liquid adsorption based on homogenous active sites on the adsorbent surface and each of this active site is only available for one absorbate molecule to be occupied. The model proposed monolayer adsorption on a surface assuming that all the adsorption sites have identical solute affinity and the adsorption at one site does not affect the adsorption at an adjacent site. Indeed, an empty site on the adsorbent surface is only occupied by one molecule of phenol and no further adsorption takes place at that particular site [8]. Linearized form of Langmuir model can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \tag{2}$$

where q_m (mg g^{-1}) represents maximum amount of adsorption required to form a homogeneous monolayer at the modified CCM, k_L (L mg^{-1}) is Langmuir constants to give an account on adsorption energy. The intercept and slope of the linear plot between C_e/q_e vs. C_e gives Langmuir constant, k_L and q_m. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L):

$$R_L = \frac{1}{1 + k_L C_o} \tag{3}$$

The value of R_L specify that the types of isotherm to be either unfavorable $R_L > 1$, linear $R_L = 1$, favorable $0 < R_L < 1$ or irreversible $R_L = 0$.

Freundlich isotherm is known as an empirical equation used for nonideal systems with highly heterogeneous surfaces [8]. Freundlich isotherm demonstrated adsorption process occurred on the heterogeneous surfaces and the adsorption capacity is related to the concentration of adsorbate at equilibrium. Linear form of Freundlich model can be expressed as:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \tag{4}$$

where k_F is a constant related to adsorption capacity, $\frac{1}{n}$ is a constant related to adsorption intensity. The values of k_F and $\frac{1}{n}$ can be determined from the intercept and slope of linear graph $\ln q_e$ vs. $\ln C_e$, respectively. Value of $n > 1$ obtained represented favorable adsorption process.

Table 2 summarizes the constants of the Langmuir and Freundlich isotherms. Langmuir and Freundlich model correlation coefficient values (r^2) for the adsorption of phenol on CCM-NH_3 and CCM-NaOH were listed in Table 2. It can be seen that the correlation coefficient values (r^2) of the two models are both very close to unity. Therefore, both models fitted well the experimental data.

The values of R_L were between 0.084–0.363 and 0.033–0.197 for CCM-NaOH and CCM-NH_3, respectively. A favorable nature of adsorption process was depicted. The n value for CCM-NaOH and CCM-NH_3 were found to be 2.95 and 3.53, respectively. All n values were greater than unity, again confirming phenol was favorably adsorbed. A comparison of equilibrium adsorption capacities between unmodified and modified CCMs was demonstrated in Fig. 7.

Ammonia solution reacted with surface functional groups and active sites in which N functional groups formed. The difference in nitrogen content between unmodified and modified samples is related to nitrogen incorporation during ammonia treatment into carbon structure. For instance, amide and nitrile groups were created by the reaction of ammonia with carboxylic acid sites available on the carbon surface:

$$-\mathrm{COO^-}\ \mathrm{NH_4^+} \rightarrow -\mathrm{CO}-\mathrm{NH_2} \rightarrow -\mathrm{C} \equiv \mathrm{N}$$

$$-\mathrm{OH} + \mathrm{NH_3} \rightarrow \mathrm{NH_2} + \mathrm{H_2O}$$

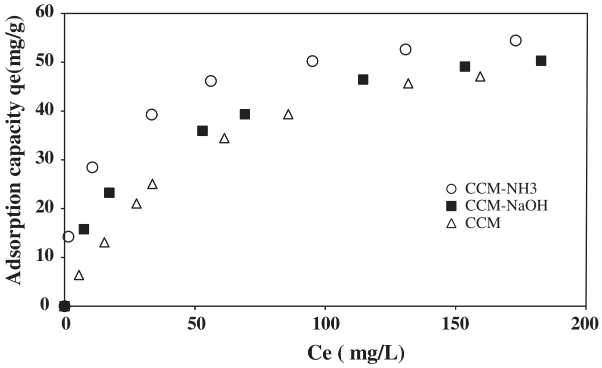

Fig. 7. Comparison of equilibrium adsorption capacities between unmodified CCM [8] and modified CCM.

After treatment with NaOH, the alkaline solution may also react with carbon as follows:

$$2\mathrm{NaOH} + \mathrm{C} \rightarrow \mathrm{Na_2O} + \mathrm{CO} + 2\mathrm{H_2}$$

These bands are corresponding to C=O and (C=O)–O groups, indicating the introduction of oxygen-containing functional groups to the surface of the carbon, which may provide more active sites for facilitating phenol adsorption.

The maximum monolayer adsorption capacities, q_m, for phenol on CCM-NH_3 and CCM-NaOH were 56.82 ± 0.9 and 54.64 ± 0.8 mg g^{-1}, respectively. The CCM-NH_3 and CCM-NaOH, respectively, showed an average of 16.5 and 9.7% higher phenol adsorption capacity compared to CCM. The adsorption capacities followed the order of CCM-NH_3 > CCM-NaOH > CCM. The increase of phenol adsorption capacity can be attributed to the increase in basic surface functional groups.

3.6. Adsorption kinetics

Kinetic models show a relationship between adsorption rate and equilibrium time. The solute uptake rate and the residence time of the adsorption process at the solid–solution interface are described by kinetic models [17]. Two common kinetic models,

Table 2
Isotherm parameters for phenol adsorption on modified CCM

Adsorbent	Langmuir constants			Freundlich constants		
	k_L (L g^{-1})	q_m (mg g^{-1})	r^2	k_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	$1/n$	r^2
CCM-NH_3	0.082	56.82	0.992	13.47	0.238	0.982
CCM-NaOH	0.031	54.64	0.964	8.17	0.339	0.975

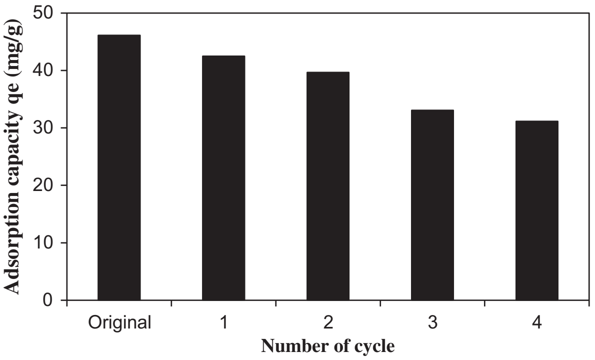

Fig. 8. Regeneration studies plot of CCM-NH_3. (Conditions: initial phenol concentration—200 mg L^{-1}, speed of shaker—200 rpm, temperature—30℃, and contact time—24 h).

namely the pseudo-first order and the pseudo-second-order models were applied to analyze the kinetic data. The pseudo-first-order rate equation was widely applied to describe the adsorption in liquid/solid system based on solid capacity [34]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where k_1 (1 min^{-1}) is the pseudo-first-order rate constant. The values of adsorption capacity, rate constant, and correlation coefficient (r^2) were determined from the plot $\log(q_e - q_t)$ vs. t.

Linearized pseudo-second-order model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant. The slope and intercept of the plot t/q_t vs. t denotes the rate constant and adsorption capacity, respectively.

The parameters obtained from the linearized plots (figures not given) are listed in Table 3. The calculated adsorption capacity ($q_{e,cal}$) and regression coefficient (r^2) are considered to confirm applicability of kinetic models. The values of experimental ($q_{e,exp}$) and calculated ($q_{e,cal}$) adsorption capacities are closer to each other, indicating the adsorption system obeyed the pseudo-second-order model. A relatively higher r^2 values (>0.99) for pseudo-second-order kinetic model was obtained for various initial phenol concentrations over the entire adsorption period. This suggests that the pseudo-second-order model, based on assumption that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate, provides the best correlation of the data [17,34,35]. Observably, the values of pseudo-second-order rate constant (k_2) for CCM-NaOH and CCM-NH_3 showed a decrease from 4.67 × 10^{-4} to

Table 3
Kinetics parameters for phenol adsorption at various initial concentrations

		Pseudo-first-order			Pseudo-second-order		
C_o (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	$k_1 \times 10^{-3}$ (1 min^{-1})	r^2	$q_{e,cal}$ (mg g^{-1})	$k_2 \times 10^{-4}$ (g mg^{-1} min^{-1})	r^2
CCM-NaOH							
50	15.78	19.62	7.6	0.933	16.89	4.67	0.989
100	23.23	23.83	6.48	0.938	24.51	4.13	0.995
150	27.94	33.17	6.48	0.960	30.3	2.16	0.988
200	38.26	33.32	5.07	0.947	38.31	3	0.997
250	40.42	43.45	6.68	0.965	42.37	2.51	0.997
300	44.09	38.12	6.45	0.997	45.45	3.72	0.999
350	51.29	41.64	5.53	0.987	52.36	3.02	0.999
CCM-NH_3							
50	14.23	10.03	4.84	0.945	14.25	11.16	0.999
100	28.44	18.41	3.68	0.918	29.07	4.9	0.999
150	36.26	23.76	2.3	0.903	36.23	2.48	0.997
200	46.15	32.94	2.07	0.916	44.44	1.52	0.994
250	47.22	32.54	2.3	0.930	45.66	1.71	0.997
300	52.62	32.52	2.07	0.865	50.51	1.68	0.996
350	54.45	30.58	2.3	0.853	51.55	2.2	0.997

3.02×10^{-4} g mg^{-1} min^{-1} and from 11.10×10^{-4} to 2.20×10^{-4} g mg^{-1} min^{-1}, respectively. This reduction occurred when the phenol concentration increased from 50 to 350 mg L^{-1}, indicating lower adsorption rate at higher initial concentration. Kinetic studies on unmodified CCM also showed better applicability of pseudo-second-order kinetic model [8]. This suggested that the phenol adsorption mechanism on CCM was not affected by modification using NaOH and ammonia solution.

3.7. Reusability of adsorbent

The reusability for CCM-NH_3 was carried out at the initial concentration of 200 mg L^{-1}. After each run, CCM-NH_3 was separated from the solution, washed with de-ionized water, and dried before it was reused for the next adsorption process. The adsorbent was employed for four successive cycles under the same experimental and regeneration methods. The results indicated a gradual deactivation of about 26% after four cycles as shown in Fig. 8. The adsorption capacity was decreased from 42.5 ± 0.6 to 31.2 ± 0.5 mg g^{-1} when the adsorbent was used for four cycles. The blockage of some active sites (pores) may cause a gradual drop in adsorption process. This drop reached a plateau state after third cycle.

4. Conclusions

The basic treatments of CCM with ammonia aqueous solution and sodium hydroxide lead to formation of basic surface functional group, which contributes to the increase in adsorption capacity of phenol. The adsorption of phenol on CCM-NH_3 and CCM-NaOH was pH dependent with optimum adsorption capacity at pH 4. Increase in initial phenol concentration from 50 to 350 mg L^{-1} leads to an increase of 16.5 and 9.7% for CCM-NH_3 and CCM-NaOH compared to unmodified CCM, respectively. The adsorption capacity followed the order of CCM-NH_3 > CCM-NaOH > CCM. Due to the addition of functional groups (OH and NH_3) on the carbon surface, the proton affinities of groups were caused that phenol is easily adsorbed on CCM-NH_3 and CCM-NaOH compared to CCM. Isotherm studies favor both models Langmuir and Freundlich isotherms for phenol adsorption over the surface of CCM-NaOH and CCM-NH_3. The adsorption kinetics can be very satisfactorily approximated by the pseudo-second-order model for both CCM-NaOH and CCM-NH_3 for all initial concentrations. Regeneration studies of the CCM-NH_3 sample showed 26% drop in adsorption capacity after four cycles.

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