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Comparative removal of phenols and its chlorinated derivatives by carbon-coated monolith: equilibrium, kinetics and regeneration studies

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ABSTRACT

The adsorptive performance of phenol, 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) onto carbon-coated monolith (CCM) was comparatively evaluated by batch mode. Experiments were carried out by varying pH, contact time, initial adsorbate concentration and reaction temperature. Regeneration performance of CCM was also assessed. The studies showed optimum 2,4-DCP adsorption, followed by 4-CP and phenol at pH 5. The adsorption equilibration time for phenol, 4CP, 2 and 4-DCP were 600, 470 and 400 min, respectively. The equilibrium adsorption capacities were increased 13.1–37.6 mg/g for 50–250 mg/L (phenol), 51.9–93.7 mg/g for 250–450 mg/L (4-CP) and 84.3–117.5 mg/g for 400–600 mg/L (2,4-DCP), respectively. The adsorption at different temperatures was monolayer as depicted by linear and non-linear isotherm models. Kinetic studies showed better applicability of pseudo-second-order kinetics model. The adsorption increases with increase in reaction temperature from 30 to 50˚C showing endothermic adsorption process. Desorption and regeneration studies showed optimum phenol recovery with ethanol with 12.9% loss in adsorption after four consecutive cycles.

Keywords: Phenol; 4-Chlorophenol; 2,4-Dichlorophenol; Carbon-coated monoliths; Chemisorption

1. Introduction

Extensive use of phenols and their chlorinated derivatives for industrial and agricultural applications has raised a global issue of environmental concern as these compounds are highly toxic and their toxicity tends to increase with increase in their degree of chlorination [1]. A wide range of chlorinated phenols are classified as persistent organic pollutant (POPs) and may cause public health hazards even at lower concentrations [2]. Studies showed that contamination of phenols can reduce the source of clean water and can cause inhibition of the normal microbial activities, aquatic organism mortality and carcinogenicity among animals [3,4]. Concerning the toxic effects of phenols, Malaysia's Department of Environment (DOE) has set stringent regulation on the use of phenol. The government stated discharge limits for the sewage

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and industrial effluent as 0.001 mg/L for Standard A quality and 1.0 mg/L for Standard B quality under Sewage and Industrial Effluent Regulation of 2009 and Environmental Quality Act (EQA) of 1979 [5]. United States Environmental Protection Agency (USEPA), has classified phenols and their derivatives as priority pollutants [6].

Various treatment technologies have been applied for the removal of phenolic compounds from wastewater. Solvent extraction treatment gives a significant removal for higher levels of phenol (>500 mg/L), biological and physico-chemical treatment for intermediate levels (5–500 mg/L) and adsorption treatment for low levels of phenol [3]. Among them, adsorptive treatment of phenolic compounds is still a versatile and widely acclaimed process. Ease of design and operation and its ability to effectively remove pollutants even at lower concentrations are some of the merits of adsorption process [7,8].

Activated carbon (AC), a commercially acclaimed adsorbent being used for water decontamination as it has comparatively high porosity, large internal surface area and relatively high mechanical strength [9]. Nevertheless, higher regeneration cost and fouling of industrial columns are still the major challenges for using AC as an adsorbent. Carbonaceous monolith has an upper hand over AC in this regard. Large external surface area, short diffusion path and low-pressure drop across column are the major merits of carbonaceous monolith [10]. It can also be placed in any position (either horizontal or vertical) or in a mobile system without losing shape [11]. In this work, we have comparatively tested the adsorptive potential of carbon-coated monolith (CCM) for the removal of phenol and its chlorinated derivatives [4-cholorophenol (4-CP); 2,4-Dichlorophenol (2,4-DCP)] from aqueous phase. Cordierite monolith was carbonized by dip-coating process and was termed as CCM. The CCM was characterized using various techniques. Kinetics and isotherm parameters were elucidated. The feasibility of CCM for industrial applications was testified by desorption and regeneration studies.

2. Experimental

2.1. Adsorbent

The ceramic monoliths (bare monoliths) were purchased from Beihai Huihuang Chemical Packing Co. Ltd, China. Chemically monolith composed of 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 of 1.02 ± 0.02 mm, channel density of 62 cell/cm (400 cpsi) and wall thickness of 0.25 ± 0.02 mm.

2.2. Chemicals and reagents

The chemicals and reagents used were of analytical reagent (AR) grade or stated. Phenol (99%), 4-chlorophenol (4-CP, 99%) and 2,4-Dichlorophenol (2,4-DCP, 98%) (Acros organic, Belgium) were used to prepare individual stock solutions (1,000 mg/L). Physical properties of phenols were reported in Table 1. Furfurly alcohol (FA, 98%) (Acros organic, Belgium), polyethylene glycol (PEG) (MW: 8000), pyrole (Py, 99%) (Acros organic, Belgium) and nitric acid (HNO_3, 66%) were used for carbonization of monolith.

2.3. Synthesis of CCM

The monolith was carbonized using dip-coating technique [12]. The ceramic monolith was initially dried at 105°C for 4 h to remove moisture. Furfuryl alcohol and PEG 8000 with percentage volume ratio 40:60 were homogenously mixed. Pyrrole was added to this mixture as a binder. Concentrated HNO_3 was added after every 5 min. The mixture was continuously stirred for an hour while reaction temperature was maintained in between 21 and 23°C [13]. The monolith was then coated by immersing it in a polymerized mixture for an hour [14]. The excessive polymerized solution choking monolith channels was removed by passing pressurized air. The monolith was then dried in an oven at 105°C for 24 h. The coated monolith was then carbonized under nitrogen atmosphere in a furnace for 3 h at 650°C with a heating rate of 10°C/min. The CCM was further activated

Table 1
Physical properties of phenols [7]

Phenols	Molecular weight (g/mol)	Molecular size (Å)	Solubility (g/L)	pK_a
Phenol	94.1	5.76 × 4.17	93	9.89
4-cholorophenol (4-CP)	128.6	6.47 × 4.17	27	9.37
2,4-dichlorophenol (2,4-DCP)	163	6.47 × 4.82	15	7.90

with argon (containing 10% oxygen) at 350˚C for 4 h [15].

2.4. Characterization of CCM

The pore sizes distribution and surface area of CCM were evaluated by Brunauer–Joyner–Halenda (BJH) and Brunauer–Emmet–Teller (BET) isotherms, respectively. The surface functional groups on CCM were detected by Fourier transform-infra red (FT-IR) analysis. The surface active sites on CCM were determined by Boehm's acid–base titration. The point of zero charge (pH_{pzc}) of CCM was determined by solid addition method [16].

2.5. Adsorption, desorption and regeneration studies

Adsorption, desorption and regeneration studies were carried out in batch mode. Parameters including agitation speed, pH, initial concentration and contact time were assessed. The sample solutions (200 mL) of desired concentrations were placed in 250-mL stopper cork conical flasks. The CCM (0.65 g approx.) was then added to a sample solution and was equilibrated in a water bath shaker at 150 rpm under ambient temperature conditions. The effect of pH was studied by adjusting initial adsorbate pH from 1 to 9 using 1.0 N HCl and 1.0 N NaOH in 200-mL adsorbate solution. The sample solution with 50-mg/L initial concentration was equilibrated for 48 h during pH studies. The equilibrium and contact time studies were carried out by varying initial adsorbate concentration from 50 to 600 mg/L. The samples were equilibrated in a water bath shaker at 150 rpm under ambient temperature conditions (i.e. 30˚C). For equilibrium studies, 500 μL of samples were withdrawn and diluted to appropriate concentration after 32 h and for kinetic studies, same volume of samples have been withdrawn at a pre-determined time interval.

The adsorption capacity at equilibrium (q_e, mg/g) was calculated as:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where C_0 and C_e are the initial and equilibrium adsorbate concentrations (mg/L), respectively, V is the volume of the solution (L) and m is the mass of adsorbent (g).

The adsorption capacity at pre-determined time intervals was calculated as:

$$q_t = \frac{V(C_0 - C_t)}{m} \tag{2}$$

where C_t is the adsorbate concentration (mg/L) at time t (min).

Desorption and regeneration studies were carried out using 0.1 M sodium hydroxide (NaOH), 0.1 M sodium chloride (NaCl), distilled water (DW) at pH 2 and ethanol (C_2H_5OH, 95.5%) as eluting agents. The experiments were carried out under ambient temperature conditions (30˚C). A CCM (0.65 g) was initially saturated with adsorbate solution for 48 h at 150 rpm in a water bath shaker. The exhausted CCM was washed several times to remove unadsorbed traces of adsorbate and was treated with aforementioned eluents for desorption. The regeneration efficiency (RE%) of CCM for different eluents was measured for four consecutive cycles. The regeneration efficiency (RE%) was calculated as:

$$\text{RE\%} = \frac{q_r}{q_e} \times 100 \tag{3}$$

where q_e and q_r are the adsorption capacities of fresh and regenerated CCM (mg/g), respectively.

2.6. Analytical methods

The concentration of phenols in the sample solutions before and after the adsorption was measured by UV-spectroscopy (UV-Spec) (Thermo Scientific Helios Alpha, USA). The pH of the solutions was adjusted and determined by a pH bench meter (EUTECH Instrument, USA).

3. Results and discussion

3.1. Characterization of adsorbent

3.1.1. Infra-red spectroscopy

The FT-IR spectra of CCM before and after phenols adsorption were illustrated in Fig. 1. As adsorbates belong to an identical family (phenolic compounds), spectra peaks were almost similar with difference in intensities. Several peaks ascribed to C–H plane bending vibrations of aromatic group in CCM were aroused between 970 and 660 cm^{-1} [17]. Peaks observed at 1,375 cm^{-1} and 1,260 –1,140 cm^{-1} represents C–O stretching vibrations of carboxyl and phenolic groups. A wide spectrum after the phenols adsorption was attributed to O–H stretching vibrations of hydrogen-bonded hydroxyl groups observed

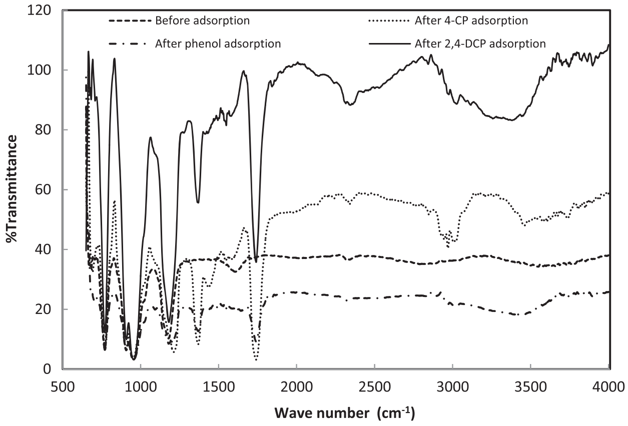

Fig. 1. FT-IR spectra of CCM.

between 3,660 and 2,860 cm^{-1} [18]. A peak near 1,750 cm^{-1} ascribed to stretching vibration of aryl ketone and C=O stretching of carbonyl group generally present on carbonaceous materials was observed after phenols adsorption. The appearance of peaks at 1,750 cm^{-1} and 1,375 cm^{-1} and broad spectrum between 3,660 and 2,860 cm^{-1} implied the creation of O–H, C–O and C=O bonds, after phenols adsorption, which is in agreement with the molecule structure of phenol. The intensity of the aroused spectral peaks observed after phenols adsorption increases with increase in adsorption capacity on CCM.

3.1.2. Surface analysis

Measurement of nitrogen adsorption/desorption isotherm at −196˚C is a standard method to estimate surface characteristics of adsorbent. During this study, type IV category isotherm was observed indicating mesoporous nature of CCM (Fig. 2(a)). Fig. 2(b) showed CCM pore size distribution plot. The pore size in range 2–10 nm dominates over CCM surface while, a part of it falls in range < 2 nm. Based on IUPAC pore size classification, the CCM could be classified as mesoporous with appreciably less number of micropores. The observed BET surface area and total pore volume of CCM were 469.8 m^2/g and 2.90 cm^3/g, respectively.

Boehm titration experiment indicates dominance of acidic sites (especially phenolic and carboxylic) over CCM surface (Table 2). Higher number of acidic groups on CCM leads to more active sites on the carbon surface.

3.2. Effect of initial pH

The point of zero charge of CCM was found to be pH 6.5 (Fig. 3(a)). The surface charge of CCM depends on the solution pH and pH_{pzc}. At $pH < pH_{pzc}$, surface of carbon was positively charged, and negatively charged at $pH > pH_{pzc}$.

In this study, the adsorption of phenol, 4-CP and 2,4-DCP was determined in pH range of 1.0–9.0 as shown in Fig. 3(b). It could be noticed that the adsorption of phenol was almost stable over a pH range of 2.0–6.0. At pH 1, a slight decrease in phenol adsorption was observed, this might be due to a higher concentration of positively charged hydronium ions causing larger static repulsive force. Also at low pH, it was believed that a reasonable strong interaction exists between adsorbent and phenols structure. In addition, hydrogen bonding by the phenolic protons with oxygen presented on the carbon surface was probable [19]. Above pH 7.0, phenols were dissociated to a higher degree and surface of CCM was charged more negatively which results in increase of electrostatic force between them [20]. The similar phenomena was observed for the adsorption of 4-CP and 2,4-DCP. A satisfied adsorptive performance for 4-CP and 2,4-DCP was observed in between pH 2 and 6. Therefore,

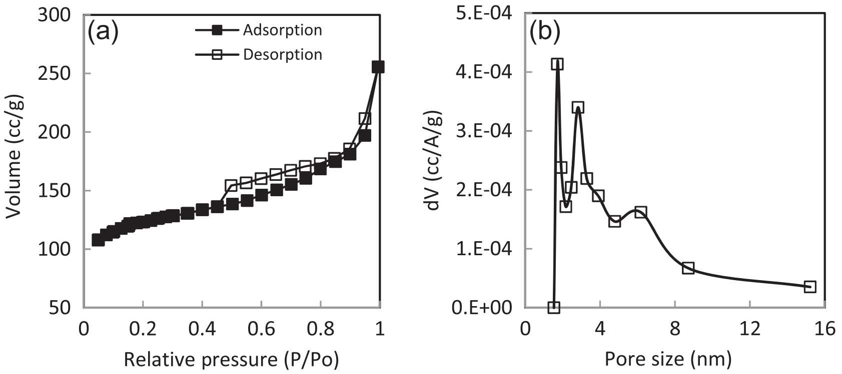

Fig. 2. Nitrogen adsorption/desorption (a) pore size distribution and (b) plots of CCM.

Table 2
Surface active sites concentration on CCM

Active sites	Concentration (mmol/g)
Total acidic sites	*1.2005*
Carboxylic	0.4244
Lactonic	0.0621
Phenolic	0.7140
Total basic sites	*0.0096*

pH 5.0 was chosen for further studies. These results are in good agreement with previous studies [21–23].

3.3. Effect of contact time at various initial concentrations

The effect of contact time on phenols adsorption was studied at various initial concentrations. The uptake was rapid initially contributing to external surface adsorption. However, the uptake was slower at the final phase attaining plateau at equilibrium. This was contributed to internal surface adsorption. The adsorption equilibration times for phenol (initial concentration range 50–250 mg/L), 4-CP (initial concentration range 250–450 mg/L) and 2,4-DCP (initial concentration range 400–600 mg/L) adsorption were 600 min, 470 min and 400 min, respectively (Fig. 4(a–c)). The adsorption capacity increases with increase in initial adsorbate concentration. The increase in initial phenol concentration from 50 to 250 mg/L leads to increase in adsorption capacity from 13.1 to 37.6 mg/g, respectively. The adsorption capacity for 4-CP concentration range from 250 to 450 mg/L, and increased from 51.9 to 93.7 mg/g while, for 2,4-DCP with concentration range 400– 600 mg/L the adsorption capacity increased from 84.3 to 117.5 mg/g, respectively. The difference in degree of adsorption between phenol, 4-CP and 2,4- DCP could be explained in terms of nature hydrophobic character of phenols [24]. In aqueous solution, the adsorbate with higher hydrophobicity has stronger tendency to be adsorbed and retained on the carbon surface or in the pores [7]. The reported solubility of phenol in aqueous medium is higher when compared to other derivatives (Table 1) and it is the reason for enhanced adsorption of substituted phenols. The adsorption capacities followed the order of 2,4-DCP > 4-CP > phenol.

3.4. Adsorption isotherm

Adsorption isotherm considers a relationship between adsorption capacity and concentration of the remaining adsorbate at constant temperature [25]. The Langmuir and Freundlich models were two common mathematical expressions applied to describe adsorption isotherms.

Langmuir isotherm model was an empirical isotherm derived from a proposed kinetic mechanism. The model proposed a coherent theory of adsorption onto a flat surface based on a kinetic viewpoint where there was a continual process of bombardment of molecules onto the surface and corresponding evaporation (desorption) of molecules from the surface to maintain zero rate of accumulation on the surface at equilibrium [26]. It was originally developed for gas adsorption system based on four assumptions:

(1) The surface of the adsorbent was uniform with equal adsorption sites.
(2) The adsorbed molecules did not interact under constant temperature.
(3) At maximum adsorption, there was only a monolayer of adsorbed material formed. Molecules of adsorbate do not deposit on each other, the adsorption sites were identical.

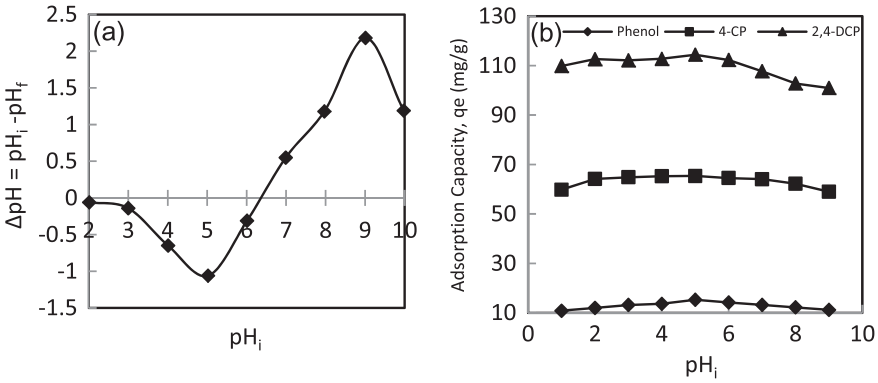

Fig. 3. Point of zero charge (pH_{PZC}) plot of CCM (a), effect of pH_i on phenols adsorption on CCM (b).

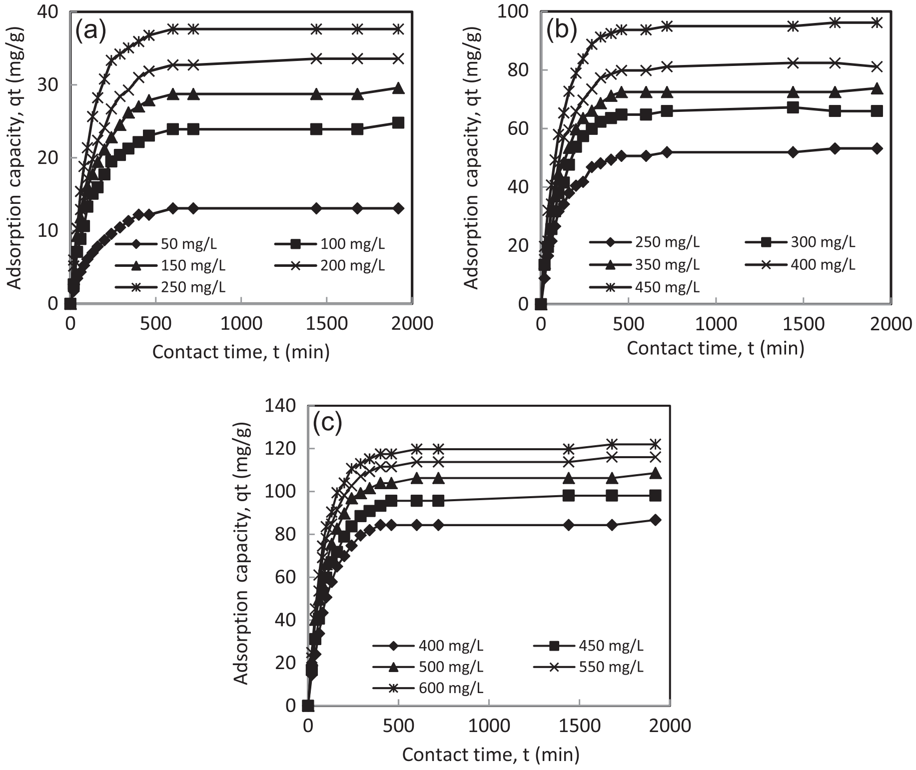

Fig. 4. Effect of contact time on phenol (a) 2-CP (b) and 2,4-DCP (c) adsorption on CCM.

(4) All the adsorption occurred through the same mechanism.

For solid (adsorbent)–liquid (adsorbate) adsorption system, the Langmuir isotherm in non-linearized form could be expressed by Eq. (4) [27]:

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

where q_m and k_L are the maximum adsorption capacity to form a complete monolayer on the surface (mg/g) and the Langmuir constant related to the energy of adsorption (L/g), respectively.

Linearized form of Langmuir model can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \tag{5}$$

where q_m and k_L could be determined from the slope and intercept of linearized equation plot (C_e/q_e against C_e).

Freundlich isotherm was known as the earliest isotherm describing the relationship of adsorption equilibrium. Unlike Langmuir isotherm, Freundlich isotherm described the adsorption on heterogeneous surface through a multilayer adsorption mechanism [28].

The Freundlich isotherm in non-linearized form was expressed by Eq. (6):

$$q_e = k_F c_e^{1/n} \tag{6}$$

where k_F and n are Freundlich constant related to adsorption capacity of the adsorbent [(mg/g) (L/mg)$^{1/n}$] and the adsorption intensity which varied with the heterogeneity of the material, respectively [17].

Linearized form of Freundlich equation could be given by Eq. (7):

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{7}$$

where k_F and n could be determined from the slope and intercept of the linearized plot (log q_e against log C_e).

For a given temperature range (30–50°C), the Langmuir model correlation coefficient values (r^2) for the adsorption of phenol, 4-CP and 2,4-DCP ranging 0.994–0.996, 0.998–1.000 and 0.993–0.997, respectively. However, the r^2 values for the Freundlich model were comparatively lower (Table 3). Based on the data from these models, the adsorption of phenols was found to follow Langmuir isotherm model (Table 3).

The applicability of Langmuir isotherm model was further confirmed by non-linear isotherm plots (Fig. 5 (a–c)). The value of R_L ranged between 0 and 1, indicating a favourable adsorption of these phenols on CCM (Table 3). The maximum monolayer adsorption capacity, q_m at 30˚C for phenol, 4-CP and 2,4-DCP was 65.79, 114.94 and 156.25 mg/g, respectively. In addition, the uptakes of phenols were found to increase with the increasing of temperature, indicating endothermic nature of the adsorption process. Table 4 compared the adsorption capacities obtained for phenol and their derivatives on various adsorbents.

3.5. Adsorption kinetics

The kinetics studies were carried out at various initial concentrations to investigate the controlling mechanism for adsorption process. The two common kinetic models, Lagergren first-order and pseudo-second-order model were applied to analyse the kinetic data.

Lagergren first-order rate equation was most widely used to describe the adsorption in liquid–solid system based on solid capacity [25] is given by as:

$$\frac{d_{qt}}{dt} = k_1(q_e - q_t) \tag{8}$$

where k_1 is the Lagergren rate constant (1/min), q_e and q_t are the amount of solutes adsorbed on the surface of the adsorbent at equilibrium (mg/g) and at particular time, t (mg/g).

To obtain a linearized equation, pseudo-first-order rate equation was integrated with boundary condition, i.e. $t = 0$ to t and $q_t = 0$ to q_t [36].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{9}$$

Pseudo–second-order rate equation is one of the most widely used kinetic expressions derived by Ho and Mckay [37]. In this rate equation, adsorption capacity was assumed to be directly proportional to the number of active sites occupied on the adsorbent [25].

The pseudo-second-order rate equation could be expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

where k_2 is the pseudo-second-order rate constant of adsorption (g/mg min).

In order to obtain a linearized equation, pseudo-second-order rate equation was integrated with boundary condition, i.e. $t = 0$ to t and $q_t = 0$ to q_t:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \times t \tag{11}$$

Data showed comparatively higher r^2 values for pseudo-second-order model (Table 5). The values of experimental ($q_{e,exp}$) and calculated ($q_{e,cal}$) adsorption capacities are appreciable close for pseudo-second-order model. These observations confirmed applicability of pseudo-second-order kinetic model. Applicability of pseudo-second-order model for phenols adsorption was reported elsewhere [7,24,38].

3.6. Intraparticle diffusion model (Weber and Morris model)

The model described mass transfer of solute from bulk solution to solid, and was extensively used to represent the diffusion in adsorptive processes. The model captured the different mass transfer resistances for uptake by aqueous-suspended particles. It was appropriate for situations where both water-and particle-side processes were important.

The model is expressed as [39]:

$$q_t = k_{id} t^{0.5} + C \tag{12}$$

where k_{id} is the intraparticle diffusion rate constant (mg/g min$^{0.5}$) and C is the intercept which represents the value of the thickness of the boundary layer. The value of intraparticle diffusion rate constant, k_{id} could be calculated from the slope of the q_t vs. $t^{0.5}$ plot.

Plots for the adsorption of phenols at various concentrations showed multilinearities (Fig. 6(a–c)) indicating that intraparticle diffusion is not the only rate-limiting step. Initially, sharp linear curves showed a rapid transport of adsorbate molecules from bulk solution to the surface of adsorbent (macropores). The adsorbate was then diffused into interior part through the pores (mesopores and micropores). The second linear portion revealed the gradual adsorption of

Table 3
Isotherm parameters for the adsorption of phenol, 4-CP, 2,4-DCP

	Langmuir isotherm				Freundlich isotherm		
Temperature (°C)	K_L (L/g)	q_m (mg/g)	r^2	R_L	K_F (mg/g) (L/mg)$^{1/n}$	$1/n$	r^2
Phenol							
30	0.019	65.36	0.995	0.134–0.660	2.63	0.606	0.963
40	0.025	66.67	0.997	0.101–0.593	3.53	0.564	0.959
50	0.037	67.11	0.997	0.074–0.498	4.75	0.535	0.953
4-chlorophenol							
30	0.047	114.94	0.998	0.038–0.115	24.33	0.288	0.875
40	0.059	121.95	0.999	0.029–0.094	26.86	0.291	0.868
50	0.078	126.58	1.000	0.022–0.075	29.29	0.301	0.913
2,4-dichlorophenol							
30	0.016	156.25	0.995	0.081–0.180	20.03	0.335	0.973
40	0.018	163.93	0.994	0.072–0.162	20.59	0.351	0.989
50	0.023	172.41	0.998	0.058–0.132	26.44	0.321	0.988

phenols. Finally, formation of plateau on the curves indicated that the adsorption process attained equilibrium stage. The reason was due to extremely low concentration of phenolic ions in the solution. The plots did not pass through the origin confirming more than one process type was involved during the adsorption [17].

3.7. Regeneration studies

To check the economic feasibility of the process regeneration, studies on CCM were performed using ethanol, 0.1 M NaOH, DW (pH: 2), 0.1 M NaCl as eluents. Optimum amount of phenol was recovered when using ethanol (93%) as an eluent while recovery was minimum (61%) with saline 0.1 M NaCl as eluent.

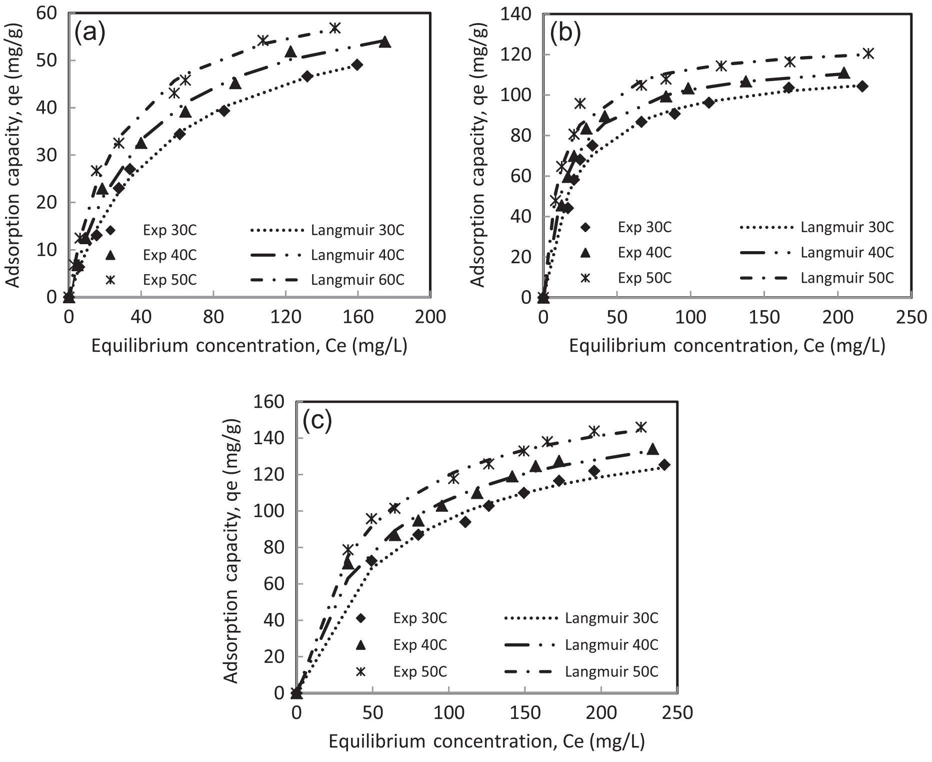

Fig. 5. Non-linear isotherm models for phenol (a), 2-CP (b) and 2,4-DCP (c).

Table 4
Comparison of maximum monolayer adsorption capacity of various adsorbents for the removal of phenol and its derivatives from aqueous phase

Adsorbent	Adsorbate	Experimental conditions	Maximum monolayer adsorption capacity (q_m, mg/g)	Reference
Activated carbon (AC)	Phenol	–	6.19	[29]
Palm seed AC	Phenol	–	18.3	[30]
Lignite AC	Phenol	25˚C	42.32	[31]
Beet pulp AC	Phenol	25˚C	89.96	[32]
MgAl-mixed oxide	Phenol	–	134.1	[22]
AC	Phenol	–	149.25	[33]
Activated sludge	Phenol,4-CP		Phenol – 236.8 4-CP – 287.2	[34]
Magnetic polysulfone microcapsule	Phenol,4-CP		Phenol – 79.36 4-CP – 370.4	[35]
Rattan sawdust AC	4-CP		188.7	[19]
CCM	Phenol,4-CP,2,4-DCP		Phenol – 65.8 4-CP – 115.0 2,4-DCP – 156.3	Present study

The recovery was 83 and 61% when DW (pH 2) and 0.1 M NaOH were used as eluents, respectively (Fig. 7). After four consecutive regeneration cycles, 12.9% loss in phenol adsorption was observed when ethanol was used as eluent, showing minimal deterioration to monolith surface coating by ethanol, while 49.4 and 57.4% loss in adsorption after four consecutive cycles was observed when DW (pH: 2) and 0.1 M NaOH were used as eluents, respectively. The drop in adsorption when 0.1 M NaCl was used as eluent was similar to 0.1 M NaOH. The loss in adsorptive performance of CCM under acidic and alkaline conditions showed the interference of these eluents with surface active sites. Also, compared to acidic,

Table 5
Kinetic parameters for the adsorption of phenol, 4-CP, and 2,4-DCP

	Kinetic models						
		Pseudo-first-order			Pseudo-second-order		
Concentration (mg/L)	$q_{e,\text{exp}}$ (mg/g)	k_1 (1/min)	q_{cal} (mg/g)	r^2	k_2 (g/mg min)	$q_{e,\text{cal}}$ (mg/g)	r^2
Phenol							
50	13.07	0.0060	13.08	0.985	0.00081	13.57	0.999
100	24.80	0.0067	22.82	0.993	0.00047	25.32	0.999
150	30.43	0.0071	28.22	0.990	0.00035	31.25	0.999
200	34.45	0.0074	32.92	0.989	0.00033	35.46	1.000
250	38.49	0.0081	35.70	0.995	0.00039	39.37	1.000
4-chlorophenol							
250	51.92	0.0088	50.82	0.987	0.00033	53.19	0.999
300	65.99	0.0097	70.65	0.993	0.00027	67.57	0.999
350	75.03	0.0092	75.53	0.985	0.00021	76.34	1.000
400	82.40	0.0099	87.18	0.986	0.00021	84.03	0.999
450	98.66	0.0106	102.61	0.992	0.00018	99.01	0.999
2,4-dichlorophenol							
400	89.15	0.0101	92.02	0.991	0.00016	90.91	0.999
450	100.44	0.0104	97.70	0.992	0.00016	102.04	1.000
500	110.99	0.0108	108.24	0.995	0.00015	112.36	1.000
550	118.24	0.0111	111.50	0.996	0.00016	120.48	1.000
600	124.25	0.0113	113.73	0.997	0.00016	126.58	1.000

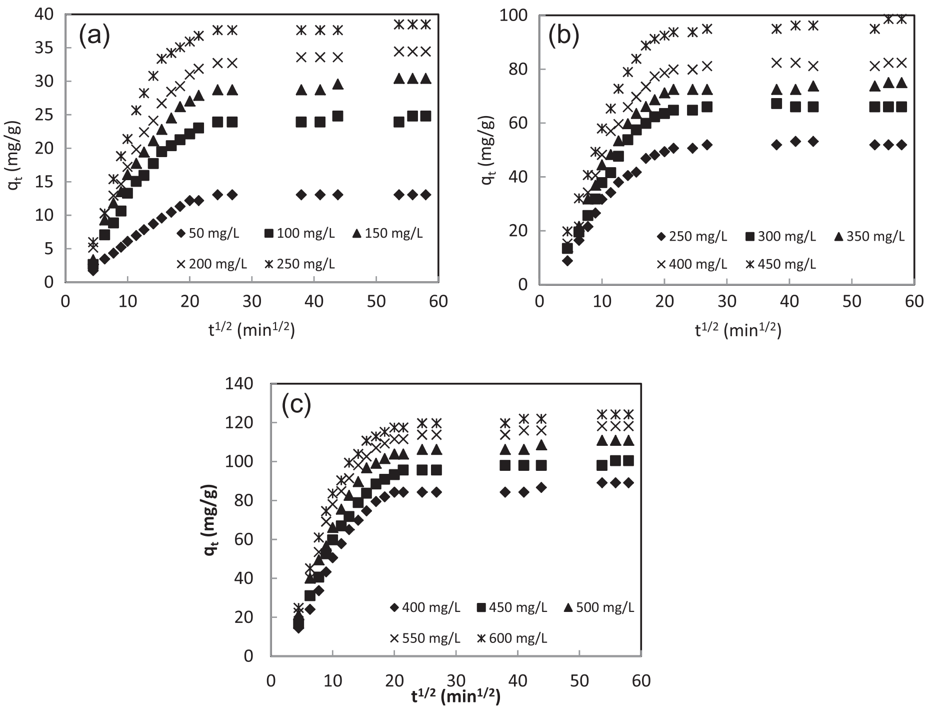

Fig. 6. Weber and Morris plots for phenol (a) 2-CP (b) and 2,4-DCP (c) adsorption on CCM.

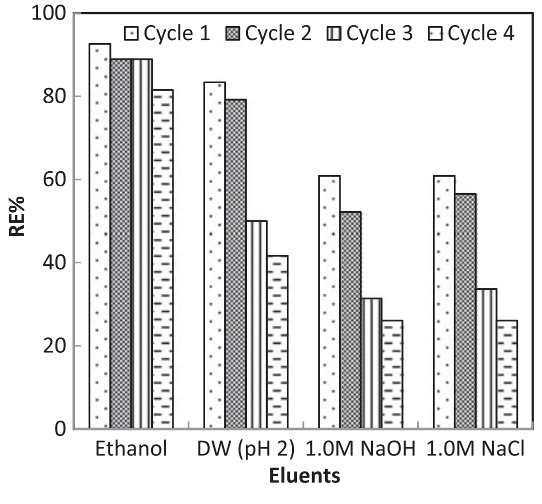

Fig. 7. Regeneration efficiency plot of CCM.

alkaline and saline medium, the solubility of phenol is higher in ethanol. Therefore, optimum phenol was recovered with ethanol. While, after four consecutive cycles only 12.9% loss in phenol adsorption was observed when ethanol was used as eluent, showing excellent CCM potential for isolating phenol.

4. Conclusions

The adsorption of phenols on CCM was solubility dependent. The adsorption of phenol was least as it was highly soluble in water. The adsorption followed the order 2,4-DCP > 4-CP > phenol. Optimum adsorption was observed at pH 5. The equilibration time for phenol, 4-CP and 2,4-DCP was found to be 600, 470 and 400 min, respectively. Kinetics studies revealed applicability of pseudo-second-order kinetics model, confirming chemisorption process. The intraparticle diffusion was not the only rate-limiting step for phenols adsorption as shown by Weber and Morris model. The adsorption increased with increase in reaction temperature. Isotherm data showed Langmuir model as a best-fitted model. Desorption study showed optimum-phenol recovery with ethanol as eluent while, regeneration study (ethanol as eluent) showed appreciably high phenol adsorption after four consecutive cycles.

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