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Adsorption potential of maize cob carbon for 2,4-dichlorophenol removal from aqueous solutions: Equilibrium, kinetics and thermodynamics modeling

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ABSTRACT

The present study deals with the adsorption potential of thermally activated carbon developed from maize cob for the removal of 2,4-dichlorophenol (2,4-DCP) from aqueous solutions. Studies were conducted to delineate the effects of contact time, 2,4-DCP initial concentration, pH and temperature. The kinetics of 4-DCP adsorption from a solution onto an adsorbent was explored experimentally. Non-linear form of pseudo-second-order model showed a better fit with good correlation co-efficient. Bangham's and intra-particle diffusion model were also used. Non-linear form of Langmuir isotherm model was applied and the data correlate well and the maximum adsorption capacity was found to be 17.94 mg/g for the particle size of 250–500 μm. Acidic pH was favorable for the adsorption of 2,4-DCP. Studies on pH effect and desorption showed that chemisorption mechanism was involved in the adsorption process. Thermodynamic study showed that adsorption of 2,4-DCP on maize cob carbon is more favored. The change in entropy (ΔS°) and heat of adsorption (ΔH°) of maize cob carbon were estimated as 26.91 J/(K mol) and 6.78 kJ/mol, respectively.

1. Introduction

Phenol and phenolic derivatives belong to a group of common environmental contaminants [1]. Even low concentrations can be an obstacle to the use or reuse of water. Phenols give an unpleasant taste and odor to drinking water and can exert negative effects on different biological processes. Most of these compounds are known or suspected to be human carcinogens [2]. Toxicity generally increases with the degree of chlorination and it has been reported that the OH group plays an important role in the toxicity of chlorophenols to fish [3]. It is known that 2,4-D disturbs metabolism, can decrease ATP and NADH levels and may also increase the levels of AMP, NAD^+, lactate dehydrogenase (LDH). An alarming symptom was the increase in the level of methemoglobin and the change of oxygen affinity of hemoglobin under the influence of 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenol. Toxic influence of 2,4-dichlorophenol may provoke disturbances in bilayer phospholipid structure that plays an important role in the proper function of cell membrane [4]. Phenolics constitute the 11th of the 126 chemicals which have been designated as priority pollutants by the United States Environmental Protection Agency [5]. Phenols in the presence of chlorine form chlorophenol, which is quite pronounced with a medicinal taste and objectionable when, get mixed with drinking water. Phenol and phenolic compounds are well-known components in a wide variety of waste waters including these from coal conversion processes, coking plants, petroleum refineries and several chemical industries, as pharmaceuticals, resin and dye manufactures. Chlorophenols constitute a significant category of pollutants and are also major components of paper pulp bleach plant effluents. In addition, 2,4-dichlorophenols have been extensively used as wood preservatives and pesticides and as precursors for the synthesis of herbicides [6]. A typical pharmaceutical industrial effluent containing 2,4-dichlorophenols is listed in Table 1. There are many methods such as oxidation, precipitation, ion exchange and solvent extraction to remove phenolic materials from aqueous solution. However, in water treatment the most widely used method is adsorption onto the surface of activated carbon. In view of the high cost and tedious procedures for the preparation and regeneration of activated carbons there is a continuing search for low cost potential adsorbents. Agricultural wastes have emerged as a better choice. There are a quite large number of studies

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Table 1
Physio-chemical characteristics of phenolic wastewater [37]

Parameters	Values
pH	7.3
EC (μS/cm)	286
Sulphate (mg/l)	58
Chloride (mg/l)	54
TDS (mg/l)	234
COD (mg/l)	485
BOD (mg/l)	59
DCP (mg/l)	15

regarding the preparation of activated carbons from agricultural wastes.

The high cost of commercial activated carbon has stimulated interest in examining the feasibility of using cheaper raw materials. Substitute materials tested include palm seed coat, bagasse, palm pith, banana pith, bagasse fly ash, and coir pith [7–12]. Activated carbons remove many of the impurities occurring in water and wastewater. Because of the high cost and variable performance of carbon regeneration, single use materials are desirable. Phenols are particularly susceptible to irreversible adsorption onto some activated carbons [13]. Highly porous structure of activated carbon may represent over design for many applications in water treatment [10]. It may be sufficient to use a larger dose of the less-expensive substitute and achieve the same treatment goal. In the search for new and low cost agricultural wastes as source material for activated carbon, attempts have been made to produce activated carbon from maize cob. Extensive characterization studies have been performed as per the standard methods to assess the quality of activated carbon. The adsorptive property of the activated carbon was tested by adsorption of 2,4-DCP from aqueous solution. A thorough study of adsorption kinetics and equilibrium sorption isotherm revealed the potential use of this carbon as an adsorbent. Efficiency of carbon mainly depends on surface area and binding forces present within the particles of adsorbent, as well as chemical characteristics of adsorbate.

This work reports the results obtained on the preparation of activated carbon from maize cob and their ability to remove 2,4-DCP from aqueous solution in batch study. The influence of several operating parameters such as initial concentration, contact time, adsorbent dosage, pH and temperature was investigated. Equilibrium isotherms and kinetic models were used to identify the possible mechanism of the adsorption process.

2. Materials and methods

2.1. Preparation and characterization of carbonized material

Maize cob was collected from nearby areas, dried in sunlight for 5 h and ground. The dried maize cob powder was sieved to 250–500 μm size. It was subjected to carbonization at 700 °C for 1 h using a muffle furnace under closed conditions. The carbonized material was taken out, sieved to 250–500 μm size again, stored in an air-tight container in a dessicator and used for adsorption studies. Physical properties of carbon prepared from maize cobs were analyzed. The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were determined using computer-controlled nitrogen gas adsorption analyzer at −196 °C (Quantachrome, Boynton Beach, USA). Moisture content, ash content, and apparent density were determined following Wilde et al. [14]. Ion-exchange capacity was determined following Kinniburg et al. [15]. All the chemicals used were of analytical reagent grade procured from Sigma, USA and Merck, India. All the solutions were prepared in double distilled water.

2.2. Experimental procedure

Adsorption experiments were carried out by agitating 100 mg of carbon with 50 ml of 2,4-DCP solution of concentration ranging from 10 to 40 mg/l and pH 2 at 200 rpm, 30 °C in a thermostated rotary shaker (ORBITEK, Chennai, India). 2,4-DCP concentration was estimated spectrophotometrically by monitoring the absorbance at 283.8 nm using UV–vis spectrophotometer (Hitachi, model U-3210, Tokyo). pH was measured using pH meter (Elico, model LI-107, Hyderabad, India). The 2,4-DCP solution was separated from the adsorbent by centrifugation at 20,000 rpm for 20 min and its absorbance was measured. Non-linear form of Langmuir equation was employed to study the equilibrium adsorption. Effect of pH was studied by adjusting the pH of 2,4-DCP solutions using dilute HCl and NaOH solutions and the solutions were agitated with 100 mg/50 ml adsorbent dose at 80 and 100 min, respectively, for 10 and 20 mg/l 2,4-DCP concentrations. For desorption studies, the spent carbon from the equilibrium sorption experiments using 10–20 mg/l 2,4-DCP, was separated by centrifugation of the mixture and washed gently with water to remove any free unadsorbed 2,4-DCP. Several such samples were prepared. Then the spent adsorbent was agitated for 80 or 100 min with 50 ml of distilled water, adjusted to different pH values. The desorbed DCP in the solvent was estimated spectrophotometrically at 283.8 nm. Desorption studies were also conducted in 50 ml of 1N NaOH solution. For temperature studies, adsorption of 10 mg/l of 2,4-DCP by 50 mg of adsorbent was carried out at 30, 40, 50 and 60 °C in the thermostated rotary shaker. Preliminary experiments showed that there was no adsorption due to container walls. Experiments were carried out in duplicate and mean values were taken for calculations. Maximum deviation was 4%.

3. Results and discussion

3.1. Physico-chemical characteristics of carbon

Characteristics of carbon prepared from maize cob are presented in Table 2. The measured surface area of maize cob carbon was 468 m^2/g and is comparable to various low cost agricultural by-products-based adsorbents namely, porogen-free banana pith carbon (37 m^2/g) [10], palm pith carbon (188 m^2/g) [9], peanut hull carbon (208 m^2/g) [16], silk cotton hull carbon (228 m^2/g) [17], eich-

Table 2
Properties of maize cob carbon

Parameter	Value
pH	7.6
Moisture (%)	9.57
Bulk density (g/ml)	0.375
Specific gravity	1.06
Porosity (%)	64.62
Decolorizing power (mg/g)	112.5
Solubility in water (%)	1.37
Solubility in 0.25N HCl (%)	2.28
Ion exchange capacity (mequiv/g)	0.29
Iodine number (mg/g)	406
Surface area (m^2/g)	468
Ash content (%)	6.9
Micropore volume (cm^3/g)	0.079
Total pore volume (cm^3/g)	0.110
Micropore area (%)	83.7
Micropore volume (%)	71
Average pore dia (nm)	2.69
Average micropore dia (nm)	1.13
Sodium (mg/g)	122
Potassium (mg/g)	11
Calcium (mg/g)	33

hornia (266 m^2/g) [18] and cassava (270 m^2/g) [19]. The moisture content of the carbon was found to be 9.57% (Table 2). It was then observed from the literature that if the moisture content of the adsorbent is high, it will dilute the action of carbon and it necessitates utilizing some extra load of carbon [17,20]. The decolorizing capacity was 112.5 mg/g, which indicates that the carbon prepared had good adsorption capacity and it could be used for adsorption of organics. The characteristics (Table 2) show that carbon has a high surface area, and most of the surface area (84%) and pore volume (71%) is made up by pores smaller than 2 nm in pore width, the so-called micropores. The maximum of pores is found below 2 nm pore width. So, the particles are mostly microporous. The total ash content was 6.9%, which represents the good quality of carbon. Carbons with high ash content are considered to have less sorption capacity. Among the elements analyzed sodium content was much higher

3.2. Effects of shaking time and concentration of 2,4-DCP on adsorption

Effect of shaking time on adsorption of 2,4-DCP onto maize cob was studied over an shaking time of 80–120 min, using 100 mg of maize cob carbon, 10–40 mg/l 2,4-DCP concentration at pH 2, 30 °C and 200 rpm shaking speed. Adsorptive uptake of 2,4-DCP (mg/g) increased with increase in shaking time and reached equilibrium. The equilibrium time was 80 and 100 min for 10 and 20 mg/l of 2,4-DCP concentration, respectively and 120 min for both 30 and 40 mg/l of 2,4-DCP concentration. It is clear that the removal of 2,4-DCP depends on the concentration of the adsorbate. The equilibrium time for 2,4-DCP calculated from this study is either the same or less than that reported for 2,4-DCP adsorption onto coir pith, i.e. after 120 min [12], and 5 h for baggase fly ash and activated carbons [11].

3.3. Effect of temperature

Increase of temperature slightly increased the removal of 2,4-DCP. The diffusion coefficient D_p for intra-particle transport of 2,4-DCP species into the adsorbent particles has been calculated at different temperatures by using the equation [21]:

$$t_{1/2} = \frac{0.03 r_o^2}{D_p} \tag{1}$$

where $t_{1/2}$ is the time for half adsorption (s), r_o is the radius of the adsorbent particle (cm) and D_p is the diffusion coefficient (cm^2/s). If pore diffusion is to be rate-limiting step, the pore diffusion coefficient (D_p) should be in the range 10^{-11} to 10^{-13} cm^2/s. In the present work, diffusion coefficient was found to be 10^{-12} cm^2/s which shows that the pore diffusion coefficient of 2,4-DCP is the rate-limiting step. The pore diffusion coefficient for adsorption of 2,4-DCP did not change with increase in temperature from 30 to 60 °C, but decreased slightly with increase in the concentration of 2,4-DCP.

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. In this phase study, a series of experiments were conducted at 30, 40, 50, and 60 °C to study the effect of temperature on the rate and the kinetics. Increase in temperature increased the percent removal. The change in standard free energy, enthalpy and entropy of adsorption were calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_c \tag{2}$$

where R is gas constant and K_c is the equilibrium constant and T is the temperature in K.

According to van't Hoff equation,

$$\log_{10} K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{3}$$

Positive values of ΔH° (6.78 kJ/mol) show the endothermic nature of adsorption. The positive values of (1.410, 1.594, 1.862 and 2.160 kJ/mol) ΔG° indicate the non-spontaneous nature of adsorption for 2,4-DCP at 30, 40, 50 and 60 °C for the equilibrium constant values of K_c (1.75, 1.85, 2.00 and 2.24). The positive values of ΔS° (26.91 J/(K mol)) suggest the increased randomness at the solid/solution interface during the adsorption of 2,4-DCP on maize cob carbon. Srivastava et al. [11] reported the change in entropy (ΔS°) and heat of adsorption (ΔH°) for phenol adsorption on bagasse fly ash as 1.8 and 0.5 MJ/kg, respectively. Similar results of ΔH° (46.50 kJ/mol) and ΔS° (0.23 J/(K mol)) for 2,4-DCP adsorption onto red mud was reported, but negative values of ΔG° (−21.98, −23.82, −26.48 and −28.50 kJ/mol) confirm the feasibility and spontaneous nature of the process [22]. Non-linear form of pseudo-second-order kinetic model was also applied for temperature studies and it shows a perfect fit for 2,4-DCP adsorption at different temperature studies and the equilibrium data obtained for all the kinetics are presented in Table 3.

3.4. Effect of pH

Optimization of pH for adsorption medium plays vital role in the adsorption studies. The pH of the adsorption medium is the most significant parameter in the treatment of chlorophenols by the adsorbent [23]. The per cent removal decreased with increase in pH (Fig. 1). The PZC (point of zero charge) of maize cob carbon was recorded as 2.1 (Fig. 2). Above PZC, the overall charge of carbon surface will be negative, which resulted in decrease in 2,4-DCP adsorption. Higher adsorption of 2,4-DCP at pH 2 has also been reported by others [9,10,24]. In the acid range pH_{equ} increases with the increasing pH_{in}, i.e. neutralization and sorption process are parallel processes (Fig. 3). The surface chemistry of the activated carbons essentially depends on their heteroatom content, mainly on their surface oxygen complex. The surface charge would depend on the solution pH and the surface characteristics of the carbon. A negative charge will result from the dissociation of surface oxygen

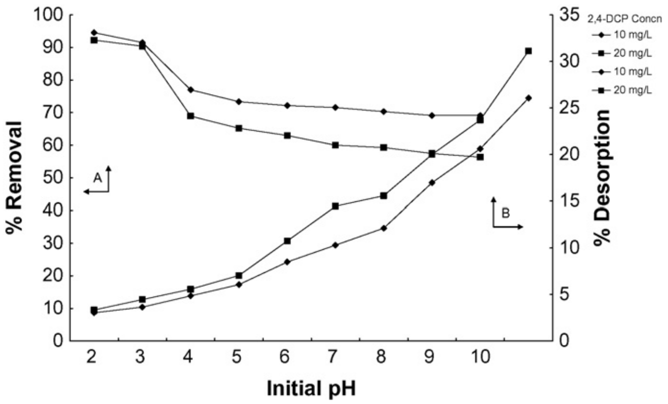

Fig. 1. (A) Effect of pH on removal of 2,4-DCP: adsorbent dose, 100 mg/50 ml; 10 mg/l, agitation time 80 min; 20 mg/l, agitation time 100 min. (B) Effect of pH on desorption of 2,4-DCP from 2,4-DCP-loaded adsorbent. Adsorbent dose, 100 mg/50 ml; 10 mg/l, agitation time 80 min; 20 mg/l, agitation time 100 min.

Table 3
Kinetic parameters for the removal of 2,4-DCP by maize cob carbon

Parameter	q_e (exp) (mg/g)	k (g/(mg min))	q_e (cal) (mg/g)	R^2
Second-order kinetic model				
Initial DCP[a] conc (mg/l)				
10	4.84	0.055	4.95	0.999
20	9.27	0.041	9.22	0.998
30	12.93	0.033	12.64	0.997
40	15.79	0.037	15.38	0.999
Temp (°C)[b]				
30	7.01	0.027	6.76	0.995
40	7.12	0.032	6.91	0.997
50	7.34	0.042	7.11	0.997
60	7.55	0.076	7.46	0.999

Concentration (mg/l)	k_o (ml/(g l))	α	R^2	Temp (°C)	k_o (ml/(g l))	α	R^2
Bangham's constants							
10	104.95	0.2699	0.9445	30	210.47	0.3282	0.9626
20	103.91	0.2263	0.992	40	243.61	0.3119	0.9923
30	86.53	0.2209	0.9714	50	330.06	0.2607	0.9647
40	90.32	0.1725	0.9804	60	531.37	0.1867	0.9754

Concentration (mg/l)	k_{id} (mg/g min)	R^2	Temp (°C)	k_{id} (mg/g min)	R^2
Intra-particle diffusion constants					
10	0.3369	0.9083	30	0.4459	0.9961
20	0.5050	0.9932	40	0.4239	0.9877
30	0.6321	0.9890	50	0.3792	0.9917
40	0.5979	0.9791	60	0.2656	0.8949

[a] Condition: adsorbent dose = 100 mg; pH = 2.0; temp = 30 °C.

[b] Condition: adsorbent dose = 50 mg; pH = 2.0; 2,4-DCP conc = 10 mg/l.

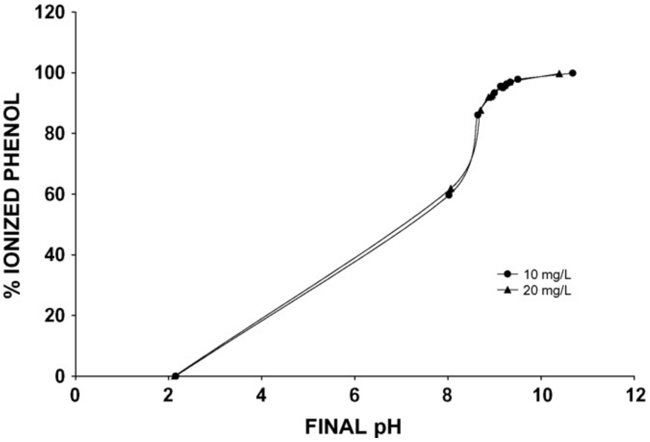

Fig. 2. Effect of final pH on ionization of 2,4-dichlorophenol; temp, 30 °C.

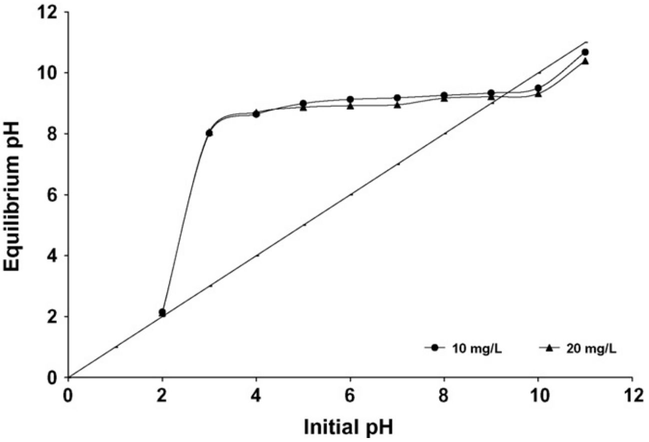

Fig. 3. Effect of initial pH on equilibrium pH.

complexes of acid character such as carboxyl and phenolic groups and these surface sites are known to be Bronsted type. The positive surface charge may be due to surface oxygen complexes of basic character like pyrones or chromenes, or due to the existence of electron-rich regions within the graphene layers acting as Lewis basic centers, which accept protons from the aqueous solution [25].

The degree of ionization of phenols depends on the pH of the medium. Based on the relationship [26].

$$CP_0 = \frac{CP_T}{\{1 + 10^{(pH - pK_a)}\}} \tag{4}$$

where CP_0 is the concentration of unionized 2,4-DCP species, CP_T is the total concentration of 2,4-DCP taken, pH is the final pH, i.e. equilibrium pH after adsorption and pK_a is 7.85. The concentration of ionized 2,4-DCP species was calculated at different final pH values and a plot of the percent ionized 2,4-DCP versus final pH is shown in Fig. 2. Effect of initial pH on final pH in the presence and absence of 2,4-DCP shows (Fig. 3) that the final pH is generally higher than the initial pH in the blank, i.e. in the absence of 2,4-DCP. This is due to the leaching of cations like Na^+ and K^+ from the carbon and subsequent replacement with the protons from the bulk solution on the adsorbent surface. Adsorption of neutral 2,4-DCP at pH 2 (unionized; see Fig. 2) did not cause any change in pH, as expected. It appears that chemisorption is the only mode in the adsorption process at pH 2. At pH > 2, adsorption of 2,4-dichlorophenolate ions release OH^- ions from the adsorbent surface and this increases the final pH further compared to blank. At lower pH values, the chlorinated phenols either neutral or positively charged. Since at acidic pH values 2,4-DCP is present mostly as the neutral species and the adsorbent surface carries positive charge, there is no electrostatic repulsion between the adsorbate and the adsorbent. In effect the removal is higher at lower pH values. The chloride (–Cl) ion on the benzene ring, which increases the acidic character is responsible for forming anion on the oxygen atom of the –OH group and also has s strong affinity for silica surfaces [27]. At a lower pH, there is a reasonably strong interaction between the adsorbent and the polar resonance contributed phenol-structure. Similar result was observed for 2,4-DCP using rice husk [28]. At a value of pH 11, the phenols dissociate, forming phenolate anions, while the surface functional groups are either neutral or negatively charged. The electrostatic repulsion between the identical charges lowers the adsorption capacity. Despite the electrostatic repulsion at alkaline pH, a significant removal was observed. This indicates that chemisorption might also be involved in the removal process.

3.5. Desorption studies

Desorption experiments were performed for a better understanding of the adsorption processes. Disposal of the 2,4-DCP-loaded carbons is an important issue that needs to be addressed; otherwise the exhausted carbon would create a new round of environmental problem. Regeneration of spent carbon and recovery of phenol would make the treatment process economical. Also desorption studies help elucidate the mechanism of adsorption. The per cent desorption increased, when the pH was increased from 2 to 11(Fig. 1). Only the physisorbed phenol unlike the chemisorbed species might be desorbed from the adsorbent surface. Studies on both pH effect and desorption suggest that the both physisorption and chemisorption are involved for the removal of 2,4-DCP by the maize cob carbon. Desorption experiments in 1N NaOH solution resulted in 77.8 and 69.5% recovery of the sorbate from 10 and 20 mg/l 2,4-DCP-loaded carbons, respectively.

3.6. Adsorption dynamics

The non-linear form of pseudo-second-order kinetic model [29,30] is expressed as

$$q_t = \frac{q_e^2 kt}{1 + q_e kt} \quad (5)$$

where q_e is the amount of 2,4-DCP sorbed at equilibrium (mg/g); q_t is the amount of 2,4-DCP sorbed at time t (mg/g); k is the second-order equilibrium rate constant (g/mg min). Calculated correlations are closer to unity for second-order kinetics model (Fig. 4; Table 3) therefore the adsorption kinetics could well be approximated more favourably by second-order kinetic model for 2,4-DCP. The k (g/mg min) and q_e values as calculated are listed in Table 3. Similar phenomena have been observed in the adsorption of 2,4-dichlorophenol on coir pith, palm pith and banana pith carbon [9,10,12]. Non-linear form of pseudo-second-order kinetic model studied at different temperature also showed correlations closer to unity. Similarly the difference between experimental q_e and the calculated q_e were very less, indicating the better fit of pseudo-second-order kinetic model (Fig. 5; Table 3).

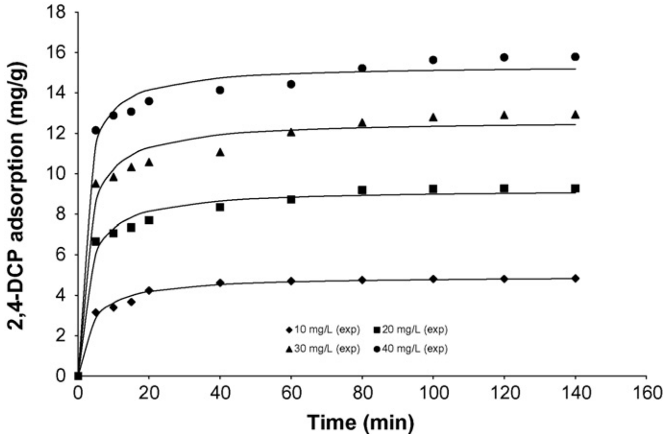

Fig. 4. Pseudo-second-order plots for removal of 2,4-DCP—at different initial 2,4-DCP concentrations: adsorbent dose, 100 mg/50 ml; initial pH, 2.0; temp, 30 °C. Lines predicted by pseudo-second-order model.

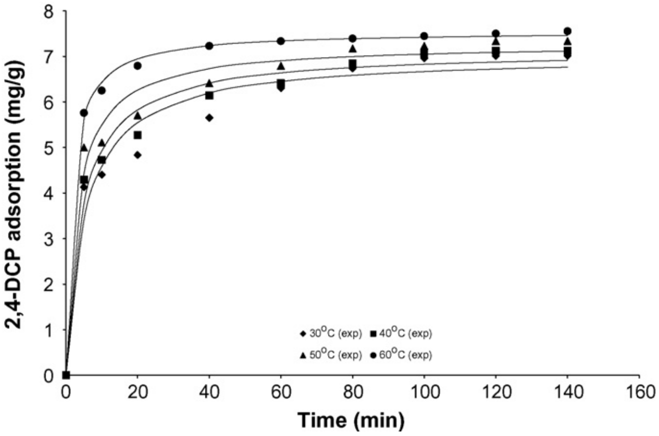

Fig. 5. Pseudo-second-order plots for removal of 2,4-DCP—at different temperatures: adsorbent dose, 50 mg/50 ml; initial pH, 2.0; initial 2,4-DCP concentration, 10 mg/l. Lines predicted by pseudo-second-order model.

3.7. Intra-particle diffusion study

An empirically found functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionally with $t^{1/2}$, the Weber–Morris plot, rather than with the contact time, t [31].

$$q_t = k_{id} t^{1/2} + C \quad (6)$$

where k_{id} is the intra-particle diffusion rate constant. According to Eq. (6), a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} and intercept C when adsorption mechanism follows the intra-particle diffusion process. Values of intercept give an idea about the thickness of boundary layer, i.e., the larger the intercept the greater is the boundary layer effect. The linear plots of mass of 2,4-DCP adsorbed per unit mass of adsorbent, q_t versus $t^{1/2}$ are attributed to the macropore diffusion which is the accessible sites of adsorption. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. The values if k_{id} as obtained from the slope of straight lines are listed in Table 3.

3.8. Bangham's equation

Kinetic data were further used to know about the controlling step occurring in the present adsorption system using Bangham's equation [32].

$$\log\log\left(\frac{C_0}{C_0} - q_t m\right) = \log\left(\frac{k_0 m}{2:303V}\right) + \log(t) \quad (7)$$

where C_0 is the initial concentration of adsorbate in solution (mg/l), V is the volume of solution (ml), m is the weight of adsorbent per liter of solution (g/L), q_t (mg/g) is the amount of adsorbate retained at time t, and α (<1) and k_0 are constants. The double logarithmic plot according to above equation yielded perfect linear curves for methylene blue removal by carbon showing that the diffusion of adsorbate into pores of the adsorbent is not the only rate-controlling step [33]. The Bangham's constants calculated from the plots are represented in Table 3.

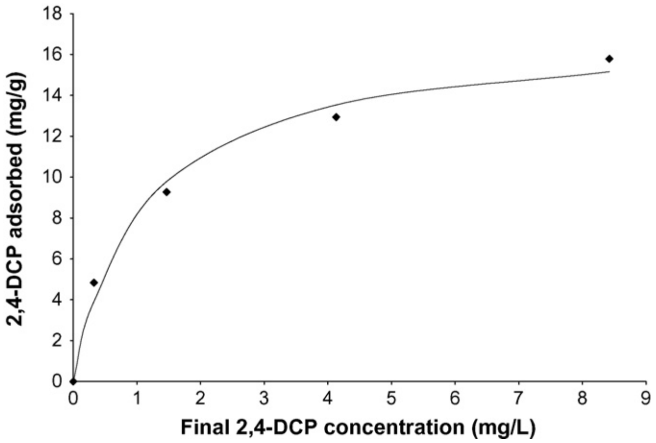

Fig. 6. Adsorption isotherm for removal of 2,4-DCP by maize cob carbon. Lines predicted by Langmuir model.

3.9. Adsorption models

The equilibrium adsorption isotherm is fundamentally very crucial in the design of adsorption systems. The equilibrium adsorption is usually described by an isotherm equation characterized by certain parameters whose values express the surface properties of the adsorbent and its affinity to the adsorbate. In this study, to investigate the adsorption isotherm of the phenolic compounds, Langmuir isotherm model was examined and the isotherm parameters were determined.

3.9.1. Langmuir isotherm

The Langmuir adsorption isotherm [34] has been successfully applied to many pollutant adsorption processes and has been the most widely used to describe the adsorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites on the surface of the adsorbent. It is then assumed that once adsorbate molecule occupies a site, no further adsorption can take place at that site. The rate of adsorption to the surface should be proportional to a driving force and area. The driving force is the concentration in the solution, and the area is the amount of bare surface.

The non-linear Langmuir equation is represented as follows:

$$q = \frac{q_{\max} b C_f}{1 + b C_f} \qquad (8)$$

where C_f is the concentration of 2,4-DCP solution (mg/l) at equilibrium, $q_{\max}$ is the maximum 2,4-DCP uptake (mg/g) and b is the Langmuir equilibrium constant. The non-linear Langmuir plot showed a smooth curve with a close fit to the experimental data (Fig. 6). Values of $q_{\max}$ and b were calculated as 17.94 mg/g and 0.907, respectively. The adsorption capacity of maize cob carbon is higher than paper mill sludge (4.49 mg/g) [35] and comparable with some carbonized agricultural materials like coir pith (19.12 mg/g) and palm pith (19.16 mg/g) [9,12]. Higher adsorption capacity (q_o) of 339 mg/g was observed using apricot stone as an adsorbent [36].

The good adsorption capacity of the carbon may be attributed to the large micropore volume (71%). Considering the molecular dimension of 2,4-DCP, the size of it was not more than 0.7 nm at any angle, whereas the average micropore size of the prepared carbon was more (1.13 nm) than the size of 2,4-DCP (Fig. 7). Thus it is clear that micropores play a considerable role in liquid-phase adsorption of 2,4-DCP. Thus large micropore volume could be the main cause for the relatively lower adsorption capacity.

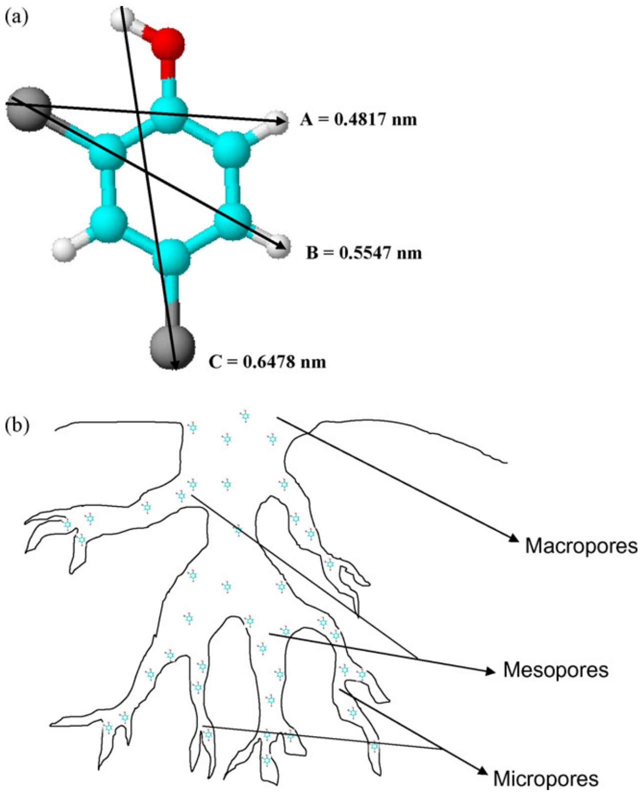

Fig. 7. Molecular dimension of 2,4-DCP (a) and its possible transport through the pores of maize cob carbon (b).

4. Conclusions

Higher percentage of 2,4-DCP removal by maize cob carbon was possible provided that the initial concentration in the solution was low. Optimum pH for 2,4-DCP removal was found to be pH 2.0. The present study shows that the maize cob carbon is an effective adsorbent for the removal of 2,4-DCP from aqueous solution. The percentages of 2,4-DCP adsorption increased with time and reached equilibrium, which varied with initial 2,4-DCP concentrations. Langmuir isotherm fitted well with experimental data. The adsorption capacity of maize cob carbon was 17.94 mg/g for the particle size of 250–500 μm. Its adsorption capacity was on par with many other reported carbonaceous materials. However, it is very important to mention here that the maize cob is an easily and a freely available inexpensive material, and its cost is very low in comparison to the cost of its regeneration. Adsorption kinetics followed second-order kinetic model. The kinetic data would be useful for the fabrication and designing of wastewater treatment plants. It is concluded that the activated carbon prepared from maize cob could be exploited for commercial applications. This carbon will go a long way in the tertiary treatment of potable water as well as industrial wastewater.

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