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Comparable Study of 4-chlorophenol Removal from Petrochemical Wastewater Using Mesoporous and Microporous Carbons: Equilibrium and Kinetics Investigations

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Abstract

In this study, an ordered mesoporous carbon structure with excellent adsorption properties towards chlorophenol compounds was synthesized using a hard template. The physico-chemical properties of the synthesized samples were studied using Small Angle X-ray Diffraction (SAXRD), Transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM) and nitrogen adsorption–desorption analysis. The capability of adsorption of 4-chlorophenol on mesoporous carbon has been investigated by varying the reaction time, initial concentration of 4-chlorophenol, adsorbents loading and the pH of the solution; and the results compared with commercial activated carbon as a microporous carbon.

Freundlich, Langmuir, Tempkin and dubinin-radushkevich adsorption isotherms were used to model the equilibrium adsorption data for 4-chlorophenol compound. The kinetic analysis showed that the adsorption process was fitted with the pseudo-second-order kinetic model. The equilibrium data were investigated by the main adsorption isotherm models on the mesoporous and microporous carbons as adsorbents, which revealed that the Freundlich model was better to describe the 4-chlorophenol adsorption than other models. Also, the obtained results indicated that the adsorption capacity and equilibrium time for mesoporous carbon were better than microporous carbon, 90 mg/g after 25 minute compare to 60 mg/g after 60 minute, respectively.

Keywords: 4-chlorophenol; Adsorption; Mesoporous carbon; Microporous carbon; Waste water; Removal

Introduction

Chlorophenols (CPs) are a particular group of toxic materials which exist as important materials in water pollutions. These compounds cause severe harmful effects, such as carcinogenicity [1].

Chlorophenols have been used in many applications, such as in herbicides, insecticides, wood preservative and synthesis intermediates in the Pharmaceutical sciences [2]. These materials are resistant and hardly biodegradable, lead to a great threat to the human life, and cause to change the taste and odor of water and degrade the quality of water [3,4].

Attention to finding effective removal techniques for removing of these compounds is increased. Various physical and chemical treatment techniques such as catalytic oxidation, photocatalytic, membrane separation, biodegradation, solvent extraction and adsorption have been used for the reduce of organic pollutants from water [3,5-9].

Among these techniques, adsorption process is a simple, effective, prominent and economical method, and it is usually applied for the removal of organic pollutants from solutions. One of the traditional technologies for the removal of contaminants in water is based on adsorption process using carbon active.

Activated carbons indicate a good adsorption capacity due to their high surface area, pore structure and surface properties. These carbonic adsorbents are suitable for removal of the contamination from water and wastewater [10].

However, the activated carbons have low efficiency for the adsorption of large molecules, because of their low specific pore volume, disordered pore structure and micropores, which molecular sizes of these types of molecules are larger than the micropore sizes [11-13].

Therefore, the use of activated carbons is restricted due to their micropore size, weak adsorption selectivity, poor mechanical strength, and inefficient regeneration [9,14].

Recently, development of effective structures as adsorbents with short equilibrium times for the adsorption of toxic compounds from solutions is important.

In this regard, compared with microporous activated carbons, mesoporous carbons have attracted much research attention due to their uniform pore structure, large pore size, high adsorption capacity, recoverability and appropriate selectivity for the adsorption of toxic compounds from solutions [4,15].

The adsorption capacity of mesoporous carbon materials depends on the different parameters such as their surface area, pore size distributions, surface structures, molecular weight, pKa, polarity and molecular size [9,16].

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The ordered mesoporous carbons are desirable materials which can be frequently used to adsorb large molecules from polluted environments. These materials have been considered owing to their potential in various applications, especially in the adsorption of large molecules which their sizes are larger than the micropores; and particular properties, such as regular frameworks, high surface areas and narrow pore size distributions.

Mesoporous carbon structures can be prepared using silica mesoporous structures as hard template.

Mesoporous carbon CMK-1 was synthesized using MCM-48 as a template by Ryoo et al. [17]. Mesoporous carbons CMK-1 can be used as adsorbents for removal of various organic pollutants [18-23]. Then, the synthesis of various ordered mesoporous carbon structures from mesoporous silica templates using sucrose as the carbon source are possible [17,24,25]. Using the hard template, synthesis of these well-ordered pore structure mesoporous carbon materials with tunable pore diameters, high pore volume and surface area can be possible [24,26-28].

In this work, highly ordered mesoporous carbon was synthesized using mesoporous silica template with tunable pore diameter, high hydrothermal stability and thick walls. The prepared material was characterized using SAXRD, SEM, TEM and nitrogen adsorption–desorption analysis.

In this experiment, 4-chlorophenol was considered as a representative of the chlorophenol compounds and the adsorption of 4-chlorophenol on the mesoporous carbon was investigated. The results were compared with those of activated carbon as microporous carbon. Moreover, the effects of the various parameters such as effect of initial concentration of 4-chlorophenol, adsorbent loading, pH of the solution and reaction time were also reported. Kinetic studies were carried out to investigate the effect of various parameters on adsorption of 4-chlorophenol on the adsorbents; the correlation between experimental data and the isotherm models were determined.

Materials and Methods

Chemicals

Tri-block copolymer P 123 (EO 20 PO 70 EO 20, EO = ethylene oxide, PO = propylene oxide, 5800) was obtained from Aldrich. Tetraethyl orthosilicate (TEOS) as a silica source was purchased from Merck. 4-Chlorophenol was used as adsorbate.

Characterizations techniques

The mesostructure of samples were studied by small angle X-ray diffraction using a Rigaku D/Max-2400 diffractometer with Cu-Ka radiation. The patterns were recorded between 0.5 to 10°.

Transmission electron microscopy (TEM) characterizations were performed on a Hitachi-600 electron microscope, with an accelerating voltage of 100 kV.

The samples morphology was also determined by JSM- 6701F scanning electron microscope (Jeol, Japan).

The nitrogen adsorption/desorption experiments were obtained at 77K with a micromeritics Tristar 3000 apparatus. The sample degassing was done at 373K overnight before to surface area measuring.

Preparation of mesoporous carbon

Ordered mesoporous carbon was prepared by the following procedure [24]. Typically 1.0 g of mesoporous silica template was impregnated with the mixture of sucrose, sulfuric acid and water, and keeping the mixture in oven for 6 h at 100°C, followed by heating at 160°C for 6 h. To obtain the fully polymerization and carbonization process, the impregnation step was repeated once again. The template-polymer composites were then carbonized at 900°C under nitrogen or argon flow for 6 h. To remove the silica template, the pyrolyzed product was washed with hydrofluoric (HF) acid at room temperature, to remove the silica template, finally dried at 120°C. The obtained carbon material was designated as mesoporous carbon.

Adsorption procedure of 4-chlorophenol

The influence of several operating parameters such as initial concentration of 4-chlorophenol solution, adsorbent loading, reaction time and pH of solution on the adsorption performance of mesoporous carbon for removal of 4-chlorophenol was investigated.

Parallel series of batch adsorption tests were carried out in 500 mL glass bottles with mesoporous carbon. A series of 4-chlorophenol solutions with concentration ranging from 20 to 200 mgL^{-1} (ppm) and the same pH were prepared by dissolving different amounts of 4-chlorophenol in the deionized water.

A series of 4-chlorophenol solutions with the pH ranging from 2 to 12 and the same initial concentration were prepared by adding various amounts of NaOH or HCl.

Appropriate amount of mesoporous carbon as the adsorbent was weighed accurately and carefully added to these two series of solutions. Then, a series of 4-chlorophenol solutions with the same pH and concentration and different loadings of adsorbent were prepared for investigation of the effect of adsorbent loading. In each bottle, the volume of solution was maintained at 500 mL and prepared solutions were shacked vigorously before stirring for different times.

The resulting mixtures were continuously stirred in constant conditions. The experiments were set at a temperature of 25 ± 1°C and a speed rate of 350 rpm for 2 h to ensure that the adsorption process reached the equilibrium.

After adsorption process, the residual concentration of 4-chlorophenol was filtered to avoid potential interference from suspended scattering particles and analyzed with a UV-VIS spectrophotometer (Analytikjena - spectrod: 210) with the wavelength corresponding to the maximum absorbance at 280 nm, based on a standard calibration curve whose correlation coefficient square (R^2) was 0.999.

The concentration of adsorbed 4-chlorophenol was calculated by subtracting the amount found in the solution after adsorption from the amount before addition of the adsorbent.

Comparing the results to data from liquid chromatography in a HPLC (SCL-10AVP; Shimadzu, Kyoto, Japan) showed that the results were consistent. The HPLC system consisted of a dual-piston pump, an auto-sampler, and variable-wavelength UV–Vis spectrophotometric detector set at 280 nm.

Finally, the optimized adsorption results for mesoporous carbon were repeated for mesoporous carbon. The amount of the adsorbed 4-chlorophenol on to mesoporous and micoporous carbon was calculated using Eq. (1) (Crisafully, Milhome et al.).

Where qe is the adsorption capacity of the adsorbent at equilibrium (mgL^{-1}); Co and Ce are the initial and the equilibrium concentration of the solute (mgL^{-1}), respectively; V is the solution volume (L) and m is the adsorbents loading (g).

To measure the adsorption kinetics of 4-chlorophenol onto the adsorbent, 500 mL of 4-chlorophenol solution with an initial concentration of 100 ppm was introduced into the bottle and about 0.3 g of the adsorbent was weighed accurately and added to the solution very carefully. The solution was stirred continuously at a temperature of 25 ± 1°C and a speed rate of 500 rpm.

A 5 mL of solution sample was taken off at various time intervals and filtrated of the solution to determine adsorption kinetics. The residual concentration of 4-chlorophenol was determined and the amount of adsorption at time (t) calculated. The adsorption capacity and the removed percent of 4-chlorophenol at pre-determined time intervals were calculated using Equations (2) and (3), respectively.

Where, Co, Ct and are the initial concentration (mgL^{-1}), the adsorbate concentration at time t (mgL^{-1}) and the amount of adsorption at time t (mgg-1), respectively [29].

Kinetic model development

Sorption in a 4-chlorophenol/adsorbent system results in the transfer of 4-chlorophenol to the surface of the adsorbent, where it increases in concentration until a dynamic equilibrium was reached between the adsorbent and 4-chlorophenol remaining in the liquid phase. In order to study the mechanism of adsorption processes such as adsorption on the surface, chemical reaction and diffusion mechanisms, and determine the rate-controlling steps, kinetic models were used. The equations of these models and their important parameters are defined in Table 1 [30-32]. In this work, kinetic data obtained from experimental batch studies were tested using pseudo-first-order, pseudo-second-order and Elovich models. In addition, the validity of these models was investigated by studying the kinetics under two initial adsorbate concentrations.

The adsorption isotherms

An adsorption isotherm describes the material adsorption equilibrium at the surface of adsorbent at constant temperature which is very important to determine the adsorption mechanism and adsorbent capacity. The experimental equilibrium data can be fitted with various isotherms models to find the best model to describe the

Kinetic model	Equation	parameters	
Pseudo-first-order	$\ln(q_e-q_t) = \ln(q_e) - k_1 t$ (4)	K_1 (min^{-1})	rate constant
		q_e (mg/g) q_t (mg/g)	q_e and q_t are the sorption capacity or the amounts adsorbed of 4-chlorophenol at equilibrium and at a time t
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$ (5)	K_2 (g/mg.min)	rate constant
		q_e (mg/g) q_t (mg/g)	q_e and q_t are the sorption capacity or the amounts adsorbed of 4-chlorophenol (mg/g) at equilibrium and at a time t
Intra-particle diffusion	$q_t = k_{id} t^{1/2} + C$ (6)	K_{id} (mg g^{-1} $min^{-0.5}$)	rate constant
		C (mg g^{-1})	intra-particle diffusion constant
Elovich	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$ (7) assumption of $\alpha\beta t >> 1$ $q_t = \beta \ln(\alpha\beta) + \beta \ln t$ (8)	α (g/mgmin)	initial adsorption rate
		β (g/mg)	desorption constant

Table 1: Kinetic models and their equation.

Adsorption isotherms	Equation	Parameters	
Langmuir model	$\frac{C_e}{q_e} = \left(\frac{1}{K_L q_m}\right) + \left(\frac{1}{q_m}\right) C_e$ (9)	k_L (L.mg^{-1})	Langmuir adsorption constant
		q_m(mg.g^{-1}) q_e (mg.g^{-1}) C_e (mg.L^{-1})	q_m, q_e and C_e are the Langmuir constant representing maximum monolayer capacity, the adsorbed amount at equilibrium concentration and equilibrium concentration C_e.
Freundlich model	$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$ (10)	K_f (mg/g) n	K_f and n are the Freundlich constants related to adsorption capacity (mg/g) and intensity, respectively.
Tempkin model	$q_e = \frac{RT}{b} \ln(A_T C_e)$ (11) $q_e = B_T \ln A_T + B_T \ln C_e$ (12)	B_T (J/mol), R (8.314 J/mol K) T (K) A_T ($L.mg^{-1}$)	B_T = RT/b, which is heat of adsorption, R is the universal gas constant, T is the absolute temperature and A_T is equilibrium binding constant
Dubinin-Radushkevich model	$\ln q_e = \ln(q_s) - \left(K_{ad} \varepsilon^2\right)$ (13)	q_e (mg/g), q_s (mg/g) K^{ad} (mol^2/kJ^2) $\in$(kJ^2/mol^2)	q_e, q_s , K_{ad} and ε are the adsorbed amount at equilibrium, theoretical isotherm saturation capacity, activity coefficient related to mean adsorption energy and Polanyi potential, respectively.
	$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right]$ (14)	R (J/mol K) T (K) C_e (mg/L)	R, T and C_e indicate the gas constant, absolute temperature and adsorbate equilibrium concentration, respectively.
	$E = \frac{1}{\sqrt{2K}}$ (15)	E (J/mol)	The mean free energy of adsorption [E (J/mol)], which is energy per molecule of adsorbate for removing a molecule from its location in the adsorption space to the infinity, can be calculated from K value using Eq. (15)

Table 2: Adsorption isotherms and their equation.

adsorption process performance. The equations of these models and their important parameters are defined in Table 2 [32]. In this work, the Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich models were used to analysis the adsorption mechanism in the experiment.

Results and Discussion

Characterization of the prepared mesoporous carbon

Figure 1 depicts the low-angle XRD pattern of ordered mesoporous carbon. It can be seen from this figure that this material shows well resolved reflections characteristic of 2D-hexagonal lattice. In particular, the diffraction pattern indicates that the mesoporous carbon is replicated the parent structure of silica template.

Figure 2 illustrates the nitrogen-sorption isotherms mesoporous carbon. The uniform distribution of mesopores was confirmed by type-IV isotherms with H1 class of hysteresis loop.

The capillary condensation also occurs at relative pressure ($P/P_0 > 0.35$). The different pore volumes of these materials lead to different BET surface areas. N_2 adsorption–desorption measurements prove the ordered meso-strusture along with relatively narrow pore size distribution.

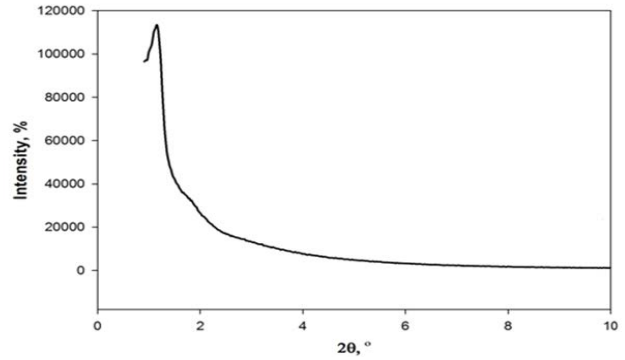

Figure 1: Low-angle X-ray diffraction pattern of ordered mesoporous carbon.

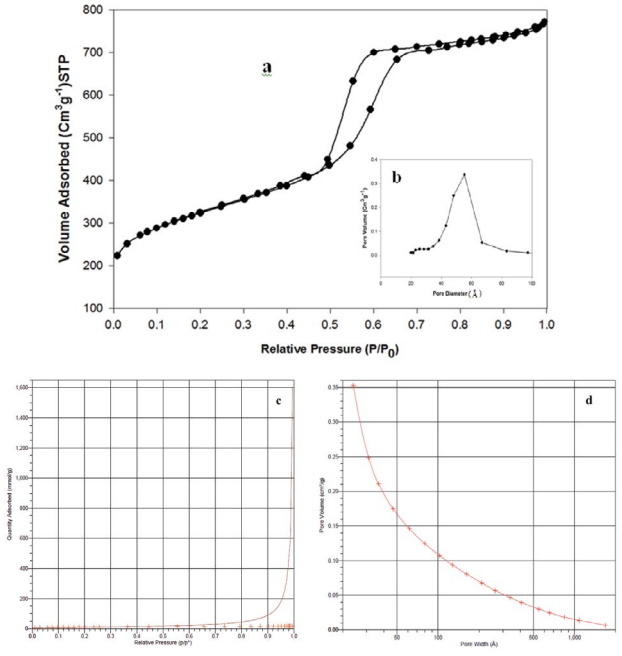

Figure 2: Adsorption–desorption isotherms of nitrogen at 77 K on mesoporous Carbon (a-b), microporous carbon (c-d).

Average pore diameter (nm)	Pore volume (cm^3 g^{-1})	Surface area (m^2 g^{-1})	Adsorbent
4.2	1.19	1113.7	Mesoporous carbon
2.74	0.6	874.79	Microporous carbon (A.C)

Table 3: BET surface area, pore volume and pore diameter of the adsorbents.

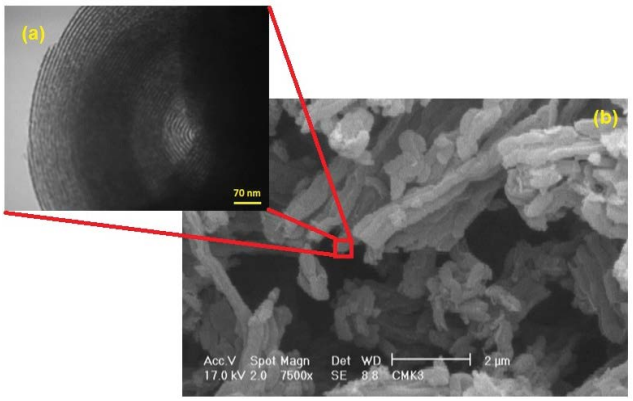

Figure 3: (a) TEM and (b) SEM images of mesoporous carbon.

The textural parameters of the ordered mesoporous carbon including the specific surface area, average pore size diameter and pore volume are presented in Table 3 and compared with the commercial activated carbon. The BET surface area, pore volume and average pore diameter in commercial activated carbon have lower value than the mesoporous carbon.

Figures 3a-3b represents the SEM and TEM micrograph of mesoporous carbon. The rod-like morphology as well as the well ordered hexagonal symmetry could be seen in the figures. The carbon mesoporous is the inverse replica of the mesoporous silica template with the pore diameter of around 4.2 nm. The microstructural analysis is almost compatible with the nitrogen sorption data (Table 3).

Effect of pH on the adsorption process

pH is one of the most important factors for studing the adsorption process. Chlorophenols have acidic proton which can be ionized when the pH of the solution is equal or more than its pKa (the pKa for 4-chlorophenol is equal to 9.40).

The effect of pH on the 4-chlorophenol adsorption by mesoporous and microporous carbons was examined in 100 mL 4-chlorophenol solution with a specific concentration of 100 mg/L and pH range of 2.0-12.0 and result is shown in Figure 4.

The results indicate that the amount of adsorbed 4-chlorophenol on the mesoporous carbon was increased by increasing pH from 2 to 7 and reached a maximum at pH = 7. The optimum pH for 4-chlorophenol adsorption was obtained at pH 5-7.

Figure 4 shows the adsorption isotherms of 4-chlorophenol on the commercial activated carbon in comparison with mesoporous carbon. The obtained results showed that the pH effect on the absorption process had a similar trend but in lower capacity than mesoporous carbon. Hence, the adsorption isotherm of 4-chlorophenol on mesoporous carbon is comparable with microporous carbon.

Results show that, at pH 2 to 5, the adsorption of 4-chlorophenol

on the mesoporous carbon was low and this may be due to compete proton exit in solution with 4-chlorophenols. With increasing the pH to 6, the adsorption become maximum. When the pH of the solution increased from 7 to 10; the most of the 4-chlorophenol molecules are in ionized form.; so the repulsion between the mesoporous carbon surface and the anionic chlorophenol ions cause the adsorption decrease. So the optimum pH was choosed 6 for subsequent experiments.

Effect of reaction time

Equilibration time was investigated to obtain the maximum adsorption and the kinetics of adsorption process. Hence, the adsorption of 4-chlorophenol on mesoporous and microporous carbons were studied as a function of reaction time and results are shown in Figure 5. The results showed that the 4-chlorophenol adsorption rate is rapid at the first, as such; the required time for equilibrium is about 25 minute, in which the 82% adsorption is completed. Thus, the equilibrium time for all the adsorption tests was kept at 2 h.

The obtained results showed that tis mesoporous carbon exhibits

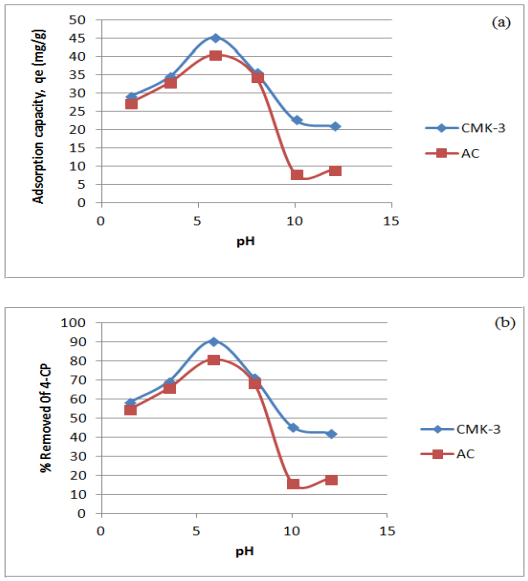

Figure 4: Effect of pH on the adsorption capacity of 4-Chlorophenol over mesoporous and microporous carbons (a) and its removal percent (b) (Adsorbent loading = 0.5 g/L, 4-CP concentration = 100 ppm, agitation speed = 350 rpm, temperature = 25◦C).

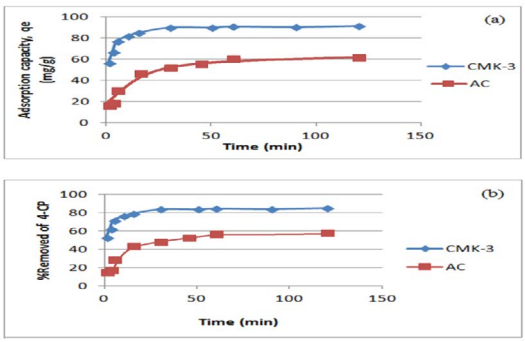

Figure 5: Effect of reaction time on the adsorption capacity of 4-Chlorophenol over mesoporous and microporous carbons (a) and its removal percent (b) (4-CP concentration = 100 ppm, adsorbent loading = 0.3 g/L, pH = 6, agitation speed = 350 rpm, temperature = 25◦C).

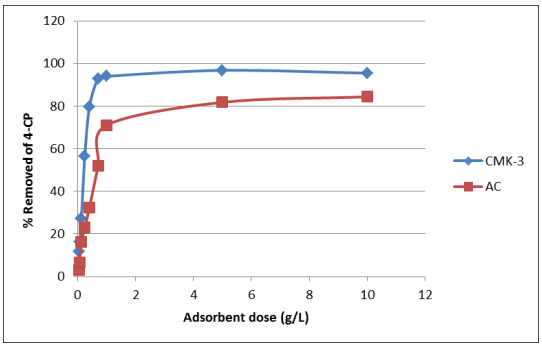

Figure 6: Adsorption isotherms (Removal %) of 4-Chlorophenol versus mesoporous and microporous carbons loading (4-CP concentration = 100 mg/L, agitation speed = 350 rpm, pH = 6, temperature = 25◦C).

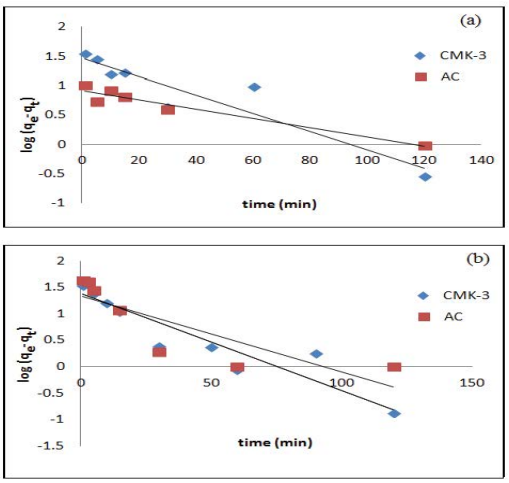

Figure 7: Experimental data fitted to Pseudo-first-order kinetics for the adsorption of 4-chlorophenol onto mesoporous and microporous carbons (adsorbent loading= 0.6 g L^{-1}, reaction time = 2 h and 4-Chlorophenol concentrations: (a) 20 ppm, (b) 100 ppm).

significant adsorption capability for 4-chlorophenol in water/wastewater compare to microporous carbon.

The adsorption capacity for synthesized mesoporous carbon and microporous carbon are 90 mg/g and 60 mg/g, respectively. The time required for equilibrium adsorption for the mesoporous carbon (25 min) is lower than microporous carbon (60 min) and other carbon structures [33].

Effect of adsorbent loading

For selecting the best amount of sorbent for adsorption of 4-chlorophenol from aqueous solution, a series of adsorption experiments at the optimum pH (=6), room temperature and 100 mgL^{-1} solution of 4-chlorophenol were conducted by varying the sorbent loading from 0.05 to 10 gL^{-1}. The obtained results showed that the removal% increases as mesoporous carbon amountas adsorbent increases up to 0.7 gL^{-1}, then remained constant. The obtained results for removal percent of 4-chlorophenol versus adsorbent loading for mesoporous and microporous carbons as sorbents are shown in Figure 6.

Adsorption kinetics

The adsorption kinetic of 4-chlorophenol on mesoporous and microporous carbons was studied by fitting the experimental data with

pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich models.

Experimental data for pseudo-first-order kinetic: According to Figure 7 which is obtained from the Eq. (4), the k_1 and q_e values are calculated from slope and intercept of linear plot of ln (q_e-q_t) versus t.

In the initial stages and rapid adsorption step, the model obeyed first-order for two adsorbents, but was not applicable for the whole of adsorption process which indicates that the adsorption of 4-chlorophenol is not a first-order reaction. The calculated kinetic model constants for the adsorption of 4-chlorophenol on adsorbents for pseudo-first-order model are given in Table 4.

The $q_{e,exp}$ values are different from calculated data. These results indicate that the adsorption of 4-chlorophenol onto mesoporous and microporous carbons is not a pseudo-first-order reaction.

Microporous carbon		Mesoporous carbon		Parameters	Kinetic model
100 ppm	20 ppm	100 ppm	20 ppm		
0.0322	0.0161	0.0414	0.0345	K1(min^{-1})	Pseudo-first-order
0.704	0.937	0.876	0.875	R^2	
57.91	23.03	152.33	88.97	qe (exp.)(mg/g)	
21.78	8.22	24.66	29.38	qe (Cal.)(mg/g)	
0.997	0.996	0.999	0.997	R^2	Pseudo-second-order
0.00002	0.0099	0.00006	0.0043	K2 (g/mg.min)	
57.91	23.03	152.33	88.97	qe (exp.)(mg/g)	
66.667	23.81	166.67	90.91	qe (Cal.)(mg/g)	
4.892	1.121	3.177	3.294	Kid (mg g^{-1} min-0.5)	Intra-particle diffusion
18.35	12.08	123.9	53.92	C (mg g^{-1})	
0.812	0.927	0.772	0.948	R^2	
36.59	650.8	1806.9	9864.7	(g/mgmin)	Elovich
0.0914	0.467	0.112	0.135	(g/mg)	
0.949	0.824	0.876	0.905	R^2	

Table 4: Calculated parameters for the adsorption of 4-chlorophenol on mesoporous and microporous carbons at two concentrations in different kinetic models.

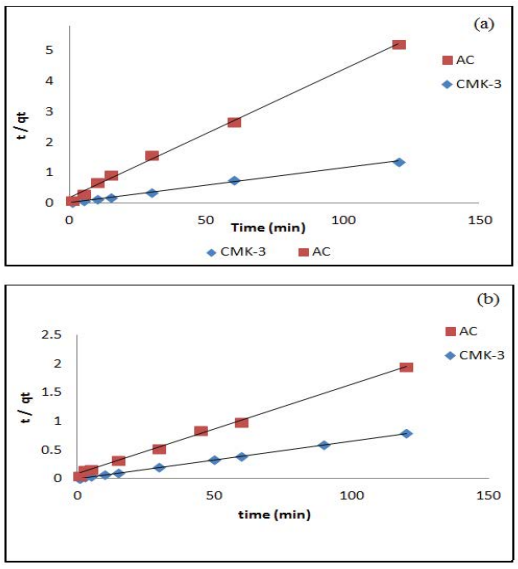

Figure 8: Experimental data fitted to Pseudo-second-order kinetics for the adsorption of 4-chlorophenol onto mesoporous and microporous carbons (adsorbent loading = 0.6 g L^{-1}, reaction time = 2 h and 4-Chlorophenol concentrations: (a) 20 ppm, (b) 100 ppm).

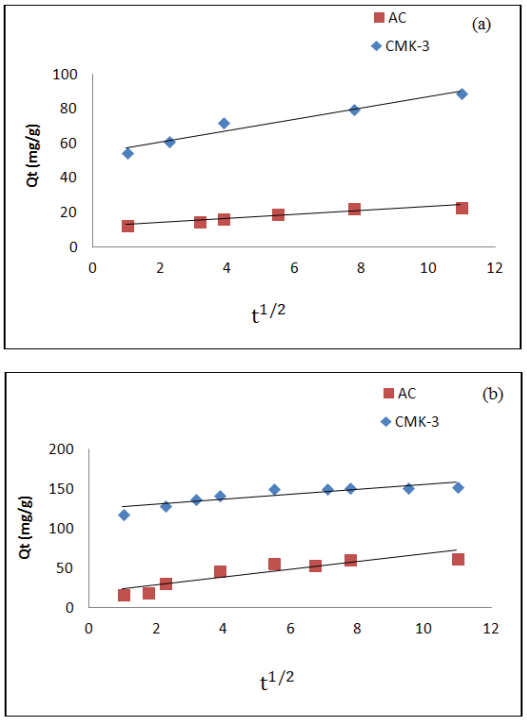

Figure 9: Experimental data fitted to Intra-particle diffusion model for 4-chlorophenol adsorption onto mesoporous and microporous carbons (adsorbent loading = 0.6 g L^{-1}, reaction time = 2 h and 4-Chlorophenol concentrations: (a) 20 ppm, (b) 100 ppm).

The results show that the calculated (q_e) value is different from experimental data (Table 4), which confirms that the adsorption of 4-chlorophenol onto mesoporous and microporous carbons does not fit the first-order reaction.

Experimental result for pseudo-second -order kinetic: The k_2 and q_e values are calculated from linear plot of t/q_t versus t (Figure 8) which is obtained from the Eq. (5). The values of R^2 and q_e are indicated in Table 4 and showed that this equation produced appropriate results. Obtained results show that at all studied ranges for two adsorbents, values of R^2 for the pseudo-second-order kinetic model had higher amounts (between 0.996 and 0.999) and the calculated q_e values were mainly near to experimental data. This indicates that the 4-chlorophenol adsorption onto mesoporous and microporous carbons obey the pseudo-second-order kinetic model over the entire adsorption time. The calculated q_e values match with the experimental data ($q_{e,exp}$). These confirm that the adsorption perfectly matches with pseudo-second-order reaction.

Experimental data for intra-particle diffusion kinetic: The adsorption kinetic of 4-chlorophenol on adsorbents in two concentrations was studied by fitting the experimental result with intra-particle diffusion model (equation. 6). The obtained results are shown in Figure 9 and Table 4.

This model assumes that the adsorption of 4-chlorophenol on the adsorbents is based on the migration of molecules from solution to the adsorbents' surface, diffusion, transport of the molecules to the pores and adsorption of molecule on active site of adsorbents via various mechanisms.

The plot of q_t versus $t^{1/2}$ in Figure 9 indicates that in low concentration of 4-chlorophenol, R^2 is better fitted with experimental results for two adsorbents. The straight line confirms that the transport

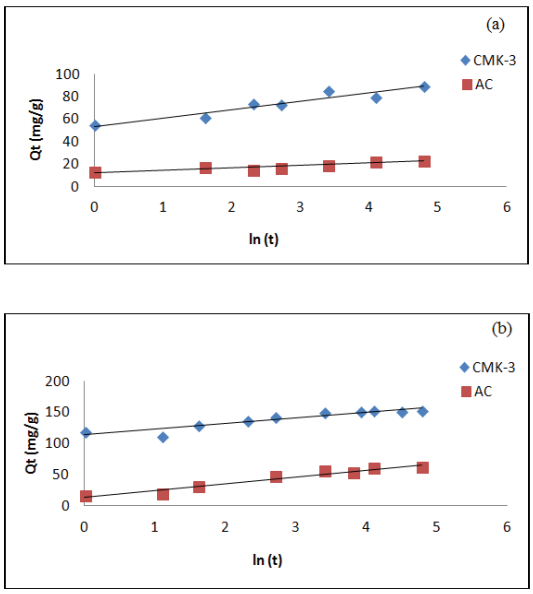

Figure 10: Experimental data fitted to Elovich kinetics for the adsorption of 4-chlorophenol onto mesoporous and microporous carbons (adsorbent loading = 0.6 g L^{-1}, reaction time = 2 h and 4-Chlorophenol concentrations: (a) 20 ppm, (b) 100 ppm).

Microporous carbon	Mesoporous carbon	Parameters	Isotherms
0.94	0.952	R^2	Langmuir
166.67	333.33	q_{max} (mg g^{-1})	
0.0097	0.0157	KL (L mg^{-1})	
0.995	0.993	R^2	Freundlich
1.546	1.645	N	
3.892	12.379	KF (L mg^{-1})	
0.822	0.949	R^2	Tempkin
59.82	70.91	BT	
13.868	6.702	AT (L mg^{-1})	
0.816	0.984	R^2	Dubinin-Radushkevich
47.229	45.209	Qs (mg g^{-1})	
0.00002	0.000002	K	
158.1	500	E (j mol^{-1})	

Table 5: Adsorption isotherm parameters for the adsorption of 4-chlorophenol on mesoporous and microporous carbons.

of 4-chlorophenol to the outer surface of adsorbents, diffusion and entering into particles (intra-particle diffusion) through the pores [32].

Experimental data for Elovich kinetics: The Elovich constants are obtained from the slope and the intercept of the linear plot of q_t versus ln(t) and the obtained results reported in Figure 10 and Table 4.

Kinetic parameters of 4-chlorophenol adsorption process on the mesoporous and microprous carbons in the Table 4 shows that the adsorption process for both of the adsorbents in concentrations of 20 and 100 ppm 4-chlorophenol obeyed the pseudo-second-order kinetic. Values of correlation coefficient indicate that the pseudo-second-order kinetic model with the highest value of R^2 (0.999-0.996) is the most suitable model for description of 4-chlorophenol adsorption onto the mesoporous and microporous carbons in two concentrations. The calculated q_e values match with the experimental data ($q_{e,exp}$). These confirm that the 4-chlorophenol adsorption process on the mesoporous and microporous carbons are in good agreement with pseudo-second-order reaction.

The analysis of adsorption isotherms

In order to obtain of adsorption capacity and investigate the adsorption behavior of 4-chlorophenol over mesoporous and microporous carbons, the adsorption isotherms have been investigated. Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm models have been employed in this study. The fitted parameters using these models are listed in Table 5.

Theoretical isotherm curves were compared with the experimental results for 4-chlorophenol adsorption on the mesoporous and microporous carbons.

According to the obtained results, the adsorption of 4-chlorophenol on the mesoporous and microporous carbons obeys Freundlich isotherm with high correlation coefficient, R^2 = 0.993 and 0.995, respectively. Due to Freundlich isotherm, adsorption process occurs based on ion binding onto the surface of adsorbent which suggests a multilayer adsorption.

Conclusion

This work described the preparation of mesoporous carbon and its characterization using SAXRD, SEM, TEM, and nitrogen adsorption techniques.

The adsorption of 4-chlorophenol using mesoporous carbon was studied and the obtained results compared with the microporous carbon. The effect of operating parameters such as reaction time, initial concentration of 4-chlorophenol, adsorbents loading and the pH of the solution has been investigated. The adsorption is more effective at pH 5 to 7.

Experiments showed that prepared mesoporous carbon was suitable for the adsorption of 4-chlorophenol from polluted water which has higher adsorption capacity 90 mg/g compare to activated carbon 60 mg/g with better equilibrium time, 25 minute compare to 60 minute for activated carbon.

Also, main adsorption isotherms were tested on these adsorbents, which indicated that the Freundlich model was well fitted than other models. The obtained results also indicated that the adsorption process for 4-chlorophenol well fitted by pseudo- second-order kinetic model.

It seems that 4-chlorophenol has been adsorbed on the mesoporous carbon, because of hydrogen bonds between hydroxyl group of 4-chlophenol and mesoporous carbon surface. Equilibrium sorption of mesoporous carbon may explain by hydrophilic interaction. It can be inferrd that the presence of free electron pairs of surface oxygen groups of the mesoporous carbon can act as active site, which play an important role in the adsorption process and leads more interaction between 4-chlorophenol and adsorbent. In addition, the large pore volume of mesoporous carbon and its open pore structures leads to diffusion of 4-chlorophenol into the pores.

Due to higher adsorption efficiency of mesoporous carbon, it can be state that the mesoporous carbon adsorbent is good candidates for applications in 4-chlorophenol removal from polluted water and wastewater.

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