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Effect of chlorine content of chlorophenols on their adsorption by mesoporous SBA-15

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Abstract

Studies on the effect of the chlorine content of chlorophenols (CPs) on their adsorption from aqueous solution by mesoporous SBA-15 are important in understanding the mechanisms of CP adsorption. In this study, three CPs with different degrees of chlorine content (i.e., 2-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol) were investigated. The effects of parameters such as temperature and solution pH were studied. The results showed that CP adsorption by SBA-15 increased with increasing number of chlorine substituents and depended strongly on the temperature and solution pH. Thermodynamic parameters such as Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were also calculated. By comparison of the adsorption coefficient of CPs with varying physical-chemical properties (size, hydrophobicity and electron density), we propose that hydrophobic interactions between CPs and the SBA-15 surface, as well as electron donor-acceptor (EDA) complexes between oxygen of the siloxane surface of SBA-15 (e^- -donor) and the π -system of the CPs (e^- -acceptor), were dominant adsorption mechanisms.

Key words: chlorophenols; mesoporous SBA-15; adsorption; pH; temperature

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Introduction

In the past decades, mesoporous silica-based materials (MMS) such as MCM-41, MCM-48 and SBA-15 have attracted considerable attention for their potential use in organic pollutant removal from aqueous solution. MMS are attractive due to their regular mesoporous structure, high specific surface areas, thermal and mechanical stability, highly uniform pore distribution and tunable pore size, as well as extraordinarily wide possibilities of functionalization (Walcarius and Mercier, 2010). It has been reported that MMS can be used as potential adsorbents for various organic pollutants such as lysine (O'Connor et al., 2006), nitrobenzene (Qin et al., 2007), pharmaceuticals (Bui and Choi, 2009) and dyes (Huang et al., 2011). In addition, MMS can be applied as catalyst supports for organic compound degradation (Li et al., 2007; Rosal et al., 2010; Tao et al., 2011). With increasing applications of MMS, one fact has emerged quite clearly that MMS might be promising porous solids for organic pollutant removal in environment remediation.

Recently, application of MMS as adsorbents or catalyst supports for removal of chlorophenols (CPs) has been reported in several studies (Cooper and Burch, 1999; Mangrulkar et al., 2008; Chaliha and Bhattacharyya, 2008; Shukla et al., 2010). CPs are used extensively in many

industries and are pollutants of concern because of their toxicity, recalcitrance and possible accumulation in the environment (Annachhatre and Gheewala, 1996; Darowski et al., 2005). The presence of CPs, even at low concentrations, can also be an obstacle to the use and/or reuse of water because of their disagreeable taste and odor. Furthermore, CPs can exert negative effects on different biological processes and are considered to be priority pollutants in drinking water since most of these compounds are recognized as carcinogens. Thus, the removal of CPs from wastewater is considered to be necessary before discharge to the environment. Cooper and Burch (1999) reported that MMS possessed large adsorption capacity for efficient elimination of 4-chlorophenol from aqueous solution and that the adsorption capacity can be regenerated by ozonation. Mangrulkar et al. (2008) indicated that uncalcined MCM-41 showed significant adsorption capacity for 2-chlorophenol as compared to calcined MCM-41 due to the hydrophobicity created by the surfactant template in MCM-41. Chaliha and Bhattacharyya (2008) reported that introduction of Mn(II) into MCM-41 produced an effective catalyst for the wet oxidation of 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. Shukla et al. (2010) indicated that Fe-loaded SBA-15 produced promising results for heterogeneous activation of H_2O_2 for oxidation of 2,4-dichlorophenol in water. However, to the best of our knowledge, there are no data available in the

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literature about the relative adsorbability of CPs on MMS, and the importance of the number of chlorine substituents on CP adsorption is poorly understood. In particular, it is important to understand adsorptive interactions between CPs and MMS used as catalyst supports, which helps to better assess the catalytic process.

As compared to other MMS, SBA-15 is characterized by having wider pores and thicker walls (Wan and Zhao, 2007). It has been reported that SBA-15 prepared from triblock copolymer P123 at 40–100°C has uniform pore sizes from 6.5 to 10 nm. The pore walls are in the range of 3.1 to 4.8 nm in thickness, which provide high thermal stability and hydrothermal stability, being suitable for use in aqueous media. Therefore, in the current study, SBA-15 was selected as the adsorbent. Three CPs with different numbers of chlorine substituents (i.e., 2-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol) were selected as target compounds to investigate the effect of the chlorine content of CPs on their adsorption by SBA-15. The effects of operating parameters such as temperature and solution pH were also studied in batch experiments. Finally, the possible adsorption mechanisms were discussed.

1 Materials and methods

1.1 Materials

All chemicals were used as received without further purification. 2-Chlorophenol (MCP), 2,6-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP) were purchased from Sigma-Aldrich with a reported purity >98%. The triblock poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) copolymer (EG₂₀-PG₇₀-EG₂₀, molecular weight 5800 g/mol) was purchased from Sigma-Aldrich. Tetraethoxysilane (TEOS) was purchased from Tianjin Kermel Chemical (China) with a reported purity >99%. Deionized distilled water was purified by a Millipore Milli-Q system. The physicochemical properties of the CPs used are listed in Table 1.

The SBA-15 material was synthesized as previously described (Zhao et al., 1998). Typically, EG₂₀-PG₇₀-EG₂₀ was dissolved in HCl solution, into which a TEOS solution was added dropwise. The molar gel composition was EG₂₀-PG₇₀-EG₂₀:60TEOS:350HCl:9000H₂O. The white precipitate was homogenized by vigorous stirring for 24 hr at 308 K and then heated at 353 K in a Teflon-coated stainless steel autoclave for 24 hr under autogenous pressure. Subsequently, the white precipitate was filtered, washed with distilled water, and dried at 353 K overnight.

Finally, the as-synthesized sample was calcined in air to remove the polymeric structure-directing agent occluded in the pore system of the mesoporous silica. It was heated at a rate of 1 K/min to 813 K and kept at that temperature for 6 hr. The XRD pattern of SBA-15 is displayed in Fig. 1. It is clearly seen that SBA-15 shows three distinct peaks corresponding to (100), (110) and (200) reflections, typical of hexagonally mesostructured material. The BET surface area of SBA-15 was 744 m²/g and the average pore diameter was 5.1 nm, both obtained with a Micromeritics 2020 ASAP surface area and pore size analyzer. The pH_{zpc} (zero point of charge) was estimated to be around 4.0 (Jiao and Regalbuto, 2008).

1.2 Adsorption experiments

Adsorption isotherms of CPs on SBA-15 were obtained using a batch equilibration technique at temperatures of 288, 298, and 308 K. A given amount of adsorbent (0.05 g) was placed in a 50 mL flask, into which 10 mL of aqueous CP solutions with varying initial concentrations were added. The pH values of the suspensions were adjusted to 5.0 by addition of 0.1 mol/L HCl or NaOH solutions. Experiments were performed in a constant-temperature water bath shaker for 2 hr at a mixing speed of 180 r/min. Kinetic studies (data not shown) indicated that the adsorption process of CPs was rapid and approached equilibrium after/within 1 min. After adsorption equilibrium was reached, solutions were filtered and analyzed for the remaining concentration of CPs. Solid-phase CP concentrations at equilibrium, q_e (μmol/g), were calculated according to Eq. (1):

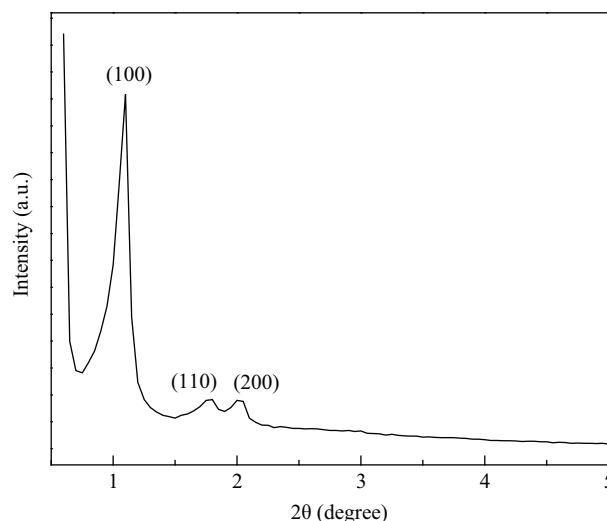


Fig. 1 XRD diffraction pattern of SBA-15.

Table 1 Physicochemical properties of chlorophenols

Compound	MW (g/mol)	Density (g/cm ³)	MV (cm ³ /mol)	MD (Å)	S_w (g/L)	log <i>D</i>	p <i>K</i> _a	<i>K</i> _{HW}
2-Chlorophenol (MCP)	128.6	1.287	99.9	6.82	11.3	2.22	8.5	0.71
2,6-Dichlorophenol (DCP)	163.0	1.458	111.8	7.08	1.9	2.89	7.0	3.16
2,4,6-Trichlorophenol (TCP)	197.4	1.596	123.7	7.32	0.8	3.76	6.6	14.13

MW: molecular weight; MV: molar volume, calculated from MW and density; MD: molecular diameter, calculated from MV assuming that molecules are spherical; S_w : aqueous solubility, obtained from EPI Suite™ v4.10; *D*: octanol/water partition coefficient, listed in SciFinder Scholar at pH 5.0 and 298 K; p*K*_a: negative logarithm of dissociation constant, listed in SciFinder Scholar at pH 5.0 and 298 K; *K*_{HW}: *n*-hexadecane-water partition coefficient, estimated from previous publications (Abraham et al., 1990; Borisover and Graber, 2003).

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where, C_0 ($\mu\text{mol/L}$) and C_e ($\mu\text{mol/L}$) are the initial and equilibrium aqueous-phase concentrations of CPs, respectively; V (L) is the volume of the aqueous solution; M (g) is the mass of adsorbent used in the experiments. To take into account solute loss from processes other than adsorption by SBA-15 (i.e., adsorption to glassware and evaporation), a blank sample without any adsorbent was also run together with the experimental samples. The analysis of the blank sample showed negligible loss of the adsorbate.

To study the effect of solution pH, batch adsorption of individual CPs was studied in a series of 50 mL flasks containing 5 g/L SBA-15 with 10 mL of a 40 $\mu\text{mol/L}$ CP solution. Experiments were first performed with and without buffer at an ionic strength 0.01 mol/L. The results demonstrated no significant difference between the samples with and without buffer. Then, the pH of the solutions was adjusted from 3.0 to 8.7 using buffer solutions. All experiments were performed twice in a constant-temperature water bath for 2 hr at a mixing speed of 180 r/min.

The solution pH was measured at the beginning and end of each experiment. The results showed that pH values remained practically unchanged during the course of the adsorption experiments.

1.3 Analytical method

Aqueous CP concentrations were analyzed by direct injection of aqueous samples on a reversed phase HPLC equipped with UV-Visible detection at the wavelength 270 nm, with flow rate of 1.0 mL/min. HPLC analyses were performed on a Waters HPLC system consisting a Waters 1525 binary pump, Waters 2487 dual wavelength absorbance detector, Waters Breeze chromatography software and a Symmetry[®] C₁₈ column (5 μm , 4.6 \times 150 mm, Waters). The mobile phase contained double-distilled water acidified to an apparent pH of 2.5 with phosphoric acid and methanol. The following water:methanol volume ratios were used: 45:55 for MCP; 35:65 for DCP; and 20:80 for TCP.

2 Results and discussion

2.1 Effect of number of chlorine substituents on CP adsorption isotherms on SBA-15

Adsorption isotherms of CPs on SBA-15 at temperature 298 K are shown in Fig. 2. The data clearly illustrate that adsorption isotherms were nonlinear with curvatures concave to the abscissa. Isotherm data confirm that CP adsorption by SBA-15 increased with increasing number of chlorine substituents. This order was positively related to molecular size, which can be expected in the absence of size exclusion effects (the larger, more highly substituted CPs are less soluble in water and interact more strongly with the adsorbent pore surfaces). The same trend has also

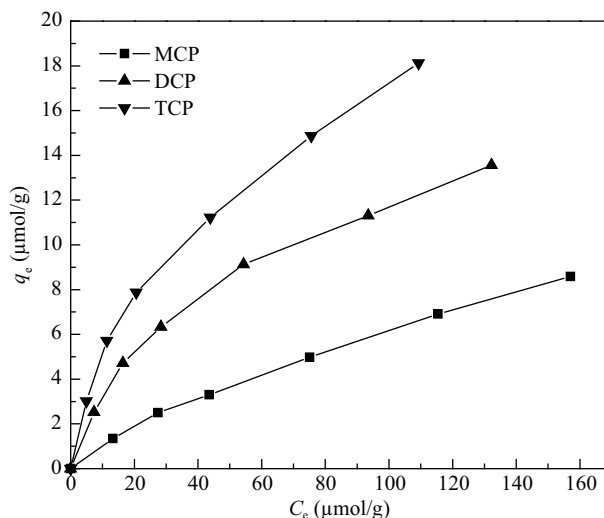


Fig. 2 Effect of number of chlorine substituents on CP adsorption isotherms on SBA-15. Adsorption conditions: adsorbent dose 5 g/L; pH 5.0; temperature 298 K.

been reported in the removal of CPs by other adsorbent materials such as CdS (Davis and Huang 1990), clay (Danis et al., 1998) and activated carbon (Liu et al., 2010).

2.2 Effect of temperature on CP adsorption

Adsorption isotherms of CPs on SBA-15 at temperatures of 288, 298 and 308 K are shown in Fig. 3. The CP uptake decreased with increasing temperature, indicating that CP removal by adsorption on SBA-15 is favored at lower temperatures. Also, isotherm data at all three temperatures confirm that CP adsorption by SBA-15 increased with increasing number of chlorine substituents. To describe the adsorption isotherm data the Langmuir (Eq. (2)) and Freundlich (Eq. (3)) isotherm models were selected:

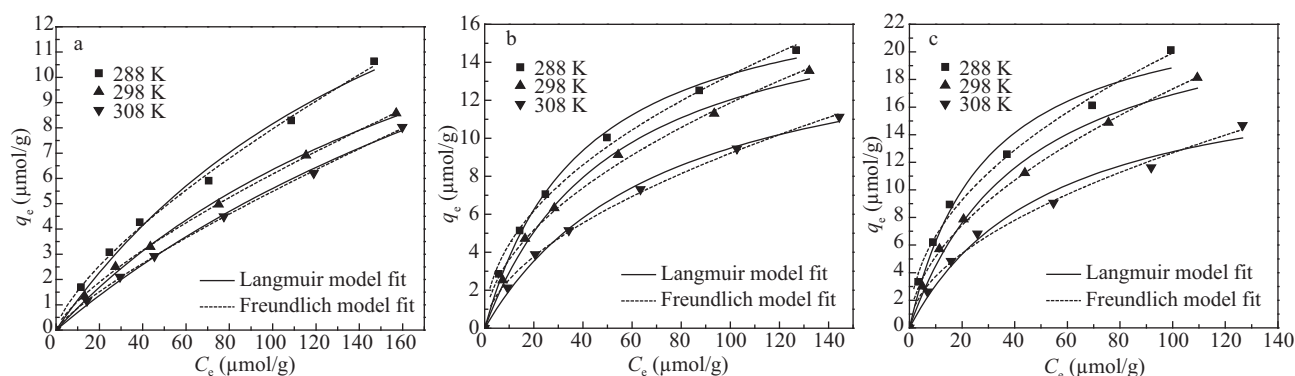
$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

where, q_e ($\mu\text{mol/g}$) is the equilibrium concentration of CPs on SBA-15; C_e ($\mu\text{mol/L}$) is the equilibrium concentration of CPs in solution; Q_0 ($\mu\text{mol/g}$) is the maximum adsorption capacity; K_L (L/ μmol) is the Langmuir affinity constant; K_F ($(\mu\text{mol/g})/(\mu\text{mol/L})^{1/n}$) is the Freundlich capacity coefficient and n is the Freundlich linearity index. As the K_F value increases, the adsorption capacity of the adsorbent for a given CP increases. The isotherm parameters obtained from the Langmuir and Freundlich model fits to the data are given in Table 2. As indicated by the correlation coefficients (> 0.98), CP adsorption isotherm data at different temperatures were described well by both isotherm models, although the Freundlich model generally provided the better fit. The K_F values for the three CPs decreased with increasing temperature, suggesting that uptake of CPs on SBA-15 is an exothermic process. Also, K_F values illustrate that the adsorption capacity of TCP was approximately 1.5 times that of DCP, and the adsorption capacity of DCP was approximately 5 times that of MCP. The value of n for the Freundlich isotherm was found to be greater than 1, indicating that CP adsorption on SBA-15

Table 2 Langmuir and Freundlich parameters describing CP adsorption isotherms on SBA-15 at different temperatures

Adsorbate	Temperature (K)	Langmuir model			Freundlich model		
		Q_0 ($\mu\text{mol/g}$)	K_L (L/ μmol)	R^2	K_F (($\mu\text{mol/g}$)/($\mu\text{mol/L}$) $^{1/n}$)	n	R^2
MCP	288	23.2	0.00542	0.991	0.303	1.41	0.996
	298	20.4	0.00452	0.997	0.210	1.36	0.999
	308	25.0	0.00289	0.998	0.138	1.25	0.999
DCP	288	18.7	0.0250	0.996	1.475	2.09	0.993
	298	18.3	0.0191	0.996	1.099	1.93	0.993
	308	16.4	0.0137	0.996	0.715	1.80	0.997
TCP	288	24.2	0.0350	0.983	2.228	2.10	0.992
	298	24.4	0.0227	0.989	1.542	1.90	0.997
	308	19.6	0.0188	0.983	1.101	1.88	0.990

**Fig. 3** Effect of temperature on MCP (a), DCP (b) and TCP (c) adsorption isotherms on SBA-15. Adsorption conditions: adsorbent dose 5 g/L; pH 5.0.

was favorable at all studied temperatures. Also, a higher value of n indicates greater heterogeneity of adsorption site energies (Carter et al., 1995). Values of Q_0 showed some increase for MCP and TCP and some decrease for DCP with increasing temperature. This phenomenon may be due to the lower solute loadings. At lower adsorbed concentrations, it seems to be difficult for the Langmuir isotherm model to exactly determine the maximum adsorption capacity (Haderlein and Schwarzenbach, 1993; Li et al., 2004). The K_L values for the three CPs decreased with increasing temperature.

Thermodynamic parameters, including standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were calculated to gain further insights into the adsorption behavior of CPs on SBA-15. Thermodynamic parameters were calculated based on the variation of the thermodynamic equilibrium constant K_0 with changes in temperature (Biggar and Cheung, 1973). For adsorption processes, K_0 can be defined as follows:

$$K_0 = \frac{\alpha_s}{\alpha_e} = \frac{\gamma_s C_s}{\gamma_e C_e} \quad (4)$$

where, α_s is the activity of the adsorbed solute at equilibrium; α_e is the activity of the solute in solution at equilibrium; C_s ($\mu\text{mol/L}$) is the quantity of adsorbed CP per liter of solvent in contact with the adsorbent surface at equilibrium; C_e ($\mu\text{mol/L}$) is the CP concentration in solution at equilibrium, γ_s is the activity coefficient of the adsorbed solute; and γ_e is the activity coefficient of the solute in solution. C_s can be calculated according to Biggar and Cheung (1973). When the concentration of the solute in solution approaches zero, the activity coefficient, γ , will

approach unity. Consequently, K_0 can be evaluated by plotting $\ln(C_s/C_e)$ against C_s and extrapolating C_s to zero. Its intercept with the vertical axis gives the value of $\ln K_0$. The calculated values of $\ln K_0$ are given in Table 3. The thermodynamic parameters describing the adsorption of CPs on SBA-15 at different temperatures were calculated from:

$$\Delta G^0 = -RT \ln K_0 \quad (5)$$

$$\ln K_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

where, R (J/(K·mol)) is the universal gas law constant and T (K) is the solution temperature. The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the linear variation of $\ln K_0$ with $1/T$. Calculated thermodynamic values are presented in Table 3. It is noted that negative ΔG^0 values were obtained in all cases, indicating the feasibility and spontaneous nature of CP adsorption on SBA-15. The negative values of ΔH^0 indicate that the adsorption process is exothermic, which is also supported by the decrease in CP adsorption that was observed with increasing temperature. Furthermore, the absolute values of ΔH^0 are increasing in the order of MCP < DCP < TCP, suggesting a higher affinity of more highly chlorine-substituted CPs towards SBA-15. The negative values of ΔS^0 indicate the decrease of the degree of randomness at the solid/solution interface during the adsorption of CPs on SBA-15.

2.3 Effect of pH on CP adsorption

Due to the dissolution of SBA-15 at pH > 9.0 (Jiao and Regalbuto, 2008), a pH range of 3.0 to 8.7 was selected for

Table 3 Thermodynamic parameters for the adsorption of CPs on SBA-15

Adsorbate	<i>T</i> (K)	ln <i>K</i> ₀	Δ <i>G</i> ₀ (kJ/mol)	Δ <i>H</i> ₀ (kJ/mol)	Δ <i>S</i> ₀ (J/(K·mol))
MCP	288	6.61	−15.82	−23.99	−28.50
	298	6.23	−15.43		
	308	5.96	−15.25		
	288	8.09	−19.36		
DCP	298	7.70	−19.07	−31.29	−47.28
	308	7.24	−18.53		
	288	8.74	−20.92		
	298	8.23	−20.38		
TCP	298	8.23	−20.38	−35.76	−51.55
	308	7.77	−19.89		

this study. Figure 4 shows the adsorption edges of CPs (i.e., the K_d values as function of pH, K_d (L/g) is the adsorption coefficient, $K_d = q_e/C_e$). A strong pH dependence of the K_d value was observed in the pH region. For MCP, the effect of pH on the adsorption was insignificant when the pH was below 7.0. For DCP and TCP, changing the pH over the range of 3.0–5.0 slightly affected the K_d value. However, a marked decrease in the K_d values for the three CPs was observed when the pH was increased above their pK_a . At pH 8.7, more than 98% of DCP and TCP are in their deprotonated forms and the K_d values for DCP and TCP were negligible, suggesting that the deprotonated species do not adsorb to the solid phase. The reduced K_d of the three CPs with pH over their pK_a could be due to the increased electrostatic repulsion between the dissociated CPs and negatively charged SBA-15. Dissociation of the CPs would increase their hydrophilicity, which may also decrease the adsorption with pH over the pK_a of the CPs. The difference in adsorption edges of CPs could be attributed to the different pK_a values (i.e., more highly chloro-substituted CPs have lower pK_a values and could be dissociated at lower pH).

The pH_{zpc} of SBA-15 was estimated to be around 4.0. Changing the pH over the range of 3.0–7.0 should have significantly affected the protonation-deprotonation transition of SBA-15 surface groups such as –OH. However, it appears that such a transition had little effect on the adsorptive affinity of MCP, suggesting that the adsorbent surface functionality plays an insignificant role in the adsorption of neutral forms to SBA-15.

2.4 Effect of chlorine content

The chlorine content of CPs causes two major changes in their physical-chemical properties (Tang and Huang, 1996). First, increasing the number of chlorine substituents will decrease the solubility of CPs significantly. Second, an increase in chlorine substituents on an aromatic ring will decrease the electron density on the ring because chlorine is an electron-withdrawing group. Therefore, the chlorine content may cause a significant difference in CP adsorption by SBA-15.

The mechanism of adsorption of organic pollutants on inorganic materials usually has contributions from electrostatic interaction, ion exchange, coordination by surface metal cations, ion-dipole interaction, hydrogen bonding, electron donor-acceptor (EDA) complexes, and

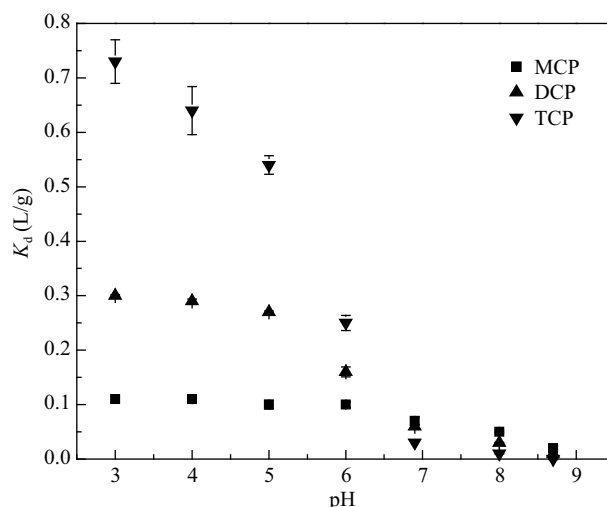


Fig. 4 Effect of solution pH on CP adsorption by SBA-15. Adsorption conditions: initial CP concentration 40 μ mol/L; adsorbent dose 5 g/L; temperature 298 K; ionic strength 0.01 mol/L.

hydrophobic interactions (Calvet, 1989; Parida et al., 2006; Keiluweit and Kleber, 2009). The SBA-15 surface is generally composed of hydroxyl groups and siloxane linkages, and hence several possible mechanisms should be considered in the adsorption of CPs by SBA-15: (1) hydrophobic interaction between CPs and the SBA-15 surface; (2) EDA interaction between oxygen on the siloxane surface of SBA-15 (e^- -donor) and π -system of CPs (e^- -acceptor); and (3) hydrogen bonding between CPs and the hydroxyl groups of SBA-15. In order to discuss the effect of chlorine content on CP adsorption, a single point adsorption coefficient (K_d) was calculated at $C_e = 0.015 S_w$ based on the fitting results using the Freundlich isotherm model. The values of K_d were 0.035 L/g for MCP, 0.111 L/g for DCP and 0.267 L/g for TCP.

Since the SBA-15 surface is not completely hydrophilic and has some hydrophobic character, hydrophobic interactions are believed to make contributions to the adsorption of CPs (Davis and Huang, 1990; Serrano et al., 2004). In aqueous solution, the adsorbate with higher hydrophobicity has a greater tendency to be adsorbed. As presented by the solubility (Table 1), the hydrophobicity of the three CPs in this study increases with increasing number of chlorine substituents, which may enhance the adsorption of the CPs. Hydrophobic interaction can be evaluated based on the hydrophobic parameter of organic chemicals, $\log D$ (Wang et al., 2010). The $\log D$ values (from 2.22 to 3.76) become higher with increasing number of chlorine substituents from MCP to TCP (Table 1), consistent with the increase in the K_d values of CP adsorption by SBA-15. Therefore, the hydrophobic effect is considered to be a dominant factor for the adsorption of CPs on SBA-15. In order to single out other interaction mechanisms between adsorbates and adsorbents, normalization of K_d values by the hexadecane-water partition coefficient (K_{HW}) was carried out (Wang et al., 2010). The normalized adsorption coefficient, K_d/K_{HW} , could factor out a hydrophobic effect, because hexadecane is incapable of interactions such as H-bonding, polar interaction, and EDA interaction (Chen et al., 2007). The results of K_d/K_{HW} showed that the value

of K_d/K_{HW} for MCP was about three times higher than for TCP, suggesting that other interaction mechanisms may play a role in addition to the hydrophobic effect. If not, the values of K_d/K_{HW} of the selected CPs should be similar.

The EDA complex mechanism assumes that the aromatic ring of CPs acts as an electron acceptor and the basal siloxane surface on SBA-15 serves as a donor (Haderlein and Schwarzenbach, 1993; Keiluweit and Kleber, 2009). Haderlein and Schwarzenbach (1993) proposed that adsorption of nitroaromatic compounds (NACs) by kaolinite was contributed to by coplanar EDA formation with oxygen ligands at the external siloxane surface of kaolinite as e^- -donors and the π -system of the NACs as e^- -acceptor. And finally, the presence of two or more nitro groups enhanced affinities substantially due to the decrease of π -electron density in the aromatic rings. In the current study, the chloro group is an electron-withdrawing group and the ring structures within CPs are excellent π -acceptors. The SBA-15 surface is considered to have a negatively charged surface prone to adsorption of electron deficient species (Parida et al., 2006). The primary adsorption sites are basal siloxane surfaces, which are shown to have a large electronegative potential and can be a significant n -donors (n presents nonbonding electrons at siloxane surfaces) (Keiluweit and Kleber, 2009). Therefore, n - π EDA interactions can be formed between CPs and the SBA-15 surface. As the number of electron-withdrawing chlorine substituents increases, the π -electron density in the aromatic ring decreases and as a result, affinity for the nonbonding electrons at siloxane surfaces in SBA-15 is higher. It has been shown that the adsorption coefficient of CPs by SBA-15 increased with increasing number of chlorine substituents, and TCP showed the highest affinity to the SBA-15 surface. Therefore, we propose that EDA interactions were another primary mechanism for the enhanced adsorption of CPs on SBA-15, where oxygen of the siloxane surface of SBA-15 serves as e^- -donor and the π -system of the CPs acts as e^- -acceptor.

Hydrogen bonding has been suggested as being responsible for phenol adsorption on soils (Boyd, 1982). It is responsible for adsorption which may be due to (1) the π -electron of a aromatic ring and the hydrogen atom of the hydroxyl groups of SBA-15 or, (2) the oxygen atoms of aromatics and the hydrogen atoms of the hydroxyl groups or, (3) the hydrogen atom attached to the oxygen atom of aromatics and the oxygen atoms of the hydroxyl groups (Davis and Huang, 1990; Parida et al., 2006). If the CP oxygen atom or π -electron system of the aromatic ring forms a donor complex, a chlorine substituent would decrease the electron density, resulting in less H-bond adsorption and consequently less CP adsorption. However, the adsorption coefficient of CPs by SBA-15 increased with increasing number of chlorine substituents in the molecules. On the other hand, if the hydrogen atom attached to the oxygen atom of aromatics and the oxygen atoms of the hydroxyl groups forms an acceptor complex, the uptake of CPs by SBA-15 would decrease with decreasing pH at pH lower than pH_{zpc} due to the competitive adsorption between CPs and hydrogen ions. However, it is

noteworthy that the adsorption coefficient remained almost constant at pH lower than pH_{zpc} (Fig. 4). Finally, it can be inferred that hydrogen bonding does not seem to be the dominant mechanism for CP adsorption on SBA-15 under the condition of this study.

3 Conclusions

The effect of the chlorine content of CPs on their adsorption by mesoporous SBA-15 was evaluated. The adsorption of CPs was found to be significantly dependent on the number of chlorine substituents, temperature and solution pH. Increasing the number of chlorine substituents in the molecules increased their adsorption by SBA-15 because increasing the number of chlorine substituents decreases the solubility of CPs significantly as well as the electron density on their rings. Increasing temperature decreased the adsorption of CPs. At pH lower than pK_a , the adsorption of CPs was slightly changed by pH. At pH higher than pK_a , the adsorption of CPs decreased significantly with increasing pH. Adsorption isotherms were well described by the Freundlich model in the studied concentration range. Negative values of ΔG^0 and ΔH^0 confirmed the spontaneous and exothermic nature of the adsorption process. Finally, the combined experimental evidence suggested that hydrophobic interaction between CPs and the SBA-15 surface as well as electron donor-acceptor (EDA) complex formation between the siloxane surface of SBA-15 (e^- -donor) and CPs (e^- -acceptor) were dominant adsorption mechanisms.

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