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# Sorption of chlorophenols on microporous minerals: mechanism and influence of metal cations, solution pH, and humic acid

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**Abstract** Sorption of 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP) on a range of dealuminated zeolites were investigated to understand the mechanism of their sorption on microporous minerals, while the influence of common metal cations, solution pH, and humic acid was also studied. Sorption of chlorophenols was found to increase with the hydrophobicity of the sorbates and that of the microporous minerals, indicating the important role of hydrophobic interactions, while sorption was also stronger in the micropores of narrower sizes because of greater enhancement of the dispersion interactions. The presence of metal cations could enhance chlorophenol sorption due to the additional electrostatic attraction between metal cations exchanged into the mineral micropores and the chlorophenolates, and this effect was apparent on the mineral sorbent with a high density of surface cations (2.62 sites/nm$^2$) in its micropores. Under circum-neutral or acidic conditions, neutral chlorophenol molecules adsorbed into the hydrophobic micropores through displacing the "loosely bound" water molecules, while their sorption was negligible under moderately alkaline conditions due to electrostatic repulsion between the negatively charged zeolite framework and anionic chlorophenolates. The influence of humic acid on sorption of chlorophenols on dealuminated Y zeolites suggests that its molecules did not block the micropores but created a secondary sorption sites by forming a "coating layer" on the external surface of the zeolites. These mechanistic insights could help better understand the interactions of ionizable chlorophenols and metal cations in mineral micropores and guide the selection and design of reusable microporous mineral sorbents for sorptive removal of chlorophenols from aqueous stream.

**Keywords** Sorption · Microporous minerals · Chlorophenol · Hydrophobic effect · Metal cations · Humic acid

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## Introduction

Chlorophenols are a class of widely occurring water pollutants released from industrial sources, including oil refining, coal conversion, and petrochemical production (Juang et al. 1996; Banat et al. 2000; Wang et al. 2007; Shah et al. 2011; Yousef et al. 2011). They are also widely used as intermediates in the production of dyes, plastics, pharmaceuticals, pesticides, and insecticides (Radhika and Palanivelu 2006; Anbia and Lashgari 2009; Lua and Jia 2009; Liu et al. 2010; Yang et al. 2015). In addition, conversion of phenols to chlorophenols could occur during chlorination of drinking water treatment, resulting in a medicinal taste and smell (Anbia and Lashgari 2009; Singh et al. 2012; Chen et al. 2013).

Pollution of surface water by chlorophenols poses risks to the environment and human health, as they can inhibit the normal activities of microbial community and cause death of aquatic life and have carcinogenicity to animals (Radhika and Palanivelu 2006; Wang et al. 2007; Liu et al. 2010). 2-Chlorophenol (2-CP) and 2,4-dichlorophenol (2,4-DCP) are among the most commonly detected chlorophenols in water (Kadmi et al. 2015). The detected concentrations of chlorophenols in freshwaters and drinking waters range from low nanograms per liter to low micrograms per liter (Kawaguchi et al. 2005; Elci et al. 2011), while they occur at nanograms per liter to micrograms per liter, even up to milligrams per liter, in wastewaters (Quintana et al. 2007; Regueiro et al. 2009; Limam et al. 2010). Although the member countries of European Union (EU) have restricted the use of chlorophenols, they are still widely used in many countries, including the United States (US) and China (Holopainen et al. 2013; Igbinosa et al. 2013).

Because of their toxicity to organisms even at relatively low concentrations, chlorophenols have been regulated as priority pollutants by the US Environmental Protection Agency (USEPA) and the EU (Hamdaoui and Naffrechoux 2007; Singh et al. 2012; Yang et al. 2015). The USEPA set an upper permissible limit of 0.5 mg/L for chlorophenols in public water supplies in 1987 (Chang et al. 2015). The current drinking water guideline values in the US for 2-CP and 2,4-DCP are 0.1 and 0.5 μg/L, respectively (Pera-Titus et al. 2004). The EU has set target limits in drinking water of 0.5 and 0.1 μg/L for total content of chlorophenols and individual ones, respectively (Peng et al. 2007; Elci et al. 2011).

Activated carbons, zeolites, biomaterials, clay minerals, and some industrial solid wastes have been used as sorbents for removal of ions and organics from water (Banat et al. 2000; Kadirvelu et al. 2000; Aksu and Yener 2001; Mohan and Singh 2002; Sljivic et al. 2009; Yousef et al. 2011; Quintelas et al. 2012). Among these sorbent materials, activated carbons are the most widely used and exhibit good adsorption capacities for many organic pollutants due to their porous structures and large surface areas (Aksu and Yener 2001; Anbia and Ghaffari 2009; Nath and Bhakhar 2010; Zhou et al. 2014). However, the application of activated carbons can be limited by a range of factors, including high cost, poor adsorption selectivity, poor mechanical strength, and expensive and difficult regeneration (Ferro-Garcia et al. 1996; Anbia and Ghaffari 2009; Anbia and Lashgari 2009; Ahmad et al. 2011; Shah et al. 2011). In contrast, zeolites have a number of potential advantages as sorbents, such as good mechanical strength, good thermal stability, and high sorption selectivity (Wang and Peng 2010; Misaelides 2011). In addition, zeolites can be regenerated easily and reused for water purification (Ozaydin et al. 2006; Damjanovic et al. 2010). Zeolites as sorbents also have some valuable physicochemical properties, including cation exchange capacity, selectivity

with molecular dimension and well-defined pore structures, high surface areas, and tailorable surface hydrophobicity (Cheng and Reinhard 2006a, b; Wang and Peng 2010).

Zeolites are crystalline, microporous aluminosilicates composed of three-dimensional framework with tetrahedral $SiO_4$ and $AlO_4$ connected together by sharing oxygen atoms, with exchangeable cations (usually alkali and alkaline earth cations) and water molecules in their cages and channels (Breck 1974; Rehakova et al. 2004; Wang and Peng 2010). The charge imbalance associated with $AlO_4$ tetrahedra results in a negatively charged framework, which is compensated by the exchangeable cations on the pore wall surface (Rehakova et al. 2004; Karapınar 2009). The exchangeable cations in the zeolite cavities can be exchanged by other cations, resulting in sorption capacity for cations (Karapınar 2009). The Al species can be removed from zeolite framework through dealumination using a range of techniques, such as acid leaching and isomorphous substitution, which increases the Si/Al ratio of the zeolite and reduces the framework's negative charge (Beyer 2002). As a result, the hydrophobicity of zeolite framework and micropores increases with its Si/Al ratio, and the zeolites with Si/Al ratios above 8 are considered hydrophobic (Ruthven 1984; Cheng and Reinhard 2006a). As water and organic molecules compete with each other for sorption on surface sites and in micropore spaces, the hydrophobicity of zeolite significantly influences its uptake of organic pollutants from water. The hydrophobic pore wall surfaces have low densities of hydrophilic centers, i.e., surface silanol groups and surface cations associated with the tetrahedrally coordinated framework aluminum, and thus interact weakly with water (Cheng and Reinhard 2006a, b). As water is "loosely bound" by weak hydrogen bonding to the siloxane surface and forming limited intermolecular hydrogen bonds among themselves in the hydrophobic micropore spaces, such molecules can be easily displaced by hydrophobic organic compounds, driven primarily by entropic effect (Farrell et al. 2003; Cheng and Reinhard 2006a). In contrast, water molecules residing in the hydrophilic micropore spaces are tightly bound to the hydrophilic centers through hydrogen bonding to silanol groups and coordination to surface cations and are thus barely displaceable by hydrophobic organic molecules (Cheng and Reinhard 2006a, 2007). Therefore, the Si/Al ratio, which determines the density of surface cations present in the mineral micropores, plays an important role in controlling the sorption of hydrophobic organic compounds on zeolites (Cheng and Reinhard 2006a).

In this study, sorption of three representative chlorophenols on a series of dealuminated zeolites was measured to study the influence of sorbate hydrophobicity, hydrophobicity of microporous minerals, and pore size of microporous minerals, on their sorption. The impact of co-existing metal cations, solution pH, and humic acid on chlorophenol sorption was also investigated, while the sorption behaviors of chlorophenols on

a hydrophilic zeolite (CBV-400) and a hydrophobic one (CBV-720) with and without the presence of metal ions ($Cu^{2+}$ and $Fe^{3+}$) were compared to further corroborate the obtained mechanism of chlorophenol sorption. The results help better understand the interactions of ionizable chlorophenols and metal cations in mineral micropores with varying density of surface cations and can guide the development of microporous mineral sorbents for efficient removal of chlorophenols from aqueous stream.

## Materials and method

Four dealuminated Y zeolites (CBV-400, CBV-720, CBV-760, and CBV-780) and a dealuminated ZSM-5 zeolite (CBV-3024E), which are all pure synthetic materials supplied by Zeolyst International (Valley Forge, PA, US), were selected as model microporous mineral sorbents in this study. The key physicochemical properties of these sorbents are summarized in Table 1. They were received as binder-free powders of micrometric size and were calcined at 380 °C for 12 h to remove the non-structural water prior to use.

2-CP (99.0 %), 2,4-DCP (99.5 %), and 2,4,6-trichlorophenol (2,4,6-TCP, 98.0 %) were purchased from Aladdin Reagent (Shanghai, China). Table 2 summarizes selected properties of these compounds. Humic acid (technical) was obtained from Sigma-Aldrich (St. Louis, MO, US). Stock solutions of $Al^{3+}$, $Fe^{3+}$, $Mn^{2+}$, $Cu^{2+}$, $Mg^{2+}$, and $Na^+$ were prepared from $Al(NO_3)_3 \cdot 9H_2O$ (≥99.0 %), $FeCl_3 \cdot 6H_2O$ (≥99.0 %), $MnCl_2 \cdot 4H_2O$ (≥99.0 %), $CuCl_2 \cdot 2H_2O$ (≥99.0 %), $MgCl_2 \cdot 6H_2O$ (≥98.0 %), and NaCl (≥99.5 %), which were all obtained from Kemiou Chemical Reagent (Tianjin, China). Laboratory triple-distilled water was used in the preparation of all solutions.

Sorption of chlorophenols on the microporous minerals was conducted with batch experiments. Accurately weighted sorbents (100 mg for 2-CP, 50 mg for 2,4-DCP and 2,4,6-

TCP) were added into 40-mL brown glass vials containing 20 mL solution of chlorophenol at varying concentrations. The vials were then sealed and agitated (at 120 rpm) in a constant-temperature shaker (HZQ-F100, Taicang Experimental Equipment Factory, Taicang, China) at 25 °C for 24 h, which was found to be sufficient for the sorption to reach equilibrium in preliminary experiments (data not shown). After that, the supernatants were withdrawn from the vials and filtered with 0.22 μm PTFE membrane filters (ANPEL Laboratory Technologies, Shanghai, China) for subsequent analysis. We measured chlorophenol sorption on CBV-720 based on triplicated experiments in the preliminary study. The relative standard deviation (RSD) values were found to be less than 5 % in general for the sorption capacities (Table S1), which is consistent with the results of atrazine and *N*-nitrosodimethylamine sorption on dealuminated zeolites conducted in our group (Hu et al. 2012; Hu and Cheng 2013; He and Cheng 2016). To reduce the workload, triplicates were skipped for the rest of the experiments, while comparable reproducibility was expected for the results of all sorption experiments, which is supported by the good $R^2$ values (0.92–1.00) for the sorption isotherms (Table S2). Although each data point on the sorption isotherms was based on single measurement, each isotherm was derived from 5 or more data points, with the $R^2$ value indicating the reproducibility of the sorption experiments at varying concentrations.

The influence of metal cations on chlorophenol sorption was evaluated by conducting the sorption experiments in the presence of individual metal cations ($Al^{3+}$, $Fe^{3+}$, $Mn^{2+}$, $Cu^{2+}$, $Mg^{2+}$, and $Na^+$). To further probe the mechanism of chlorophenol sorption, sorption of 2-CP and 2,4-DCP was also conducted by adjusting the initial pH of the solution to the desired values (2.0 or 12.0) using HCl or NaOH solution, with the final pH values of the solutions after sorption equilibrium measured with a pH meter (PHS-3C, Shanghai REX Instrument Factory, Shanghai, China). With $pK_a$ values of 8.52 and 7.90, 2-CP and 2,2-DCP were expected to stay

**Table 1** Summary of the major physicochemical properties of the model microporous mineral sorbents used in this study

| Mineral sorbent | CBV-400 | CBV-720 | CBV-760 | CBV-780 | CBV-3024E |
|---|---|---|---|---|---|
| Framework type | FAU | FAU | FAU | FAU | MFI |
| Pore size, nm | 0.74–1.2 | 0.74–1.2 | 0.74–1.2 | 0.74–1.2 | 0.54–0.56 |
| Si/Al mole ratio[a] | 2.55 | 15 | 30 | 40 | 15 |
| Bulk density (g/cm³) | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 |
| Theoretical micropore volume (cm³/g) | 0.48 | 0.48 | 0.48 | 0.48 | 0.17 |
| Nominal cation form[a] | Hydrogen | Hydrogen | Hydrogen | Hydrogen | Ammonium |
| [Na₂O][a] (wt.%) | 2.8 | 0.03 | 0.03 | 0.03 | 0.05 |
| BET surface area[a] (m²/g) | 730 | 780 | 720 | 780 | 400 |
| Monovalent cation density[b] (sites/nm²) | 2.62 | 0.42 | 0.23 | 0.16 | 1.55 |

[a] From product data sheets of Zeolyst (Valley Forge, PA, US)

[b] The monovalent cation density is estimated from the Si/Al mole ratio and the general molecular formula of $[(Mg,Na_2,Ca)_{3.5}[Al_7Si_{17}O_{48}] \cdot 32(H_2O)]$ for faujasite and $[Na_4Al_4Si_{92}O_{192} \cdot 16(H_2O)]$ for ZSM-5

**Table 2** Selected physicochemical properties of 2-CP, 2,4-DCP, and 2,4,6-TCP

| Chlorophenol | Molecular weight (g/mol) | Molecular size[a] (nm) | Water solubility (at 25 °C)[b] (g/L) | $pK_a$ (at 25 °C)[a] | $\log K_{ow}$[c] |
|---|---|---|---|---|---|
| 2-CP | 128.6 | 0.576 × 0.482 | 28 | 8.52 | 2.15 |
| 2,4-DCP | 163.0 | 0.647 × 0.482 | 4.5 | 7.90 | 3.06 |
| 2,4,6-TCP | 197.4 | 0.647 × 0.547 | 0.8 | 5.99 | 3.69 |

[a] Liu et al. (2010)

[b] Dąbrowski et al. (2005)

[c] Hamdaoui and Naffrechoux (2007)

predominantly as neutral molecules under acidic conditions, while they were essentially fully deprotonated and distributed as negatively charged chlorophenolates under moderately alkaline conditions. Consequently, such conditions could help elucidate the contributions of hydrophobic interactions and electrostatic attraction to sorption of chlorophenol molecules in the mineral micropores, respectively. The influence of humic acid, a common model for natural organic matter in sorption studies, on chlorophenol sorption was also evaluated by performing the sorption experiments in the presence of humic acid at 2 and 10 mg/L.

Concentrations of chlorophenols in aqueous samples were measured using an ACQUITY ultra-performance liquid chromatograph (UPLC) with UV-Vis detector (Waters, Milford, MA, US) at the maximum absorption wavelengths of 274, 284, and 290 nm for 2-CP, 2,4-DCP, and 2,4,6-TCP, respectively (Liu et al. 2010). Analyte separation was achieved on a BEH C18 analytical column (50 × 2.1 mm, 1.7 μm; Waters, Milford, MA, US) using isocratic methanol/water (70:30 for 2-CP and 2,4-DCP; 80:20 for 2,4,6-TCP, $v/v$) as the eluent at a flow rate of 0.3 mL/min. The concentrations of metal ions were determined on a 7700X Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Agilent Technologies, Santa Clara, CA, US). All sorption isotherms were fitted with the Freundlich model, which could describe all sorption data reasonably well (Table S2). For easy comparison of the sorption capacities of the microporous mineral sorbents under various conditions, the predicted sorption capacities (from the respective Freundlich isotherm models) of the dealuminated zeolites for 2-CP, 2,4-DCP, and 2,4,6-TCP in different solution matrices at an equilibrium aqueous concentration of 10 μmol/L are summarized in Table S3 of the Electronic supplementary material.

## Results and discussion

### Sorption of chlorophenols on microporous minerals

Figure 1 shows the sorption isotherms of 2-CP, 2,4-DCP, and 2,4,6-TCP on four dealuminated Y zeolites (CBV-400, CBV-720, CBV-760, and CBV-780). As sorbate molecules

adsorbed in the pore interior interact with all the surrounding pore walls, the dispersion force fields exerted by individual part of the pore wall surfaces overlap with each other when the pore is narrow enough (Gregg and Sing 1982; Nguyen and Do 1999). Thus, the superposition of the interaction force fields from the pore walls enhances the potential energies for adsorption of molecules in the molecular dimension pores (Gregg and Sing 1982; Cheng et al. 2012). Such enhancement is affected by the ratio of the pore size to the diameter of the sorbate molecules, and the adsorption potentials in pores with sizes that are three to six times of the sorbate molecules are notably enhanced (Gregg and Sing 1982; Hu et al. 2012). The pore size of Y zeolite ranges from 0.74 nm (channels) to 1.2 nm (cages), while the widest molecular dimensions of 2-CP, 2,4-DCP, and 2,4,6-TCP are 0.576, 0.647, and 0.647 nm, respectively. Therefore, 2-CP, 2,4-DCP, and 2,4,6-TCP are expected to occupy the narrow pores of the dealuminated Y zeolites first, where the enhancement of adsorption potential energies is strongest, followed gradually by the pore spaces of larger sizes. The higher sorption of 2,4,6-TCP in the micropores of a given zeolite resulted from the stronger interaction of its larger molecules with the surrounding pore wall surfaces compared with 2-CP and 2,4-DCP.

Sorbents with hydrophobic surface have relatively strong affinity for non-polar sorbates in aqueous solution (Moreno-Castilla 2004; Liu et al. 2010). Hydrophobic interactions, which are primarily an entropic effect arising from the disruption of the hydrogen bonding networks of highly ordered water molecules in liquid water by the non-polar solute, are a key driving force for sorption of non-polar organic compounds. The $\log K_{ow}$ values of 2-CP, 2,4-DCP, and 2,4,6-TCP are 2.15, 3.06, and 3.69, respectively. The sorption of chlorophenols on all four dealuminated Y zeolites decreased in the order of 2,4,6-TCP, 2,4-DCP, and 2-CP, which can be explained by weaker hydrophobic effect in the mineral micropores with decreasing hydrophobicity of the sorbates.

Except for the varying densities of surface cations, the pore structures and pore volumes of CBV-400, CBV-720, CBV-760, and CBV-780 are essentially identical. Sorption of 2-CP, 2,4-DCP, and 2,4,6-TCP on these zeolites all increased in the order of CBV-400, CBV-720, CBV-760, and CBV-780. That is, the sorption capacities for chlorophenols
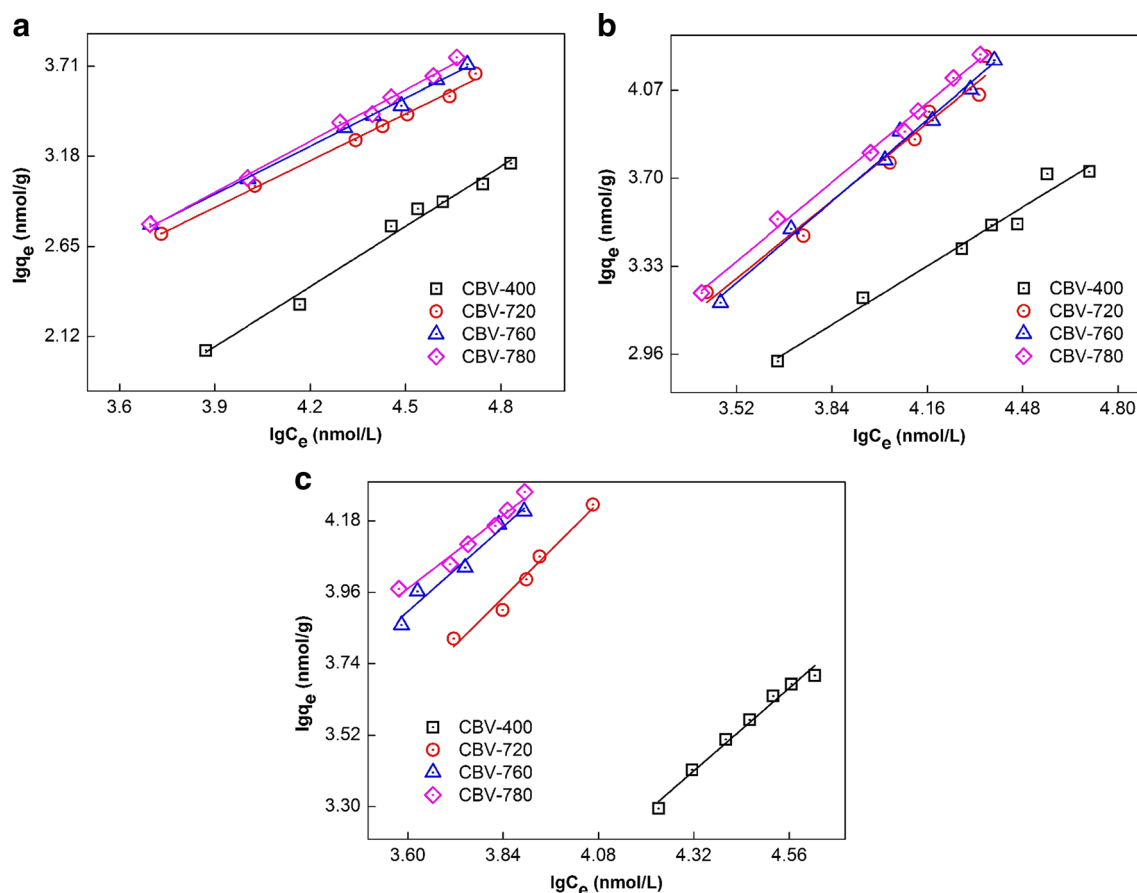
**Fig. 1** Sorption of **a** 2-CP, **b** 2,4-DCP, and **c** 2,4,6-TCP on four dealuminated Y zeolites with identical surface cation of H$^+$ but different Si/Al ratios at circum-neutral solution pH and 25 °C. The Si/Al mole ratios are 2.55, 15, 30, and 40 for CBV-400, CBV-720, CBV-760, and CBV-780, respectively. The *lines* represent Freundlich isotherm fits (the fitting parameters are summarized in Table S2 of the Electronic supplementary material)

increased with decreasing density of surface cations or increasing hydrophobicity of the zeolite micropores. Previous studies demonstrated that hydrophobic organic molecules adsorbed on microporous minerals mainly through displacement of the loosely bound water molecules from the hydrophobic micropore spaces, while the "tightly bound" water molecules were barely affected (Cheng and Reinhard 2006a, b, 2007; Cheng et al. 2012; Hu and Cheng 2013). Dealumination decreases the negative charge associated with the AlO$_4$ tetrahedra in the zeolite framework, and correspondingly the density of the exchangeable cations balancing the negative charge (Chen 1976; Ruthven 1984). In addition, as the zeolite is gradually dealuminated, non-polar siloxane surfaces are formed by cross-condensation of the neighboring silanol groups (Kerr 1967; Chen 1976), and the resulting micropore spaces surrounded by uncharged siloxane surfaces are hydrophobic (Cheng and Reinhard 2006a). With decreasing density of hydrophilic centers (surface cations and silanol groups), the water affinity of zeolite micropores decreases and consequently allows greater sorption of hydrophobic organic compounds through out-competing the

loosely bound water (Cheng and Reinhard 2006a, 2007). Among the four dealuminated Y zeolites, CBV-400 exhibited the lowest chlorophenol sorption capacities, primarily due to the strong sorption of water in its predominantly hydrophilic micropores that contain cations at a rather high density (2.62 sites/nm$^2$). In contrast, chlorophenol sorption on CBV-720, CBV-760, and CBV-780 was comparable, mainly because of the small differences in their surface cation densities (0.16–0.42 sites/nm$^2$). Together, these results indicate that the density of surface cations determines the hydrophobicity of micropores and plays a key role in controlling the uptake of chlorophenols from aqueous solutions.

Several previous studies have investigated sorption of volatile organic compounds (VOCs) on microporous minerals in the presence and absence of water and found that the presence of water could greatly reduce organic sorption (Farrell and Reinhard 1994; Werth and Reinhard 1997; Farrell et al. 2003; Li and Werth 2004; Cheng and Reinhard 2006a, b). Organic molecules could only out-compete water molecules in the micropores that are relatively hydrophobic, primarily through displacing the loosely bound water in such pore

spaces (Muller and Gubbins 1998; Muller et al. 2000; Cheng and Reinhard 2006a, b). That is, sorption of hydrophobic organic molecules in mineral micropores occurs in the presence of a vast number of molecules because of the hydrophobic effect. Under acidic and circum-neutral pH conditions, 2-CP ($pK_a = 8.52$) and 2,4-DCP ($pK_a = 7.90$) exist predominantly in the form of neutral molecules. As a result, their sorption on the dealuminated zeolites is attributed primarily to the hydrophobic interactions in the sorbent's micropores, which is also consistent with the greater sorption of these compounds on the zeolites of greater hydrophobicity (Fig. 1). Although desorption experiment could help further verify the role of hydrophobic interactions in chlorophenol sorption on the microporous minerals, it was not conducted because the relatively low desorption flux, resulting primarily from hindered molecular diffusion in the micropores of molecular dimension, might not be measured reliably in batch aqueous systems (Cheng and Reinhard 2006b, 2010). Previous studies have investigated desorption of VOCs from microporous minerals in gas-phase column experiments, and the results consistently supported that hydrophobic effect plays a key role for VOC sorption on microporous minerals in the presence of water (Farrell and Reinhard 1994; Werth and Reinhard 1997; Cheng and Reinhard 2006a, 2007).

## Impact of pore size on chlorophenol sorption

Figure 2 compares the sorption isotherms of 2-CP and 2,4-DCP on CBV-720 and CBV-3024E, which have identical framework Si/Al ratio of 15 but different pore structures and pore sizes. CBV-3024E exhibited much higher sorption capacities for both 2-CP and 2,4-DCP than CBV-720, even though its specific surface area (400 m$^2$/g) was much lower than that of the latter (780 m$^2$/g). The pore openings of CBV-

720 and CBV-3024E are 0.74 and 0.54 nm, respectively, while the narrowest dimensions of 2-CP and 2,4-DCP are both 0.482 nm. Thus, 2-CP and 2,4-DCP molecules can access the micropores of CBV-720 and CBV-3024E. As the pore dimension decreases, the degree of the overlap of the dispersion force fields acted by the pore wall surfaces increases, enhancing the adsorption potential energies of the sorbate molecules confined in the pore interior (Nguyen and Do 1999). That is why more 2-CP and 2,4-DCP adsorbed on CBV-3024E, which has narrower pore sizes than CBV-720. It is worth noting that although CBV-3024E and CBV-720 have the same framework Si/Al ratio of 15, their surface cation densities are different, which results from the large differences in their specific surface areas and structural types. CBV-3024E, which has a higher surface cation density (1.55 sites/nm$^2$) but narrower pore sizes compared with CBV-720 (cation density of 0.42 sites/nm$^2$), exhibited greater sorption capacities for both 2-CP and 2,4-DCP, suggesting the size of micropores plays an even more important role than their hydrophobicity during organic sorption. Together, these results indicate that pore size is a key factor in determining the sorption capacity of microporous minerals, and higher sorption capacities are expected for the sorbents with pore sizes closer to those of sorbate molecules when their hydrophobicity is not largely different.

## Impact of metal ions on chlorophenol sorption

Figure 3a–f show the influence of various trivalent, divalent, and monovalent metal cations ($Al^{3+}$, $Fe^{3+}$, $Mn^{2+}$, $Cu^{2+}$, $Mg^{2+}$, and $Na^+$) on 2-CP sorption on the hydrophilic Y zeolite CBV-400, while Fig. 4a–f show the corresponding results for 2,4-DCP sorption. The presence of all these metal cations promoted sorption of chlorophenols on CBV-400, with overall
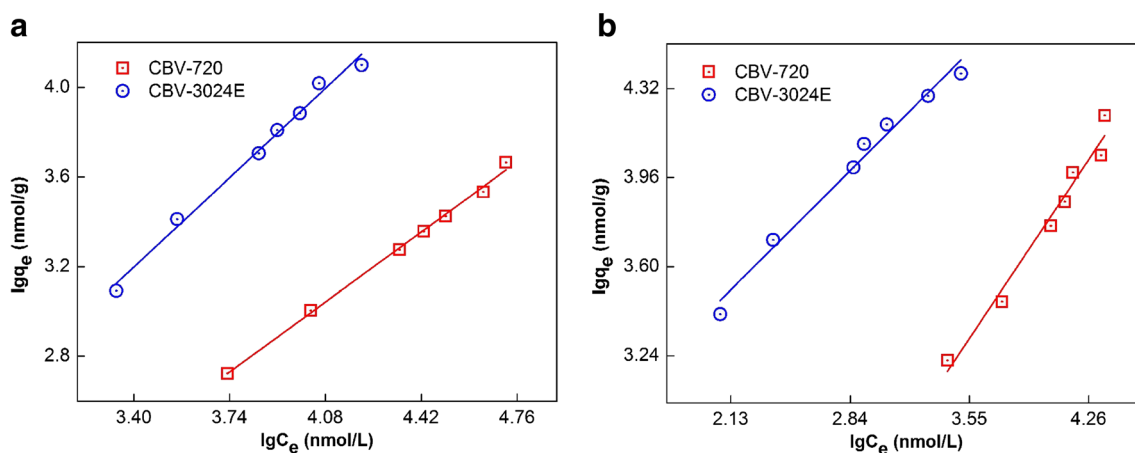


**Fig. 2** Sorption of **a** 2-CP and **b** 2,4-DCP on CBV-720 and CBV-3024E at circum-neutral solution pH and 25 °C. CBV-720 and CBV-3024E both have the Si/Al mole ratios of 15, while the pore openings are 0.74 and 0.54 nm, respectively. The *lines* represent Freundlich isotherm fits (the fitting parameters are summarized in Table S2 of Electronic supplementary material)
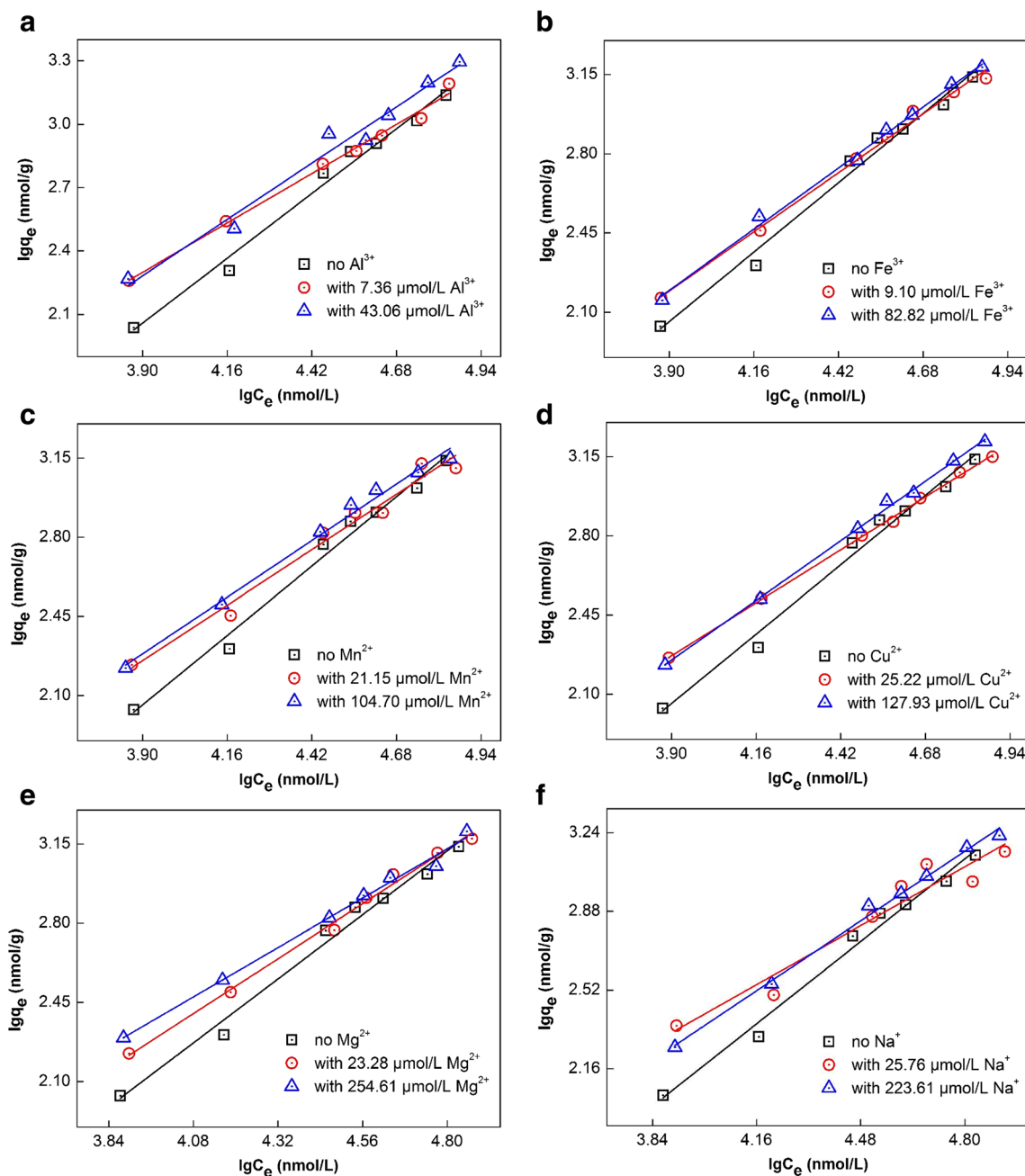
**Fig. 3** Influence of metal ions on 2-CP sorption on CBV-400 (at circum-neutral solution pH and 25 °C): **a** $Al^{3+}$, **b** $Fe^{3+}$, **c** $Mn^{2+}$, **d** $Cu^{2+}$, **e** $Mg^{2+}$, and **f** $Na^+$. The *lines* represent Freundlich isotherm fits (the fitting parameters are summarized in Table S2 of Electronic supplementary material)

stronger effect observed for the sorption of 2,4-DCP. In contrast, the presence of metal cations had little influence on sorption of 2-CP and 2,4-DCP on the hydrophobic Y zeolites, CBV-720, CBV-760, and CBV-780 (Figs. S1, S2, and S3). Apparently, sorption of chlorophenols and metal cations on the hydrophilic CBV-400 exhibited synergism (co-operative effect), while non-interactive effect was found on the hydrophobic Y zeolites (CBV-720, CBV-760, and CBV-780). Chlorophenol molecules adsorb predominantly in the

hydrophobic micropore spaces of the dealuminated Y zeolites in the presence of water, while ion exchange with the exchangeable cations is the primary sorption mechanism for the metal cations on these zeolites. The exchangeable cations on CBV-400, CBV-720, CBV-760, and CBV-780 are protons ($H^+$), which can be exchanged by multivalent cations and other monovalent cations by mass action. The enhanced sorption of chlorophenols in the micropores of CBV-400 in the presence of metal cations can be explained by the additional
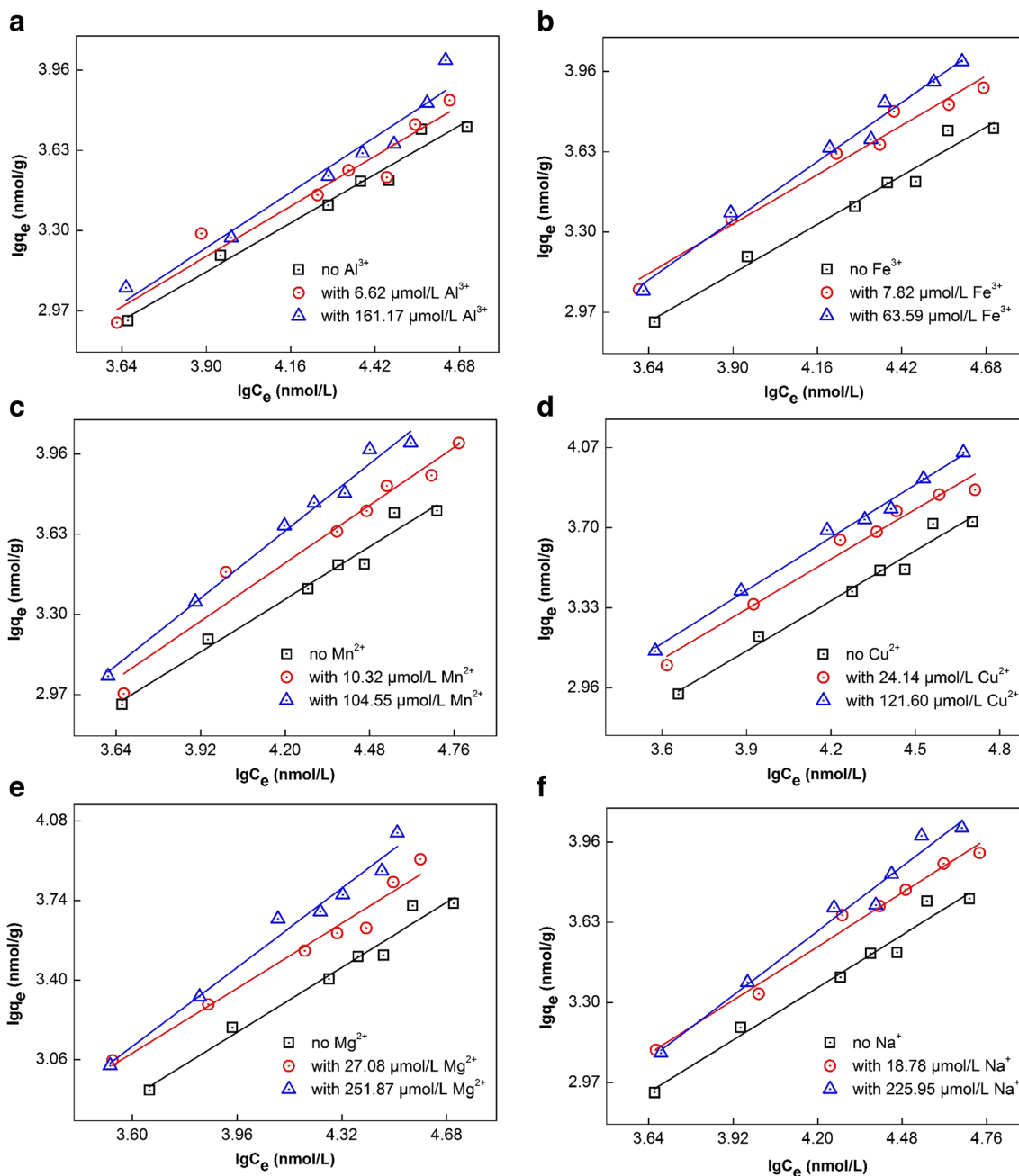
**Fig. 4** Influence of metal ions on 2,4-DCP sorption on CBV-400 (at circum-neutral solution pH and 25 °C): **a** $Al^{3+}$, **b** $Fe^{3+}$, **c** $Mn^{2+}$, **d** $Cu^{2+}$, **e** $Mg^{2+}$, and **f** $Na^+$. The *lines* represent Freundlich isotherm fits (the fitting parameters are summarized in Table S2 of Electronic supplementary material)

electrostatic attraction between the metal cations exchanged into the micropores and the negatively charged chlorophenolates. Phenols are weak acids due to the resonance stabilization of the conjugate bases, while the electron-withdrawing inductive effect of chlorine atoms in chlorophenol molecules further promotes ionization of the hydroxyl group on the benzene ring. As a result, the acidity of chlorophenols increases with the degree of chlorine substitution (the p$K_a$ values of phenol, 2-CP, 2,4-DCP, and 2,4,6-

TCP are 9.89, 8.52, 7.90, and 5.99, respectively (Liu et al. 2010)), and they can dissociate to form negatively charged chlorophenolates in water. In the absence of metal cations, binding of chlorophenolates with protons (the exchangeable cations originally present in the micropores of CBV-400) would result in formation of neutral chlorophenols, which are hydrophobic and adsorb in the hydrophobic micropore spaces. However, once the protons in the micropores had been replaced with metal cations, chlorophenolates would adsorb

onto these metal cations through electrostatic attraction while the neutral chlorophenol molecules would still adsorb in the hydrophobic micropore spaces, enhancing the overall sorption of chlorophenols.

Because the densities of surface cations in the micropores of the hydrophobic zeolites (CBV-720, CBV-760, and CBV-780) are rather low (0.16–0.42 sites/nm$^2$), the amounts of metal cations that can be exchanged into their micropores are relatively small. The interactions between chlorophenolates and the relatively small amounts of metal ions present in the micropores of these hydrophobic zeolites cannot bring significant sorption. As a result, the presence of metal cations could not significantly affect the overall sorption of 2-CP and 2,4-DCP on the hydrophobic zeolites, in contrast to the appreciable sorption enhancement observed on the hydrophilic CBV-400.

Figures 3 and 4 also show that the uptake of chlorophenols on CBV-400 increased with the concentrations of co-existing metal ions, which could be explained by sorption of more chlorophenolates due to the occupation of more cationic sites in the micropores by the metal cations. The enhancement in sorption capacity of 2.4-DCP by the presence of metal cations was consistently higher than that of 2-CP under comparable conditions. This is attributed to the greater dissociation of 2,4-DCP ($pK_a$ = 7.90) compared with 2-CP ($pK_a$ = 8.52) under comparable pH conditions. The sorption enhancement brought by trivalent cations ($Al^{3+}$ and $Fe^{3+}$) and divalent cations ($Mn^{2+}$, $Cu^{2+}$, and $Mg^{2+}$) was not significantly different from that of the monovalent cation ($Na^+$) for sorption of both 2-CP and 2,4-DCP in the micropores of CBV-400. This can be explained by the fact that metal cations adsorb in the micropores through ion exchange, and the net number of cationic sites occupied by the multivalent cations are only one third or half of that of the monovalent one under comparable conditions. Together, these results suggest that both sorption of neutral chlorophenol molecules in the hydrophobic micropore spaces and sorption of negatively charged chlorophenolates on the exchanged metal cations through electrostatic attraction contributed to the sorption of chlorophenols in the micropores of hydrophilic CBV-400 in the presence of metal ions. In contrast, chlorophenol sorption in the micropores of the more hydrophobic zeolites, CBV-720, CBV-760, and CBV-780, occurred predominantly through displacement of the loosely bound water molecules by the neutral chlorophenol molecules as only very small amounts of metal cations could exchange into their primarily hydrophobic micropores.

The sorption behaviors of chlorophenols and metal cations on the dealuminated Y zeolites indicate that the mineral's hydrophobicity (i.e., density of surface cations) plays a critical role in the competitive sorption process. When the micropores have a low density of surface cations and are hydrophobic, chlorophenols and metal ions adsorb independently. However, chlorophenol sorption can be markedly enhanced by the

presence of metal cations in the micropores of the much less hydrophobic zeolite (CBV-400) because of the easy ionization of 2-CP and 2,4-DCP, and the electrostatic attraction between chlorophenolates and metal cations exchanged into the micropores. Therefore, the mineralogical and chemical features of the sorbents, the properties of the sorbates, the interactions between the sorbates, as well as solution conditions, can all influence the sorption of organic pollutants on microporous mineral sorbents.

When the initial concentrations of metal cations were kept constant, the uptake of metal cations on the four dealuminated Y zeolites remained approximately constant with increases in the concentrations of chlorophenols (Tables S4, S5, S6, S7, S8, S9, S10, and S11). Ion exchange with the exchangeable cations ($H^+$) is the primary sorption mechanism for metal cations on the dealuminated Y zeolites. Neutral chlorophenol molecules adsorb in the hydrophobic micropore spaces, which are devoid of surface cations and surface hydroxyls, while the metal cations occupy the exchangeable cationic sites. Therefore, sorption of chlorophenol molecules could barely affect the exchange of metal cations with the $H^+$ originally present in the micropores of the dealuminated Y zeolites in the binary sorption process, despite the fact that the metal cations, once exchanged into the micropores, could bring sorption of chlorophenolates through electrostatic attraction.

## Impact of solution pH on chlorophenol sorption

As chlorophenols are weak acids, solution pH can significantly affect their sorption on microporous minerals by altering their chemical speciation. Figure 5 shows that sorption of chlorophenols on CBV-400 and CBV-720 in solutions with initial pH values of 2.0 and 12.0. The pH values of 2-CP solutions with initial pH of 2.0 raised to 3.8 upon equilibrium with CBV-400, while those equilibrated with CBV-720 raised to 2.2 to 2.3 (Table S12). Buffer capacity for alkaline solutions was also observed for these zeolites. The pH values of 2-CP solutions with initial pH of 12.0 decreased to 10.7 to 10.8 upon equilibrium with CBV-400, while those equilibrated with CBV-720 decreased to 10.2 to 10.3 (Table S13). Comparable results were also observed for 2,4-DCP solutions with initial pH values of 2.0 and 12.0 (Tables S14 and S15). The buffering capacity of the dealuminated zeolites with protons as exchangeable cations can be attributed to surface protonation-dissociation reactions and dissolution of framework Al under strongly acidic and alkaline conditions (Witter and Kirchmann 1989; Shevade and Ford 2004). The greater buffering capacity of CBV-400 under acidic conditions probably resulted from its higher content of framework Al, and thus more leachable Al on the framework surface, compared with CBV-720. The presence of metal cations appears to have small impact on the final solution pH under acidic conditions (Tables S12 and S14), while their effect under alkaline
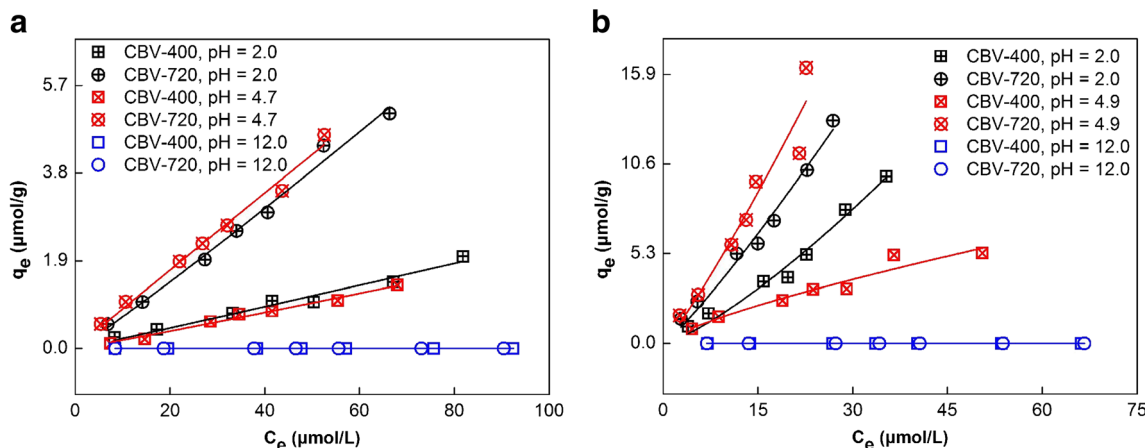
**Fig. 5** The effect of initial solution pH on the sorption of **a** 2-CP and **b** 2,4-DCP on the dealuminated Y zeolites (CBV-400 and CBV-720) at 25 °C. The *lines* represent Freundlich isotherm fits (the fitting parameters are summarized in Table S2 of Electronic supplementary material). It should be noted that the values of initial solution pH are denoted on these figures

conditions was not studied because they would readily precipitate out of solution.

Despite of the buffering effect of zeolites, the final pH values of the solutions with initial pH of 2.0 or 12.0 were still in the moderately acidic or alkaline ranges. Therefore, both 2-CP ($pK_a$ = 8.52) and 2,4-DCP ($pK_a$ = 7.90) in aqueous solutions existed almost completely in the form of neutral species under moderately acid conditions, but as negatively charged chlorophenolates under moderately alkaline conditions. Due to the significant electrostatic repulsion between the chlorophenolates and the negatively charged zeolite framework, little chlorophenol sorption could occur under moderately alkaline conditions (i.e, in the solutions with initial pH of 12.0). In contrast, the neutral 2-CP and 2,4-DCP molecules under moderately acidic conditions (i.e., in the solutions with initial pH of 2.0) adsorbed in the hydrophobic micropore spaces of CBV-400 and CBV-720 through displacing the loosely bound water molecules. The slightly greater sorption of both 2-CP and 2,4-DCP on CBV-720 than CBV-400 under moderately acidic conditions compared with near-neutral pH conditions (4.7–4.9) consistently supports the dominance of hydrophobic effect for their sorption in the acidic solutions. These results suggest that chlorophenols, which stay predominantly in neutral forms at acidic to circum-neutral solution pH, could be effectively adsorbed by microporous minerals. In contrast, their sorption would be very poor in alkaline solutions due to the electrostatic repulsion between the negatively charged mineral surfaces and chlorophenolates. Therefore, adjustment of the pH values of wastewaters from alkaline to acidic can significantly enhance sorptive removal of chlorophenols by microporous minerals.

Figure 6 shows the sorption of 2-CP and 2,4-DCP on CBV-400 and CBV-720 with and without the presence of metal ions ($Fe^{3+}$ and $Cu^{2+}$) in the solutions with initial pH of 2.0. In contrast to the observations made at circum-neutral pH (Figs. 3 and 4), the presence of metal cations had little effect on chlorophenol sorption. The concentrations of $H^+$ were 1–2 orders of magnitude higher than those of metal cations in the solutions, thus metal cations could barely replace $H^+$ as the exchangeable cations in the micropores. Furthermore, 2-CP and 2,4-DCP existed overwhelmingly in the neutral form in both the solution phase and micropores due to the high abundance of $H^+$. As a result, the electrostatic attraction between metal cations in mineral micropores and chlorophenolates was insignificant and could bring little additional sorption of chlorophenolates. With chlorophenol sorption occuring almost exclusively through displacing the loosely bound water molecules, sorption of 2-CP and 2,4-DCP on the more hydrophobic CBV-720 was stronger compared with on CBV-400. These results also corroborate the existence of relatively strong interactions between chlorophenolates and metal cations exchanged into the mineral micropores at circum-neutral pH conditions.

Similar to the cases at circum-neutral pH conditions, sorption of metal cations on both CBV-400 and CBV-720 remained approximately constant with increases in the concentration of chlorophenols in the solutions with initial pH of 2.0 at a given metal cation concentration (Tables S16 and S17). With neutral 2-CP and 2,4-DCP molecules adsorbed only in the hydrophobic micropore spaces of CBV-400 and CBV-720 under moderately acidic conditions, sorption of the co-existing metal cations onto the exchangeable cationic sites in the hydrophilic domains of the micropores occurred independently and was thus not significantly affected by the presence of chlorophenols.

### Impact of humic acid on chlorophenol sorption

Humic acid is an important organic constituent of natural waters and can be found at concentrations ranging from several
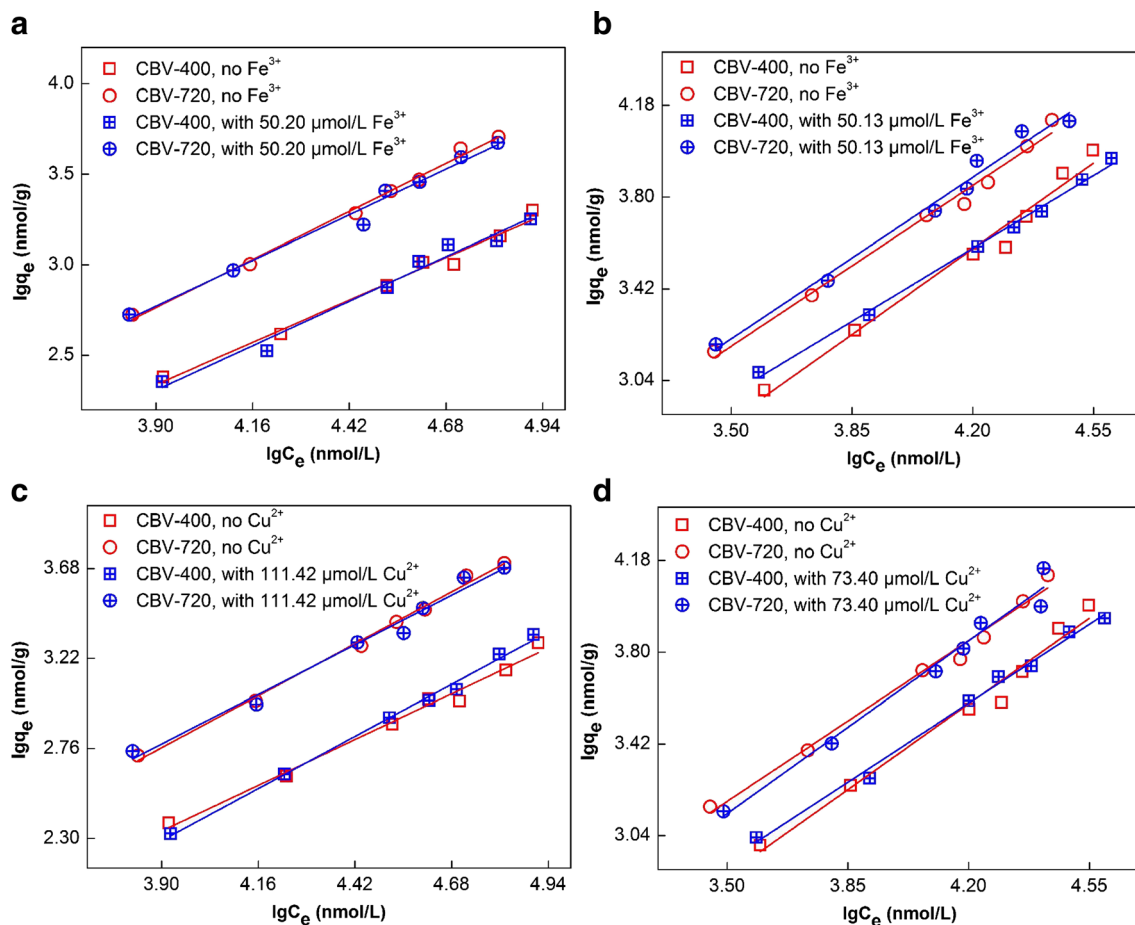
**Fig. 6** Influence of metal ions ($Fe^{3+}$ and $Cu^{2+}$) on sorption of chlorophenols on dealuminated Y zeolites (CBV-400 and CBV-720) in solutions with initial pH of 2.0 and 25 °C: **a** effect of $Fe^{3+}$ on the sorption of 2-CP, **b** effect of $Fe^{3+}$ on the sorption of 2,4-DCP, **c** effect of $Cu^{2+}$ on the sorption of 2-CP, and **d** effect of $Cu^{2+}$ on the sorption of 2,4-DCP. The *lines* represent Freundlich isotherm fits (the fitting parameters are summarized in Table S2 of Electronic supplementary material)

to hundreds of milligrams per liter (Wall and Choppin 2003). Figure 7 shows the influence of humic acid on sorption of 2-CP and 2,4-DCP on the hydrophilic CBV-400 and the hydrophobic CBV-720. The presence of humic acid promoted sorption of both 2-CP and 2,4-DCP on CBV-400, with overall stronger effect observed for the sorption of 2,4-DCP. In contrast, the presence of humic acid had little effect on chlorophenol sorption on CBV-720. At circum-neutral pH, both 2-CP and 2,4-DCP stayed predominantly as neutral molecules and adsorbed into the hydrophobic micropore spaces of CBV-400 and CBV-720 through displacing the loosely bound water molecules. Humic acid macromolecules are known to influence organic sorption on porous sorbents through competing directly for the sorption sites and blocking the pores with diameters in the range of 1.5–5.0 nm (Ding et al. 2008). The Aldrich humic acid, which is a supramolecular colloidal mixture, has been characterized as having a weight-average molecular weight of 4006–4100 g/mol and a number-average molecular weight of 1395–1630 g/mol, respectively (Nghiem et al. 2008). The equivalent Stokes radii estimated from the

Wilke-Chang and Stokes-Einstein equations were in the range of 0.95 to 1.02 nm for the Aldrich humic acid molecules (Nghiem et al. 2008). The fraction of soil humic acid with a weight-average molecular weight of 5800 has also been estimated to have a hydrodynamic radii of 2.1 nm by the Einstein equation (Kawahigashi et al. 2005). As a result, the diameters of the Aldrich humic acid molecules, as hydrated sphere colloids in aqueous solution, are expected to be around 1–2 nm. This is also consistent with the previous findings that Aldrich humic acid caused pore plugging of the nanofiltration membrane with an average pore diameter of 1.28 nm (Nghiem et al. 2008; Nghiem 2010). The fact that the presence of Aldrich humic acid did not negatively impact the sorption of 2-CP and 2,4-DCP on CBV-400 and CBV-720 suggests that the micropores of these dealuminated Y zeolites, which have pore sizes ranging from 0.74 nm (channels) to 1.2 nm (cages), were not blocked by the humic acid molecules. On the other hand, humic acid adsorbed on the external surface of these zeolites and formed a "coating layer," which brought sorption of additional chlorophenol molecules through hydrophobic
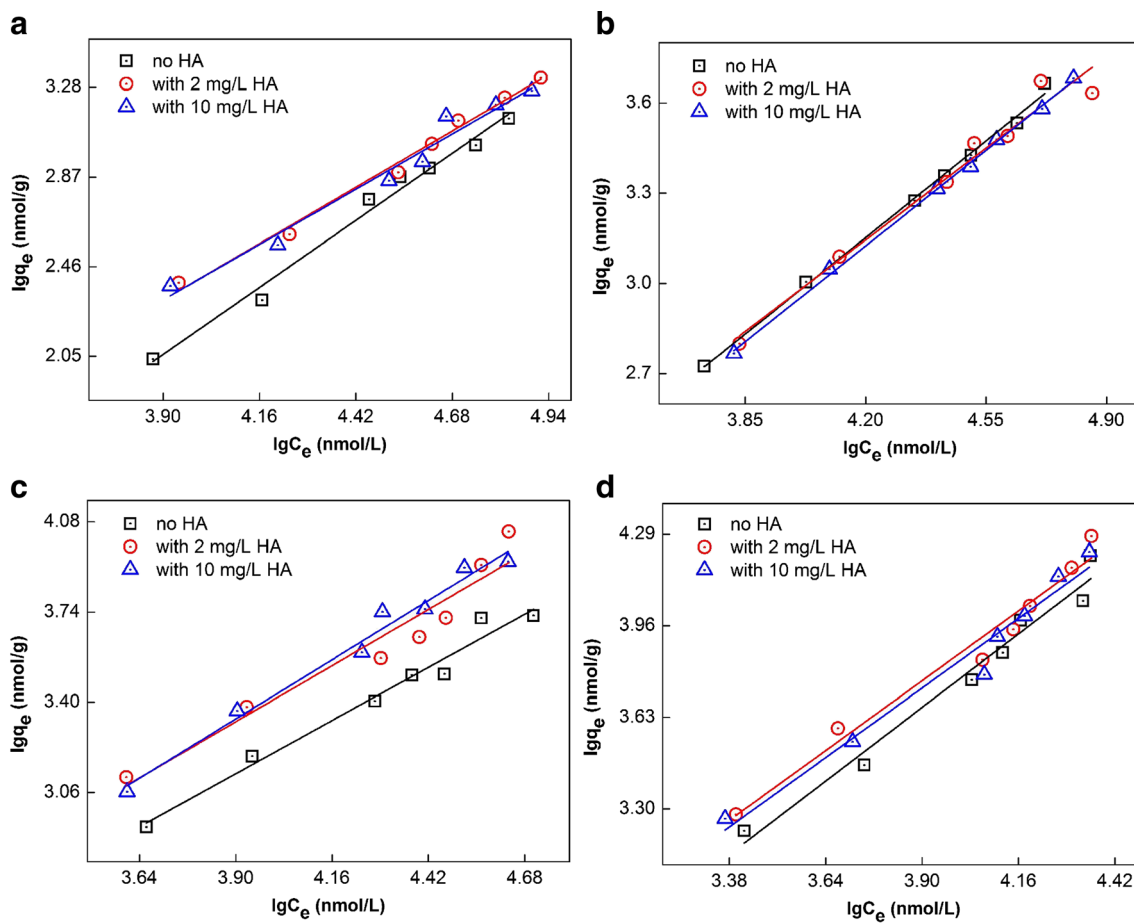
**Fig. 7** Influence of humic acid (HA) on sorption of chlorophenols on dealuminated Y zeolites at circum-neutral solution pH and 25 °C: **a** 2-CP sorption on CBV-400, **b** 2-CP sorption on CBV-720, **c** 2,4-DCP sorption on CBV-400, and **d** 2,4-DCP sorption on CBV-720. The *lines* represent Freundlich isotherm fits (the fitting parameters are summarized in Table S2 of Electronic supplementary material)

interactions. That is, besides sorption of chlorophenols in the hydrophobic micropores of the dealuminated Y zeolites, humic acid adsorbed on their external surfaces became secondary sorption sites and thus could promote sorption of chlorophenols. A recent study also concluded that Aldrich humic acid molecules could not access the internal pores of pillared clay based composites (with d-spacing ranging from 1.19 to 1.82 nm), while their sorption on the composites' external surface enhanced the sorption of bisphenol A and 2,4-DCP (Ortiz-Martínez et al. 2016).

Because the densities of surface cations in the micropores of the hydrophilic CBV-400 are relatively high (2.62 sites/ $nm^2$), much less 2-CP or 2,4-DCP could adsorb in its micropores compared with those of the more hydrophobic CBV-720 (0.42 sites/$nm^2$) under comparable conditions in the absence of humic acid. The amounts of 2-CP and 2,4-DCP that adsorbed on the humic acid coating layer of these zeolites could be relatively small when those adsorbed in their micropores were large. As a result, appreciable enhancement of 2-CP and 2,4-DCP sorption was observed on CBV-400, which had relatively low sorption capacities, but not on CBV-720.

Figure 7 also shows that the enhancement in sorption capacity of 2,4-DCP by the presence of humic acid was higher than that of 2-CP on CBV-400 under comparable conditions. This could be explained by the greater hydrophobicity of 2,4-DCP ($\log K_{ow}$ = 3.06) compared with 2-CP ($\log K_{ow}$ = 2.15), which resulted in stronger hydrophobic interactions with the humic acid coating layer on the external surface of CBV-400.

## Conclusions

Sorption of 2-CP, 2,4-DCP, and 2,4,6-TCP from aqueous solution on model dealuminated zeolites and the influence of co-existing metal cations, solution pH, and humic acid were systematically investigated in this study. Sorption of chlorophenols on the microporous minerals increased with the hydrophobicity of the sorbates and that of the mineral micropores, which is indicative of the important role played by hydrophobic interactions. For microporous minerals with comparable surface hydrophobicity (Si/ Al = 15), greater chlorophenol sorption occurred on the

one with narrower pore sizes (CBV-3024E) because of stronger enhancement of the dispersion interactions in the narrower pores. Sorption of chlorophenols on microporous minerals with relatively low densities of surface cations was not significantly affected by the presence of metal cations as their sorption in the micropores of these minerals was dominated by the mechanism of hydrophobic interactions. In contrast, chlorophenol sorption on the mineral sorbent with a high density of surface cations ($2.62$ sites/nm$^2$) in its micropores was markedly enhanced by the presence of metal cations, which is attributed to the sorption of additional chlorophenolates onto the metal cations exchanged into the micropores through electrostatic attraction. Sorption of 2-CP and 2,4-DCP on the dealuminated Y zeolites decreased to negligible under moderately alkaline conditions, as strong electrostatic repulsion existed between the chlorophenolates and the negatively charged mineral pore wall surface under such conditions. Sorption of chlorophenols on the microporous minerals was not significantly affected by the presence of metal cations under moderately acidic conditions, which resulted from the absence of significant interactions between metal ions and neutral chlorophenol molecules in the micropores. The presence of humic acid enhanced sorption of chlorophenols at circum-neutral pH on the hydrophilic CBV-400 due to the sorption of additional chlorophenols on the humic acid coating layer on the external surface of zeolite through hydrophobic interactions. In contrast, humic acid had little effect on chlorophenol sorption on the hydrophobic CBV-720 as the masses of additionally adsorbed chlorophenols were probably small compared with those adsorbed in the zeolite micropores.

These results reveal important insights on the roles played by the mineralogical and chemical features of the microporous mineral sorbents, the properties of the sorbates, and the interactions between the sorbates during sorption of organic pollutants on microporous minerals. Such mechanistic understanding can help guide the selection and design of microporous minerals for sorptive removal of chlorophenols and other ionizable organic pollutants from aqueous streams in practical application. Although single factor experiment conducted in this study helped obtain mechanistic understanding on the roles played by individual variables in chlorophenol sorption on the dealuminated zeolites, the relationship between these variables affecting the sorption process could be determined efficiently and systematically with design of experiments (DOE). Results from DOE could also help identify the optimum sorption conditions and sorbent properties for removing chlorophenols from aqueous stream with microporous minerals, which are critical for practical implementation of sorptive removal in wastewater treatment.

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