Effect of copper on the adsorption of *p*-nitrophenol onto soils

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The adsorption of p-nitrophenol onto soils decreased in the presence of copper due to its competition for the adsorption sites.

Abstract

The effect of copper on adsorption of *p*-nitrophenol on two typical Chinese soils was investigated using a batch-equilibration method. Adsorption experiments were carried out when both copper and *p*-nitrophenol were adsorbed simultaneously, and when copper was previously adsorbed on soils. It was observed that adsorption of *p*-nitrophenol decreased with increasing copper concentrations thereby indicating a competition between copper and *p*-nitrophenol for occupying the adsorption sites on soils. Moisture increased the hydrated sphere and the acidity of water surrounding the cation, which further reduced the adsorption of *p*-nitrophenol. Fourier transform infrared spectroscopy study provided the direct evidence for the coordination of *p*-nitrophenol sorbed by soils with metal cation in *n*-hexane system. It was observed that the perturbations included a red shift of the ν_{asym} (NO) band, a concomitant blue-shift of the ν_{sym} (NO) band and a blue-shift of C–N band when compared with the infrared spectra obtained from water solution.

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1. Introduction

In recent years considerable attention has been given to the fate of nitroaromatic compounds in the environment (Li et al., 2003; Zhu et al., 2000; Weissmahr et al., 1999). These compounds are widely used as pesticides, explosives, solvents, and intermediates in the synthesis of dyes (Weissmahr et al., 1997). Many of these

compounds and their transformation products are considered of significant toxicological concern. For example, *p*-nitrophenol may reach the human being as a hydrolytic product during the degradation of several organophosphorus pesticides when present in food commodities.

Adsorption of nitroaromatic compounds mainly depends on the nature and position of the substituents on the aromatic ring as well as the exchangeable cations and the type of clays and their charge present in soil. Greater adsorption of nitroaromatic compounds by clays has been attributed to the formation of an electron donor–acceptor (EDA) complex, in which polarized

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aromatic rings parallel to the basal surfaces accept electrons from the siloxane oxygen to form the complex (Haderlein et al., 1996; Weissmahr et al., 1998; Haderlein and Schwarzenbach, 1993). Subsequently, Boyd et al. (2001) also observed that the adsorption of such compounds decreased due to the increased electron-releasing abilities of *meta*- and *para*-substituents on nitrobenzene. This observation was consistent with the EDA complex formation mechanism. However, Plemenshikov and Leszczynski (1999) challenged the EDA complex formation hypothesis. They studied 1,3,5-trinitrobenzene (TNB) siloxane complex and found no electronic evidence for EDA complexation. In their study, the high affinity of 1,3,5-TNB for a model siloxane surface was attributed to the attractive Coulombic and van der Waals' forces between the surface and the planar structure of organic ligand. In addition to the proposed EDA complex formation mechanism, smectite clays may also adsorb neutral organic molecules by hydrophobic interactions (Laird and Fleming, 1999). Adsorption of nitroaromatic compounds was also related to the types and hydration characteristics of exchangeable cations (Johnston et al., 2001, 2002; Sheng et al., 2002; Saltzman and Yariv, 1975). For weakly hydrated cations (e.g., K^+ and Cs^+), the combined size of the cations and associated water molecules does not occupy all of the available space. Thus the portion of adsorption sites "available" for nitroaromatics sorption is expected to be relatively large resulting in a greater sorption. For cations with higher hydration energies (e.g., Na^+ and Mg^{2+}), the space available in the interlamellar region would be correspondingly small because of the large hydrated radii of the cations. In addition, adsorption of nitroaromatic compounds was noted to be influenced by the different types of clays and was also affected by the different type and positions of substituents on the aromatic ring. Johnston et al. (2001) used Fourier transform infrared (FTIR) spectroscopy to demonstrate the formation of interlayer cation– NO_2 complexation especially in K^+ - and Cs^+ -smectites.

Heavy metals and organic contaminants coexist in soil. Several studies have been undertaken to investigate the adsorption and desorption on soil of either heavy metals (Liu and Richard, 2000; Düring et al., 2003; Mulligan et al., 1999) or organic contaminants (Gimsing et al., 2004b; Pusino et al., 2003) separately. However, little attention has been given to determine the effect of heavy metals on the adsorption of organic contaminants on soils. Similarly not much is known about the adsorption of heavy metals on soil as affected by organic contaminants (Maqueda et al., 1998; Gimsing et al., 2004a; Morillo et al., 1994, 1997, 2000, 2002). Adsorption and desorption of copper on montmorillonite were affected by the presence of a cationic pesticide chlordimeform (Maqueda et al., 1998). The effect was evaluated when both adsorbates were adsorbed simultaneously and

when the pesticide was previously adsorbed on montmorillonite. Copper adsorption decreased when both adsorbates were adsorbed simultaneously, indicating a competition between copper and chlordimeform for interlamellar positions. Morillo et al. (1994, 1997, 2000, 2002) studied the mutual influence of glyphosate and copper adsorption on montmorillonite and soil. Glyphosate adsorption on montmorillonite decreased in the presence of Cu in solution or adsorbed on the mineral. This is attributed to the formation of Cu–glyphosate complexes that have a lower tendency to be adsorbed on montmorillonite than the free glyphosate. However, these workers also found that the presence of Cu enhances the adsorption of glyphosate on soil.

The objective of present study was to examine the effect of copper on the adsorption of *p*-nitrophenol on two typical Chinese soils namely Jiangxi and Heilongjiang soils, with different soil characteristics. The adsorption of *p*-nitrophenol from *n*-hexane and FTIR data were used to reveal the mechanism involved in elucidating the effect of copper on the adsorption of *p*-nitrophenol.

2. Materials and methods

2.1. Soil characteristics

The soils used in this study were collected from Jiangxi Province (southern China) and Heilongjiang Province (northern China). These are two typical Chinese soils with various physicochemical properties. Soil samples were air-dried, ground and screened through a 1-mm nylon fiber sieve to remove stone, plant roots and other large particles, and stored in plastic bags. Soil suspension pH was measured at a soil to water ratio of 1:1 (w/v). Organic carbon content in soils was determined by the Walkley-Black's method (Nelson and Sommers, 1982). Amorphous Fe-, Al- and Mn-oxides were determined by ammonium oxalate extraction methods (McKeague and Day, 1966). Crystalline Fe-, Al- and Mn-oxides were determined by the oxalate–ascorbic acid extraction method of Shuman (1982). The characteristics of the soils are shown in Table 1. Crystalline clay minerals were also analyzed by X-ray diffraction (XRD). The clay minerals of Jiangxi soil were dominated by kaolinite, limonite, goethite, with minor concentrations of hematite and gibbsite. In Heilongjiang soil, the clay minerals contained greater concentrations of illite, chlorite, and small amounts of kaolinite.

Nitrogen specific surface area (SSA) of soils was estimated by using a micromeritics Flowsorb II surface area analyzer, and by applying the Brunauer–Emmet–Teller (BET) equation to sorption of N_2 at a relative partial pressure of 0.3 at 77 K.

Table 1
Characteristics of soils

	Jiangxi soil	Heilongjiang soil
Sand (%)	19.5	9.8
Silt (%)	18.7	62.8
Clay (%)	42.4	27.4
pH	5.3	7.3
CEC (cmol kg ⁻¹)	14.7	32.7
Organic matter (%)	0.66	6.86
Fe (%)		
Crystal.	1.55	1.40
Amorp.	0.24	0.47
Al (%)		
Crystal.	1.36	1.58
Amorp.	0.27	0.34
Mn (mg kg ⁻¹)	40.0	326
DOC (mg kg ⁻¹)	226	891
BET surface area (m ² g ⁻¹)	31.7	19.4

2.2. Reagents

p-Nitrophenol (*p*-NO₂-C₆H₄-OH, 97%) was purchased from Beijing Xingjin Company and used directly without further purification. Its solubility in water was 16 000 mg l⁻¹ with a pK_a value of 7.15. Cu(NO₃)₂·3H₂O was of guarantee reagent grade (Beijing Chemicals, China). Methanol used was of HPLC grade.

2.3. Competitive sorption between Cu and *p*-nitrophenol

In the adsorption experiments, NaNO₃ was used as soil background electrolyte because of its environmental implications and minimum probability of complexes formation. Various concentrations of *p*-nitrophenol and Cu were added to 0.4 g of soils in 20 ml of 0.01 M NaNO₃ and 0.1 g l⁻¹ NaN₃ in 50 ml glass centrifuge tubes sealed by Teflon-lined screw caps. Each competitive adsorption experiment was repeated in triplicate. The concentrations of *p*-nitrophenol and Cu used in the competitive adsorption ranged from 0.72 to 21.6 mM and 0 to 2.0 mM, respectively. The suspension was rotated continuously for 24 h at room temperature (23 ± 1 °C) to ensure complete adsorption. The suspension was then centrifuged at 1667 g for 20 min to separate liquid and solid phases, and 1 ml of supernatant was used for the analysis of *p*-nitrophenol by HPLC.

In order to determine the competitive adsorption of Cu with *p*-nitrophenol, several portions of 20 ml of 0.01 M NaNO₃ and 0.1 g l⁻¹ NaN₃ solutions containing various concentrations of *p*-nitrophenol were added to 0.4 g soil, and the suspension was shaken for 12 h. Different amounts of Cu solution were then added to the suspensions to make the initial Cu concentrations as 0, 0.1, 0.5 and 2.0 mM, respectively. The suspension was shaken for an additional 12 h. The centrifugation procedure and collection of supernatant for HPLC analysis were the same as described above.

2.4. Adsorption of *p*-nitrophenol from *n*-hexane

A portion of 4.0 g soils was dispersed in 4.0 mM Cu(NO₃)₂ solution (200 ml). The suspensions were rotated continuously for 24 h at room temperature to ensure complete adsorption. After reaching equilibrium, the suspension was centrifuged, and the supernatant was removed. Distilled water (50 ml) was used to wash the residue soils in order to remove excess of Cu(NO₃)₂. The soils treated or untreated with Cu solution are referred here Cu-soil and soil, respectively. The Cu-soil and soil were oven-dried at 105 °C for 96 h to remove moisture. The oven-dried soils were stored in a desiccator prior to use. An aliquot of 20 µl distilled water was added to the oven-dried soils (0.4 g), and the moistened soil was subsequently ground thoroughly to make the distribution of water homogeneously. The grounded soil was placed in 50 ml glass tubes, capped with Teflon-lined screw caps, and stored in a desiccator prior to use. The partially hydrated soils and another portion of oven-dried soils were suspended in 20 ml of *n*-hexane containing various concentrations of *p*-nitrophenol in 50 ml glass centrifuge tubes. The suspensions were rotated continuously for 24 h at room temperature (23 ± 1 °C) to reach equilibrium. The suspensions were then centrifuged at 1667 g for 20 min to separate liquid and solid phases. Aliquots of the supernatants (10 ml) were dried under a gentle stream of nitrogen. A portion of 2 ml of methanol was added into the residue in order to dissolve the compound of interest. The extract was filtered with acrodisk (0.25 µm) and 1 µl of filtrate was injected into the liquid chromatograph.

2.5. FTIR measurements

Infrared spectra were obtained on a Perkin–Elmer GX2000 Fourier transform infrared (FTIR) spectroscopy equipped with deuterated triglycine (DTGS) and mercury–cadmium–telluride (MCT) detectors, a KBr beam splitter and a sample bench purged with dry air. The resolution for the FTIR spectra was 2.0 cm⁻¹, and a total of 64 scans was collected for each spectrum. The self-supporting soil films were prepared from soil suspensions. To obtain the soil suspensions, 20 ml aliquots of an aqueous suspension containing both *p*-nitrophenol and Cu sorbed on Jiangxi soil were passed through a 0.45 µm hydrophilic polyethersulfone membrane (φ = 25 mm) on a Millipore holder. Due to the small adsorption amount of *p*-nitrophenol in the presence of copper, the concentration of *p*-nitrophenol in solution was increased to 72.0 mM to ascertain IR spectra. The resulting deposits on the filters of soil–*p*-nitrophenol–Cu were allowed to be freeze-dried overnight and were removed from the filter by employing a knife edge. To obtain Cu-soil sample from *n*-hexane, 20 ml supernatant

solution was removed and the soil–*p*-nitrophenol–Cu was freeze-dried and stored in a desiccator prior to use.

2.6. Analysis

The concentrations of *p*-nitrophenol were determined by HPLC (Agilent 1100 HPLC) fitted with a diode array detector (DAD) at the maximum adsorption wavelength of 317 nm, and an extended polar selectivity reversed-phase column (15 cm × 4.6 mm i.d.). Isocratic elution was performed at a flow rate of 0.7 ml min^{−1}, the mobile phase was methanol:water (60%:40%). Controls consisted of soils and electrolyte solution but without *p*-nitrophenol. The amounts of *p*-nitrophenol adsorbed were calculated from the differences between the initial and the final equilibrium concentrations. The recoveries of *p*-nitrophenol following the adsorption procedure without soils were >98%. Under the experimental conditions described *p*-nitrophenol showed a single HPLC peak at the retention time of 6.5 min.

3. Results and discussion

3.1. Adsorption time

The adsorption of *p*-nitrophenol (10.8 mM) on two soils versus equilibrium time is presented in Fig. 1. Although the adsorption reached equilibrium in 4 h, a 24 h period was used to ensure complete equilibrium in the subsequent experiments. The results indicated that the sorption of *p*-nitrophenol was very rapid within the first 4 h. The adsorption of *p*-nitrophenol on Heilongjiang soil was lower than that on Jiangxi soil.

Fig. 1. Adsorption of *p*-nitrophenol versus equilibrium time by (■) Heilongjiang soil; (●) Jiangxi soil. Equilibrium concentration of *p*-nitrophenol: 10.8 mM.

3.2. Effect of pH on K_d

The adsorption of *p*-nitrophenol by soils was studied at various pH values. For the ionizable *p*-nitrophenol a strong pH dependence of the apparent K_d value was observed in the pH region corresponding to the pK_a of the compound. The adsorption of *p*-nitrophenol onto two soils increased significantly from pH 2.5 to 4 followed by a plateau over the pH range of 4–6 and then the adsorption of *p*-nitrophenol rapidly decreased from pH 6 to 8 (Fig. 2). The ionic fraction of *p*-nitrophenol ion (ϕ_{ions}) can be calculated from:

$$\phi_{ions} = 1 / [1 + 10^{(pK_a - pH)}] \quad (1)$$

Obviously, ϕ_{ions} increases as the pH value increased. Considering pK_a of 7.15 of *p*-nitrophenol, it appears that *p*-nitrophenol was present in neutral form when pH was less than 6. However, it was present in the form of the dissociated anionic species when pH of equilibrium solution was higher than 8. The small K_d of *p*-nitrophenol at higher pH values could be explained by electrostatic repulsion between the reactive surface site and the negatively charged *p*-nitrophenol molecule. The protons present in the aquatic system at pH lower than 4 will compete with *p*-nitrophenol for binding to the adsorption sites of soils. Therefore, the K_d value of *p*-nitrophenol is expected to decrease slightly at lower pH.

3.3. Competitive adsorption

Competitive adsorption of *p*-nitrophenol and copper was evaluated when both adsorbates were adsorbed on Heilongjiang and Jiangxi soils simultaneously. The results are shown in Fig. 3a and b. The adsorption of *p*-nitrophenol onto Heilongjiang and Jiangxi soils decreased with the increase of copper concentrations

Fig. 2. Effect of equilibrium solution pH on K_d values of *p*-nitrophenol on Heilongjiang (■) and Jiangxi (●) soil ($n = 3$); 0.4 g soil, 20 ml of 0.01 M NaNO₃, initial concentration of 10.8 mM *p*-nitrophenol.

from 0 to 2.0 mM. Almost no adsorption of *p*-nitrophenol in Jiangxi soil was observed when the Cu concentrations were greater than 0.5 mM. In contrast, copper had a relatively smaller suppression effect on the adsorption of *p*-nitrophenol on Heilongjiang soil.

p-Nitrophenol adsorption isotherms in the presence of copper can be described by a constant distribution coefficient as expressed by the following equation:

$$K_d = C_{\text{sorb}}/C_{\text{aq}} \quad (2)$$

where C_{sorb} and C_{aq} are the concentration of *p*-nitrophenol in soil (e.g., mM kg⁻¹) and in solution (e.g. mM l⁻¹), respectively. The competition of copper with *p*-nitrophenol for adsorption is reflected by the diminishing K_d values from 10.9 to 2.3 for Heilongjiang soil and from 18.3 to 0.01 for Jiangxi soil when the copper concentrations increased from 0 to 2.0 mM.

To determine whether copper can compete with *p*-nitrophenol for adsorption sites, a series of experiments were conducted. The two soils were first equilibrated with *p*-nitrophenol for 12 h and then copper solutions were added to the equilibrated suspension to make the initial copper concentrations of 0.1, 0.5 and 2.0 mM. The suspension was further equilibrated for an additional 12 h (Fig. 3c and d). It was found that the competitive adsorption between *p*-nitrophenol and

copper was quite similar as indicated by the simultaneous adsorption of both adsorbates. This is due to the fact that copper with positive charge has stronger adsorption affinity than *p*-nitrophenol for adsorption sites on soils. Thus, Cu²⁺ can compete with *p*-nitrophenol for the same adsorption sites, even when *p*-nitrophenol was previously adsorbed on soils. This suggests that the addition of copper to soils would release the adsorbed *p*-nitrophenol from soils, a phenomenon that could be considered of great environmental importance.

Haderlein and Schwarzenbach (1993) and Haderlein et al. (1996) also observed similar effects of exchangeable cations on adsorption of nitroaromatic compounds. In the presence of strongly hydrated cations (e.g., Na⁺, Mg²⁺, etc.), no significant specific adsorption of nitroaromatic compounds was observed, while for more weakly hydrated cations (e.g., K⁺, Cs⁺, etc.), the adsorption of nitroaromatic compounds were greatly increased.

Fourier transform infrared (FTIR) linear dichroism measurements indicated that the adsorbed substituted nitroaromatic molecules were oriented coplanar to the siloxane surface of clay minerals (Johnston et al., 2002). The parallel orientation of nitroaromatic molecules relative to the clay mineral layers manifests a requirement for adsorption domains of sufficient size on the siloxane

Fig. 3. Effect of different concentration of Cu on adsorption constants (K_d values) of *p*-nitrophenol. *p*-Nitrophenol and Cu were added simultaneously: (a) Heilongjiang soil, (b) Jiangxi soil; *p*-nitrophenol was adsorbed previously: (c) Heilongjiang soil, (d) Jiangxi soil.

surfaces between cations. In this study, the larger sizes of copper with a high hydrated energy 2100 kJ mol^{-1} may obscure a greater portion of the siloxane surfaces and shrink the size of the effective adsorption domains so that much less adsorption sites were available to accommodate *p*-nitrophenol molecules.

As shown in Fig. 3, adsorption of *p*-nitrophenol on highly-negative charged Heilongjiang soil was considerably less than that on low-negative charged Jiangxi soil. The characteristics of soils are listed in Table 1. Two mechanisms may be responsible for this phenomenon. First, the low charge of Jiangxi soil decreased the hydrated cations adsorbed thereby providing larger adsorption domains for *p*-nitrophenol, which was consistent with report of Sheng et al. (2002). Second, Jiangxi soil has greater surface area as compared with Heilongjiang soil, which means that Jiangxi soil can provide more site-specific adsorption for *p*-nitrophenol.

3.4. Adsorption of *p*-nitrophenol in *n*-hexane

To validate the hypothesis stated above, a further study was performed on the adsorption of *p*-nitrophenol from *n*-hexane on dried and partially hydrated soils (10% water) in the absence and presence of Cu. The results are shown in Fig. 4.

Freundlich equation (solid line) fit the adsorption isotherms (solid square, circle and triangle, Fig. 4):

$$Q = K_f C^n \quad (3)$$

where Q is the amount of *p*-nitrophenol adsorbed by soil, C is the equilibrium concentration, n is a constant of the isotherm curvature, and K_f is the Freundlich adsorption coefficient, an index of sorption capacity of soils.

The Freundlich adsorption coefficients are listed in Table 2. The adsorption capacity of *p*-nitrophenol decreased from 396.2 to 59.9, and from 2489.4 to 131.5 when dried Jiangxi and Heilongjiang soils were hydrated

with 10% water, respectively. The addition of exogenous copper further decreased the adsorption capacity of *p*-nitrophenol. The adsorption capacity of Jiangxi and Heilongjiang soils followed the order: dried soil > dried soil with simultaneously addition of exogenous copper (afterwards it was referred to as Cu-soil) > hydrated soil > hydrated soil with addition of exogenous copper (afterwards it was referred to as hydrated Cu-soil). The adsorption of *p*-nitrophenol onto soils from *n*-hexane solvent was greater than that from water (Fig. 3), which could be partially attributed to the interaction of *p*-nitrophenol with both solvent and sorbent (Banat et al., 2000). Water solubility of *p*-nitrophenol is high (115 mM) due to its hydrogen bonding between water and *p*-nitrophenol molecules, which is promoted by the dipole moment of 1.8 D for water and 5.67 D for *p*-nitrophenol. Because of the non-polar property of *n*-hexane, its interaction with *p*-nitrophenol is very weak. Accordingly, the solubility of *p*-nitrophenol in *n*-hexane is limited (0.62 mM) compared with that in water. To achieve adsorption, the interaction between *p*-nitrophenol and soils should be stronger than that between *p*-nitrophenol and solvents. Saltzman and Yariv (1976) also found that with increasing polar character of solvent, the amount of adsorbed parathion decreased in accordance with the dielectric constants of these solvents (hexane, 1.89; water, 80.37). *p*-Nitrophenol is adsorbed on negatively charged surfaces through hydrogen bonding and/or charge transfer complexes.

The adsorbed amount of *p*-nitrophenol on partially hydrated soils was greater than that on partially hydrated Cu-soils, which can be ascribed to the high polarity of Cu. The electronegativity of Cu is 1.9, which makes the dissociation of H more readily from soil minerals and water molecules associated with Cu. The high acid strength of the $-\text{OH}$ group of *p*-nitrophenol does not favor the formation of H-bond with the water-associated Cu because the highly polarizing Cu increased the ability of donating proton. The acidity of water molecules coordinated with metal cations was also

Fig. 4. Equilibrium sorption isotherms of *p*-nitrophenol from *n*-hexane on dried and partially hydrated soils (10% water). (a) Heilongjiang soil; (b) Jiangxi soil. (■) dried soil, (●) dried Cu-soil, (▲) hydrated soil, (▼) hydrated Cu-soil.

Table 2

Freundlich constants and correlation coefficients for *p*-nitrophenol adsorption on different adsorbents from *n*-hexane ($n = 3$)

Adsorbent	Jiangxi soil			Heilongjiang soil		
	K_f	n	R	K_f	n	R
Dried soil	396.2	0.530	0.99	2489.4	0.858	0.99
Dried soil-Cu	213.2	0.474	0.98	579.1	0.641	0.99
Hydrated soil	96.9	0.839	0.99	150.8	0.860	0.99
Hydrated soil-Cu	59.92	0.913	0.99	131.5	0.883	0.99

evaluated by Pusino et al. (2004). Furthermore, due to the addition of water, the ion radii of Cu increased from 0.72 to 6.0 Å. The large hydrated sphere of Cu occupied more space thus less adsorption sites were “available” for *p*-nitrophenol sorption. On the other hand, the large hydrated sphere was unfavorable to the interaction between Cu and the $-\text{NO}_2$ group of *p*-nitrophenol.

It is evident from Fig. 4 that the adsorption of *p*-nitrophenol on two dried soils was slightly higher than that on two dried Cu-soils. This appears to be due to the addition of Cu that occupied several adsorption sites and thus reduced the adsorption of *p*-nitrophenol. Johnston et al. (2002) suggested that the sorption of nitroaromatic compounds is attributed to two types of surface interaction: non-specific van der Waals’ interactions between the neutral portion of the organic guest species and the clay siloxane surface; and the site-specific interactions between cations and organic substituents carrying partial negative atomic ‘charge. Although Cu can also interact with $-\text{OH}$ or $-\text{NO}_2$ of *p*-nitrophenol, Fig. 4 indicated that the interaction is slightly weak compared to the non-specific interaction.

FTIR spectroscopy was used to study the molecular scale interaction of nitroaromatic compound with sorbent. The vibrational modes of the $-\text{NO}_2$ groups are sensitive to the charge of their local environment, which can be used to study the local environment of the soil surface.

When Cu cation is adsorbed on soils in *n*-hexane system, the $-\text{NO}_2$ group of *p*-nitrophenol apparently coordinates directly to metal cation and to the residual polarized water molecules surrounding these cations. The interaction of the $-\text{NO}_2$ substituent with interlayer Cu ion induced a blue-shift of the ν_{sym} (NO) band position from 1337 cm^{-1} for Cu-soil in water solution to 1344 cm^{-1} in *n*-hexane. A concomitant shift in the opposite direction of the ν_{asym} (NO) band from 1516 to 1514 cm^{-1} was observed. The shifts were consistent with the observations reported by Johnston et al. (2001). Due to the electron-withdrawing property of Cu cation, the C–N bonds are somewhat strengthened (shortened, with more double-bond character) in the NO_2 –Cu complex compared with the isolated, and uncomplexed *p*-nitrophenol molecules. This causes the C–N stretching components in the complexes to increase in frequency from 1384 to 1389 cm^{-1} . In addition, the blue-shift is also reinforced by electrostatic repulsion between Cu cation and the partial positive charge of N center. As shown by Boyd et al. (2001), the asymmetric $-\text{NO}_2$ modes are dominated by the N–O components, while the potential energy distribution of the symmetric $-\text{NO}_2$ modes is comprised of not only N–O stretching components, but also C–N stretching components. Thus the blue-shift of ν_{sym} (NO) band to higher frequency was partly due to the strengthened C–N bond upon complexation. Therefore, the shifts observed in Fig. 5 for the $-\text{NO}_2$

Fig. 5. FTIR spectra of *p*-nitrophenol sorbed on Jiangxi soil in the $2000\text{--}600\text{ cm}^{-1}$ region. (a) dried soil; (b) dried soil-Cu; (c) FTIR spectra of *p*-nitrophenol in aqueous solution on Cu-soil. (d) FTIR spectra of *p*-nitrophenol in *n*-hexane system on Cu-soil.

vibrational peaks interacting with Cu-exchanged soil can be rationalized in terms of inner-sphere complexation between the $-\text{NO}_2$ group and Cu. These data provide molecular-level support for the hypothesis that *p*-nitrophenol sorption on soils is affected, in part, by interactions with cations. The influence of cations on the $-\text{NO}_2$ stretching bands is also observed through earlier IR studies of *p*-nitrophenol (Saltzman and Yariv, 1975) and parathion (Saltzman and Yariv, 1976) sorption on montmorillonite.

The changes in $-\text{NO}_2$ stretching frequencies for *p*-nitrophenol upon adsorption by Cu-soil suggest that site-specific interactions between Cu and $-\text{NO}_2$ groups may be responsible, in part, for the high affinity of *p*-nitrophenol for soils.

Sorption isotherms of *p*-nitrophenol on two partially hydrated (10% water) soils from *n*-hexane are also shown in Fig. 4. Due to the competition of highly polar water for mineral phase surfaces, the presence of 10% water in soils markedly reduced the adsorption of *p*-nitrophenol. As shown in Fig. 6, the effect of water ratio on the adsorption of *p*-nitrophenol by two soils was conducted at a constant initial *p*-nitrophenol concentration of 0.62 mM. The ability of *p*-nitrophenol to be adsorbed from *n*-hexane decreased as the amount of water increased. Most *p*-nitrophenol adsorption had been suppressed when soils were hydrated by 10% water.

In summary, the adsorption of *p*-nitrophenol on soils decreased greatly in the presence of Cu in aqueous system. Infrared spectra indicated that *p*-nitrophenol sorbed by soils coordinated with metal cation directly in *n*-hexane system. In the aqueous system, the larger hydration sphere of copper shrunk the size of the effective adsorption domains. Furthermore, the high acid strength of the $-\text{OH}$ group of *p*-nitrophenol does not favor the formation of H-bond with water associated copper because the highly

polarizing heavy metal increase the ability of donating proton.

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Fig. 6. Effect of moisture content on the adsorption of *p*-nitrophenol by (■) Heilongjiang soil; (●) Jiangxi soil.

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