Simultaneous adsorption of phenol and cadmium on amphoteric modified soil☆

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ABSTRACT

Surface modification is an effective way to enhance adsorption of pollutants by soil. In this study, we investigated the individual adsorption of cadmium ion (Cd^{2+}) and phenol and also in combination by the clay layer of a loessial soil treated with the amphoteric modifier, duodalkylbetaine (BS-12). Three levels of BS-12 modification were compared in this experiment: (1) unmodified soil (CK), (2) modification with an amount of BS-12 equivalent to 50% of the soil's CEC (50BS) and (3) modification with an amount of BS-12 equivalent to 100% of the soil's CEC (100BS). Cd^{2+} adsorption was 0.92–1.70 times higher in the amphoteric modified soil compared to unmodified soil. Adsorption isotherms for Cd^{2+} displayed a L1-type shape. Phenol adsorption was 1.25–4.35 times higher in the amphoteric modified soil compared to the unmodified control. The adsorption isotherms of phenol on amphoteric modified soils were generally linear, but changed to L1-type isotherms for modified soil in the Cd^{2+} + phenol treatment at 40 °C. The results clearly showed that amphoteric modified soil had the ability to simultaneously adsorb Cd^{2+} and phenol. Cd^{2+} adsorption by the amphoteric modified soil was related to the initial concentration of Cd^{2+} in the supernatant. Cd^{2+} adsorption in the 100BS treatment exceeded adsorption in the 50BS treatment when Cd^{2+} initial concentrations were higher than approximate 200 $\mu g\,mL^{-1}$. Phenol adsorption by modified soils decreased in the order: 100BS > 50BS > CK and was primarily determined by the surface hydrophobicity of the soil. For the unmodified soil, total adsorption in the Cd^{2+} + phenol treatment was slightly lower compared to treatments that contained only Cd^{2+} or phenol. This indicated an antagonistic effect between the adsorption of Cd^{2+} and phenol, which was reduced after amphoteric modification. A comparison of temperature effects on Cd^{2+} and phenol adsorption indicated that Cd^{2+} was both physically and chemically adsorbed by the amphoteric modified soil, but phenol was primarily adsorbed physically.

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1. Introduction

Simultaneous contamination of soil with both organic pollutants and heavy metals has become a serious environmental problem. The adsorption of these pollutants by soil can minimize their harmful effects by reducing their movement in the soil, thus reducing their potential for plant uptake or groundwater contamination.

Boyd et al. [1] treated clay and soil samples with a cationic surfactant in order to change the surface of the soil material from hydrophilic to hydrophobic. The studies showed that the adsorption of organic pollutants was 10- to 100-fold higher on modified clay or soil compared to unmodified clay or soil [2–5]. Several researchers investigated the modification of bentonite with a mixture of two surfactants to enhance the adsorption of organic pollutants [6–8]. Other investigators have systematically investigated the factors that affect the adsorption of organic pollutants on modified clay or soil. These factors include clay and soil type [7,9–12], polarity of organic pollutants [13], pH, adsorbed form of the modifiers on the clay surface [14,15], surface charge density of clays [13,16], interlayer microstructural changes [17] and pore structure of clays [18].

The adsorption of hydrophilic heavy metals by cationic modified soil is related to the form of the heavy metal ion. For anionic heavy metals, such as the oxyanions $CrO_4{}^{2-}$ and $SeO_4{}^{2-}$, adsorption by the cationic modified soil is related to the amount of modification. When the amount of the cationic surfactant is greater than cation exchange capacity (CEC) of the clay or soil, then the excess surfactant will be adsorbed by hydrophobic bonds on the organic phase formed by the adsorption of the cationic surfactant on the exchange

sites of the soil or clay. The positive charges of the excess cationic surfactant become adsorption sites for oxyanions. The adsorption of oxyanion by the cationic modified soil is through an ion-exchange process [19–21].

Meng and Zhang [22] observed that the long carbon chains of the cationic surfactant created a hydrophobic effect at the soil surface that repelled cationic heavy metals such as cadmium ion (Cd^{2+}). Cd^{2+} was physically and chemically adsorbed to parts of the soil surface that were not covered by the cationic surfactant, but Cd^{2+} adsorption was reduced as the amount of modifier increased. These results, supported by other researchers [23–24], indicated that treatment with a cationic surfactant results in an increase in the adsorption of organic pollutants by soil, but a decrease in the adsorption of heavy metals. Thus, when organic pollutants and heavy metals coexist in the soil, treatment of the soil with a cationic surfactant may increase heavy metal mobility and the risk of environmental pollution.

The simultaneous adsorption of multiple organic pollutants by a cationic modified soil has been investigated by several researchers. The results showed that adsorption patterns varied depending on the type of pollutant [11] and that multiple organic pollutants had a synergistic effect on adsorption. The adsorption of aliphatic compounds on organic clay exhibited a type III isotherm, but a dual S-type isotherm was observed for the adsorption of aromatic compounds. This showed that the adsorption of organic compounds on modified clay enhanced the adsorption ability of the organic phase formed by the cationic surfactant on the clay surface [25–26]. The adsorbed amounts of total benzene–toluene–ethylbenzene–xylene (BTEX) mixture were generally higher than those for the individual compounds, but compared to benzene and toluene, the large-size alkylbenzene showed greater partitioning affinity due to their high hydrophobicity [27].

The treatment of soil with a cationic surfactant is not effective in the case of simultaneous pollution with both organic and heavy metal pollutants because cationic heavy metals are weakly adsorbed, but simultaneous adsorption probably be achieved with an amphoteric modifier due to its special molecular structure. In this paper, the term surface modifier refers to the compound used to modify the soil or clay surface, the soil that is modified with the amphoteric surface modifier is referred to as amphoteric modified soil. Molecules of the amphoteric modifier consist of both hydrophobic and hydrophilic groups. The hydrophobic group consists of a long carbon chain containing 8–18 carbon atoms. The hydrophilic portion has two charged groups, one is positively charged and the other group is negatively charged. Amphoteric modified soil is formed when the positively charged groups of the amphoteric modifier are adsorbed by electrostatic forces to the negatively charged sites on the soil surface.

The amphoteric modifier's hydrophobic carbon chain forms an organic phase on the soil surface that increases the adsorption of organic pollutants. At the same time, heavy metal cations from the soil solution are attracted to the free, negatively charged groups of the amphoteric modifier by electrostatic forces. Furthermore, the adsorption of heavy metal cations is also increased because the atom with a lone electron pair in the amphoteric modifier, e.g. oxygen or nitrogen atom, increases adsorption by producing complex bonds with heavy metal cation and by forming a stable pentagonal ring between the amphoteric modifier and heavy metal cation. As a result, amphoteric modified soil has the ability to simultaneously absorb both organic and heavy metal pollutants.

There are few reports on the effect of amphoteric modifier on adsorption when the soil is simultaneously polluted with heavy metals and organic pollutants. Sheng et al. [28] found the montmorillonite, modified with carboxylic group-bearing carboxydecyltriethylammonium (CDTEA), had dual adsorptive
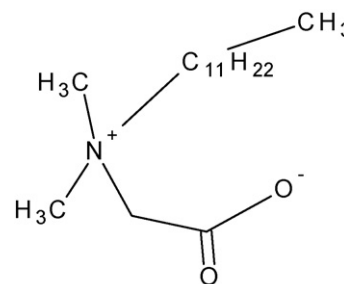

Fig. 1. Molecular structure of BS-12. BS-12 is commercial name of duodalkylbetaine.

properties for Pb^{2+} and chlorobenzene. In a previous paper, we described the theoretical principles for the use of an amphoteric modifier to adsorb organic and heavy metal pollutants in soil, and compared the adsorption of Cd^{2+} and phenol on soil modified with amphoteric modifier to that modified with cationic modifier when these two pollutants occurred separately, the study showed amphoteric modification could increase Cd^{2+} and phenol adsorption separately and demonstrated the amphoteric modified soil has the potential for simultaneously adsorbing heavy metals and organic pollutants [29].

In this paper, we investigated the individual adsorption of Cd^{2+} and phenol in their single treatment and the simultaneous adsorption characteristics in their mixture solution at different temperatures by a soil modified with the amphoteric modifier, duodalkylbetaine (BS-12). The results provide evidence that amphoteric surfactants can be used to treat soils containing both organic and heavy metal pollutants.

2. Materials and methods

2.1. Amphoteric modifier

The amphoteric modifier used in this experiment was duodalkylbetaine. Its molecular structure is shown in Fig. 1. The compound, which is commercially known as BS-12, 30% (w/v) in water solution, Analytical Reagent, was provided by the Sichuan Jinkun Chemical Engineering Co. Ltd., Chengdu, Sichuan Province, China.

2.2. Soil samples

The soil was the clay layer of loessial soil that collected from experiment fields located next to Northwest A&F University, Yangling, Shaanxi Province, China. The sampling depth was 1.1–1.3 m. The soil was air-dried and passed through a 1-mm sieve. The characteristics of the soil were as follows: pH 8.24, clay content (<0.01 mm) = 530.4 g kg^{-1}, CEC = 28.09 cmol$_c$ kg^{-1}, OM = 8.8 g kg^{-1}, and $CaCO_3$ = 3.2 g kg^{-1}. The primary components of clay were illite and smectite, and included a small quantity of albite and calcite. CEC was determined by the method of sodium acetate (pH 8.2)-flame photometry.

2.3. Modification of soil

Three levels of BS-12 modification were compared in this experiment: (1) unmodified soil (CK), (2) modification with an amount of BS-12 equivalent to 50% of the soil's CEC (50BS) and (3) modification with an amount of BS-12 equivalent to 100% of the soil's CEC (100BS).

A solution containing BS-12 was prepared by dissolving the compound in 1 L deionized water at 40 °C. The weight of BS-12 in solution was calculated by equation: $W_{soil} \times$ soil's

CEC × modification ratio × 272.45 × 10⁻², where W_{soil} is the weight of soil modified, kg; 272.45 is the molecular weight of BS-12, g mol⁻¹. The solution was then mechanically stirred into 1 L soil suspension that contains 0.5 kg soil. After equilibrating for 3 h (result from a preliminary kinetic experiment), the amphoteric modified soil samples were vacuum filtered, washed five times with deionized water, dried at 60 °C, and passed through a 1-mm sieve.

2.4. Adsorption isotherms

The experiment included three pollutant treatments: (1) heavy metal pollutant (Cd^{2+}) only, (2) organic pollutant (phenol) only, and (3) heavy metal + organic pollutant (Cd^{2+} + phenol) mixture. A series of Cd^{2+} aqueous solutions at 5, 10, 20, 50, 100, 200, 300, 400 and 500 μg mL⁻¹ were prepared using cadmium sulfate ($3CdSO_4·8H_2O$). Phenols in water solutions were also prepared at 5, 10, 20, 50, 100, 200, 300, 400 and 500 μg mL⁻¹. The concentration in the Cd^{2+} + phenol treatment was expressed as '$a + b$', where 'a' is the concentration of Cd^{2+} in the mixture, and 'b' is the concentration of phenol in the mixture. A series of solutions containing Cd^{2+} + phenol were prepared with concentrations of 5 + 5, 10 + 10, 20 + 20, 50 + 50, 100 + 100, 200 + 200, 300 + 300, 400 + 400 and 500 + 500 μg mL⁻¹. NaNO₃ at concentration of 0.01 mol L⁻¹ was added in the solution to keep ionic strength constant.

Adsorption isotherms were obtained by conducting adsorption tests on the modified soil at 20 and 40 °C using the batch equilibrium method. For example, in the case of the Cd^{2+} treatment, 2 g of modified soil was taken into glass centrifuge tubes. Twenty milliliters from each of the seven Cd^{2+} dilutions was added into separate tubes. Equilibrium was reached by shaking the suspensions for 24 h in a water bath at the prescribed temperature. The samples were centrifuged at 2500 rpm and then the pH and Cd^{2+} concentration of the supernatant were measured. Each isotherm was determined using four replicates. Adsorption isotherms for the phenol and Cd^{2+} + phenol treatments were obtained by the same method.

2.5. Determination

The concentration of Cd^{2+} in the supernatant was measured by flame atomic adsorption spectrometry with a Hitachi Z-5000 atomic absorption spectrometer. Background absorption was corrected by the Zeeman effect. The concentration of phenol in the supernatant was measured by 4-aminoantipyrine spectrometry with a SP-2100 UV–VIS spectrophotometer. A reagent blank was used to adjust absorbance to zero. The amount of Cd^{2+} or phenol adsorbed by the soil was calculated as the difference between the initial and final concentration of the pollutant(s) in the supernatant. Analytical quality was monitored by inserting standards among the samples.

3. Results and discussion

3.1. Equilibrium adsorption characteristics of Cd^{2+} by the amphoteric modified soil

The adsorption isotherms of Cd^{2+} to amphoteric modified soil for both the single pollutant and mixed pollutant treatments are shown in Fig. 2. Adsorption isotherms of phenol to amphoteric modified soil are shown in Fig. 4. We defined adsorption ratio, K_r, as the ratio of the amount of the pollutant (Cd^{2+} or phenol) adsorbed at equilibrium by the amphoteric modified soil in single pollutant or mixed pollutant treatments compared to the amount adsorbed by the unmodified soil at the same pollutant equilibrium concentration in single pollutant treatment. K_r expresses the different adsorption characteristics for organic pollutants and heavy metals between
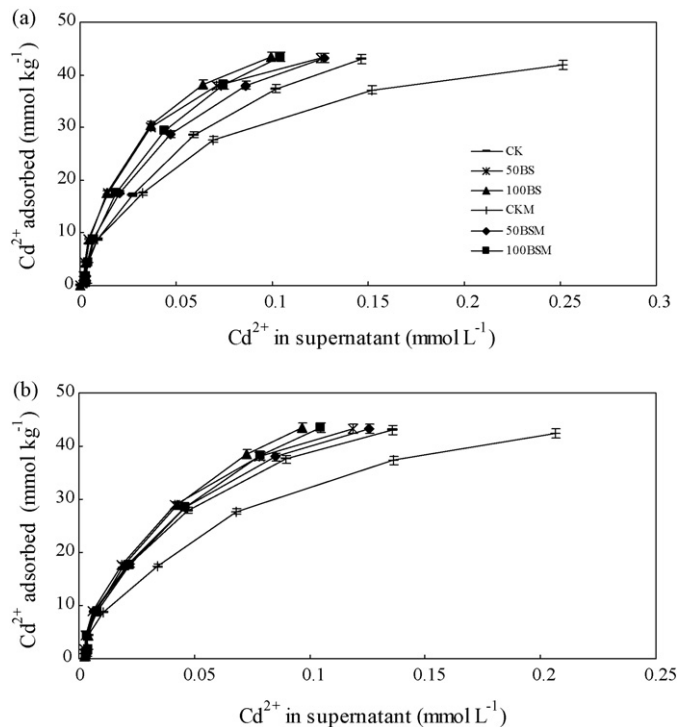
Fig. 2. Cd^{2+} adsorption isotherms on different amphoteric modified soils in Cd^{2+} and Cd^{2+} + phenol treatments. (a) At 20 °C and (b) at 40 °C. There are unmodified soil (CK) and two kinds of modified soils, i.e. soils modified with an amount of BS-12 equivalent to 50% of the soil's CEC (50BS) and equivalent to 100% of the soil's CEC (100BS), used in experiment. We used the abbreviations CK, 50BS and 100BS to represent experiments in pollutant single (Cd^{2+} or phenol) treatment, while the abbreviations CKM, 50BSM and 100BSM were used to represent the same experiments in pollutants mixture (Cd^{2+} + phenol) treatment. Cd^{2+}, cadmium ion.

amphoteric modified soil and unmodified soil. K_r values for Cd^{2+} and phenol are shown in Figs. 3 and 5, respectively.

In this study, the other species of Cd have been ignored, because the pH values of supernatant were in the range 7.0–7.6 after equilibration. It is less than the critical pH that the precipitation, $Cd(OH)_2$, start to form (the critical pH 8.56, When Cd^{2+} concentration reaches 500.0 μg mL⁻¹, pK_{sp} = 13.2).

The adsorption isotherms of Cd^{2+} for amphoteric modified and unmodified soil were L1-type in both the Cd^{2+} and Cd^{2+} + phenol treatments (Fig. 2). Cd^{2+} adsorption increased across the range of Cd^{2+} concentrations in this study, but the maximum Cd^{2+} adsorption did not reach for this soil. Cd^{2+} adsorption was higher in the 50BS and 100BS treatments compared to the unmodified soil at both temperatures. Fig. 3 showed that Cd^{2+} adsorption in the 50BS treatment was 1.05–1.7 times in Cd^{2+} single treatment, 1.00–1.31 times in Cd^{2+} + phenol treatment more than the unmodified soil, while adsorption in the 100BS treatment was 1.0–1.68 times in Cd^{2+} single treatment, 0.92–1.31 times in Cd^{2+} + phenol treatment higher than the unmodified soil. These results demonstrated that the modification of soil by BS-12 increased the soil's ability to adsorb Cd^{2+}, thus supporting our hypothesis.

In BS-12 modified soil, Cd^{2+} can be adsorbed by net negative charges on the bare soil surface as well as negative charges and complex groups on BS-12 modifier. A preliminary study showed that the CEC of CK, 50BS, 100BS soils were 28.09, 30.25 and 28.02 cmol_c kg⁻¹ respectively, demonstrated that the modification by BS-12 had little effects on the amounts of negative charges. Hence, the increase of Cd^{2+} adsorption in modified soil is due to the enhancing effect of complex groups on BS-12.
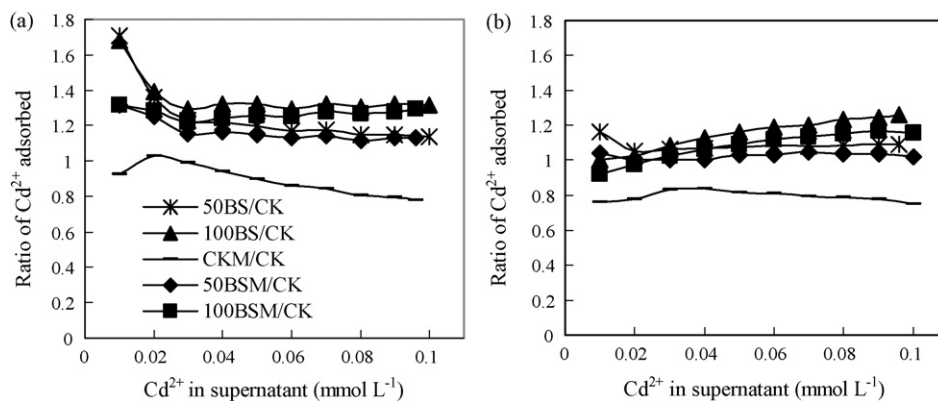
Fig. 3. The ratio of Cd^{2+} adsorption by modified soil in Cd^{2+} and Cd^{2+} + phenol treatments and by unmodified soil in Cd^{2+} treatment. (a) At 20 °C and (b) at 40 °C.

Results in Fig. 2 indicated that Cd^{2+} adsorption by amphoteric modified soil was related to the initial concentration of Cd^{2+} in both Cd^{2+} and Cd^{2+} + phenol treatments. When the initial concentration of Cd^{2+} added to the soil solution was <200 $\mu g\,mL^{-1}$ (1.78 $mmol\,L^{-1}$), i.e. corresponding to 0.01–0.03 $mmol\,L^{-1}$ Cd^{2+} equilibrium concentration in Fig. 2, Cd^{2+} adsorption declined in the order: 50BS > 100BS > CK. In contrast, when the initial concentration of Cd^{2+} added to the soil solution was >200 $\mu g\,mL^{-1}$, adsorption declined in the order: 100BS > 50BS > CK. Fig. 3 also showed when Cd^{2+} initial concentrations in the soil solution were >200 $\mu g\,mL^{-1}$, K_r of Cd^{2+} was higher in the 100BS treatment compared to the 50BS treatment at both temperatures in both Cd^{2+} and Cd^{2+} + phenol treatments. The results showed that the relative amount of Cd^{2+} adsorbed by the 50BS and 100BS treatments varied depending on the initial concentration of Cd^{2+} in the soil solution. At low initial concentrations, the adsorption of Cd^{2+} was higher in the 50BS treatment compared to the 100BS treatment. In contrast, adsorption was higher in the 100BS treatment when Cd^{2+} initial concentrations increased. The presence of phenol in the Cd^{2+} + phenol treatment did not affect this characteristics of Cd^{2+} adsorption. We suggested the reasons as follows.

Amphoteric modifier has both negatively charged and positively charged groups, two exchange reactions may be taken place in the modification of soil: (1) the positively charged group of amphoteric modifier combines with the negatively charged site on the surface of soil, the negatively charged group of the modifier will extend into the soil solution due to repulsion by the negatively charged sites on the soil surface. Therefore, the negatively charged group on amphoteric modifier become free adsorption site on the modified surface of soil instead of that on bare surface of soil, (2) the negatively charged group of amphoteric modifier combines with the positively charged site on the surface of soil, thus the positively charged adsorption sites on bare surface of soil are replaced by positively charged groups on amphoteric modifier. Hence, the modification has little effect on amount of soil surface charge. The outcome can be supported by the CEC values of both modified (50BS, 100BS) and unmodified soils (CK). Weers [30] reported the pK_a of BS-12 was 1.8, but Kato [31] found the isoelectirc zone of BS-12 was in pH 5.5–10.5. These indicate that the positively charged groups on BS-12 have equal charge strength with the negatively charged groups under the pH of supernatant after equilibration, even though the carboxylic groups of BS-12 have been completely deprotonated. Furthermore, the loessial soil has constantly charged surface due to its high clay content, i.e. net and high negative charges, thus the modification is primarily taken place by combining positively charged groups of amphoteric modifier with the negatively charged sites on the surface of soil.

Variations in the adsorption characteristics of soils treated with different amounts of amphoteric modifier (BS-12) are related to the density of the negatively charged hydrophilic groups and the hydrophobic carbon chains of the amphoteric modifier on the soil surface. Cd^{2+} adsorption by the modified soil is enhanced by negatively charged hydrophilic groups on BS-12 with an increase of modified ratio from 50% to 100%, while the repulsion to Cd^{2+} adsorption on modified soil is simultaneously increased by the hydrophobic carbon chains. Because the attractive force, i.e. electrostatic attraction between positive charges of Cd^{2+} and negative charges on the surface of modified soil and the complex attraction between Cd^{2+} and complex group on BS-12, is much greater than the repulsive interaction between the positively charged Cd^{2+} and hydrophobic carbon chain of modifier, Cd^{2+} adsorption is higher in 100BS compared to in 50BS treatments at high Cd^{2+} initial concentration. A reverse sequence to Cd^{2+} adsorption on 50BS and 100BS treatments at low initial concentration probably result from the competitive adsorption of the cations (Na^+, etc.) coexisted in soil solution, and this competitive effect could be neglected at high Cd^{2+} concentration due to higher Cd^{2+} adsorption. Even though the order of Cd^{2+} adsorption is 50BS > 100BS in the low Cd^{2+} concentration region, the absolute amount of Cd^{2+} adsorbed in the 50BS and 100BS treatments is higher than in the unmodified soil.

Regardless of temperature and modification treatment, Cd^{2+} adsorption was higher in the Cd^{2+} treatment compared to the Cd^{2+} + phenol treatment in both the modified and unmodified soil (Fig. 2). Fig. 3 also showed that the K_r values in Cd^{2+} treatment were higher than those in Cd^{2+} + phenol treatment. In addition, the K_r values of unmodified soil in Cd^{2+} + phenol treatment were less than 1 (Fig. 3). These indicated that phenol reduced Cd^{2+} adsorption in this soil. Furthermore, compared with Cd^{2+} adsorption in Cd^{2+} treatment, when the Cd^{2+} equilibrium concentration in supernatant was high, the decrease of Cd^{2+} adsorption in Cd^{2+} + phenol treatment in modified soil was smaller than that in unmodified soil. This is in agreement with the characteristics of the Cd^{2+} adsorption isotherms in Fig. 2. These results showed that the phenol in the soil solution had an antagonistic effect on Cd^{2+} adsorption by the unmodified soil. However, treatment of the soil with the amphoteric modifier reduced the effect of phenol on Cd^{2+} adsorption. We discuss the antagonistic effect between Cd^{2+} and phenol adsorption in next section.

The effect of temperature on Cd^{2+} adsorption is also shown in Fig. 2. Temperature increased Cd^{2+} adsorption in both the Cd^{2+} and Cd^{2+} + phenol treatments for the unmodified soil. The increase in Cd^{2+} adsorption, referred to as the positive temperature effect, demonstrated that Cd^{2+} adsorption was primarily due to chemical adsorption in the unmodified soil. This finding supports our

previous study [22]. In contrast, Cd^{2+} adsorption on the ampho-teric modified soil decreased as temperatures increased in the Cd^{2+} + phenol treatments, we refer to this as the negative tem-perature effect. The temperature effects are related to the Cd^{2+} equilibrium concentration in the Cd^{2+} treatment. Negative temper-ature effect on Cd^{2+} adsorption occurred at low Cd^{2+} concentrations while positive temperature effect occurred at high Cd^{2+} concen-trations. This demonstrated that Cd^{2+} adsorption by amphoteric modified soil was due to both physical and chemical adsorption.

Modification of the soil with BS-12 does not decrease the total amount of negatively charged adsorption sites on the surface of the modified soil. Due to the high clay content and high negative charge of the soil, electrostatic attraction is the main adsorption-type for Cd^{2+} adsorption by this soil. This type of adsorption, produced by electrostatic forces, is physical adsorption. The BS-12 molecule also contains both carboxyl and amidocyanogen groups. The atom with a lone electron pair in the carboxyl group and the amidocyanogen group of BS-12 molecule (such as oxygen or nitrogen atom) forms a chemical bond with Cd^{2+}, producing a stable pentagonal ring struc-ture between the amphoteric modifier and the heavy metal cation. This type of adsorption is chemical adsorption. Therefore, total Cd^{2+} adsorption in the modified soil includes both physical and chemical adsorption mechanisms. The negative temperature effect on Cd^{2+} adsorption is primarily appeared in low Cd^{2+} concentration region, because the physical adsorption is easy to happen.

3.2. Equilibrium adsorption characteristics of phenol on amphoteric modified soil

The pK_a of phenol is 9.99 [32], thus the most phenols exist as neutral species (molecule) under the pH of supernatant (7.0–7.6) after equilibration. Fig. 4 showed that phenol adsorp-tion isotherms on amphoteric modified soil were linear except for the Cd^{2+} + phenol treatment at 40 °C. This indicated a rela-tively constant proportion between the amount of phenol adsorbed on the surface of modified soil and the amount of phenol in the soil solution. In the Cd^{2+} + phenol treatment, the shape of the phenol adsorption isotherms changed from linear at 20 °C to L1-type at 40 °C. This indicated that in the Cd^{2+} + phenol treatment, the amphoteric modified soil's adsorption affinity for phenol was affected by temperature.

Phenol adsorption declined in the order 100BS > 50BS > CK for both the phenol and Cd^{2+} + phenol treatments regardless of tem-perature (Fig. 4). This indicated that phenol adsorption due to the hydrophobicity of modified soil increased as the amount of modifier increased. Fig. 5 showed that phenol adsorption in the 50BS treatment was 1.38–3.28 times in phenol single treatment, 1.25–2.56 times in Cd^{2+} + phenol treatment more than that in the
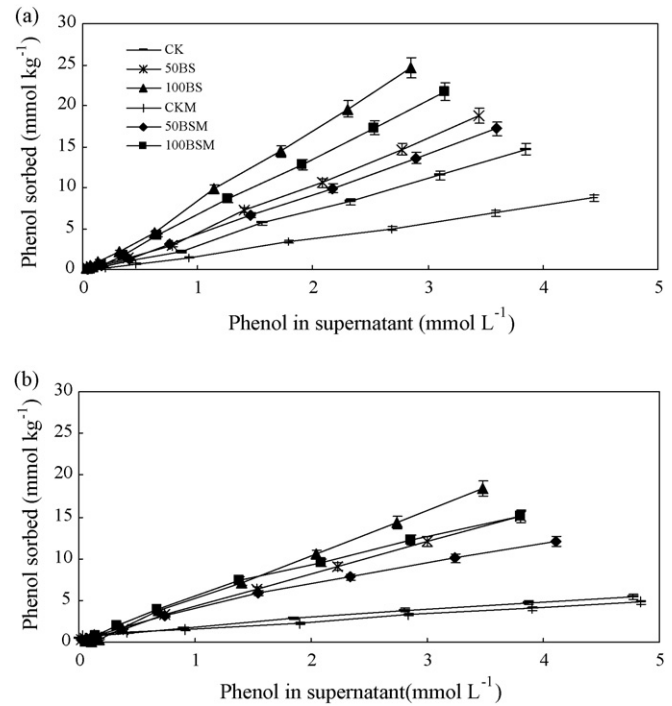

Fig. 4. Phenol adsorption isotherms on different amphoteric modified soils in phe-nol and Cd^{2+} + phenol treatments. (a) At 20 °C and (b) at 40 °C.

unmodified soil respectively, while adsorption in the 100BS treat-ment was 2.29–4.35 times in phenol single treatment, 1.84–3.46 times in Cd^{2+} + phenol treatment higher than the unmodified soil. This result showed that the modification of soil with BS-12 increased the adsorption of organic pollutants and supported our hypothesis. Adsorption of organic pollutants is lower in the ampho-teric modified soils compared to soils modified with the cationic surfactant, but the latter do not have the ability to simultaneously adsorb both heavy metals and organic pollutants. Therefore, the treatment of soil with an amphoteric modifier is superior to treat-ment with a cationic surfactant when soil contains both heavy metals and organic pollutants.

At the same temperature and modification ratio, phenol adsorp-tion was higher in the phenol treatment compared to the Cd^{2+} + phenol treatment for both the amphoteric modified and the unmodified soil (Figs. 4 and 5). This indicated that the presence of Cd^{2+} had a negative effect on phenol adsorption. This was sim-ilar to our observation that phenol had an antagonistic effect on Cd^{2+} adsorption in the Cd^{2+} + phenol treatment. The results demon-
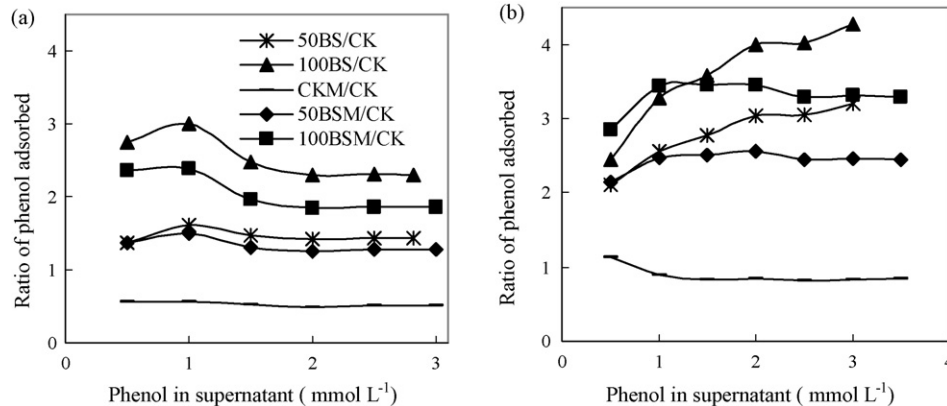

Fig. 5. The ratio of phenol adsorption by modified soil in phenol and Cd^{2+} + phenol treatments and by unmodified soil in phenol treatment. (a) At 20 °C and (b) at 40 °C.

strate that there is an inter-antagonistic effect between phenol and Cd^{2+} adsorption. When the two pollutants were present in the soil simultaneously, both phenol and Cd^{2+} adsorption were reduced in amphoteric modified and unmodified soils.

Even though Cd^{2+} and phenol are not adsorbed at the same sites, an inter-antagonistic effect between Cd^{2+} and phenol adsorption is demonstrated in this study and supported by other researchers [24,33]. Oyanedel-Craver et al. [24] indicated that the metals (Cd, Pb and Zn) and benzene were both adsorbed by surface adsorption in benzyltriethylammonium (BTEA)–bentonite. Although the metals and benzene are not sorbed at same sites, they are both interacting with the surface of the clay. The presence of benzene could cause crowding at the surface and result in a steric hindrance which could decrease the amount of metal that could interact with the surface. When partitioning-type clay, hexadecyltrimethylammonium (HDTMA)–bentonite, was used, competition between the non-polar organics (benzene) and metal were caused by the adsorption of benzene on the HDTMA–bentonite surface. Small amounts of benzene, which are polarizable due to electron delocalization, are adsorbed by an electrostatic attraction between benzene and the clay mineral surface and may compete with the surface sorption of heavy metals. Andini et al. [33] reported the adsorption of chlorophenol on the surface of benzyldimethyloctadecylammonium (BDMOA)–bentonite created competition between the heavy metals, and organic molecules. But a contrary result was also observed, Yoo et al. [34] did not find the competition between Cd, Pb and phenol sorption onto HDTMA–bentonite.

In this study, although phenol primarily interact with the organic phase created by the alkyl chains of BS-12 modifier, (1) phenol is a relatively soluble non-polar compound [34], the soil OM could adsorb both Cd^{2+} and phenol simultaneously. This could account for Yoo's observation [34], since bentonite is a relatively pure clay mineral, phenol is difficult to be adsorbed on bare clay surface; (2) amphoteric modifier adsorbed on the surface of bare soil could adsorb both Cd^{2+} (by negative charges and complex groups) and phenol (by alkyl chains), the hydrogen bond may be formed between –COOH on BS-12 molecule and phenol to some extent. Therefore, the interaction of both Cd^{2+} and phenol with same surface [24,33] or same modifier molecule is the reason for inter-antagonistic effect.

A comparison of the temperature treatments showed that phenol adsorption decreased as temperature increased, indicating that phenol adsorption in this soil was mainly due to physical adsorption. This supports the hypothesis of Meng et al. [29] that phenol adsorption is determined by the partition of phenol between the surface of the modified soil and soil solution.

Compared with phenol adsorption in the phenol treatment at high equilibrium concentration, although Cd^{2+} reduced phenol adsorption, the decrease of phenol adsorption in Cd^{2+} + phenol treatment in unmodified soil was greater compared to that in modified soil (Fig. 4). This result demonstrated that the modification of soil with BS-12 could decrease the antagonistic effects of Cd^{2+} on phenol adsorption simultaneously.

At 40 °C, Fig. 4 indicated that for both modified soil and unmodified soil, the phenol adsorption isotherms in the Cd^{2+} + phenol treatment were close to that in the phenol treatments. These indicated that the antagonistic effect of Cd^{2+} on phenol adsorption was also reduced by high temperatures. This is probably related to differences in the effect of temperature on the mechanism for Cd^{2+} and phenol adsorption.

4. Conclusions

The modification of soil with the amphoteric modifier, BS-12, increased the adsorption of both phenol and Cd^{2+} compared to unmodified soil. These results support the hypothesis that amphoteric modified soil has the ability to simultaneously adsorb organic pollutants and cationic heavy metals. Cd^{2+} adsorption is enhanced by negatively charged hydrophilic groups on BS-12 with an increase of modified ratio from 50% to 100% and related to the Cd^{2+} initial concentration. In contrast, the adsorption of phenol on amphoteric modified soil is controlled by hydrophobicity resulting from the density of the hydrophobic carbon chains on the soil surface. A comparison of single pollutant (Cd^{2+} only or phenol only) with mixed pollutant (Cd^{2+} + phenol) treatments showed an inter-antagonistic effect between Cd^{2+} adsorption and phenol adsorption on unmodified soil. Modification of soil with BS-12 can decrease the antagonistic effects significantly. The adsorption of Cd^{2+} on unmodified soil is mainly due to chemical adsorption, while Cd^{2+} is both physically and chemically adsorbed on the amphoteric modified soil. Physical adsorption is the primary mechanism for phenol adsorption in both modified and unmodified soils.

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Glossary

Amphoteric modified soil: The soil was modified with amphoteric surface modifier.

Amphoteric surface modifier: Its molecular structure consist of both hydrophobic and hydrophilic groups, the hydrophobic group consists of a long carbon chain containing 8–18 carbon atoms, and the hydrophilic portion has two charged groups, one is positively charged and the other group is negatively charged.

Modified soil: The soil was modified with surface modifier.

Surface modifier: The compound used to modify the soil or clay surface.