



Sorption and cosorption of the nonionic herbicide mefenacet and heavy metals on soil and its components

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Abstract

Sorption and cosorption of the nonionic herbicide mefenacet and two typical metals (copper and silver) on black soil and its components (kaolinite and humic acid) were investigated. It was found that because of their different valences and properties, Cu^{2+} and Ag^+ presented different effects on the sorption of mefenacet. Due to the competition of Cu^{2+} , along with the shells of dense water formed by its surface complexation, for sorption surface area with mefenacet, the addition of Cu^{2+} decreased the sorption amount of mefenacet on soil and its components, especially on humic acid. However, the addition of Ag^+ significantly enhanced the sorption of mefenacet, which was attributed to the softness of the cation that weakened the hydrophilicity of the local region around Ag^+ -complexed functionalities, and thus mitigated the competitive sorption of water. In addition, the sorption of mefenacet on soil with or without the two metals was generally decreased with increasing pH, which was caused by the hydrolysis of carbonyl and carboxyl groups on the surface of the sorbents, π - π interaction between mefenacet and the soil organic matter, and so on. On the other hand, the presence of mefenacet seemed to have little effect on the sorption of Cu^{2+} and Ag^+ , indicating that Cu^{2+} and Ag^+ might be sorbed strongly on the tested sorbents and the mefenacet added was too low in concentration to affect the sorption of the metals.

Key words: mefenacet; copper; silver; soil; kaolinite; humic acid; adsorption; pH

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Introduction

Mefenacet, 1-(2-benzothiazolyl-oxy)-*N*-methyl-*N*-phenylacetamide, is one of the acetanilide herbicides. It has been widely used in paddy fields to control weeds, particularly in the tropical and temperate zones such as the south of China and some other Asian countries (Okamura et al., 1999, 2002). In recent years, much attention has been paid to its environmental behaviors because of the frequent detection of mefenacet in many rivers and lakes (Okamura et al., 1999, 2002). Mefenacet is bio-refractory and environmentally stable with a half-life of 46–174 days in different soils (Zhang et al., 2001a). Ecotoxicological studies suggested that mefenacet could shorten the height and root length of rice plants and disturb the balance of active oxygen in the plants (Zhang et al., 2001b). Additionally, it is reported that mefenacet is harmful to shrimp, algae and even *Daphnia magna* (Okamura et al., 1999, 2002; Shigehisa and Shiraishi, 1998).

Sorption-desorption of herbicides between soil particles and water not only greatly affect their transport and persistence in soil (Pignatello and Huang, 1991), but also directly determine their contamination levels in

groundwater (Arias-Estévez et al., 2008). Previous studies (Kibe et al., 2000; Lu et al., 2001) reported that soil organic matter played an important role in the sorption of mefenacet on soils, and the sorption coefficient was increased with increase of the content of soil organic matter (SOM) (Pignatello and Huang, 1991). Herbicides commonly coexist with heavy metals in contaminated soils. Previous studies mainly focused on the sorption and desorption of simplex contamination on soils, i.e., either the sorption and desorption of herbicides or that of heavy metals (Arias-Estévez et al., 2006; Bradl, 2004; Dube et al., 2001; Huang et al., 2002; Sorensen et al., 2006). Reports on the effects of heavy metals on the sorption of herbicides on soils and minerals are relatively limited (Morillo et al., 1997, 2000; Pateiro-Moure et al., 2007; Pose-Juan et al., 2010; Zhou et al., 2004).

Up to now, many studies have focused on the interaction behaviors of metals and ionic herbicides in soil-water systems. Morillo et al. (1997, 2000) reported on the effect of Cu^{2+} on the adsorption of glyphosate (GPS) on soils with different characteristics. It was found that the interactions of GPS with soils were related to the content of iron and aluminum amorphous oxides as well as organic matter, and that the presence of Cu^{2+} could enhance the adsorption of GPS on soils. The formation of GPS-Cu complexes,

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the presence of adsorption sites and the decrease of pH with the addition of Cu^{2+} were cited as possible reasons for the enhancement of GPS adsorption on soils. Zhou et al. (2004) reported the adsorption and cosorption of GPS and cadmium (Cd^{2+}) on different soils. It was also found that the content of organic matter and the cation exchange capacity (CEC) were the primary factors that affected the adsorption of GPS on soils, and the presence of Cd^{2+} could improve the adsorption of GPS on soils due to the decrease of the equilibrium pH caused by its addition. In addition, the presence of GPS decreased the adsorption of Cd^{2+} on soils. One reason was attributed to the fact that the added GPS led to a decrease in the pH and thus correspondingly decreased the negative charges on the soil surface. Another reason might be the formation of Cd-GPS complexes which had low affinity for soil particles. Miriam et al. (2007) reported on the effect of Cu^{2+} on the sorption and desorption of several herbicides such as paraquat (PQ), diquat (DQ) and difenzoquat (DFQ) in vineyard acid soils. It was found that extracting Cu^{2+} from the soil could decrease the desorption of PQ and DQ, however, the affinity of DFQ was decreased because of the released vacant adsorption sites. Tests of the comparative adsorption of Cu^{2+} and herbicides on soil revealed that Cu^{2+} could displace herbicides from sorption sites (Pateiro-Moure et al., 2007).

However, few efforts have been made to determine the effect of heavy metals on the sorption of nonionic herbicides such as mefenacet on soils. Soils contaminated by copper and silver have both been reported (Pietrzaka and McPhaila, 2004; Teng et al., 2002). These two metals might affect the transport and persistence of herbicides in soils in different modes due to their different valences and properties. Therefore, the present study selected Cu^{2+} and Ag^+ as heavy metal models to investigate their effect on the sorption of mefenacet on soil and some soil components. As the basic clay with the simplest structure and as the most important soil organic matter, kaolinite and humic acid were selected as representative components of soil. Hopefully, the present study could provide some basic knowledge for the remediation of soils contaminated by heavy metals and nonionic herbicides.

1 Materials and methods

1.1 Materials and reagents

The soil used was the surface layer of soil (0–20 cm), which was sampled from Gongzhuling, Jilin Province (Northeast of China, black soil). The sampled soil was first air-dried, ground and screened through a 60-mesh nylon fiber sieve to remove stones, plant roots and other large particles. Then the screened soil was stored as the stock sample for further study. The pH value of the soil was measured at a soil to water ratio of 1/40 (V/V), which was the same ratio as used in the sorption experiments. The content of soil organic carbon (OC) was determined by the dichromate oxidation method. The cation exchange capacity (CEC) of the soil was determined by the NH_4Ac

exchange method (Lu, 2000). The contents of Cu^{2+} and Ag^+ were determined by the national standard method of China, using atomic absorption spectrophotometry (AAS, Thermo M Series, USA). The physicochemical properties of the selected soil were as follows: pH, 5.60; OC, 15.5 g/kg; clay, 39.8%; Cu content, 22.7 mg/kg, and no Ag was detected in the soil.

Kaolinite (chemical purity) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Humic acid was obtained from Shanghai Jufeng Chemical Technical Co., Ltd. (China). Mefenacet was provided by Jiangsu Changlong Chemicals Co., Ltd. (China), with a reported purity of > 96%, and was monitored by high performance liquid chromatography (HPLC, Agilent 1200, USA) to assure that no interference impurity occurred. Mefenacet exhibits a low water solubility of 4.0 mg/L (at 20°C), K_{ow} of 1700, and a melting point of 134.8°C. The chemical structure of mefenacet is shown in Fig. 1. Methanol (HPLC grade) was obtained from Tedia Company, USA. NaNO_3 , $\text{Cu}(\text{NO}_3)_2$, AgNO_3 and other reagents used in the study were analytical grade.

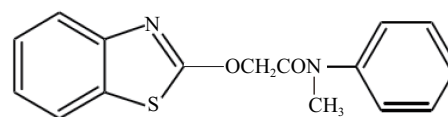


Fig. 1 Molecular structure of mefenacet.

1.2 Kinetic sorption experiments

All the sorption experiments were conducted in 22 mL glass vials with PTFE-lined screw caps. Typically, 0.5 g black soil, 0.5 g kaolinite, 0.02 g humic acid and 20 mL 0.02 mol/L NaNO_3 aqueous solutions were added to the glass vials. The initial concentration of mefenacet was controlled at 2.0 mg/L by adding the appropriate dosage of the stock solution of mefenacet. The stock solution of mefenacet was prepared in methanol with a total concentration of 2051.32 mg/L. It is worth noting that the dosage of methanol should be not more than 0.001 L/L in order to minimize cosolvent effects. Next, the glass vials were shaken by an end-over-end shaker at room temperature for 0.5–96 hr. At given time intervals, vials were taken out from the shaker and centrifuged at 1500 × g (Sigma 3K15, Germany) for 20 min, and a portion of the supernatant was finally taken for HPLC analysis. All the tests were conducted in duplicate.

1.3 Effect of Cu^{2+} and Ag^+ on the sorption of mefenacet

Batch experiments were carried out to investigate the effect of Cu^{2+} and Ag^+ on the sorption of mefenacet on soils. Typically, 0.5 g soil, 0.5 g kaolinite, 0.02 g humic acid and 20 mL of 0.02 mol/L NaNO_3 aqueous solution containing a series of concentrations of mefenacet and different concentrations of Cu^{2+} or Ag^+ were mixed in the 22 mL glass vials. The experimental groups are listed in Table 1. To exclude the effect of hydrolytic acidification caused by Cu^{2+} and Ag^+ , the pH value of the mixture was adjusted to the natural point by addition of 1.0 mol/L HCl.

Table 1 Experiment groups for investigating the effect of heavy metals on the sorption of mefenacet

Sorbent	Initial concentration of heavy metals	Initial concentration of mefenacet (mg/L)	pH value of equilibrium solution
Black soil (0.5 g)	0	0.1–2.0	5.60±0.20
	Cu10	0.1–2.0	5.60±0.20
	Cu50	0.1–2.0	5.60±0.20
	Ag10	0.1–2.0	5.60±0.20
	Ag50	0.1–2.0	5.60±0.20
Kaolinite (0.5 g)	0	0.1–2.0	8.70±0.10
	Cu10	0.1–2.0	8.70±0.10
	Cu50	0.1–2.0	8.70±0.10
	Ag10	0.1–2.0	8.70±0.10
	Ag50	0.1–2.0	8.70±0.10
Humic acid (0.02 g)	0	0.1–2.0	3.40±0.10
	Cu10	0.1–2.0	3.40±0.10
	Cu50	0.1–2.0	3.40±0.10
	Ag10	0.1–2.0	3.40±0.10
	Ag50	0.1–2.0	3.40±0.10

Cu10, Cu50 indicate that the initial concentrations of Cu^{2+} of the solution were 10, 50 mg/L respectively; Ag10, Ag50 indicate that the initial concentrations of Ag^+ of the solution were 10, 50 mg/L, respectively.

or 1.0 mol/L NaOH (5.60 for black soil, 8.70 for kaolinite, and 3.40 for humic acid). The suspensions were then mixed by an end-over-end shaker at room temperature until the adsorption equilibrium was obtained. After centrifugation, the supernatants were taken for HPLC analysis.

The effects of pH on the sorption of mefenacet on the sorbents as affected by heavy metals were also investigated either in the absence or in the presence of heavy metals. The experimental groups are shown in Table 2.

1.4 Effect of mefenacet on the sorption of Cu^{2+} and Ag^+

The effect of mefenacet on the sorption of Cu^{2+} and Ag^+ onto the sorbents was investigated on the basis of a fixed concentration of mefenacet of 2.0 mg/L. The initial concentrations of the heavy metals in the experimental groups were set at 50 mg/L. The effect of pH on the sorption of Cu^{2+} or Ag^+ on soils in the presence of mefenacet was investigated. The experimental groups are shown in Table 3.

1.5 Analytical methods

The concentrations of mefenacet were determined by an HPLC system with a diode array detector (DAD) (Agilent 1200, USA). An Agilent SB-18 column (4.6 mm × 150

Table 2 Experiment groups for investigating the effect of the pH value on the sorption of mefenacet as affected by heavy metals

Sorbent	Initial concentration of heavy metals	Initial concentration of mefenacet (mg/L)	pH value of equilibrium solution
Black soil (0.5 g)	0	2.0	2.50–10.0
	Cu50	2.0	2.50–10.0
	Ag50	2.0	2.50–10.0
Kaolinite (0.5 g)	0	2.0	2.50–10.0
	Cu50	2.0	2.50–10.0
	Ag50	2.0	2.50–10.0
Humic acid (0.02 g)	0	2.0	2.50–10.0
	Cu50	2.0	2.50–10.0
	Ag50	2.0	2.50–10.0

Table 3 Experiment groups for investigating the effect of pH on the sorption of heavy metals as affected by mefenacet

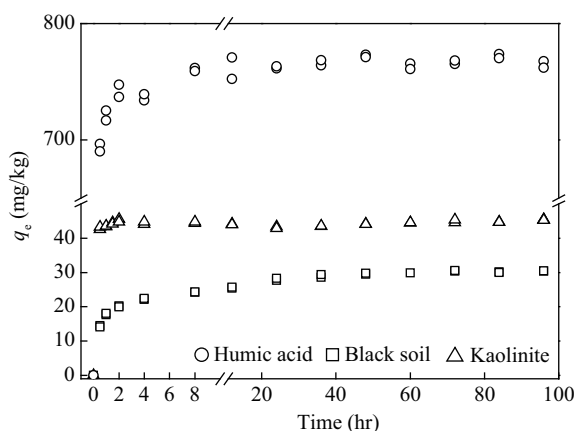
Sorbent	Initial concentration of heavy metals	Initial concentration of mefenacet (mg/L)	pH value of equilibrium solution
Black soil (0.5 g)	Cu50	0	2.50–10.0
	Cu50	2.0	2.50–10.0
	Ag50	0	2.50–10.0
	Ag50	2.0	2.50–10.0
	Ag50	2.0	2.50–10.0
Kaolinite (0.5 g)	Cu50	0	2.50–10.0
	Cu50	2.0	2.50–10.0
	Ag50	0	2.50–10.0
Humic acid (0.02 g)	Ag50	2.0	2.50–10.0
	Cu50	0	2.50–10.0
	Cu50	2.0	2.50–10.0
	Ag50	0	2.50–10.0

mm, 5 μm) was used for the separation. Isocratic elution was performed at a flow rate of 1.0 mL/min with methanol–water (75/25, V/V) as the eluent. The injection volume was 20 μL , the column temperature was 30°C, and the detector wavelength was 220 nm. The concentrations of Cu^{2+} and Ag^+ were determined by AAS with flame atomic absorption spectrometry (Thermo M Series, USA). Based on the obtained calibration curves, the amount of mefenacet, Cu^{2+} and Ag^+ adsorbed was calculated from the difference in concentrations between the initial and equilibrium solutions.

2 Results and discussion

2.1 Equilibrium time of the sorption experiments

Figure 2 illustrates the sorption amount of mefenacet on the black soil, kaolinite and humic acid as a function of equilibrium time. As can be seen, the sorption of mefenacet on black soil and humic acid exhibited two stages, i.e., an initial fast sorption step and a following slow sorption step. Typically, the sorption of mefenacet was rapid during the initial 30 min and the corresponding sorption amount of mefenacet corresponded to about 1/3 of the total equilibrium amount. After that point, the sorption rate was still relatively fast until about 10 hr.

**Fig. 2** Equilibrium time of mefenacet sorption on black soil, kaolinite and humic acid. Initial mefenacet 2.0 mg/L, black soil 0.5 g, kaolinite 0.5 g, humic acid 0.02 g.

Then desorption began to play an important role and the sorption amount of mefenacet started to change slightly. Figure 2 shows that the sorption of mefenacet on kaolinite almost reached equilibrium in the first 30 min, and then with the extension of the equilibrium time, the sorption amount stayed constant. A conclusion was derived from Fig. 2 that the fast sorption step dominated the sorption behavior of mefenacet on the soil and its components rather than the slow step. In general, both the organic matter and the mineral components affect the sorption process of hydrophobic organic compounds (HOCs). The fast sorption in the first stage can be attributed to the adsorption of solute on mineral surfaces (Huang et al., 1996) or the partition of solute into the rubbery domain of the soil organic matter (Weber and Huang, 1996), while the slow sorption in the second stage reflected the gradual diffusion of solute into soil organic matter matrices and soil micropores (Pignatello and Xing, 1996). According to the equilibrium curves, 72 hr was selected as the equilibrium time for the sorption of mefenacet on the black soil and 48 hr was selected for humic acid and kaolinite.

2.2 Effect of Cu^{2+} and Ag^+ on the sorption of mefenacet on soil and its components

2.2.1 Effect of Cu^{2+} and Ag^+ on the sorption isotherms of mefenacet

The sorption isotherms of mefenacet on the black soil, kaolinite and humic acid with different concentrations of

Cu^{2+} and Ag^+ are shown in Fig. 3. It was found that all the isotherms were fitted well with the Freundlich model and the corresponding parameters are listed in Table 4.

$$q = K_f C_e^n$$

where, q (mg/kg) is the sorbed amount in the soil, C_e (mg/L) is the equilibrium concentration in the solution, K_f [(mg/kg)(mg/L) $^{-n}$] is the Freundlich affinity coefficient, and n is an empirical exponent which indicates isotherm nonlinearity. Figure 3 shows that the sorption isotherms of mefenacet on the black soil and kaolinite slightly shifted with the addition of Cu^{2+} , while the isotherms on humic acid significantly changed and K_f decreased by 28% when 50 mg/L of Cu^{2+} was added. In addition, the addition of Ag^+ resulted in an increase of the sorption amounts of mefenacet on the three sorbents, and the K_f values increased by 20%–60% and 60%–90% as 10 and 50 mg/L of Ag^+ was added, respectively.

Heavy metals might influence the adsorption of organic chemicals on soils in several ways. When metal ions coexist in solutions with organic chemicals, they could be adsorbed on the SOM or minerals through the formation of complexes or by ion-exchange. In addition, they might also be complexed with organic ligands in the solution to form soil-metal-ligand or soil-ligand-metal complexes. For instance, Morillo et al. (2000) found that the presence of Cu^{2+} increased the sorption of the herbicide glyphosate on soils through the formation of a low-solubility complex.

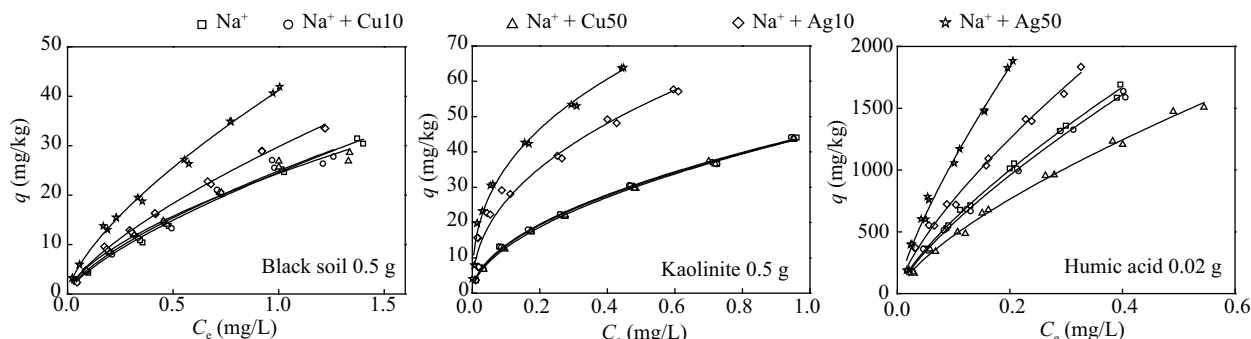


Fig. 3 Effects of heavy metals on the sorption isotherms of mefenacet. Initial pH: 5.60 for black soil, 8.70 for kaolinite, 3.40 for humic acid; Na^+ concentration 0.02 mol/L.

Table 4 Freundlich model parameters of sorption isotherms at different metal ion concentrations

Sorbent	Initial concentration of heavy metals	K_f ((mg/kg)(mg/L) $^{-n}$)	n	R^2
Black soil	0	24.58 ± 0.24	0.68 ± 0.03	0.9870
	Cu10	24.90 ± 0.51	0.73 ± 0.03	0.9865
	Cu50	24.41 ± 0.42	0.67 ± 0.02	0.9908
	Ag10	29.80 ± 0.27	0.73 ± 0.01	0.9974
	Ag50	41.17 ± 0.45	0.76 ± 0.03	0.9921
Kaolinite	0	44.45 ± 0.34	0.52 ± 0.01	0.9981
	Cu10	44.71 ± 0.35	0.51 ± 0.01	0.9981
	Cu50	44.48 ± 0.27	0.54 ± 0.01	0.9988
	Ag10	72.03 ± 3.31	0.44 ± 0.03	0.9595
	Ag50	86.15 ± 2.89	0.38 ± 0.02	0.9810
Humic acid	0	3291.28 ± 61.41	0.74 ± 0.01	0.9977
	Cu10	3197.41 ± 73.15	0.75 ± 0.02	0.9965
	Cu50	2369.05 ± 52.62	0.70 ± 0.02	0.9948
	Ag10	4028.24 ± 148.46	0.73 ± 0.02	0.9932
	Ag50	6287.44 ± 393.95	0.77 ± 0.03	0.9878

Chen et al. (2008) reported that Cd^{2+} and atrazine could also form a complex, thus decreasing their adsorption on sorbents. It should be noted that no obvious change was observed from the UV-Vis absorption spectrums of the mefenacet solution with Cu^{2+} and Ag^+ in the present study, which suggests that complexation reactions might not occur between mefenacet and $\text{Cu}^{2+}/\text{Ag}^+$. The non-linear sorption of mefenacet on soils suggests that specific interactions might occur between mefenacet and SOM (Bradl, 2004; Chiou and Kile, 1998). The numerous hydroxyl ($-\text{OH}$) and carboxyl ($-\text{COOH}$) groups in humic acid might potentially interact with the oxygen of the carbonyl ($-\text{C}=\text{O}$) and the carbon of the carbon-nitrogen bond ($-\text{C}-\text{N}$) in mefenacet to form hydrogen bonds. In addition, mefenacet might also combine with humic acid by π - π electron donor-acceptor interactions. Cu^{2+} could bond with $-\text{OH}$ and $-\text{COOH}$ on the soil surfaces to occupy the adsorption sites on soils. In addition, the surface complexation of Cu^{2+} forms hydration shells of dense water to compete with mefenacet for the adsorption surface area. The occupation of adsorption sites by hydrated Cu^{2+} would result in a decrease of the mefenacet sorption on humic acid.

By contrast, the presence of Ag^+ demonstrated an opposite trend by facilitating the adsorption of mefenacet. The differing mechanisms could be explained from the following aspects. According to the "hard-soft-cation" concept, the smaller the ratio of charge to radius of the cation, the softer the cation (Chen et al., 2007). Ag^+ is a cation with a lower charge, however, it has a larger radius than Cu^{2+} and natural alkaline metals existing in humic acid. Therefore, it is easy for Ag^+ to replace the original metal ions in humic acid through outer-sphere complexation, which will make the complex functional groups less soluble and decrease the effective size of cation hydration shells of dense water, and finally result in the weakening of competitive sorption of water molecules. Furthermore, in agreement with the Lewis acid-base concept, Ag^+ has high polarizability and acts as a soft acid, so it could interact with mefenacet which contains π -electrons and functions as a soft base. In addition, the S and N atoms in the thiazole ring in the molecular structure of mefenacet can provide lone pair electrons to the unoccupied orbital of Ag^+ . The formation of the coordination bond with Ag^+ results in the enhancement of the sorption of mefenacet indirectly. However, the

effect of Cu^{2+} on the mefenacet sorption on the black soil and kaolinite was insignificant (Fig. 3). Because Cu^{2+} is a hard acid and has a smaller radius compared with Ag^+ , electrostatic interaction is the dominant factor controlling the sorption mechanism of Cu^{2+} on the soil and kaolinite. The competition of Cu^{2+} with mefenacet was not strong enough to affect the sorption amount of mefenacet on the two sorbents.

2.2.2 Effect of pH on the sorption of mefenacet on soil and its components as affected by heavy metals

Figure 4 illustrates the effect of pH on the sorption of mefenacet on soil and its components in the presence or absence of Cu^{2+} and Ag^+ . It was observed that the sorption of mefenacet on soil and its components generally decreased with increasing pH in the presence or absence of Cu^{2+} and Ag^+ . It has been reported that mefenacet was very stable and did not hydrolyze in the pH range of 3–10 in 5 days (Huang et al., 2002). Therefore, electrostatic interaction might be not the main mechanism between mefenacet and the soil surface. The effect of pH on the sorption of mefenacet could be explained from the following aspects. First, $-\text{COOH}$ and $-\text{C}=\text{O}$ on the surface of the sorbents would hydrolyze with increasing pH value, which could decrease the possibility of the formation of hydrogen bonds with mefenacet and finally result in the decrease of the sorption of mefenacet. Secondly, π - π interaction probably occurs between the π -donor groups of the herbicide and the π -acceptor groups of SOM. In general, the phenyl ring connected with the electron-donating group in the mefenacet molecule can serve as a π -acceptor group. SOM contains an abundance of potentially strong π -acceptor groups, including quinones, protonated aromatic amines and N-heteroaromatic rings, as well as aromatic rings substituted with two or more electro-withdrawing groups such as carbonyl and carboxyl ($\text{Ar}-\text{COOH}$, $\text{Ar}-\text{COOR}$, $\text{Ar}-\text{CONR}_2$) (Seliger et al., 1995). Decreasing the pH value below neutral can increase the abundance of π -accepting sites in humic substances by protonation of carboxyl, arylamine, and heteroaromatic N functional groups on aromatic rings (Zhu et al., 2004), and thus enhance the π - π electron interactions between SOM and mefenacet. When increasing the solution pH value above the neutral point, most of the SOM was dissolved into the alkaline solution, which lead to the sorption of mefenacet decreasing.

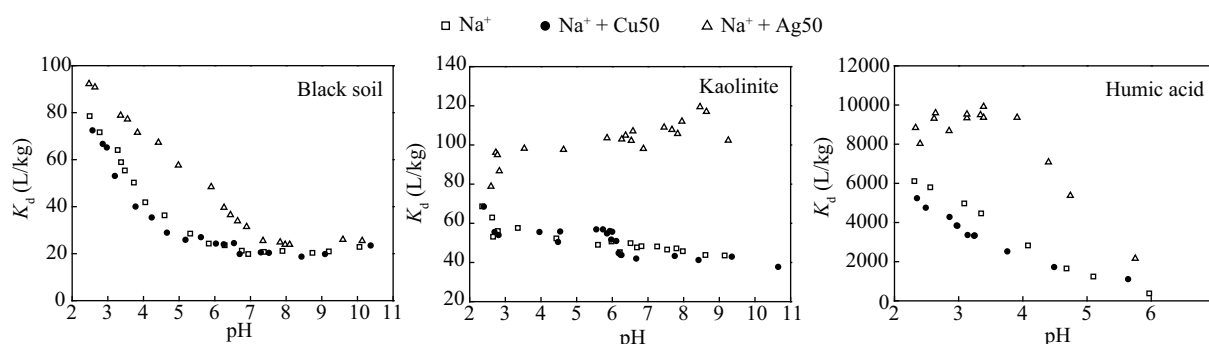


Fig. 4 Effects of pH on sorption of mefenacet with different metal ions. K_d : sorption coefficient, Na^+ 0.02 mol/L. Initial mefenacet 2.0 mg/L, black soil 0.5 g, kaolinite 0.5 g, humic acid 0.02 g.

Figure 4 also shows that the addition of Cu^{2+} has a small effect on the sorption of mefenacet on the black soil and kaolinite. The distribution coefficient was almost unchanged. However, the addition of Cu^{2+} decreased the sorption coefficient (K_d) of mefenacet on humic acid (the K_d values decreased by 20% at the pH range of 2.5–4.0). The addition of Ag^+ always enhanced the sorption of mefenacet on the three sorbents, especially for pH 2.0–6.0; the K_d value for the three sorbents in the presence of Ag^+ was 2–3 times higher than that without Ag^+ . It should be noted that the sorption of mefenacet on the black soil was decreased gradually when the pH value was increased, and the K_d value in the presence or absence of Ag^+ exhibited the same trends. However, the sorption of mefenacet on kaolinite and humic acid in the presence of Ag^+ was increased with the increase of pH in certain ranges, and then started to show a declining trend. It is very interesting to note that the turning point was approximately the respective natural pH of the two sorbents, i.e., about 8.7 for kaolinite and 3.4 for humic acid. The possible causation for this observation might be explained as follows. When the pH value of the solution was lower than the natural pH of the sorbent, many H^+ would be present on the sorbent surface, and ion-exchange reactions between metal and H^+ would occur easily, which would result in adsorption of the metal on the sorbent. Combined with the stronger interaction between Ag^+ and mefenacet referred to above, the addition of Ag^+ directly resulted in the enhancement of mefenacet sorption. But it did not show a similar observation for the black soil. The exact mechanisms need to be further studied.

In the actual environment, the presence of Cu^{2+} or Ag^+ would decrease the pH value of the soil because of hydrolysis, which might result in the increase of the mefenacet sorption on the soil. Generally, herbicides cannot be biodegraded before desorption from soils (Zhang et al., 2001a). Therefore, mefenacet would be retained for a long period and accumulated gradually in soil polluted by heavy metals, which might lead to unexpected environmental impacts. Through adjusting the pH to neutral, the sorption of mefenacet can be decreased, by which could enhance

the degradation potential of mefenacet by bacteria.

2.3 Effect of mefenacet on the sorption of Cu^{2+} and Ag^+

The sorption of heavy metals on the sorbents at different concentrations of mefenacet was studied and the results are shown in Table 5. It was found that the sorption amounts of Cu^{2+} or Ag^+ on the three sorbents were relatively constant when the initial concentration of mefenacet ranged from 0.1 to 0.2 mg/L, and the relative standard deviation was less than 10%. The results indicate that mefenacet had little effect on the sorption of Cu^{2+} or Ag^+ on the tested sorbents. Such a conclusion is also illustrated in Fig. 5 with nearly superposed data points when investigating the effects of pH on the sorption of Cu^{2+} and Ag^+ on different sorbents. Possible causation was attributed to the strong sorption capacity of the tested sorbents for Cu^{2+} and Ag^+ and a concentration of mefenacet too low to cause an obvious effect.

In addition, it was observed that the sorption of Cu^{2+} and Ag^+ on the sorbents increased with the increase of pH until saturation was reached (Fig. 5). The same phenomenon was reported by Wei et al. (2000). Under acidic conditions, H^+ might compete with heavy metals for sorption sites on the sorbent surface and thus restrain the sorption of metals. The competition from H^+ became weakened with increasing pH. Under basic conditions, the OH^- potentially induced the metal cations to deposit, which indirectly resulted in the increase of the total sorption amount of the heavy metals.

3 Conclusions

The presence of Cu^{2+} had small effects on the sorption of mefenacet on the black soil and kaolinite, but significantly decreased the sorption of mefenacet on humic acid. However, Ag^+ as a “soft” cation increased the sorption of mefenacet on soil and its components significantly. The sorption of mefenacet on soil with or without the two metals was generally decreased with increasing pH. In the practical environment, the presence of Cu^{2+} and Ag^+ would decrease the pH value of the soils through

Table 5 Sorption of heavy metals at different concentrations of mefenacet

Sorbent	Initial concentration of heavy metals	Initial concentration of mefenacet (mg/L)	pH value of equilibrium solution	Sorption amount of heavy metals (mg/L)
Black soil	0	0.1–2.0	5.60 ± 0.20	–
	Cu10	0.1–2.0	5.60 ± 0.20	394 ± 10
	Cu50	0.1–2.0	5.60 ± 0.20	1062 ± 29
	Ag10	0.1–2.0	5.60 ± 0.20	306 ± 9
	Ag50	0.1–2.0	5.60 ± 0.20	1062 ± 29
Kaolinite	0	0.1–2.0	8.70 ± 0.10	–
	Cu10	0.1–2.0	8.70 ± 0.10	394 ± 2
	Cu50	0.1–2.0	8.70 ± 0.10	1989 ± 14
	Ag10	0.1–2.0	8.70 ± 0.10	131 ± 7
	Ag50	0.1–2.0	8.70 ± 0.10	308 ± 34
Humic acid	0	0.1–2.0	3.40 ± 0.10	–
	Cu10	0.1–2.0	3.40 ± 0.10	8377 ± 102
	Cu50	0.1–2.0	3.40 ± 0.10	35511 ± 1378
	Ag10	0.1–2.0	3.40 ± 0.10	3779 ± 104
	Ag50	0.1–2.0	3.40 ± 0.10	10025 ± 458

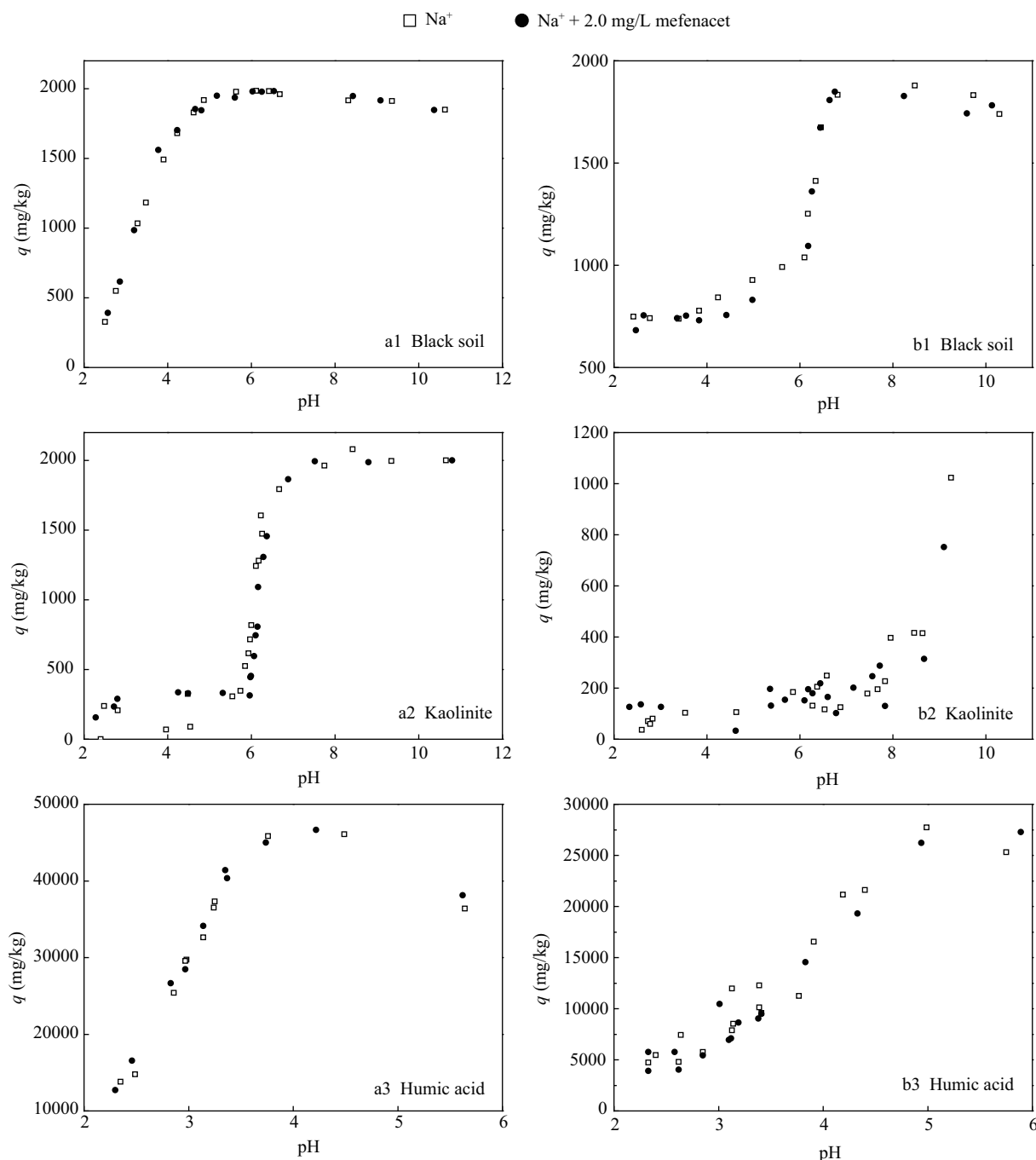


Fig. 5 Effects of pH on the sorption of Cu^{2+} (a) and Ag^{+} (b) with and without mefenacet. Na^{+} 0.02 mol/L, initial Cu^{2+} 50 mg/L, initial Ag^{+} 50 mg/L, black soil 0.5 g, kaolinite 0.5 g, humic acid 0.02 g.

hydrolysis, which might increase the sorption of mefenacet on soils. The present study showed that increasing pH could decrease the sorption of mefenacet on soils, thereby, adjusting the pH value to neutral (pH 7.0) is probably a good way for the inhibition or desorption of mefenacet on/from soils. In addition, the presence of mefenacet had insignificant effects on the sorption of Cu^{2+} and Ag^{+} on soil and its components and the increase of pH could increase the sorption of the metal ions on the soils.

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