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Cadmium adsorption in montmorillonite as affected by glyphosate

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Abstract: Behaviors of soil heavy metals are often affected by coexisting herbicides due to their physical and chemical interaction. Effect of glyphosate, an herbicide containing -PO_3^{2-} and -COOH groups, on cadmium adsorption in montmorillonite was studied in detail. The results showed that the cadmium adsorption quantity in montmorillonite increased with increasing soil solution pH and cadmium concentration as usual, but decreased with glyphosate, which is due to the formation of a low affinity complex of Cd and glyphosate and decreasing solution pH induced by glyphosate addition. When the equilibrium solution pH was below 6.7, glyphosate has little effect on cadmium adsorption, but when the equilibrium solution pH was above 6.7, glyphosate significantly decreased cadmium adsorption quantity in montmorillonite. In addition, the adding order of Cd and glyphosate also influenced Cd adsorption quantity in montmorillonite.

Keywords: cadmium; interaction; glyphosate; montmorillonite

Introduction

Cadmium is a toxic heavy metal, and its environmental exposure or soil contamination will cause diseases of human beings and animals. At the meantime, cadmium can restrain plant growth and reduce enzyme activities. It was estimated that the area of cadmium contaminated agricultural soil in China reached to 1.3×10^4 hm^2 in 1988. New data indicated that the area largely increased in recent years.

Generally speaking, soil pollution is caused by over one pollutant in most cases, which is also called as combined soil pollution. More and more scientists concerned on this topic, but mainly on interaction of heavy metals (Abdel-Sabour, 1998; Chen, 1996; 1998; Zhou, 2002a; 2002b). Studies of interaction of metals and organic pollutants are not yet so much. A series of researches on influence of *o*-phenylenediamine and pyrocatechol on copper and cadmium behaviors in soils were finished in our laboratory recently (Wang, 2003; Zhou, 2003).

Glyphosate is a wide-used herbicide in China and even through the world (Carlisle, 1998). The half-lives of this herbicide varied from weeks to years, depending on soil types, microorganism kinds and quantities. In some cases, plant and microorganism cannot use glyphosate directly (Hensley, 1978).

Glyphosate contains -PO_3^{2-} and -COOH groups, which can easily react with Cu, Cd and other metal ions to form complexes (Morillo, 1997; 2000). According to the recommended field application rates from 0.34 to 1.12 kg active ingredient (AI)/hm^2 for control of annual weeds, and 1.12 to 4.48 kgAI/hm^2 for perennials, 1 kg/hm^2 of a pesticide will give a concentration in the top 13 cm of a field of roughly 0.45 mg/kg (Carlisle, 1998). Thus, the highest application rate should give rise to a soil concentration of roughly 2 mg/kg. This does not take into account soil adsorption, which may concentrate glyphosate in the top of the soil to much higher levels. So, 0.01—0.05 mmol/L glyphosate were used in our experiments and its influence on cadmium adsorption in montmorillonite was investigated.

1 Materials and methods

1.1 Cadmium adsorption isotherms in montmorillonite as affected by glyphosate

0.1 g montmorillonite was weighed in each of 24 centrifuge tubes. The tubes were divided into 3 groups and each group consisted of 8 tubes. In each group, 5 ml 0.01 mol/L $NaNO_3$ solution containing different concentration of Cd was added in different tubes and set up a series of Cd concentration. And then, 5 ml 0.01 mol/L $NaNO_3$ solution without glyphosate was added in each tube in the first group, 5 ml 0.01 mol/L $NaNO_3$ solution containing 0.05 mmol/L glyphosate was added in each tube in the second group, and 5 ml 0.01 mol/L $NaNO_3$ solution containing 0.25 mmol/L glyphosate was added in each tube in the third group. 15 ml 0.01 mol/L $NaNO_3$ solution was then supplied in each tube. The final solution volume in each tube was 25 ml and Cd concentration series consisted of 0, 1.0, 2.0, 3.0, 4.0, 5.0 8.0, and 10 mg/L in each group. Glyphosate concentration was 0, 0.01 and 0.05 mmol/L in the first, the second and the third groups, respectively. Each treatment was run in replicate.

1.2 Effect of pH on cadmium adsorption in montmorillonite

0.1 g montmorillonite was weighed in each of 24 centrifuge tubes. The tubes were divided into 3 groups and each group consisted of 8 tubes. In each tube, 5 ml 0.01 mol/L $NaNO_3$ solution containing 0.05 mmol/L Cd was added at first. And then, 5 ml 0.01 mol/L $NaNO_3$ solutions containing 0, 0.05 and 0.25 mmol/L glyphosate were added in each tube of the first, the second and the third groups, respectively. In following, different volume of 0.01 mol/L NaOH or HCl solution was added in different tube to adjust solution pH varying from 3 to 9 in each group. After that, 0.01 mol/L $NaNO_3$ solution was supplied and the final solution volume in each tube was 25 ml. The final Cd concentration was 0.01 mmol/L in each tube, and the glyphosate concentration was 0, 0.01 and 0.05 mmol/L in the first, the second and the third groups, respectively.

1.3 Effect of glyphosate on cadmium adsorption in

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montmorillonite in different adding order

Cadmium-glyphosate-montmorillonite: 0.1 g montmorillonite was weighed in each tube. 100 ml 0.01 mol/L $NaNO_3$ solution containing 0.05 mmol/L Cd^{2+} and 0.05 mmol/L glyphosate was thoroughly mixed and stayed for 2 h for chemical equilibrium. And then, 5 ml above solution was added in each centrifuge tube containing 0.1 g montmorillonite. Different volume of 0.01 mol/L HCl or NaOH was added in different tube to adjust the solution pH varying from 3 to 9. The final solution volume was 25 ml by supplying 0.01 mol/L $NaNO_3$ solution, and the concentrations of both Cd and glyphosate in each tube were 0.01 mmol/L.

Cadmium-montmori-llonite-glyphosate: 0.1 g montmorillonite was weighed in each tube. And then, 5 ml 0.1 mol/L $NaNO_3$ solution containing 0.05 mmol/L cadmium was added in each tube, different volumes of 0.01 mol/L HCl or NaOH were added in different tube to adjust solution pH varying from 3 to 9, and 0.1 mol/L $NaNO_3$ was then supplied to give the solution volume to be 20 ml. These centrifuge tubes were continuously shaken for 2 h at 25℃. After that, 5 ml 0.01 mol/L $NaNO_3$ solution containing 0.05 mmol/L glyphosate was added in each tube. The final solution volume was 25 ml, and the concentrations of both Cd and glyphosate in each tube were 0.01 mmol/L.

Glyphosate-montmorillonite-cadmium: 0.1 g montmorillonite was weighed in each tube. And then, 5 ml 0.01 mol/L $NaNO_3$ solution containing 0.05 mmol/L glyphosate was added in each tube, different volume of 0.01 mol/L HCl or NaOH was added to adjust solution pH varying from 3 to 9, and 0.01 mol/L $NaNO_3$ was then supplied to give the solution volume to be 20 ml. These centrifuge tubes were shaken for 2 h at 25℃. After that, 5 ml 0.01 mol/L $NaNO_3$ solution containing 0.05 mmol/L Cd was added in each tube. The final solution volume was 25 ml and the concentrations of both Cd and glyphosate in each tube were 0.01 mmol/L.

All centrifuge tubes were continuously shaken for 2 h at 25℃, and then centrifuged and filtrated through a filtrate film. The Cd concentration in the centrifuged solution was determined by AAS. All solution pH after equilibrium were determined by a pH meter with a combined pH electrode.

2 Results and discussion

2.1 Adsorption isotherms of cadmium in montmorillonite

Fig. 1 shows the adsorption isotherms of cadmium in montmorillonite in the absence and presence of glyphosate. It is found that cadmium adsorption quantity in montmorillonite obviously decreased when glyphosate was presented in the equilibrium solution. Moreover, the more the glyphosate presented, the lower the cadmium adsorption in montmorillonite.

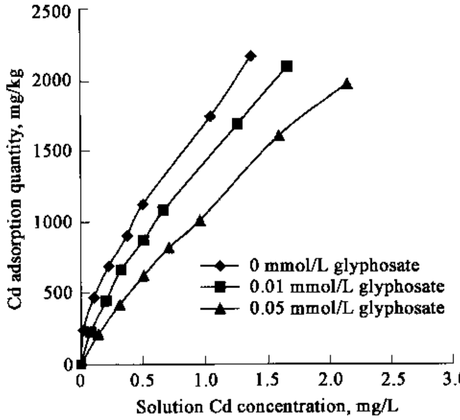

Fig. 1 Cadmium adsorption isotherms in montmorillonite in the absence and presence of glyphosate

The adsorption isotherms of Cd were simulated using Freundlich equation, and the results showed a very good correlation between Cd adsorption quantity and solution Cd concentration. The simulation equations are shown in Table 1.

Table 1 Simulation of cadmium adsorption isotherms in montmorillonite in the absence and presence of glyphosate

Glyphosate conc., mmol/L	Simulation equations	Correlation coefficient
0	$Q = 1640.2\ C^{0.519}$	$R^2 = 0.9850$
0.01	$Q = 1448.1 C^{0.725}$	$R^2 = 0.9992$
0.05	$Q = 1077.2\ C^{0.819}$	$R^2 = 0.9994$

Notes: *Q*. cadmium adsorption quantity in montmorillonite, mg/kg; *C*. cadmium concentration in equilibrium solution, mg/L

Glyphosate is a weakly acid. When it was added in the equilibrium solution, it decreased solution pH, which is clearly shown in Table 2. Morillo *et al*. (Morillo, 2002) studied Cu adsorption in soil in the absence and presence of several glyphosate concentrations with uncontrolled equilibrium pH. A strong decrease in Cu adsorption was also observed as the concentration of glyphosate increased.

As shown in Table 2, when glyphosate was added, equilibrium solution pHs in the second and third groups decreased about 0.58 and 1.10 unit in average, respectively. The higher the initial glyphosate concentration, the more acidic the equilibrium become, creating a more protonated montmorillonite surface, and hence more positive, making adsorption of Cd^{2+} species more difficult. Moreover, at lower pH, the protons in solution compete with cadmium for the adsorption sites(Zhou, 2003).

2.2 Effect of pH on Cd adsorption in montmorillonite

In order to understand the interaction mechanism of glyphosate and Cd in montmorillonite, pH effect on Cd adsorption in montmorillonite was studied in the absence and

Table 2 Change of solution pH in the absence and presence of glyphosate

Gly. con., mmol/L	pH Cd concentration, mg/L 0	1	2	3	4	5	8	10
0	8.65 ± 0.16	8.31 ± 0.02	7.83 ± 0.04	7.60 ± 0.07	7.54 ± 0.03	7.38 ± 0.04	7.28 ± 0.03	7.26 ± 0.03
0.01	8.50 ± 0.18	7.25 ± 0.04	7.11 ± 0.01	7.02 ± 0.01	6.96 ± 0.02	6.89 ± 0.01	6.78 ± 0.01	6.72 ± 0.02
0.05	8.56 ± 0.06	6.61 ± 0.04	6.53 ± 0.02	6.49 ± 0.04	6.39 ± 0.05	6.32 ± 0.00	6.13 ± 0.01	6.04 ± 0.01

presence of glyphosate. The results are shown in Fig.2. It is interesting to observe that solution pH affected Cd adsorption quantity, and glyphosate did not affect it at pH < 6.7. However, when solution pH was above 6.7, cadmium adsorption quantity was significantly decreased in the presence of glyphosate compared with that in the absence of glyphosate. It means that glyphosate affected Cd adsorption quantity in montmorillonite at high pH.

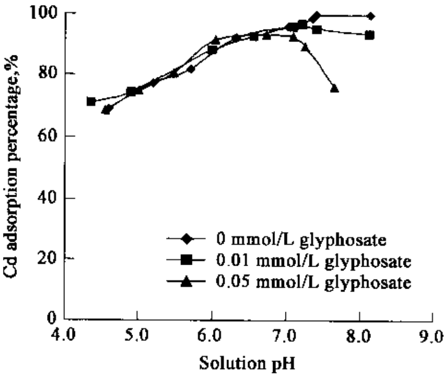

Fig.2 Dependence of cadmium adsorption percentage on pH in the absence and presence of glyphosate

Cadmium can react with glyphosate to form complexes. But, glyphosate existed in solution in several different speciations, and varied with solution pH. Fig.3 shows the speciation of solution glyphosate with pH. At pH < 6, glyphosate existed in solution mainly as H_3G and H_2G^-; while at pH > 6.0, glyphosate existed in solution mainly as HG^{2-} and G^{3-}. These glyphosate speciations reacted with Cd^{2+} to form complexes, and the complexation constants increase in the order of H_3G < H_2G^- < HG^{2-} < G^{3-} (Undabeytia, 2002).

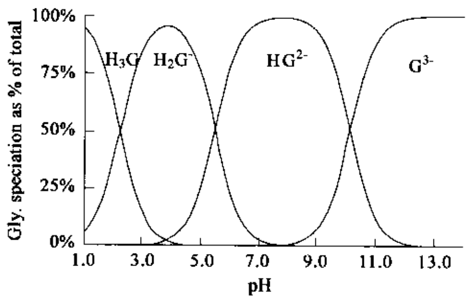

Fig.3 Dependence of glyphosate speciation as % of total on pH

Because the presence of glyphosate did not affect Cd adsorption in montmorillonite at pH < 6.7, the complexes of Cd and H_3G or H_2G^- were difficult to form or the formed complex had almost the same affinity as Cd^{2+} to adsorb in montmorillonite; when pH was above 6.7, cadmium adsorption quantity in montmorillonite decreased in the presence of glyphosate, suggesting that the negatively charged complexes of Cd and HG^{2-} or G^{3-}, formed in the pH, did not adsorb or had much less affinity to adsorb in montmorillonite than Cd^{2+}.

The Cd^{2+} ion concentration in the equilibrium solution was analyzed by a Cd^{2+} ion selective electrode. It decreased with increasing solution pH, as shown in Fig.4, which is ascribed that more Cd^{2+} was adsorbed in montmorillonite with increasing solution pH and correspondingly reduced solution Cd^{2+} concentration; meanwhile, glyphosate reacted with solution Cd^{2+} to form complexes and also reduced Cd^{2+} concentration in solution. It has previously reported that the concentration of free Cu^{2+} in solution was drastically reduced in the presence of glyphosate, due to the formation of Cu-glyphosate.

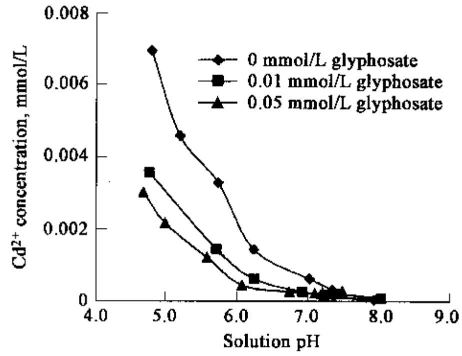

Fig.4 Solution Cd^{2+} concentrations in the absence and presence of glyphosate

Glass(Glass, 1984) studied the metal complex formation by glyphosate through differential pulse polarography. Two Cd-glyphosate complexes with $E_{1/2}$ of −0.72 and −0.94 V were determined. It was concluded that when glyphosate was added into cadmium solution, some new complexes were produced, and decreased the solution Cd^{2+} ion concentration. Although the Cd^{2+} ion concentration decreased when glyphosate was added(Fig.4), the cadmium adsorption quantity in the montmorillonite did not decrease when the equilibrium solution pH < 6.7(Fig.2). It showed that Cd-glyphosate almost has the same affinity with cadmium to montmorillonite in this pH range.

Fig. 5 shows the dependence of Cd speciations on solution pH. The initial concentrations of cadmium and glyphosate were 0.01 mmol/L and 0.05 mmol/L, respectively. It is observed that Cd adsorption quantity was smaller at pH < 6 or > 7 than that at pH ranging from 6 to 7. The concentration of Cd^{2+} decreased with increasing pH. However, concentration of Cd-glyphosate complexes increased with increasing solution pH, suggesting that Cd-glyphosate complexes were easily formed at high pH and at the meantime did not adsorb in montmorillonite.

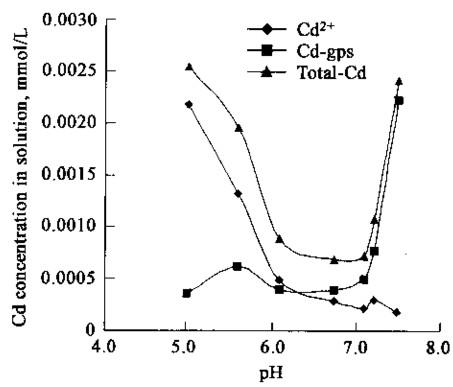

Fig.5 Different Cd speciation in equilibrium solution in the absence and presence of glyphosate

2.3 Effect of glyphosate on cadmium adsorption in montmorillonite in different adding order

Fig. 6 shows the effect of glyphosate on cadmium adsorption in montmorillonite in different adding order. It is very clear that Cd adsorption quantities in montmorillonite were different among different adding orders, although the trend was similar as Cd adsorption quantity increased with increasing pH at first and then decreased. Among the three different adding orders, adding glyphosate in montmorillonite solution at first and then adding cadmium solution resulted in a lowest Cd adsorption quantity. It suggested that glyphosate adsorption in montmorillonite retarded cadmium adsorption, possibly because adsorbed glyphosate in montmorillonite occupied adsorption sites of cadmium. Allen and Vivek (Allen, 1995) studied cadmium adsorption in hematite in the presence of humic materials. Humic acid binds directly on the oxide surface, and the competition and site blockage also decreased Cd adsorption.

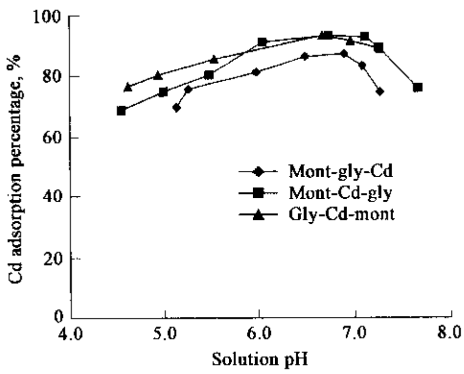

Fig. 6 Effect of solution pH on cadmium adsorption percentage in montmorillonite in different adding order

When cadmium was added in equilibrium solution at first and then equilibrated the mineral solution with glyphosate, cadmium adsorption quantity was much higher than the above order. But, when the solution of cadmium and glyphosate was mixed at first, and then was added in mineral solution, the adsorption quantity of cadmium was the highest at pH < 6.0 and did not have difference at pH > 6.0. It suggested that the presence of Cd-glyphosate complexes increased Cd adsorption in montmorillonite.

3 Conclusions

Cadmium adsorption isotherms in montmorillonite were satisfactorily simulated with Freundlich equations, and cadmium adsorption quantity in montmorillonite increased with increasing solution pH.

The presence of glyphosate decreased cadmium adsorption quantity in montmorillonite, mainly due to decreasing solution pH and at the meantime the formation of less affinity complexes of Cd and glyphosate.

Different adding order of montmorillonite, Cd and glyphosate resulted in various Cd adsorption quantities in montmorillonite.

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