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Effect of 2,4-Dichlorophenoxyacetic Acid on Adsorption and Release of Copper on Montmorillonite

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The soil ecosystem receives most of pesticides utilized for plant protection which produces many ecological problems. Heavy metal ions are supposed to be very toxic and carcinogenic in nature. Copper is an essential element for plants and animals, however, an increase in its levels in soils can inhibit organic matter biodegradation. Some animals are especially sensitive to copper (Baker,1990).

The environmental fate of pesticides and heavy metals is mainly determined by their capacity to be sorbed onto soil constituents. Organic matter and clay minerals are the most important components influencing pesticides and metals adsorption by soils. The potential hazard of metal and its mobility in soils depend mainly on the adsorption-desorption processes that can take place on the colloidal components. From the view point of adsorption, clay minerals are the predominant inorganic components in soils (Christensen, 1989). They are abundant and have high specific surface area, high chemical and mechanical stability, and a variety of surface and structural properties. The addition of pesticides and organic fertilizers can affect copper adsorption by the clay fraction for several reasons, e.g., competition with the metal, chelation in solution, etc. (Puls et al., 1991; Morillo et al., 1997).

Although many studies have been published on the adsorption of pesticides and heavy metals independently, little-attention has been given to the phenomena which take place when both are present together (Morillo and Maqueda, 1992; Undabeytia et al.,1996).

The objective of this study was to characterize copper adsorption-desorption on a clay mineral in the presence and absence of the pesticide 2,4-dichlorophenoxyacetic acid (2,4-D).

MATERIALS AND METHODS

The montmorillonite (97-98% purity) "FM0" sample used in this study was obtained from Guangzhou, China. Its surface area was 56.4 m^2/g, and the structural formula determined by chemical analysis was $[Na_{0.106}K_{0.089}Ca_{0.457}Mg_{0.067}][Fe^{2+}_{0.002}Fe^{3+}_{0.037}Mg_{0.347}Al_{1.656}][Si_{3.749}Al_{0.206}]O_{10}(OH)_2$

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•nH_2O. Its cation exchange capacity (CEC) was 84.4 mmol/100g, according to the analysis method developed by Theng (1997). The Walkley-Black method was used to determine the organic matter content (0. 2679g/g) (Bekbolet et al., 1999). Moisture content (8.234%) and particle size (80 mesh) analyses were performed according to Bekbolet et al., (1999). 2,4-D (99% purity) was supplied by Jingjiang pesticide factory in China. All other chemicals used herein were of analytical grade or better. The adsorbate was Cu(II) ($CuCl_2.2H_2O$).

Triplicate adsorption experiments were done in 50 ml polypropylene tubes by mixing 0.1g of montmorillonite with 20 ml of 0.01 M NaCl solutions containing 2,4-D (0.2, 0.4, 0.8, 1.0 mM) and copper (25, 50, 100, 200, 400 μM). The samples were shaken for 24 h at 25±1℃ and the shaking frequency was 110rpm. Copper and 2,4-D adsorbed were calculated from the differences between the initial and equilibrium concentrations. The adsorption isotherms were obtained by plotting the amounts of Cu adsorbed C_s (μmol g^{-1}) versus the equilibrium concentration C_e (μmol L^{-1}).

The concentrations of Cu (II) and the inorganic cations Ca^{2+} and Mg^{2+} released during 2,4-D and / or Cu adsorption were determined by atomic absorption spectrometry (AAS) (Hitachi model Z-8100, Japan). The pH was measured by a pH meter (Microcomputer pH/mv/TEMP Meter 6171, made in China for JENCO U.S.A.).

The successive adsorptions (the montmorillonit previously treated by 2,4-D) were done by mixing 0.1g of montmorillonite with 20 ml of solutions containing different concentrations of 2,4-D. After reaching equilibrium for 24 h at 25±1℃, the samples were centrifuged at 14000rmp for 15min, the supernatant was removed. The montmorillonite samples were then washed twice with distilled water. Various concentrations of Cu(II) solution under the same conditions as previously were then added for the successive adsorptions.

Desorption experiments were conducted after reaching equilibrium adsorption. Half of the supernatant was removed after centrifugation and replaced with 10 mL 0.01 M NaCl, allowing equilibrium for an additional 24 h period. Subsequently the desorption continued as in the adsorption experiment. This process was repeated twice more. The time-dependence (kinetic) studies of the adsorption and desorption experiments showed that the time of 24 h was long enough to reach the equilibrium. The desorption graphics of Cu were obtained by plotting the amount of Cu that remained adsorbed (μmol g^{-1}) versus the final concentration (μmol L^{-1}) for all desorption processes.

RESULTS AND DISCUSSION

The adsorption isotherm of Cu (II) on montmorillonite in the absence of 2,4-D is shown in Figure 1.This isotherm corresponds to the L-type according to Giles et al. (1960). The shape of the isotherm shows that as sites are filled it becomes increasingly more difficult for adsorbate to find a vacant site (Maqueda et al.,

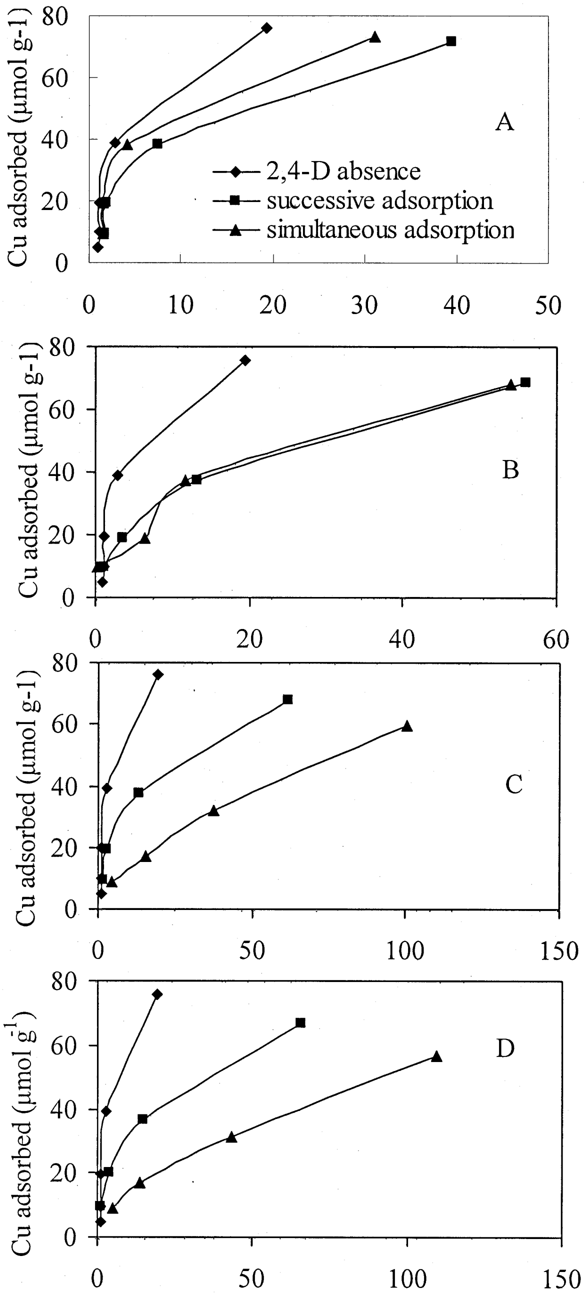

Figure 1. Isotherms of Cu (II) on montmorillonite from 2,4-D absence solutions, in comparison with successive and simultaneous Cu adsorption, at various 2,4-D concentrations: 0.2 (A), 0.4 (B), 0.8 (C) and 1.0 (D)mM.

1998). He. et al.(2001) reported that in Cu-montmorillonite, most of the Cu^{2+} ions replace the original metal ions in the interlayer or move into hexagonal cavities of Si-O sheet. A small fraction penetrates into the octahedral vacancies. This result indicates that there are three different occurrences of Cu^{2+} ions in montmorillonite: (1) entering into the interlayer; (2) adsorbing in the hexagonal cavities; and (3) penetrating into the octahedral vacancies. The first is attributed to the exchangeable adsorption, while the second and the third to the specific adsorption.

The concentrations of copper species in solution for the system of pH 6.5±0.1, estimated by using the equilibrium constants given by Lindsay (1979), are 91.6% Cu^{2+}, 5.39% $CuOH^+$, and 2.44% $CuCl^+$. Although copper adsorption possibly occurs principally through the Cu^{2+} species, the possibility of surface hydrolysis should be taken into account (Harsch and Doner, 1984).

From Figure 1 we can observe that copper adsorption decreases when the pesticide 2,4-D concentration increases. It is because that 2,4-D is an acidic pesticide, and with the increasing of 2,4-D concentrations the pHs of the system are lower (about 3). In such acidic system, Cu^{2+} is very difficult to be absorbed on the montmorillonite, and even easier to be desorbed from the montmorillonite. It suggests that pH of the system plays a significant role in the adsorption process. However, for the lowest copper concentration it seems to be independent of the pesticide 2,4-D concentration.

Freundlich isotherm model was applied for adsorption equilibrium data. The Freundlich isotherm is represented by the following equation:

$$\text{Log } C_s = \log K_f + n \log C_e$$

Where C_s is the amount of adsorbed Cu (μmol g^{-1}) and C_e the Cu concentration (μmol L^{-1}) in the equilibrium solution. K_f and n are constants characterizing the sorbate-sorbent system related to adsorption capacity and adsorption intensity, respectively. When log C_s is plotted against log C_e, a straight line with slope n and intercept log K_f is obtained. K_f reaches the value of C_s when equilibrium concentration C_e approaches to unity, thus can be considered as indicative parameter of the sorption strength. n indicates the rate of adsorption increase with solute concentration reflecting the non-linearity of the adsorption.

Langmuir isotherm model can also be used to explain the observed phenomena. The Langmuir equation is described as follows:

$$C_e / Q_e = 1 / (Q_0 b) + (C_e / Q_0)$$

Where C_e represents equilibrium concentration (μmol L^{-1}), Q_e is the amount of Cu (II) adsorbed at equilibrium (μmol g^{-1}). Q_0 and b represent Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot of C_e / Q_e vs C_e shows that the adsorption obeys the Langmiur model. Q_0 and b were determined from the slope and intercept of the Langmuir plot.

The correlation coefficients and adsorption constants of Freundlich and Langmuir

Table 1. Freundlich and Langmuir constants and their correlation coefficients for Cu (II) Adsorption on Montmorillonite in the absence and presence of 2,4-D.

2,4-D mM	K_f	n	r (Freundlich)	Q_0	b	r (Langmuir)
0.0	27.2	0.3817	0.992	16.695	0.367	0.975
0.2	14.46	0.4491	0.997	6.694	0.947	0.994
0.4	9.84	0.4949	0.997	7.215	0.7204	0.9928
0.8	9.54	0.4954	0.99	7.092	2.504	0.9964
1.0	9.45	0.4529	0.999	6.94	2.402	0.9908

Table 2. Freundlich and Langmuir Constants and their Correlation coefficients for Cu (II) Adsorption on Montmorillonite in the Absence and Presence of 2,4-D.

2,4-D mM	K_f	n	r (Freundlich)	Q_0	b	r (Langmuir)
0.0	27.2	0.3817	0.992	16.695	0.367	0.975
0.2	13.2	0.5454	0.9918	12.21	0.475	0.9934
0.4	9.165	0.4794	0.9947	7.299	0.698	0.9932
0.8	3.54	0.6057	0.9961	3.093	1.542	0.9954
1.0	3.42	0.5839	0.9992	1.204	5.144	0.991

Table 3. The pH values under various conditions in successive adsorption and simultaneous adsorption.

2,4-D+Cu^{2+}	Successive Adsorption pHs			Simultaneous Adsorption pHs		
(mM+μM)	A	B	C	A	B	C
0.2 + 50	3.89	5.78	6.51	3.41	5.71	6.49
0.2 + 100	4.13	5.87	6.59	3.51	5.76	6.57
0.2 + 200	4.39	6.06	6.81	3.63	5.98	6.79
0.2 + 400	4.62	6.12	6.87	3.43	5.72	6.72
0.4 + 50	3.69	5.71	6.45	3.37	5.66	6.41
0.4 + 100	3.96	5.79	6.56	3.39	5.68	6.46
0.4 + 200	4.18	5.98	6.61	3.49	5.9	6.55
0.4 + 400	4.34	6.03	6.68	3.53	5.95	6.64
0.8 + 50	3.52	5.69	6.41	3.33	5.65	6.35
0.8 + 100	3.48	5.67	6.37	3.31	5.64	6.29
0.8 + 200	3.41	5.59	6.31	3.29	5.61	6.25
0.8 + 400	3.37	5.57	6.27	3.25	5.54	6.21
1.0 + 50	3.34	5.52	6.17	3.12	5.3	6.12
1.0 + 100	3.29	5.46	6.04	3.11	5.26	5.92
1.0 + 200	3.25	5.39	5.94	3.1	5.23	5.87
1.0+ 400	3.21	4.87	5.59	3.08	4.42	5.54

Note: A: before adsorption; B: adsorption equilibrium; C: desorption equilibrium

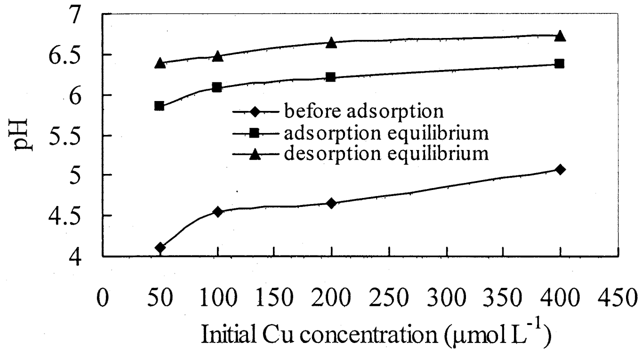

Figure 2. The pH of Cu solutions in the absence of 2,4-D under different conditions.

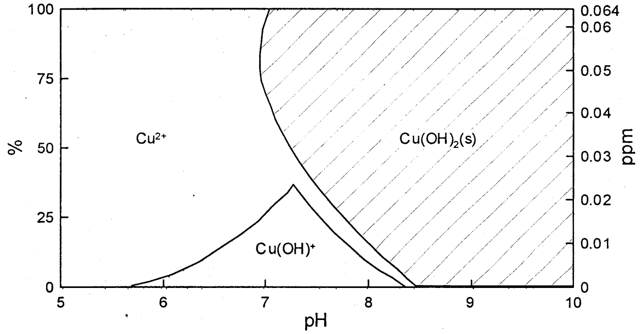

Figure 3. The various species of Cu under different pH in water.

isotherms for Cu (II) adsorption in the absence and presence of 2,4-D at different 2,4-D initial concentrations are shown in Tables 1 and 2. From figure 1 and Tables 1 and 2, it was observed that Cu adsorption was higher when the clay was previously treated with the pesticide 2,4-D than when both adsorbates were added simultaneously. This may be due to the fact that when both adsorbates were added simultaneously, the pHs of the system were lower than those of the successive adsorption systems (see Figure2 and Table 3).The higher 2,4-D concentrations, the lower the pHs of the solutions, so the adsorption of additional substance Cu^{2+} becomes more difficult.

Table 2 shows the Freundlich and Langmuir parameters for Cu adsorption isotherms when both the pesticide and copper are added simultaneously. It can be observed that the effect of the 2,4-D on Cu adsorption is reflected by the diminishing K_f values (from 27.2 to 3.42) as pesticide concentration increases. In this case the pesticide had a certain effect on Cu adsorption. The greatest Cu adsorption thus occurs in the adsorption of pesticide-free solutions. This may be due to the effect of pH of the equilibrium solutions. The pHs of the various

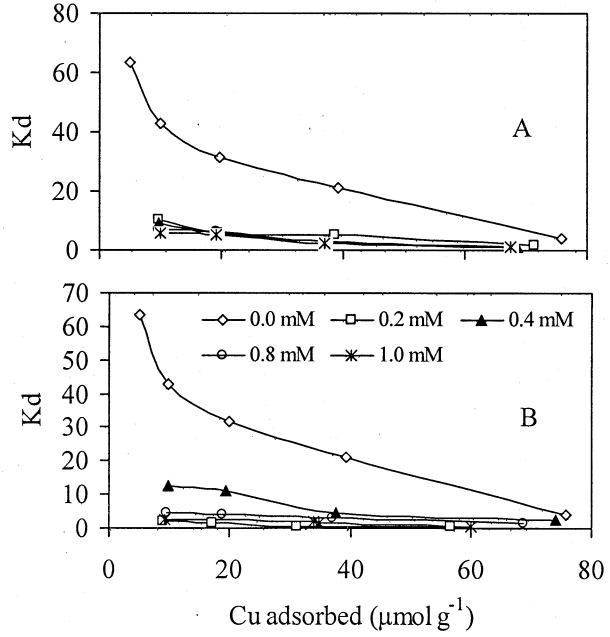

Figure 4. Cu (II) K_d values as function of the amount of Cu adsorbed in successive (A) and simultaneous (B) adsorption, at different 2,4-D concentrations.

conditions see Figure 2 and Table3:

From the Figure 2 and Table3, the pH values of both 2,4-D-free and successive adsorptions are 4.87-6.37 in the solutions of adsorption equilibrium. However, the pH of simultaneous adsorption is below 5.98 and decreased with increasing initial concentrations of 2,4-D and Cu (II), due to the hydrolysis of metals and proton release during adsorption. When the initial concentrations of Cu (II) and pesticide were 400 μmol L^{-1} and 1.0 mmol L^{-1} in simultaneous adsorption, respectively, the pH of the equilibrium solution can reduce to 4.42. From Figure 3, when the pH is 5-7, the there exists more Cu(II) (50-500μg/l) in the solution; when pH is more than 7, the complexes of Cu will increase in the solution (Liao 1992). Lee et al found that the percent adsorption of Co (II) increases with pH and that kaolinite has little affinity for the anionic complexes (Lee et al., 2002). Thus the maximum Cu adsorption in this study occurs when the 2,4-D is absent. When the 2,4-D and Cu are added simultaneously, the Cu adsorption is lowest due to the lower pH values of the solutions containing 2,4-D.

A useful parameter to evaluate the adorbant-adsorbate affinity is the distribution coefficient Kd, which is difined as

$$Kd = \frac{[\text{X-Clay}]}{[\text{X-solution}]}$$

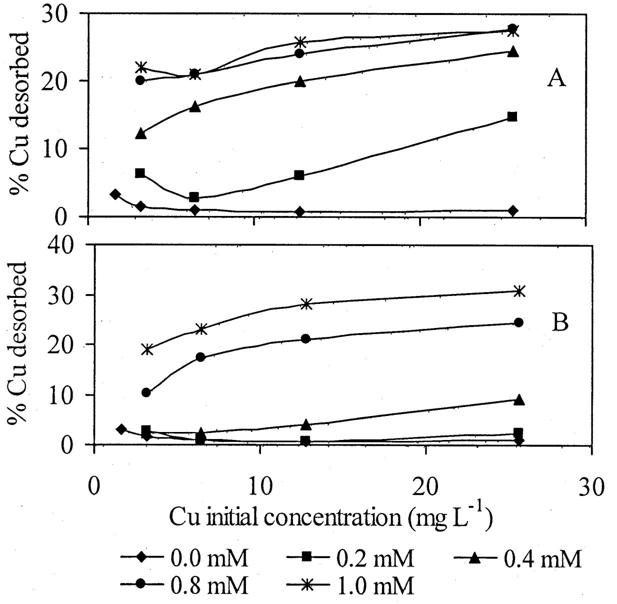

Figure 5. Percentages of Cu (II) desorbed versus the initial amounts of Cu used in successive (A) and simultaneous (B) adsorption, at different 2,4-D initial concentrations.

Where the numerator is the sorbate concentration adsorbed on the clay (μmol/l), and the denominator is the sorbate concentration in the equilibrium solution(μmol/l).

To calculate Kd for Cu, it was assumed that the Cu species in solution is in the form of Cu^{2+}, since its proportion of this species is more than 90% (Lindsay, 1979). Figure 4 shows the Kd values for Cu adsorption at different 2,4-D concentrations and different adsorption conditions. In all cases, it was found the Kd values increased with the decreasing amount of Cu^{2+} adsorpted, and Kd values decreased with increasing 2,4-D pesticide concentrations and Cu^{2+} loadings increase. This indicates that sites of high affinity play an important role in the condition at low surface coverage. From Figrue 4, it is observed that the Kd values of the successive adsorption are higher than those of the simultaneous adsorption and Kd values of 2,4-D-free adsorption are the highest. This is in agreement with the results obtained in Figure 1.

Figure 5 shows the percentage of copper desorbed versus the initial amount of copper used. The maximum percentage desorbed after three cycles of desorption is 30.1% of the Cu in simultaneous adsorption. In comparision with the 2,4-D-free desorption, the higher 2,4-Dconcentration and initial Cu^{2+} concentration, the higher desorption ratio, and the percentage desorbed of pesticide-free is lowest. This indicates that the increasing pesticide concentration in some way improves the metal desorption. From Figure 2 and Table 3, in all cases the final pH values of desorption equilibrium after three desorption cycles are 5.54-6.89. However, when the 2,4-D of higher concentration is present in the adsorption processes, the pHs of desorption equilibrium are slightly lower than those when the 2,4-D concentrations are lower or absent. At the same time, the desorption cycles involve centrifugation, removal of half of the volume of the supernatant, and addition of a corresponding volume of 10 mL of 0.01M NaCl, and thus the concentrations of Ca^{2+} and Mg^{2+} cations in suspension are reduced. A small increase in the magnitude of the surface potential (Undabeytia, 1997), due to a smaller sum of total concentrations of divalent cations, contributes to enhanced adsorption of Cu in desorption cycles.

In conclusion, the process of Cu adsorption and desorption on montmorillonite was affected largely by the pesticide 2,4-D. Cu adsorption was higher when the clay was previously treated with the pesticide 2,4-D of higher concentrations (0.8mM and 1.0mM) than when both adsorbates were added simultaneously, and the maxmium Cu adsorption occurs in the adsorption from pesticide-free solutions. Copper adsorption decreases when the pesticide 2,4-D concentration increases. The adsorption follows the Freudlich and Langmuir isotherm model.

The maximum percentage desorbed after three cycles of desorption is 30.1% of the Cu in simultaneous adsorption. The percentage desorbed was higher when the pesticide is present and increasing with pesticide concentration and metal loading. The percentage desorbed of pesticide-free is the lowest. This indicates that the pH of the solutions plays a significant role on the adsorption and desorption of Cu.

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