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Adsorption of Cu^{2+} on Montmorillonite as Affected by 2,4-Dichlorophenoxyacetic Acid (2,4-D)

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Heavy metals have long been recognized as ecotoxicological hazardous substances and their chronic toxicities and accumulation abilities in living organisms have been of great interest for many years. Heavy metals are introduced into the soils through natural phenomena and human activities, such as agricultural practices, transport, industrial activities and waste disposal. At the same time, the soil ecosystem must receive the pesticides utilized for plant protection, and indiscriminate and excessive use may produce many ecological problems. Thus combined pollution of heavy metals with pesticides increased. The fate of pesticides and heavy metals in soils is mainly determined by their capacities to be adsorbed onto soil constituents. Many studies have been published on the adsorption of pesticides and heavy metals independently (Saha et al. 2001; Undabeytia et al. 2002). Competitive adsorption among heavy metals and that of organic compounds and cosolutes of similar structure have also been widely studied (Saha et al. 2002; Xing and Pignatello 1997). Up to date, little attention has been given to the phenomena that take place when both pesticides and heavy metals are present together.

From the point of view of adsorption, clay minerals are the most important inorganic components in soils due to their abundance, high specific area and exchange capacity. Montmorillonite is an expandable 2:1 type clay mineral with one alumina octahedral sheet (gibbsite sheet) sandwiched between two silica tetrahedral sheets (siloxane sheets). 2,4-dichlorophenoxyacetic acid (2,4-D) is extensively used in agriculture to control many types of weeds. 2,4-D has a p*K*a of 2.8 and is mostly in anionic form at the pH range of most agricultural soils. 2,4-D can be carcinogenic in animals and human beings (Hoar et al. 1986), therefore attention has increasingly been paid to its adverse effects on the environmental quality and ecosystem health. The aim of this study is to examine possible interaction of copper with montmorillonite in the presence of the herbicide 2,4-D. The effect of 2,4-D on copper adsorption on montmorillonite was investigated when both 2,4-D and copper were adsorbed simultaneously and successively. Moreover, the effect of 2,4-D on copper adsorption kinetics was also investigated.

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MATERIALS AND METHODS

2,4-D was purchased from Sigma-Aldrich Inc. with a reported purity > 98%. Montmorillonite used in this study was obtained from Beijing Youlichuangjia Science and Technology Development Company (China). Cation exchange capacity (CEC) was determined by the method developed by Theng et al. (1997). The CEC of montmorillonite was 89.35 meq $(100\ g)^{-1}$. Specific surface area was obtained via Brunauner-Emmett-Teller (BET)–N_2 adsorption method (Brunauer et al. 1938) using a micromeritics Flowsorb II surface area analyzer. The determined surface area of montmorillonite was 82.56 $m^2\ g^{-1}$.

Duplicate adsorption experiments were done by mixing 100 mg montmorillonite with 20 ml 0.01 M $NaNO_3$ solutions, containing various concentrations of Cu^{2+} (0.078-0.78 mM). The Cu^{2+} was added as nitrate. The pH of adsorption system was adjusted to 5.0±0.2 with either HNO_3 or NaOH. The samples were shaken for 24 h at 25±1℃, then centrifuged for 30 min at 4000× g and filtered through a 0.45 μm of cellulose nitrate membrane. The filtrates were measured by inductively coupled plasma mass spectrometry (ICP-MS, PQ3, Fisons Instruments, UK) to determine the concentrations of Cu^{2+}. The amounts of adsorbed Cu^{2+} were calculated by the difference between the amount added initially and that remained in the equilibrium solution after the adsorption. The effect of 2,4-D on Cu^{2+} adsorption was performed under the established adsorption conditions. Various concentrations of Cu^{2+} (0.078-0.78 mM) and 2,4-D (0-2.0 mM) were added to the adsorption system simultaneously. In order to investigate the effect of 2,4-D addition sequence on Cu^{2+} adsorption, several portions of 20 ml 0.01 M $NaNO_3$ solutions containing 0.5 mM 2,4-D were added to 0.100 g montmorillonite and shaken for 24 h. After reaching equilibrium, the suspensions were centrifuged, the supernatant was removed, and the solid samples were washed twice with distilled water and treated again with Cu^{2+} under the same conditions as previously. Another successive adsorption was also performed. Various concentrations of Cu^{2+} were added to 0.100 g montmorillonite, then shaken 24h to reach equilibrium and treated again with 0.5 mM 2,4-D for another 24 h. All the above adsorption isotherms were performed at pH 5.0±0.2. The effect of pH on Cu^{2+} $(1\times10^{-4}\ mol\ L^{-1})$ adsorption in the absence and presence of 0.5 mM 2,4-D was processed under the pH values of 2-7, adjusted by either 0.10 M HNO_3 or NaOH. The sorption kinetic experiments were performed with initial Cu^{2+} concentrations of 0.156 mM at pH 5.0±0.2, and a concentration of 0.5 mM 2,4-D was added simultaneously. Samples were taken from the batch treatments over the period of 12 min to 48 h.

RESULTS AND DISCUSSION

Figure 1 shows the adsorption isotherms of Cu^{2+} by montmorillonite at equilibrium pH 5.0±0.2, both in the absence of 2,4-D and in the presence of different 2,4-D concentrations in the initial solution. As can be seen from the

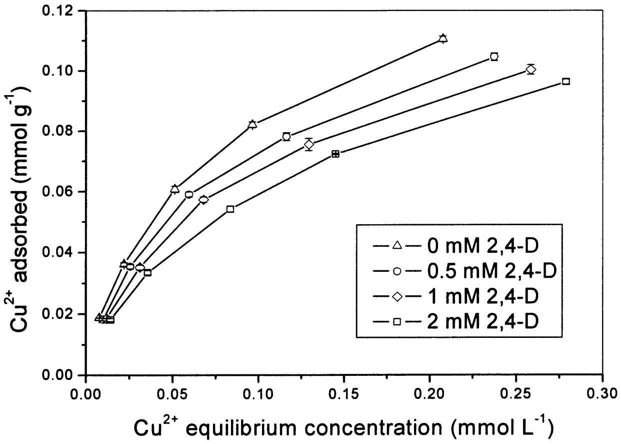

Figure 1. Adsorption isotherms of Cu^{2+} on montmorillonite at various 2,4-D concentrations. Error bars represent standard deviation of parallel measurements.

figure, when 2,4-D was present in solution together with Cu^{2+}, the adsorption of Cu^{2+} was lower than in the case of Cu^{2+} alone, the adsorption of Cu^{2+} decreased as the concentration of 2,4-D increased. In the study of glyphosate (GPS) adsorption together with Cu^{2+}, Maqueda et al. (1998a) attributed the decreased adsorption to competition for adsorption sites and formation of complexes with lower tendency to be adsorbed. However, adsorption of 2,4-D on montmrillonite (negatively charged surface) is not preferred compared with that of Cu^{2+}. Thus in our study the former mechanism cannot be dominant. 2,4-D is an acidic herbicide with a p*K*a of 2.8. At the studied pH 5.0±0.2, nearly 100% of 2,4-D is in anionic form, which can form complex with Cu^{2+} via $-COO^-$ group. The complex, however, tends not to be adsorbed by montmorillonite to the same extent as free Cu^{2+}. Therefore, the formation of complex with 2,4-D via $-COO^-$ group may explain the decreased adsorption of Cu^{2+} on montmorillonite in the presence of 2,4-D. The research of Dendrinou-Samara et al. (2001) and the reference therein demonstrated the formation of complex between Cu^{2+} with 2,4-D.

Table 1. Adjustable parameters and correlation coefficients of Freundlich and Langmuir equations for Cu^{2+} adsorption on montmorillonite in the absence and presence of 2, 4-D.

2,4-D concentration (mM)	K_f ($L\ g^{-1}$)	n	R^2	k_2 ($mmol\ g^{-1}$)	k_1 ($L\ mmol^{-1}$)	R^2
0	0.243	0.485	0.99	0.145	14.5	0.99
1	0.214	0.485	0.98	0.135	13.1	0.99
1.5	0.200	0.489	0.99	0.132	11.3	0.98
2	0.190	0.517	0.99	0.130	8.75	0.99

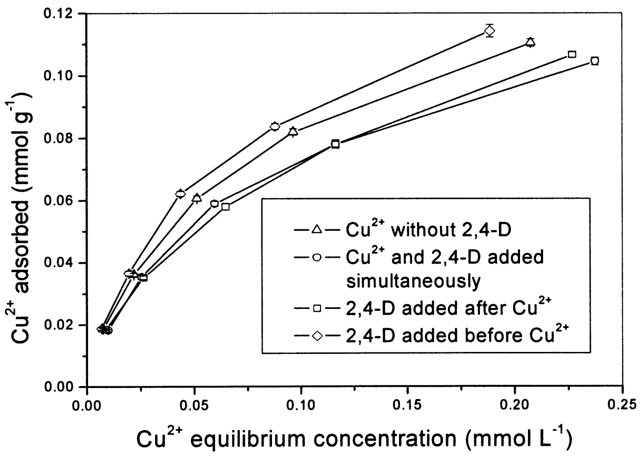

Figure 2. Adsorption isotherms of Cu^{2+} on montmorillonite from 2,4-D-free solutions, in comparison with Cu^{2+} adsorption when 0.5 mM 2,4-D added simultaneously with, after and before Cu^{2+}. Error bars represent standard deviation of parallel measurements.

Cu^{2+} adsorption by montmorillonite can be described by Langmuir (1) and Freundlich (2) adsorption equations, the general forms of which are,

$$Q = {k_1 k_2 C}\Big/{(1 + k_1 C)} \qquad (1)$$

$$Q = K_f C^n \qquad (2)$$

where Q (mmol g^{-1}) is the amount of adsorbed Cu^{2+}, C (mmol L^{-1}) is the equilibrium concentration, k_1 (L $mmol^{-1}$) is a constant relating to the binding energy of metal to minerals; k_2 (mmol g^{-1}) is the maximum adsorption capacity. K_f (L g^{-1}) is the empirical distribution parameter and it gives a measure of adsorbent capacity. n is a constant of the isotherm curvature, which gives the intensity of adsorption. Both equations can well describe Cu^{2+} adsorption on montmorillonite in the absence and presence of 2, 4-D ($R^2 > 0.98$, $P < 0.05$). The obtained values are listed in Table 1. As the concentration of 2,4-D increased from 0 to 2 mM, the K_f and k_2 values decreased from 0.243 to 0.190 and from 0.145 to 0.130, respectively. The diminishing K_f and k_2 values (significantly different at 95% confidence interval) with the increase of 2, 4-D concentrations reflected that 2,4-D had a significant effect on Cu^{2+}adsorption on montmorillonite.

Figure 2 shows Cu^{2+} adsorption isotherms on montmorillonite from 2,4-D-free solution (F) in comparison with Cu^{2+} adsorption when 0.5 mM 2,4-D added simultaneously with Cu^{2+}(S), after Cu^{2+}(A) and before Cu^{2+}(B). It was observed followed the descending order of adding sequence: B > F > A $\approx$ S. Cu^{2+}

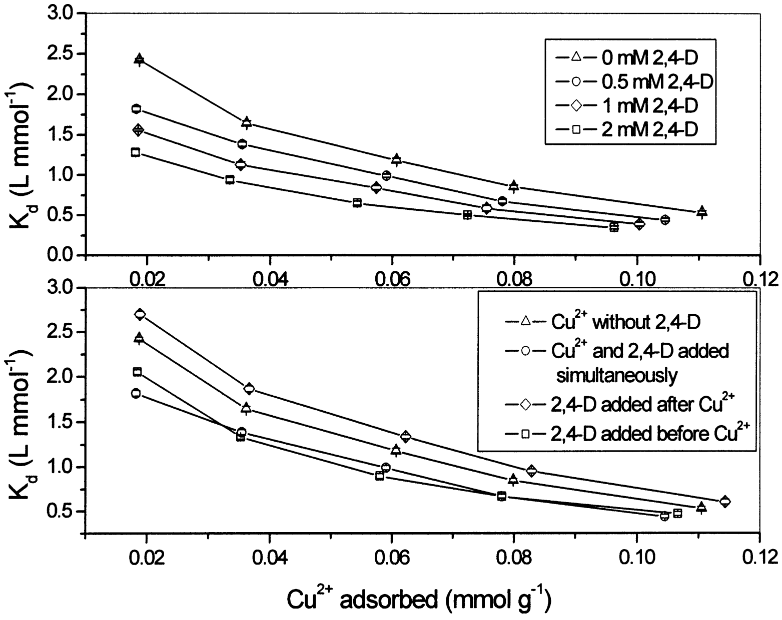

Figure 3. Cu^{2+} K_d values as a function of Cu^{2+} adsorbed at various 2, 4-D concentrations (a) and Cu^{2+} adsorbed with 0.5mM 2, 4-D added in the adsorption system in different addition sequence (b). Error bars represent standard deviation of parallel measurements.

adsorption was higher when montmorillonite was previously treated with the herbicide than the other adsorption conditions. This may be due to the fact that a part of the herbicide is adsorbed on planar positions in montmorillonite, opening the layers and making easier the subsequent penetration of Cu^{2+} (Maqueda et al. 1998b; Ni and Zheng 2003). Cu^{2+} adsorption was lower when both adsorbates were added simultaneously or when Cu^{2+} was treated before 2,4-D than its adsorption from 2,4-D-free solutions. The successive adsorption in which Cu^{2+} was treated before 2,4-D gave an adsorption isotherm similar to that when both adsorbates adsorbed simultaneously. When Cu^{2+} was previously adsorbed on montmorillonite, 2,4-D in solution may solubilise Cu^{2+} on montmorillonite by lowering the free cation concentration in solution and so displacing the equilibrium between adsorbed and solution phases (Staunton 2004). Therefore even 2,4-D was added after Cu^{2+} adsorption on montmorillonite has reached equilibrium, it can affect Cu^{2+} adsorption on montmorillonite.

Distribution coefficient (K_d) is a useful parameter to measure the affinity adsorbent-sorbate. It can be defined as

$$K_d = \frac{[M_{clay}]}{[M_{solution}]} \tag{3}$$

where $[M_{clay}]$ is the concentration of adsorbed M (Cu^{2+}), and $[M_{solution}]$ is the

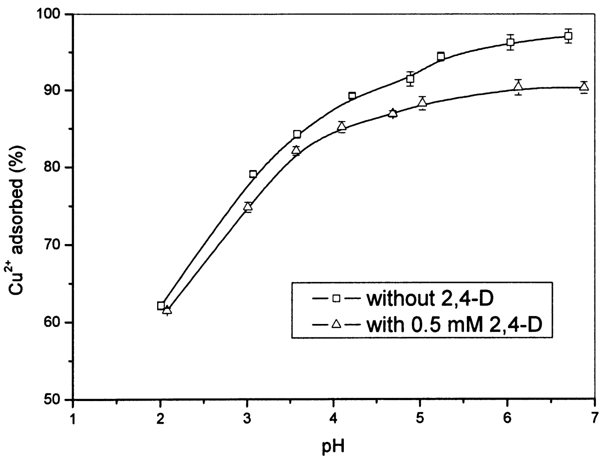

Figure 4. Cu^{2+} adsorption on montmorillonite as a function of pH in the absence and presence of 0.5 mM 2,4-D. Error bars represent standard deviation of parallel measurements.

concentration of sorbate M in the equilibrium solution. Figure 3a shows the K_d values for Cu^{2+} adsorption at various 2,4-D concentrations (0, 0.5, 1, and 2 mM). Figure 3b shows the K_d values for Cu^{2+} when 0.5 mM 2,4-D was added simultaneously with, before and after Cu^{2+}. In all cases there were high K_d values for low surface coverage, these decreased when the loading of Cu^{2+} was higher. It can be observed in Figure 3a that K_d values decreased as 2, 4-D concentration increased. The K_d values followed the order of B > F > A ≈ S (Figure 3b), which was in agreement with the results obtained in Figure 2, showing higher affinity of Cu^{2+} for montmorillonite when 2,4-D has been previously adsorbed and lower affinity of Cu^{2+} when 2,4-D was added simultaneously with and after Cu^{2+}.

Adsorption of Cu^{2+} on montmorillonite increased with pH increased from 2 to 7 both in the absence and presence of 2,4-D (Figure 4). Adsorption of Cu^{2+} on montmorillonite as a function of pH did not present to be the typical sigmoid shape. At low pH values, a high fraction of Cu^{2+} was adsorbed on montmorillonite. This phenomenon indicated the adsorption edge for Cu^{2+} may exist at a lower pH. In the presence of 2,4-D, Cu^{2+} adsorption on montmorillonite showed an obvious decrease. Such decrease enhanced with pH increased from 2 to 5 and tended to be constant when pH > 5. This was due to the fact that 2,4-D was predominantly ionic when pH > 5. The ionic species can form complex with Cu^{2+} that tends not to be adsorbed by montmorillonite to the same extent as free Cu^{2+}. Therefore again stressed the importance of the complex ability of 2,4-D on its effect on Cu^{2+} adsorption, as opposed to the competition effect.

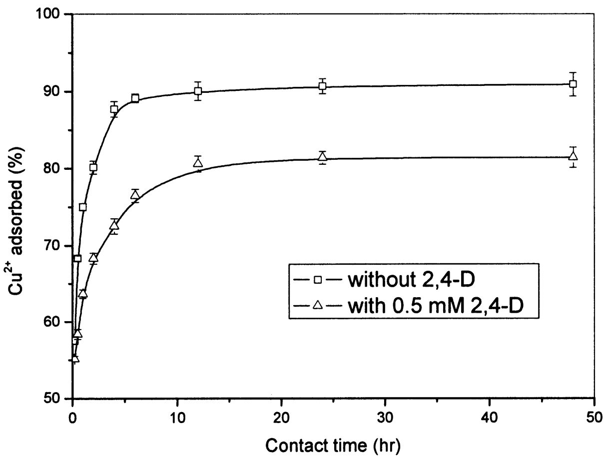

Figure 5. Cu^{2+} adsorption kinetics on montmorillonite from 2,4-D-free solution, in comparison with simultaneous Cu^{2+} adsorption in the presence of 0.5 mM 2,4-D at pH 5.0±0.2. Error bars represent standard deviation of parallel measurements.

Figure 5 shows the kinetics of Cu^{2+} adsorption on montmorillonite from 2,4-D-free solution, in comparison with simultaneous adsorption in the presence of 0.5 mM 2,4-D at pH 5.0±0.2. The adsorption percent of Cu^{2+} increased with increasing contact time and equilibrium was attained within 24 h. Cu^{2+} adsorption was typical biphasic time-dependent kinetics. That is to say the adsorption of Cu^{2+} was a two-step process: a rapid adsorption of Cu^{2+} to the external surface followed by possible slow intraparticle diffusion in the interior of the particles. The initial fast reactions were generally accepted to be film diffusion process (Lan et al. 1992). The reason might be that at the initial stages, most of the adsorption sites on mineral surface were not occupied. So as soon as Cu^{2+} approached the interface of liquid-solid by diffusing, it was captured by the solid. Therefore the active sites on montmorillonite surface were mostly occupied by previously adsorbed Cu^{2+}. When Cu^{2+} in the solution reached the interface of liquid-solid, it was necessary for Cu^{2+} to diffuse further along montmorillonite surface until it encountered the active sites which were not reacted. Apparently, this intraparticle diffusion was much slower than film diffusion. This two-stage metal uptake can also be explained as adsorption occurring onto two different types of binding sites on the adsorbent articles (Sen et al. 2002). In the presence of 2,4-D, the adsorption amount and rate reduced compared with Cu^{2+} adsorption from 2,4-D-free solution. The total amount of Cu^{2+} sorption in the presence of 2,4-D was about 10% less than that in the absence of 2,4-D. The effects could be due to the aforementioned complex ability of 2,4-D.

Data presented here show that, due to the mutual influence between pesticides and heavy metals, these phenomena must be taken into account with the increasing mixed pollution of heavy metals and pesticide.

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