韓國土壤環境學會誌 Vol.1, No.1 81~88, 1996
J. of KoSES Vol.1, No.1 81~88, 1996

原著

3개의 다른 토양에서의 카드늄과 마그네시움의 경쟁적 상호작용

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Competitve Interactions of Cadmium with Magnesium in Three Different Soil Constituents

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ABSTRACT

To study the Cd adsorption in the presence of competing ions in soil-solution interphase, three soil samples from the Bt horizon were taken and analyzed for their physical and chemical properties. Adsorption of ethylene glycol monoethyl ether(EGME) and N_2 were determined to establish the specific surface area of the soils. We attempted to establish a qeneralizing competitive sorption isotherms for soils of entirely different composition of the solid phase, resulting in the routine use as a guidelines for the fate of reactive solute in soil profiles. Many physicochemical factors including competitive adsorption bettween solutes will affect the general adsorption phenomena as shown in a single not only on the soil:solution ratio used, but also on the surface areas of its respective soil samples. This phenomenon was attributed to competition Cd for sorption sites with Mg by different soil constituents. These adsorption isotherms are able to use as examples to demonstrate that this phenomenon can complicate the development of a standardized batch adsorption procedure as well as interpreting fate and adsorption of toxic inorganic compounds.

Key word : Competitive interactions, Cadmium, Magnesium, Adsorption isotherms

요 약 문

토양과 토양용액의 경계면에서 토양내 흡착부위에 대해 경쟁적 이온이 존재할 때 카드늄의 흡착 현상을 연구하기 위하여, 토양의 Bt층으로부터 토양시료를 채취하여 토양의 물리화학적 특성을 분석하였다. 한편 Ethylene glycol monoethyl ether(EGME)와 질소가스를 가지고 각각의 토양의 특정표면적을 조사하였다. 토양층 내에서 토양입자와 반응성을 지닌 물질의 동태를 연구하는 일반적 지침으로, 물리화학적 특성이 완전히 다른 토양을 가지고 일반적인 등온흡착곡선을 취하였다. 단일 등온흡착곡선에서 보여 주었던 것처럼 물질간의 경쟁적흡착을 포함한 여러가지의 물리 화학적 요인들이 흡착에 영향을 미칠 것으로 추정된다. 한편 각각의 토양입자에 의한 카드늄 흡착의 정도는 사용된 토양과 용액의 희석 비율 뿐만 아니라 각각의 토양의 표면적에 의존한다는 것을 알 수 있었다. 이러한 결과는 서로 다른 토양에서의 카드늄이 마그네시움과의 경쟁적 흡착에서도 적용되는 것을 알 수 있었다. 이러한 등온흡착곡선은 유해한 무기성분의 흡착과 동태 해석 뿐만 아니라 표준 배취흡착과정을 연구개발하는데 복합 요인으로 작용한다는 것을 증명하기 위한 예로서 사용할 수 있다.

주제어 : 경쟁적 상호작용, 카드늄, 마그네시움, 등온흡착곡선

Introduction

The environmental hazards derived from the recent increasing disposal of heavy metals into soils-particularly Cd, which is highly toxic to humans even at very low concentrations[5] - have aroused growing concern in recent years.

The capacity of geological materials to attenuate potential pollutants has been studied by many researchers for the past 30 years. The "batch" adsorption technique is often used in laboratory studies to assess the capacity of geological materials to attenuate potential pollutants, that consists of mixing a solution of known composition and concentration with a mass of adsorbent, for a period of time, then the solution of known composition and concentration with a mass of adsorbent, for a period of time, then the solution is separated from adsorbent and chemically analyzed to determine changes in solute concentration. As a dependent variable, the specific surface area is mainly influenced by the clay content and clay mineral type. In addition, the lower the clay content or the clay content of 2:1 clay minerals is, the more significant the influence of the organic substance content as well as the iron and manganese oxide content on the specific surface area. However, the batch adsorption procedures that have been used vary considerably and are often not procedurally comparable.

The adsorption of portential groundwater pollutants may also be reduced by competitive interactions with other species for adsorption sites. Competition occurs when similarly charged species are attracted to some portion of the same type of adsorption sites on the surfaces of claysized particles.[6] However, most investigators have treated the system under a study as a single solute or single-component system, although the solutions incoming to soil environment usually contain several different kinds of constituents as multi-component system. Therefore, one of the major difficulties in applying adsorption data from single-component studies to multi-component waste effluents is that the adsorption behavior of an ion may be subject to competitive interactions with other ions, molecules, or ligands that are in the same phase, or associated, with the adsobing surface. For competitive interactions between ions, it is generally accepted that when one ion is in solution competing for sorption sites, the amounts of the second ion adsorbed by soils will be less than when the former ion is not present in solution. A number of factors, in addition to those related to the ingerent variability of soils clays affect the adsorption of a given constituent.

For inorganic species, these factors include time, temperature, temperature, method of mixing, soil:solution ratio, moisture content, and the composition and concentration of the solution.[1, 2, 3, 8]

The objectives of this study are to observe a simple batch adsorption procedure and competitive interactions between Cd and Mg and between As and P with different soil materials and soil:solution ratio to obtain solute-adsorbate partition under a given condition. Such a procedure would be meaningful in evaluating the suitability of various waste materials in land application. Another objective of the study is to determine how competition between solutes and physicochemical parameters affect adsorption data in interpreting adsorption phenomena and the routine use of the procedure.

Methods and Materials

Three soil samples from Bt horizon were collected and analyzed (Table 1): (1)the Leon loam, (2) the Cecil clay loam, and (3) Coastal plain sediment the Norfolk sandy loam, in east South Carolina. These samples vary considerable in pH, texture, surface area and organic carbon. The specific surfcae area were determined by N_2 and EGME according to Gile's Method[6]. Soil pH was determined in 5:1 water/soil suspension using 5gram of soil. Soil texture analysis was determined by the pipette method.

For single adsorption isotherm curves, samples were prepared b mixing soil:solution at the ratio of 1:5. To observe the soil:solution effect in binary system, six different soil: solution ratios were applied from 1:5 to 1:200, while the competitive adsorption isotherms were observed with 1:5. The solution were made at the given equal initial concentrations from 0 to 200 ppm with every 20ppm increment for Cd, and Mg, respectively. Five gram of soil samples, used in this study, were weighed, on a oven-dried basis, into Nalgene bottles and agitated with a reciprocal shaker for 24 hours. Neither pH or ionic strength was controlled. The bottles were removed from the shaker and a portion of the suspension was centrifuged at 10000 rpm for 30 min. after pH and eletrical conductivity measurements were made.

The solutions of Cd and Mg in the single and muluiphase studies were quantified using a Perkin-Elmer Model 306 Atomic Adsorption Spectrophotometer. Amount of adsorption was calculated by the differences between initial concentration and cation remained in the equilibrium solution.

Results and discussion

Adsorption isotherms were obtained for all the soils studied and characteristics of the three soils used in this experiment are given in Table 1 and Figure 1. The proposed adsorption mechanism for cation adsorption in that the hydrated cations are held to clay surfaces because of the negative charges of the clay. Since the sites of negative charges are at different distances from the clay surface, the energies with which cations are held differ. As the polarizing power of the cation increasing, the clay-cation bond strength increases, in the order Na<K<Rb<Cs, for divalent cations the order is Mg<Ca.

Table 1. Selected physical and chemical Properties of Soils used in the Adsorption Isotherms

Soil	pH	Organic Carbon	Soil TExture Sand	Silt	Clay	Surface area N_2	CO_2	Remark
				%		(m^2/g soil)		
Cecil	6.1	0.10	45	25	30	22.9	20.6	clay loam
Norfolk	6.4	0.10	56	21	23	10.6	10.0	sandy loam
Leon	7.4	0.18	45	38	17	7.3	6.4	loam

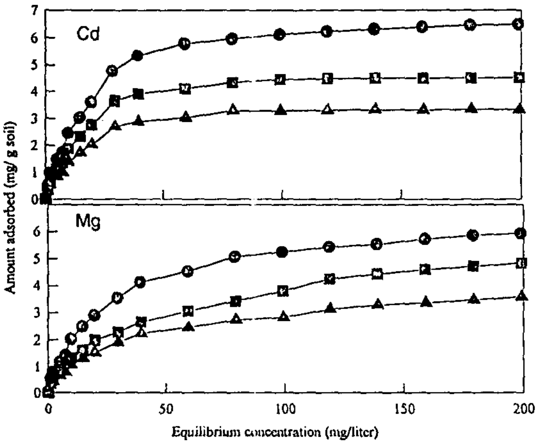

Fig. 1. Adsorption isotherms of Cd and Mg, for Cecil clay loam, Norfolk sandy loam, and Leon loam with soil: solution ratio of 1:5

●—● Cecil clay loam
■—■ Norfolk sandy loam
▲—▲ Leon loam

The shape and concentration of the adsorption isotherms for Cd and Mg cations on Cecil, Norfolk, and Leon soils have been examined at equilibrium concentration up to 200 mg/L. According to the curves, the adsorption isotherms for three soils showed the adsorption of Cd and Mg increased with increasing equilibrium concentrations in the order of Cd <Mg, suggesting the hydration power and ionic valance of cations influenced the sorption for the available sites. As shown in table 2, the maximum adsorption occurred with Cd for Cecil clay loam soils, which has the highest clay content among soil studied in this experiment. However, the amount of cations adsorbed throughout an entire equilibrium concentrations decreased with decreasing content of clay in the order of Cecil <Norfolk <Leon regardless of contents of sand and silt.

Table 2. Maximum Concentrations of Cd and Mg in Solid and Solution Phases for Three Soils

Soil	Cd Solid (mg/g soil)	Cd Solution (mg/L)	Mg Solid (mg/g soil)	Mg Solution (mg/L)	Remark
Cecil	23	195.4	19	196.2	Soil:solution = 1:5
Norfolk	4	199.2	4	199.2	〃
Leon	12	197.6	11	197.8	〃

And the adsorption isotherms obey a Langmuir type equation over this concentration ranges, and gives adsorption with respect to maxima · for Cecil, Leon and Norfolk, respectively, indicating that the adsorption mechanisms for these three soils are closely related to its inherent adsorption type and the amount of abailable surface area. Adsorption equation of the Langmuir type, applied in this study, has frequently been applied to the monomolecular adsorption of ions from solutions with general understanding. The equation takes the form

$$(x/m)=kbc/(1+kC)$$

where

x/m = amount of adsorption per unit mass of absobent

b=adsorption maximum

C=equilibrium concentration of adsorbate in solution

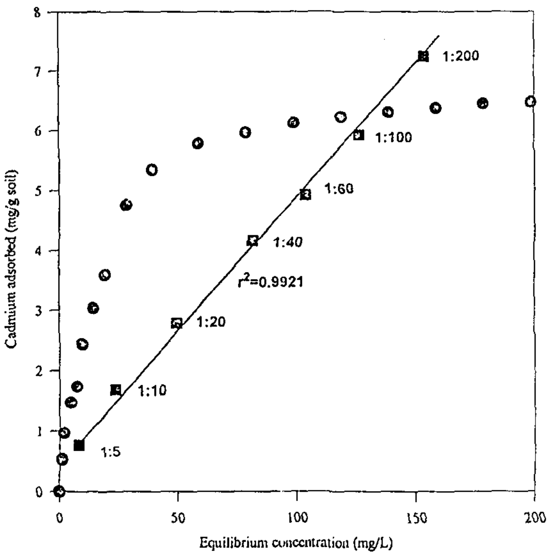

Fig. 2. Effects of soil:solution ratios on cadium adsorption by Cecil clay loam.

The solid dots were derived by using a 1:5 ratio.

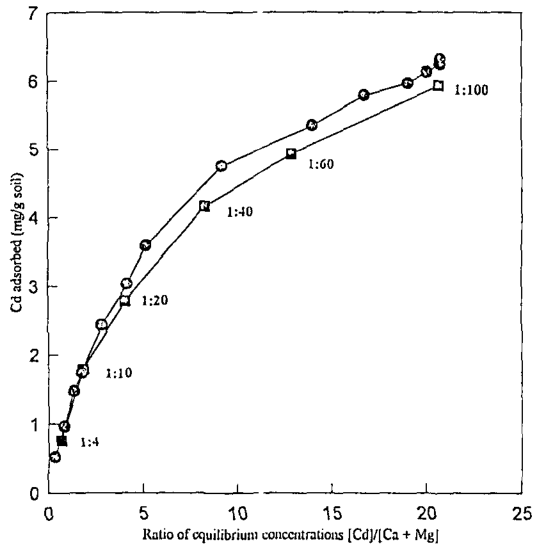

Fig. 3. Cadium adsorption by the Cecil clay loam. Adsorption curves is a transformation of figure 2, taking competitive interacions of indigenous Ca and MG into account.

The colid circle dots were derived by using a 1:5 ratio.

k=a constant relating boning energy of the adsorbent for the adsorbate.

If the experimental data fits this equation, a straight line is obtained by plotting C/(x/m) against C. The data with three soils were plotted according to the linear form of Langmuir equation. The adsorption plateau confirms to a Langmuir equation.

For the study of adsorption procedures, it became necessary to determine soil:solution ratios, such that sufficient solute was adsorbed to be both satisfactorily significant and practical. The amount of adsorbate per adsorbent may or may not be independent on the amount of adsorbent used. In some situations, the amount of adsorbate per mass of adsorbent seems to be influenced by the amount of adsorbent used in the experiment. This phenomenon has been termed the "soil:solution ratio effect".[2, 8, 12]

Therefore, we observed the soil:solution effect on the adsorption Cd by adding the same concentration of Cd for 7 levels of soil:solution ratio. The procedures were the same as the previous adsorption experiment. As shown in Figure 2, the effect of soil:solution ratio on adsorption of Cd by Cecil clay loam attributed to the increasing the adsorption of Cd with increasing the soil:solution ratios. From this result, we assume that the adsorption of Cd to the available sorption sites is closely related to the release of inherent cations on the sorption sites into solution phase, resulting in enhancement of exchange between ions in solution and solid phases.[11]

The soil:solution ratio effect has been attributed to the competitive interactions between a given solute and species that are concomitantly desorbed or exchanged during the partitioning of solutes and adsorbates. As the sample size is increased, there would be a larger source of these potentially competing constituents. The net effect is that the magnitude of adsorption (given equal initial concentratios) will decrease, as observed from a Ca-saturated montmorillonite.[4]

A similar results was observed in this study in which the adsorption characteristics of Cecil soil, containing approximately 50% 1:1 kaolinittic clay, were inveatigated using $CdCl_2$. It was found that there was strong soil:solution ratio effect on Cd adsorption(Fig. 3).

The adsorption isotherms of Cd with a 1:5 soil:solution(wt/vol) did not follow the same pattern with different soil:solution ratio, suggesting that dilution factor of soil:solution significantly influences the adsorption characteristics. We assume that the indigenous Ca and Mg in sorption sites reduced the adsorption of Cd due to the compertitive interactions. While the smaller the ratio of soil: solution, the larger the amount of indigenous Ca and Mg from soil sample were desorbed into solution, the larger the amount of indigenous Ca and Mg from soil sample were desorbed into solution phase, indicating the amount of Cd adsorbed increased. Work by Bittel and Miller[3] indicated that selectivity coefficients for Ca and Cd exchange reactions with montmorillonite and kaolinitic clay were 0. 8 and 1.3 (on a concentration basis), suggesting that these clay minerals have no strong affinity for one cation versus the other. Calcium will readily exchange with Cd and vise versa. If the adsorption isotherms plotted ad Cd adsorbed relative to Cd(Ca + Mg) in solution phase showed that the individual curves coalesced into one adjacent curves. This represented that the amounts of adsorbed and desorbed were correlated.

The affinity of the Cecil clay loam for Cd, having different chemical structures, showed that Cd adsorption using $CdCl_2$ as a solution chemical was greater than observed when $CdCO_3$ was used to prepare the cadmium solutions in figure 3. The equilubrated solutions made from the $CdCl_2$ contained little Na in solution, indicating that Na was not desorbed from the soil itself. Equilibrium concentratios of Cd and Na relative to the cadmium compound used. The difference between the two adsorption curves probably resulted from competitive effects of Na and Cd (Table 3). Because $CdCl_2$ was readily soluble in water, while the $CdCO_3$ had to be dissolved in concentrated HNO_3, then neutralized with NaOH to adjust the stock Cd solution to a pH comparable to that of the soil. Thus, the lower adsorption curve actually represents Cd removal from a binary solute system (Cd and Na), due to not its strong affinity for exchange sites in soils, but mass reaction effect of Na for sorption sites.

The effect of divalent cation on the adsorption of Cd by Cecil clay loam, Norfolk sandy loam, and Leon loam. Soil samples were added to a solution containing a different concentrations of Cd and a 100 ppm of Mg and equilibrated of 8 hours. In Fig. 5, the influence of Mg on the adsorption of Cd by these three soils showed that the presence of Mg greatly hindered the adsorption of Cd when the solution concentrations of Cd were below 50 ppm although the adsorption of Cd gradually increased with increasing equilibrium

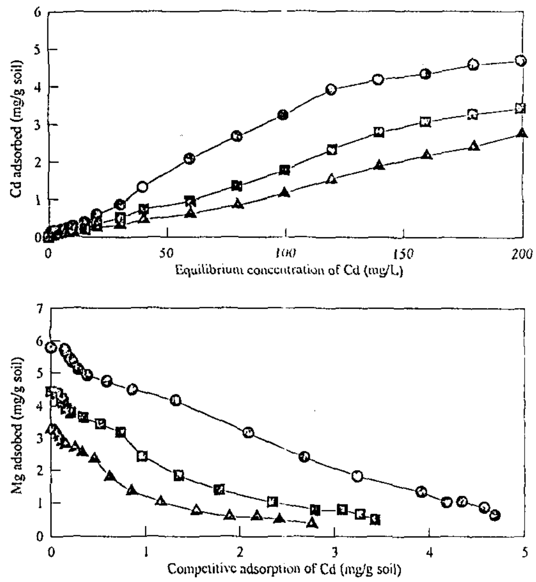

Fig. 4. Competitive adsorption of Cd in the presence of 100ppm of Mg (above) and the relative adsorption of magnesium plotted against the amount of Cd adsorbed (below).

●–● Cecil ■–■ Norfolk ▲–▲ Leon

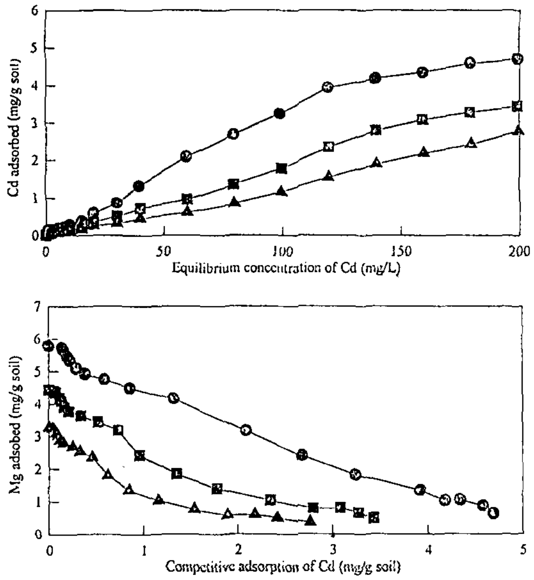

Fig. 5. Competitive adsorption of Cd in the presence of 100ppm of Mg (above) and the relative adsorption of magnesium plotted against the amount of Cd adsorbed (below).

●–● Cecil ■–■ Norfolk ▲–▲ Leon

Table 3. Equilibrium Concentrations of Cd and Na relative to the Cadmium Compound used

$CdCl_2$(ppm)		$CdCO_3$(ppm)	
Cd	Na	Cd	Na
1.87	<0.75	1.70	92.0
4.46	<0.75	4.51	214.0
9.36	1.20	11.41	220.0
24.50	<0.75	28.43	213.0
64.50	<0.75	48.33	227.0

concentrations. Conversely, the adsorption of 100 ppm Mg gradually decreased with increasing equilibrium comcentration. When Cd and other cations are present together, the decrease in Cd adsorption by an adsorbent must arise resulting from competition for the available sorption sites between ions present together. On the other hand, the maximum adsorption of Cd was in the order of Cecil <Leon <Norfolk as seen from single adsorption isotherm. Therefore we assume that the adsorption of Cd in single and binary system is much influenced by the amount of clay content in soil samples used.[7]

Summary

The adsorption isotherms with respect to concentration for Cd and Mg on Cecil clay loam, Norfolk sandy loam, and Leon loam have been examined. The isotherms of Cd and Mg for the three soils confirm to a a Langmuir-type equation, and the amount of an individual cation increased with increasing concentration at equilibrium. On the other hand, the maximum adsorption is greatly influenced by the amount of clay content, suggesting that the hydrated cations are held only to clay surfaces because of the negative charges of the clay minerals. For the effect of mono and divalent cations on the adsorption of Cd by Cecil clay loam, Norfolk sandy loam, and Leon loam, the influence of Na or Mg on the addorption of Cd by these three different soils suggested that when Cd and other cations are present together, the decrease in Cd adsorption by an adsorbent must arise resulting from competition for the available sorption sites between ions present together. Also, the adsorption of Cd in single and binary system is much influenced by the amount of clay content in soil samples used. The soil:solution ratio effect has been attributed to the competitive interactions between a given solute and species that are concemitantly desorbed or exchanged during the partitioning of solutes and adsorbates.

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