

Cadmium Adsorption and Exchangeable Cations Desorption in Soils: Effects of pH and Organic Matter Content

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In order to investigate the effects of pH and organic matter content on cadmium adsorption and exchangeable cations desorption in soils, the adsorption isotherms of cadmium and the desorption isotherms of calcium and magnesium on four New Jersey soils at four pH values were plotted, and the cadmium partition coefficients (K_d) were also calculated. The slopes of cadmium adsorption isotherms dramatically increased with increasing solution pH. Judging from Langmuir adsorption equations, the maximum adsorption quantities (b) of cadmium at high pH values were much greater than those at low pH values for the same soil. The partition coefficients increased greatly with increasing solution pH. The slopes of regression equations between partition coefficients and pH values were steep in the order of the organic matter content of the soils. The correlation coefficients (r^2) between partition coefficient and organic matter content for 1×10^{-4} M increased from 0.3027 at pH 4.0 to 0.9964 at pH 8.5 and from 0.2093 at pH 4.0 to 0.9657 at pH 8.5 for 2×10^{-4} M $\text{Cd}(\text{NO}_3)_2$. The desorption quantities of calcium and magnesium decreased with increasing solution pH and increased with increasing cadmium adsorption.

Key words : Adsorption isotherm, Partition coefficient, Langmuir adsorption equation.

1. Introduction

Cadmium, which is daily ingested from food chain or inhalation via the respiratory route, interferes with intestinal calcium absorption, vitamin D activation in the kidney and the production of mature collagen fibers in bone (Friberg et al., 1985; Friberg et al., 1986). What is worse, the half-time of cadmium both in the environment and humans is very long. But, unfortunately, the emission of cadmium into the environment increases every year because of the enlargement of industrial products in the modern society. Cadmium is used for the production of metallurgical alloys, petrochemicals, batteries, fungicides, photography, pigments for paints, inorganic chemicals, hair dyes, organic che-

micals, etc.

Cadmium has been one of the most important pollutants for the last two or three decades because of its serious toxicity, uptake by plants, persistence and bioaccumulation. Nowadays, numerous scientific papers on cadmium are published each year, and a large percent of them have focused on the cadmium adsorption by soils.

Cadmium binding by soils is affected by many factors including organic matter (Petruzzillie et al., 1978; Christensen, 1989), cation exchange capacity (Sposito, 1984; Lee, 1987), competitive cations (Christensen, 1984; Elliot et al., 1986), soil pH (Kuo and Baker, 1980; Christensen, 1989), ionic strength and ligand (Shuman, 1986; Lee et al., 1988), exchangeable cations (Sposito, 1981), anions

(Benjamin and Leckie, 1982), partial concentration and size (Hart, 1982) and amorphous oxides (Anderson and Christensen, 1988; Fu et al., 1991). Among these factors, soil pH and organic matter are the dominant factors that influence cadmium adsorption by soils. Christensen (1989) investigated the cadmium partition coefficients, K_d —defined as the ratio of the cadmium concentration in the solid phase to that in the liquid phase at equilibrium—for 63 Danish agricultural soils. K_d correlated very well with soil pH and organic matter, but no further improvement to the correlation was obtained by considering other soil parameters as clay, silt, fine sand, coarse sand, cation exchange capacity and oxides of Mn, Fe and Al. Fu and Allen (1992) reported that the cadmium adsorption by oxic sediment was strongly dependent on solution pH.

As a result of cadmium adsorption, calcium and magnesium bound in soils move from the solid phase to the soil solution. During the rainy season, calcium and magnesium, which restrain plants from cadmium uptake, wash away. The desorption of calcium and magnesium from soils are also strongly dependent on solution pH. Ca-soil complexes are slightly weaker than complexes formed by cadmium (Balistrieri and Murray, 1982), and the negative charges on soil colloids increase with increasing soil pH because of ionization of active organic functional groups (Sparks, 1986) and surface hydroxide groups.

The purpose of this paper is to determine the effect of soil pH and organic matter content on the cadmium adsorption by soils and the desorption of exchangeable cations from soils. We used four New Jersey soils and four concentrations of cadmium solution. We investigated cadmium partition coefficients, cadmium adsorption isotherms and the desorption isotherms of exchangeable cations at four pH values.

2. Materials and Methods

2.1 Samples

Four New Jersey soils used in this study were collected by the New Jersey Department of Environmental Control and Energy. These are Birdsboro silt loam, Boonton loam (Union county), Boonton loam (Bergen county) and Sassafras sandy loam. Soil samples were taken from a depth of 1 to 2 feet. The soils were air dried and agglomerates were broken by hand and by using a wooden mallet. Those particles larger than 2 mm were removed by sieving. The physico-chemical properties of these soils are summarized in Table 1.

Particle size distributions were measured using a hydrometer method (Sims and Heckendorn, 1991 a). Cation exchange capacity was determined by measuring the total nitrogen, which adsorbed at the negative charges on soil surfaces by 1 M ammonium acetate solution. Organic matter content was measured using the Walkley-Black Wet Combustion method (Sims and Heckendorn, 1991c). Surface area was measured by sorption of N_2 gas (with He carrier gas) onto the soil using a Quantasorb Model Qs-7 sorption system (Quantachrome Corp.).

2.2 Adsorption experiments

Batch adsorption experiments were conducted at room temperature. Four concentrations of cadmium solution were used at four pH values covering the range from 4.0 to 8.5. Ionic strength was maintained at 0.01 N $NaNO_3$.

A series of 200 ml polyethylene bottles were prepared with each containing 1.0 g dry soil and 100 ml of 1×10^{-5} M, 1×10^{-4} M, 2×10^{-4} M and 3×10^{-4} M $Cd(NO_3)_2$ in 0.01 N $NaNO_3$. The pH values of the samples were adjusted by adding

Table 1. Physico-chemical properties of the New Jersey soils

Soil Name	Soil pH		Exch.-Cations (me/100g)			
	H ₂ O	CaCl ₂	K	Ca	Mg	
Birdsboro Silt Loam	5.69	5.24	0.46	3.60	1.31	
Boonton Loam (Union County)	5.14	4.70	0.21	2.00	0.55	
Boonton Loam (Bergen County)	5.12	4.31	0.20	2.70	0.61	
Sassafras Sandy Loam	5.78	5.31	0.16	2.19	0.72	
CEC ¹⁾ (me/100g)	OM ²⁾ (%)	SA ³⁾ (m ² /g)	CD ⁴⁾ (me/m ²)	Soil Texture (%)		
				Sand	Silt	Clay
5.30	2.2	7.06	7.5×10^{-3}	50	32	18
4.20	8.6	6.45	6.5×10^{-3}	49	35	16
4.20	5.3	7.20	5.4×10^{-3}	60	27	13
3.10	0.6	5.31	5.8×10^{-3}	45	37	18

- 1) Cation Exchange Capacity
- 2) Organic Matter
- 3) Specific Surface Area
- 4) Charge Density

NaOH or HNO₃. Samples were shaken for 24 hours on a reciprocating shaker. After 24 hours shaking, the pH values were readjusted and the samples were shaken again for 24 hours. The samples were then filtered through 0.45 μm membrane filters. The cadmium concentration in the filtered solution were determined using a Perkin Elmer 5000 Atomic Absorption Spectrophotometer.

2.3 Adsorption isotherms

The adsorption of metal to soil is often characterized by an adsorption isotherm which is a plot of adsorption quantity against aqueous equilibrium concentration of metal at fixed temperature, pH and other conditions.

The amounts of adsorbed cadmium, C_s (μmole/g), and the aqueous equilibrium concentrations of cadmium, C_w (μmole/g) were calculated at four pH values under the adsorption experiments, above mentioned.

2.4 Calculation of K_d

The distribution of cadmium between soil and solute was expressed in terms of cadmium partition coefficients (K_d), defined as the ratio of soil cadmium to solute cadmium at equilibrium. Partition coefficients were calculated as,

$$K_d = \frac{\text{equilibrium Cd concentration in soil } (\mu\text{g/g})}{\text{equilibrium Cd concentration in solution } (\mu\text{g/ml})}$$

The cadmium partition coefficients were correlated to the organic matter contents(%) and solution pH values by linear regression analysis.

2.5 Desorption experiment

Calcium and magnesium, which moves from the solid phase to the liquid phase during cadmium adsorption, were determined by atomic absorption spectrophotometry. The procedural steps for the

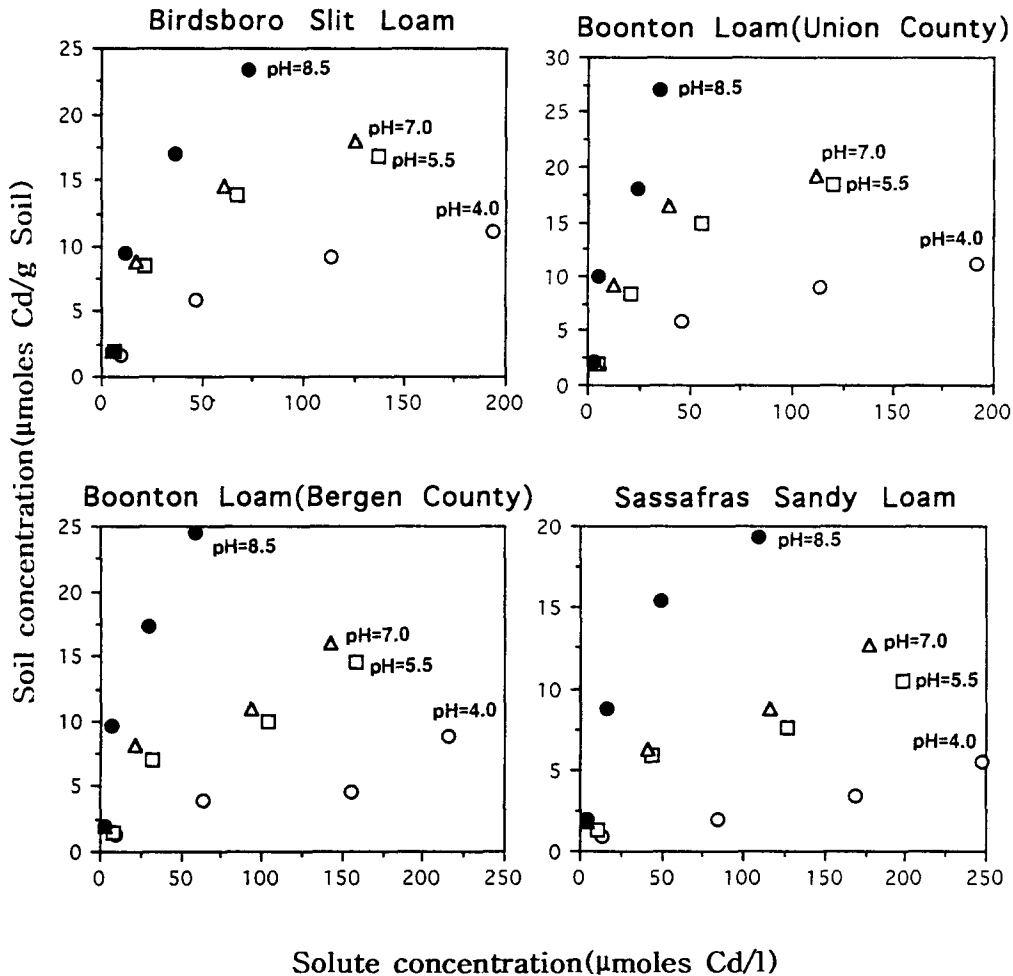


Fig. 1. Adsorption isotherms of cadmium on four New Jersey soils at four pH values. $I=0.01N$ $NaNO_3$

desorption experiment were equivalent to those used for the adsorption experiment.

3. Results and Discussion

3.1 Adsorption isotherms

Fig. 1 shows adsorption isotherms of cadmium for the four New Jersey soils at pH 4.0, 5.5, 7.0 and 8.5.

The adsorption isotherms of all the samples are

strongly dependent on solution pH. The slopes of the adsorption isotherms dramatically increase with increasing solution pH. At pH 8.5, the slopes of adsorption isotherms decrease in the order of Boonton loam (Union county), Boonton loam (Bergen county), Birdsboro silt loam and Sassafras sandy loam. This order of slopes is consistent with that of organic matter content of soils, as listed in Table 1. From the above adsorption data, we can also determine the maximum capacity of the soil to bind cadmium fitting to Langmuir adsorption isotherm.

The form of the isotherm equation used was:

$$C_s = \frac{b \cdot K \cdot C_w}{1 + K \cdot C_w}$$

where,

C_s : the adsorbed concentration of cadmium ($\mu\text{g/g}$)

C_w : the equilibrium concentration of cadmium in solution (mg/l)

b : maximum adsorbed concentration of cadmium ($\mu\text{g/g}$)

K : Langmuir constant (l/mg)

The isotherm parameters are given in Table 2.

The maximum adsorption quantities (b) increase with increasing solution pH for any soil, at constant ionic strength. At the same pH, the maximum adsorption quantities of cadmium for these New Jersey soils vary widely. At pH 8.5, the order of maximum adsorption quantities is not exactly consistent with the order of organic matter content, but the Boonton loam (Union county), which contains the greatest quantity of organic matter (8.6%), has the greatest maximum adsorption quantity, 9091 ($\mu\text{g/g}$), and Sassafras sandy loam, which contains the smallest quantity of organic matter (0.6%), has the smallest maximum adsorption quantity, 3125 ($\mu\text{g/g}$).

3.2 Partition coefficients (K_d)

3.2.1 Effect of pH

Fig. 2 shows the measured partition coefficients (K_d) at concentrations of 1×10^{-4} M and 2×10^{-4} M Cd (NO_3)₂ as a function of solution pH values.

The partition coefficients greatly increase with increasing solution pH. The partition coefficients at the concentration of 1×10^{-4} M Cd (NO_3)₂ range from 23.63 to 127.45 ml/g at pH 4.0 to 568.86 to 2073.44 ml/g at pH 8.5, and those at the concentration of 2×10^{-4} M Cd (NO_3)₂ range from 19.87 to 80.10 ml/g at pH 4.0 to 315.46 to 729.59 ml/g at pH 8.5.

By increasing the concentration of added cadmium, the amounts of cadmium adsorbed by soils increase (Fig. 1), but the cadmium partition coefficients decrease, as shown in Fig. 2. The partition coefficients at pH 4.0 decrease in the order of Boonton loam (Union county), Birdsboro silt loam, Boonton loam (Bergen county) and Sassafras sandy loam. But, at pH 8.5, the partition coefficients decrease in the order of Boonton loam (Union county), Boonton loam (Bergen county), Birdsboro silt loam and Sassafras sandy loam, which is equivalent to the order of organic matter content in these soils. The slopes of regression equations between partition coefficients and pH values both for 1×10^{-4} M and 2×10^{-4} M Cd (NO_3)₂ decrease in the order of Boonton loam (Union county), Boonton loam (Ber-

Table 2. Langmuir constants for the adsorption of cadmium on four New Jersey soils at four pH values. I=0.01N NaNO₃

Soil Name	pH=4.0		pH=5.5		pH=7.0		pH=8.5	
	b ($\mu\text{g/g}$)	k (l/mg)	b ($\mu\text{g/g}$)	k (l/mg)	b ($\mu\text{g/g}$)	k (l/mg)	b ($\mu\text{g/g}$)	k (l/mg)
Birdsboro Silt Loam	1,786	0.1065	2,788	0.1513	2,941	0.1735	8,333	0.0635
Boonton Loam (Union County)	1,515	0.1880	3,125	0.1584	2,857	0.2917	9,091	0.1209
Boonton Loam (Bergen County)	1,149	0.0893	2,439	0.0956	1,961	0.2965	5,000	0.1905
Sassafras Sandy Loam	893	0.0517	1,724	0.0874	1,613	0.2026	3,125	0.2092

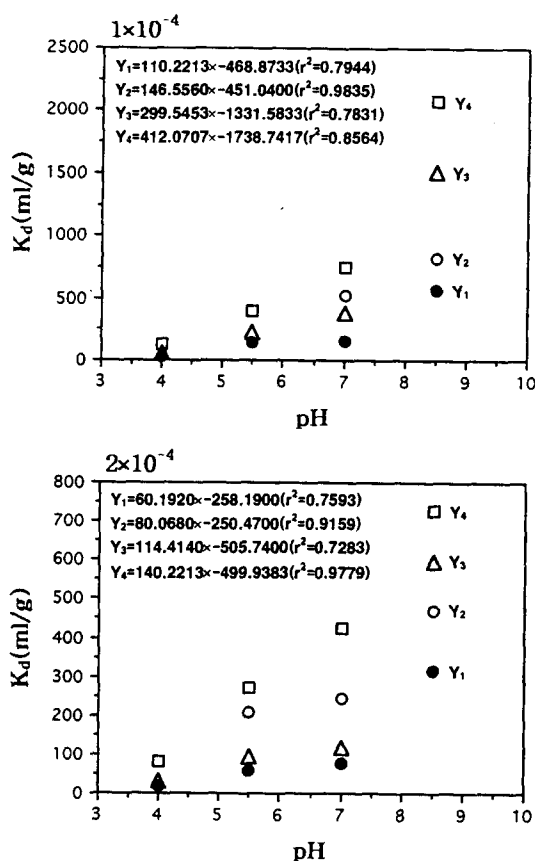


Fig. 2. Partition coefficients (K_d) for 1×10^{-4} M and 2×10^{-4} M cadmium as a function of soil pH values. ○; Birdsboro silt loam, □; Boonton loam (Union county), △; Boonton loam (Bergen county), ●; Sassafras sandy loam. $I = 0.01$ N NaNO_3 .

gen county), Birdsboro silt loam and Sassafras sandy loam.

The results of this experiment show that cadmium adsorption is strongly dependent on solution pH, and that the high dependence on pH for cadmium adsorption is closely concerned with soil organic matter content.

3.2.2 Effect of organic matter content

The organic matter contents ranged from 0.6 to

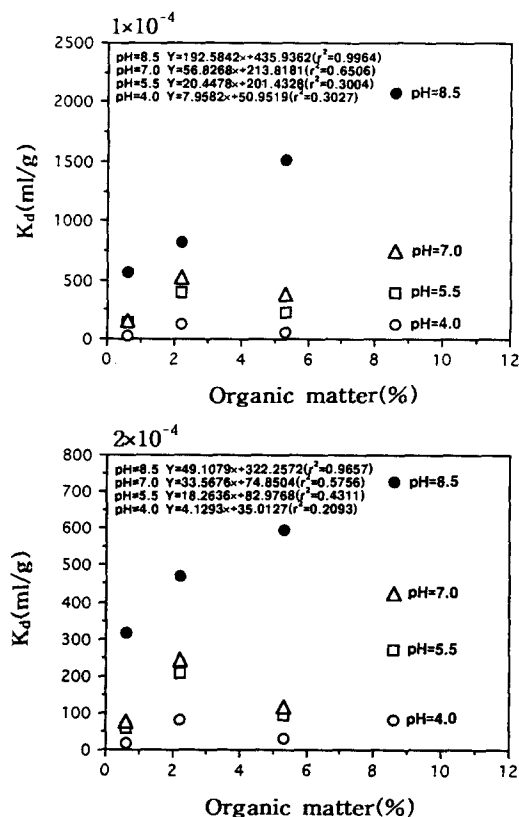


Fig. 3. Partition coefficients (K_d) for 1×10^{-4} M and 2×10^{-4} M cadmium as a function of soil organic matter content. $I = 0.01$ N NaNO_3 .

8.6% in the four soils used in this experiment (Table 1). Fig. 3 shows the measured partition coefficients at concentrations of 1×10^{-4} M and 2×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ as a function of organic matter content.

The partition coefficients at the concentration of 1×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ range from 23.63 to 568.86 ml/g at 0.6% organic matter to 127.45 to 2073.44 ml/g at 8.6% organic matter, and those at the concentration of 2×10^{-4} M $\text{Cd}(\text{NO}_3)_2$ range from 19.87 to 315.46 ml/g at 0.6% organic matter to 79.25 to 729.59 ml/g at 8.6% organic matter.

Judging from linear regression analysis, with increasing solution pH, correlation coefficients (r^2) be-

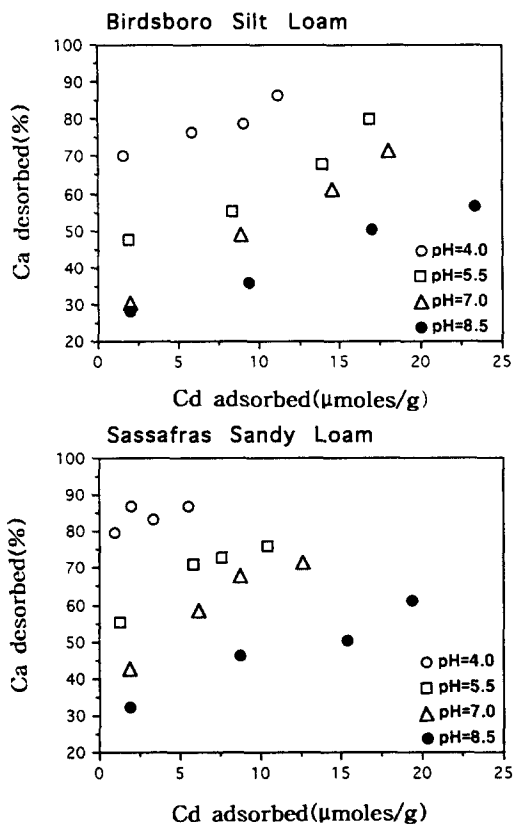


Fig. 4. Desorption isotherms of calcium on Birdsboro silt loam and Sassafras sandy loam at four pH values. $I=0.01N NaNO_3$

tween partition coefficients and organic matter contents for $1 \times 10^{-4} M$ and $2 \times 10^{-4} M Cd(NO_3)_2$ improve from 0.3027 at pH 4.0 to 0.9964 at pH 8.5 and from 0.2093 at pH 4.0 to 0.9657 at pH 8.5. At low pH, no significant correlation is observed, but, at high pH, the partition coefficient highly correlates with organic matter content. Therefore, we may consider that the organic functional groups ionize at higher solution pH values.

3.3 Desorption isotherms

The desorption isotherm of an exchangeable cation is defined as a plot of desorption quantity against aqueous equilibrium concentration of ad-

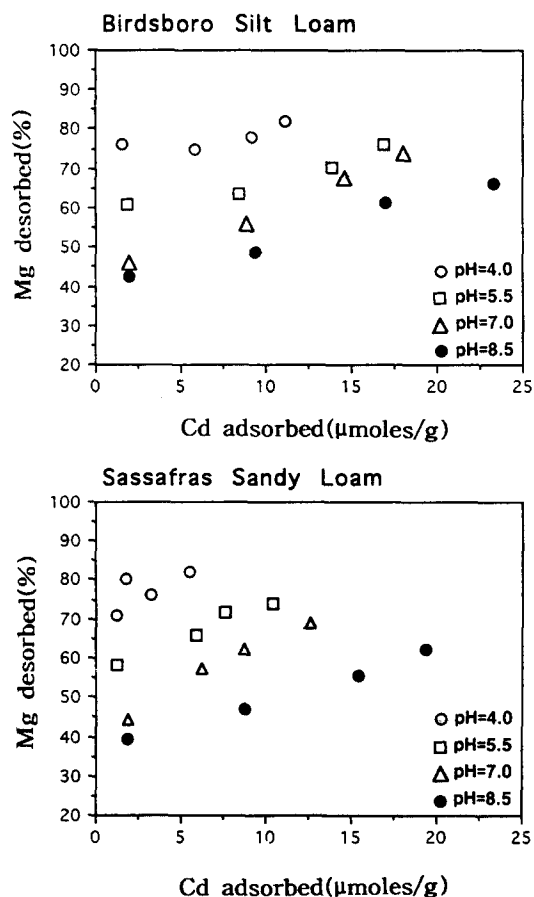


Fig. 5. Desorption isotherms of magnesium on Birdsboro silt loam and Sassafras sandy loam at four pH values. $I=0.01N NaNO_3$

ded metal, and desorption quantity is represented as the percentage of desorbed cation to total amount of cation in soil.

Fig. 4 shows desorption isotherms of calcium and Fig. 5 shows desorption isotherms of magnesium from Birdsboro silt loam and Sassafras sandy loam at four pH values.

As shown in Fig. 4 and Fig. 5, the desorption quantities of calcium and magnesium decrease with increasing solution pH and increase with increasing the amount of cadmium adsorbed. The percentages of desorbed calcium range from 70.22 to 86.35% at pH 4.0 to 28.30 to 56.61% at pH 8.5 on Birds-

boro silt loam, and from 79.74 to 86.78% at pH 4.0 to 32.25 to 60.98% at pH 8.5 on Sassafras sandy loam. The percentages of desorbed magnesium range from 76.00 to 82.03% at pH 4.0 to 42.64 to 66.28% at pH 8.5 on Birdsboro silt loam, and from 71.20 to 82.57% at pH 4.0 to 39.18 to 62.34% at pH 8.5 on Sassafras sandy loam. The result of this experiment shows that the desorption of exchangeable cations, such as calcium and magnesium, is strongly affected by both solution pH and competition with cadmium.

4. Conclusions

The purpose of this experiment was to investigate the effect of soil pH and organic matter content on the cadmium adsorption by soils and the desorption of exchangeable cations, such as calcium and magnesium, from soils. For this experiment, the adsorption isotherms of cadmium and the desorption isotherms of calcium and magnesium on four New Jersey soils at four pH values were evaluated, and the cadmium partition coefficients (K_d) were also calculated.

The slopes of cadmium adsorption isotherms dramatically increased with increasing solution pH. For pH 8.5, the slopes of adsorption isotherms decreased in the order of Boonton loam (Union county), Boonton loam (Bergen county), Birdsboro silt loam and Sassafras sandy loam. The order of slopes was consistent with that of organic matter content of the soils. Judging from Langmuir constants, the maximum adsorption quantities of cadmium at high pH values were much higher than those at low pH values for the same soil. At pH 8.5, Boonton loam (Union county) had the greatest maximum adsorption quantity, 9091 $\mu\text{g/g}$, and Sassafras sandy loam had the smallest maximum adsorption

quantity, 3125 $\mu\text{g/g}$.

The cadmium partition coefficients highly increased with increasing solution pH. The slopes of regression equation between partition coefficients and pH values decreased in the order of Boonton loam (Union county), Boonton loam (Bergen county), Birdsboro silt loam and Sassafras sandy loam. Judging from linear regression analysis, the correlation coefficients (r^2) between partition coefficients and organic matter contents improved greatly with increasing solution pH.

The desorption quantities of calcium and magnesium decreased with increasing solution pH and increased with the amount of cadmium adsorbed.

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토양에서 카드뮴의 흡착과 치환성양이온의 탈착 : pH와 유기물함량의 영향

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미국 New Jersey주에서 채취한 4종류의 토양시료를 이용하여 토양에서 카드뮴 흡착과 치환성양이온의 탈착에 미치는 pH와 유기물함량의 영향을 조사하였다. 카드뮴용액으로는 1×10^{-5} M, 1×10^{-4} M, 2×10^{-4} M, 3×10^{-4} M Cd(NO₃)₂ 용액을 사용하였고, 흡착평형시의 토양용액의 pH는 4.0, 5.5, 7.0, 8.5로 맞추었다. 카드뮴흡착등온선의 기울기는 토양용액의 pH가 증가할수록 증가하였으며, partition coefficient (K_d)도 용액의 pH가 증가할수록 크게 증가하였다. 또한 Langmuir흡착방정식에 의하여 구한 카드뮴최대흡착량도 용액의 pH가 높은 경우가 낮은 경우보다 훨씬 많았다. 그리고 pH와 partition coefficient사이의 직선회귀식의 기울기의 순서는 유기물함량의 순서와 같았다. 1×10^{-4} M Cd(NO₃)₂ 용액을 사용한 실험에서 유기물함량과 partition coefficient사이의 correlation coefficient (r²)는 용액의 pH가 4.0인 경우의 0.3027에서 pH가 8.5인 경우의 0.9964로 증가하였으며, 2×10^{-4} M Cd(NO₃)₂ 용액을 사용한 실험에서는 pH가 4.0인 경우의 0.2093에서 pH가 8.5인 경우의 0.9657로 증가하였다. 칼슘과 마그네슘의 탈착량은 토양용액의 pH가 증가할수록, 흡착된 카드뮴의 양이 증가할수록 감소하였다.