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Phosphate-induced cadmium adsorption in a tropical savannah soil

Enemona Marinus Ugbaje and Nafiu Abdu*

Department of Soil Science, Ahmadu Bello University, Zaria, Nigeria.

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The influence of phosphate (P) on cadmium (Cd) adsorption was examined in a savanna soil with long history of different fertilizer amendment. The soil was incubated with P at 0, 250 and 500 mg P kg^{-1} soil and left to equilibrate for 2 weeks. Cd was added to the P-incubated soil at concentrations ranging from 27, 49 and 83 mg Cd kg soil. Addition of phosphate as KH_2PO_4 increased Cd adsorption by the soil. The amount of Cd adsorbed at 250 mg P kg^{-1} treatment was more than the amount of Cd adsorbed at 500 mg P kg^{-1} at low equilibrium Cd concentration. The sorption maxima and the distribution coefficient also increased; but the distribution coefficient and binding energy at 250 mg P kg^{-1} were higher than those at 500 mg P kg^{-1}. Fitting the experimental data to adsorption, isotherm indicated a shift from the L-curve to the H-curve isotherm with P-amendment indicating a possible precipitation of Cd-P compounds. The Langmuir sorption maxima increased from 61 to 99.3 with P addition while the distribution coefficient also increased from 13.9 to 29.4. Our results indicated that Cd in the presence of phosphate can act as a bridging element between phosphate and organic matter.

Key words: Cadmium, adsorption isotherms, phosphate.

INTRODUCTION

The continual application of compost from municipal waste, untreated wastewater and the growing of vegetable and arable crops on abandoned dump sites has led to the buildup of heavy metals such as cadmium (Cd), lead (Pb), zinc (Zn) and nickel (Ni) in the soil (Anikwe and Nwobodo, 2002; Amusan et al., 2005; Agbenin et al., 2010; Abdu et al., 2011a). There is also some indirect evidence of possible heavy metal buildup in some agricultural soils in the savanna because of long term application of inorganic fertilizers (Ewa et al., 1999; Abdu et al., 2011a). However, investigations have shown that phosphate had not induced significant Cd enrichment in the soil even though the levels of phosphatic fertilizers added to these fields were more than those ordinarily feasible with majority of farmers in the region (Agbenin, 2006). Studies have shown that phosphate can precipitate many heavy metals, so one may consider employing phosphate fertilizers for treating Cd contaminated soils (Xiong, 1995). Of the potentially toxic metals, Cd is the most insidious in soil ecosystems (Agbenin, 2006). Plants can accumulate significant amounts of Cd without apparent toxicity symptoms (Prince et al., 2003), which can be toxic in the long-term to humans and animals. Crop plants, vegetables such as lettuce and spinach tend to accumulate more Cd than most other crops (Pinto et al., 2004; Abdu et al., 2011b). Cadmium consumption and toxicity in humans and animals have been associated with kidney and liver dysfunction, weakening of immune systems and the impairment of reproductive functions (Oliver, 1997).

Although, a number of studies have examined the influence of phosphate fertilizers on Cd immobilization by soils (Cao et al., 1993; Xiong, 1995; Bolan, 2003), the effect of this phosphate on the availability and retention of Cd on savanna soils still requires more examination. Moreover, the effectiveness and mechanism of using

*Corresponding author. E-mail: nabdu@abu.edu.ng, nafiu2002@yahoo.com.

phosphate to immobilize heavy metals such as Cd is still poorly understood. The objective of this study, therefore, was to determine the influence of phosphate on the adsorption of Cd and mechanism of Cd retention in a savanna soil under different fertilizer management.

MATERIALS AND METHODS

Site description and soil sampling

Soil samples used for this study were collected from the long-term dung (D), nitrogen (N), phosphorus (P) and potassium (K) (DNPK) experimental field of the Institute for Agricultural Research, Ahmadu Bello University, Samaru, Zaria (11°, 11’ N, 07° 38’ E) in sub-humid northern guinea savanna at an altitude of about 686 m above sea level. The trial started in 1950 and is the oldest organic and mineral fertilizer experiment in West Africa. In the first decade of the trial (1950 to 1960), cotton, sorghum and groundnut were cropped in rotation while between 1961 and 1970, cotton monoculture dominated from 1976, a rotation of groundnut and maize became a predominant cropping. Nitrogen was usually not applied when groundnut is grown as a sole crop. In 1967, lime was applied on a plot-by-plot basis depending on the actual lime requirement of each plot. Also, micronutrient like (Zn), molybdenum (Mo), boron (B) and copper (Cu) were sprayed on the crop growing on that field at that same year. The trial has been under natural fallow since 1997. The DNPK plot consists of 81 plots with a length of 272.25 m and width of 90.53 m.

The samples were taken from three plots comprising of the following fertilizer treatments: 1) Only D application, 2) N, P, K application, 3) only P application. The soil will be referred to as D, NPK and P, respectively. The soil samples were taken at a depth of 15 to 30 cm and each was replicated three times using an auger. The soil samples were air-dried and passed through a 2 mm mesh sieve and stored prior to analysis.

Chemical analyses

Soil particle size analysis was done with the standard hydrometer method as described by Gee and Bauder (1986). Soil pH was determined in water and 0.01 M $CaCl_2$ at soil solution ratio of 1:2.5 using a glass electrode pH meter. Organic carbon (OC) was determined by the Walkley-black method as described by Nelson and Sommer (1982). Extractable P was determine colorimetrically after extraction with NH_4F and HCl. Exchangeable cations (Ca, Mg, K and Na) were extracted with 1N NH_4OAC (pH 7.4). Calcium and Mg were determined by atomic absorption spectrophotometry (AAS). Sodium and K were determined using a flame photometer. Exchangeable acidity (H+Al) was determined by successive leaching of soil with 1N KCl using a 1:10 soil solution ratio. The amount of exchangeable H and Al in the leachates was determined by titration method. Cation exchange capacity was determined using the effective cation exchange capacity (ECEC) method (ECEC = ∑ exchangeable Na, K, Ca, Mg, Al and H).

The texture of the soil is sandy loam with a pH of 5.7 in water and 5.3 in $CaCl_2$, OC was 8.9 g Kg^{-1} and the ECEC is 6.3 Cmol Kg^{-1}. The extractable P of the soil was 4.05 mg Kg^{-1}.

Phosphate incubation

Fifty grams (50 g) of each soil sample was placed into 9 plastic containers. Each sample was replicated three times and labeled correctly. 100 ml of phosphate stock solution was added at two levels of concentration (250 and 500 mg P Kg^{-1}) to each sample. Another set of the soil samples were incubated with distilled water only as a control without phosphate stock solution. The samples were allowed to equilibrate for two weeks on a laboratory bench at field capacity. After two weeks, the soil samples were air-dried and passed through a 2 mm sieve. 2 g of each soil sample was weighed into a centrifuged tube and 20 ml of 0.01 M $CaCl_2$ solution was added as a background electrolyte. The samples were shaken for 2 h and later centrifuged. The supernatants were then filtered through Whatman No. 42 filter paper and phosphorus in the equilibrium solutions was determined by molybdenum-blue method of Murphy and Riley (1962). The pH of the P equilibrated soil sample was also taken after drying and sieving.

Cadmium sorption experiment

A batch experiment was used to study the adsorption of Cd onto the soil as a function of metal concentration. 5 g of each air-dried soil samples from the aforementioned experiment was placed into 3 different plastic containers and labeled correctly. 30 ml of $Cd(NO_3)_2$ solution were added at three different concentrations of 27, 49 and 83 mg Cd kg^{-1}. The samples were allowed to equilibrate for 24 h on the laboratory bench. After 24 h, the samples were centrifuged for 20 min and the supernatant was filtered. Cadmium was determined in the supernatant using atomic absorption spectrophotometer (Model 192, Pye Unicam, Cambridge, UK). Cadmium sorption data were fitted to the Langmuir and Freundlich adsorption isotherms. Langmuir equation could be represented as:

$$\frac{c}{q} = \frac{1}{kb} + \frac{c}{b} \qquad (1)$$

Where q = the amount of Cd sorbed per unit weight of soil (mg g^{-1}), c = equilibrium Cd concentration (mg L^{-1}), b = Cd adsorption maxima (mg kg^{-1}), k = coefficient relating to bonding energy (L mg^{-1}) and kb = distribution coefficient (L kg^{-1}).

The Freundlich equation is given by:

$$q = K_F C_q^{\frac{1}{n}} \qquad (2)$$

Where K_F and n are the Freundlich constants characteristic of the system involved; K_F and n are indicators of adsorption capacity and adsorption intensity, respectively.

K_F and n can easily be determined from the linearized logarithmic form of the equation given by:

$$\log q = \log K_F + \frac{1}{n} \log C_q \qquad (3)$$

Both the Langmuir and the Freundlich models were developed for a single layer adsorption. The Freundlich model has the advantage of accounting for surface heterogeneity and exponential distribution of multi-layer adsorption sites and hence, a more physical realistic description of metal adsorption by soil colloids. However, both equations normally fit experimental data set reasonably well over moderate ranges of concentration.

RESULTS AND DISCUSSION

Influence of phosphate on Cd adsorption

Cadmium adsorption has been described by adsorption isotherms such as the Langmuir and the Freundlich models. In this study, Cd adsorption by the soil was best described by Langmuir equation. Although, the Cd

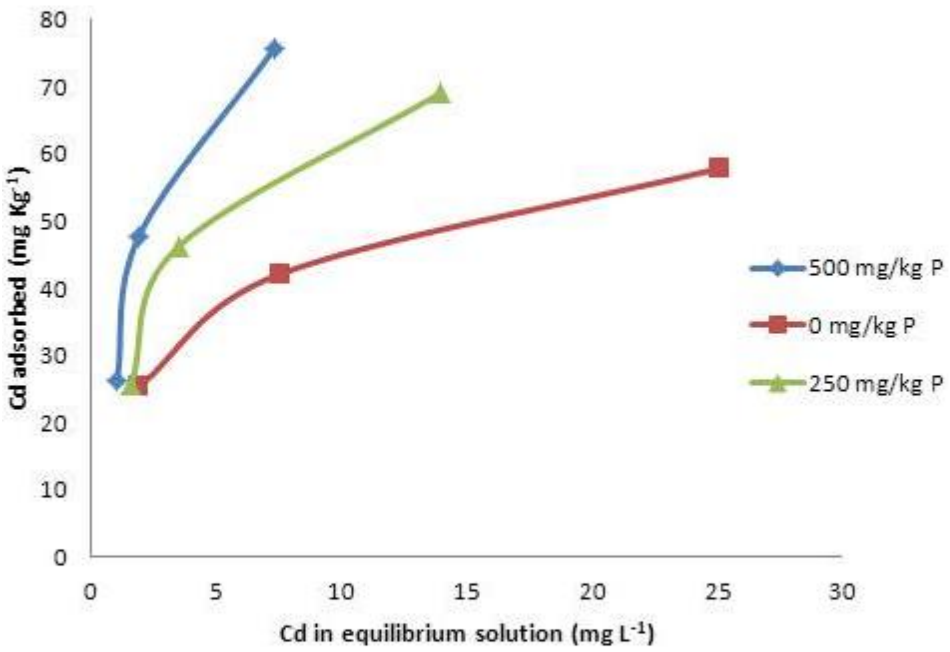

Figure 1. Cd adsorption as a function of phosphate incubation for the dung amended soil.

Table 1. Langmuir isotherm constants and coefficient of regression for adsorption of Cd on P amended soil.

Soil	0 mg P kg^{-1}				250 mg P kg^{-1}				500 mg P kg^{-1}			
	B	K	K_d	R^2	b	k	K_d	R^2	b	k	K_d	R^2
D	65.57	0.29	18.77	0.99	86.11	0.30	25.47	0.99	103.67	0.38	39.31	0.99
NPK	61.25	0.22	13.49	0.99	76.99	0.51	39.56	0.99	96.40	0.29	28.27	0.99
P	56.21	0.17	9.53	0.99	88.93	0.26	22.69	0.99	97.92	0.27	26.34	0.99

Table 2. Freundlich isotherm constants and coefficient of regression for adsorption of Cd on P amended soil.

Soil	0 mg P kg^{-1}				250mg P kg^{-1}				500mg P kg^{-1}			
	Lnk	K_F	n	R^2	lnk	K_F	n	R^2	lnk	K_F	n	R^2
D	3.05	21.13	0.32	0.99	3.14	23.13	0.44	0.93	3.37	29.17	0.51	0.92
NPK	2.86	17.44	0.34	0.94	3.34	28.16	0.35	0.91	3.21	24.68	0.47	0.99
P	2.68	14.57	0.35	0.94	3.09	21.93	0.45	0.98	3.15	23.41	0.50	0.95

adsorption data showed a highly significant fit to both Freundlich and Langmuir isotherms, comparison of coefficient of determination of Langmuir and Freundlich equation demonstrated that the Langmuir adsorption isotherm has a better fit than Freundlich equation. Phosphorus treatment changed Cd adsorption from the L-curve isotherm to the H-curve isotherm (Figure 1) indicating a strong affinity of the P-treated soil for Cd. H-curve isotherm has a large initial slope as a result of high affinity of the soil adsorbent for the adsorbate (Sposito, 2008). Phosphate has a very high affinity for soil adsorption sites. The adsorption of phosphate usually results in increasing soil negative charges (Perez-Novo et al., 2011). Phosphate would thus increase soil adsorption for heavy metal ions with positive charges. This result is in consonants with the observations of Agbenin (1998) that soil P amendment increased the net negative charge of the same soil. In the D soil, phosphate incubation resulted in increased Cd adsorption (Figure 1). The phosphate treatment also increased the distribution coefficient, sorption maxima and binding energy (Tables 1 and 2) for both the Langmuir and Freundlich equations. The sorption maxima in the Langmuir equation increased from 61 in 0 mg P kg^{-1} to 84 in the 250 mg P kg^{-1} and 99.3 in the 500 mg P kg^{-1}; similarly, with the distribution coefficient, it increased from 13.9 in the 0 mg P kg^{-1} to 29.4 in the

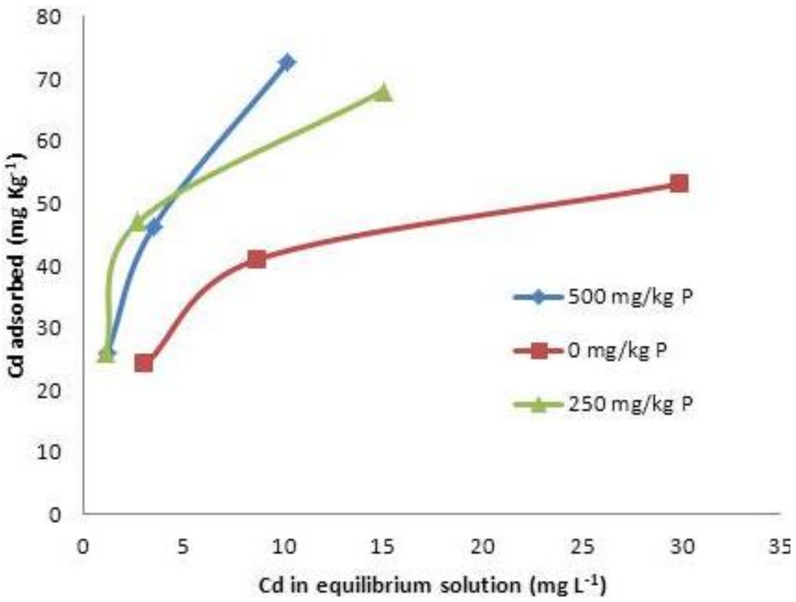

Figure 2. Cd adsorption as a function of phosphate incubation for the NPK amended soil.

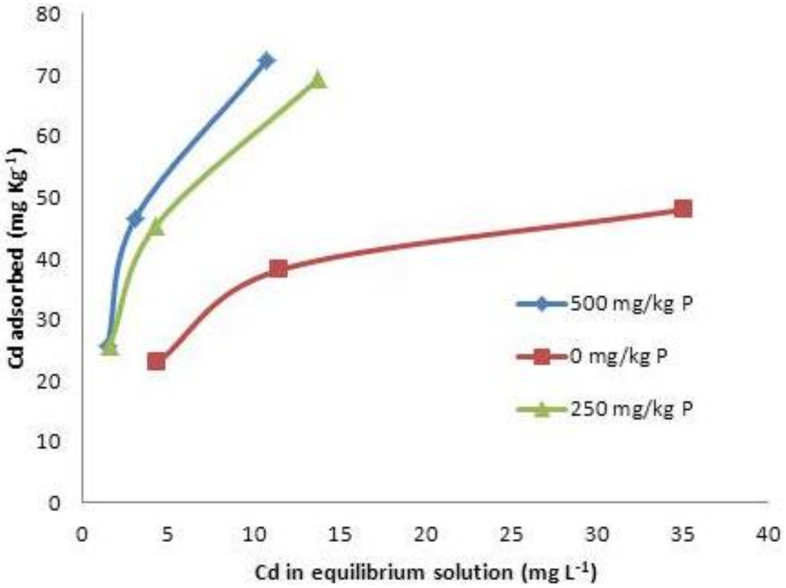

Figure 3. Cd adsorption as a function of phosphate incubation for the P amended soil.

250 mg P kg^{-1} and 31.1 in the 500 mg P kg^{-1} (Table 1).

The same trend was also observed in the P soil, phosphate treatment also resulted in increased Cd adsorption (Figure 2), increased distribution coefficient, sorption maxima and binding energy (Tables 1 and 2). Similar effects were also observed on the NPK soil. The phosphate treatment did increase the amount of Cd adsorbed (Figure 3). The amount of Cd adsorbed at 250 mg P kg^{-1} treatment was more than that adsorbed at 500 mg P kg^{-1} at low equilibrium Cd concentration.

Mechanism of Cd retention as a function of P amendment

The deviation of the adsorption isotherm from the L-curve to the H-curve suggests precipitation of Cd-phosphate compounds on the soil colloidal surface or co precipitation with solid P minerals in the soil. This co precipitation may be through the process of inclusion, adsorption or solid-solution formation (Sposito, 2008). With the P amendment, the adsorption of phosphate raised the

Table 3. The pH of the soil with and without phosphate pre-incubation.

Soil	**D**			**NPK**			**P**		
P treatments (mg kg^{-1})	**0**	**250**	**500**	**0**	**250**	**500**	**0**	**250**	**500**
PH	5.63	5.70	5.78	5.55	5.61	5.46	5.50	5.60	5.60

Table 4. Pearson correlation coefficient (r) between the Langmuir sorption maxima (b), bonding energy constant (k) and distribution coefficient (k_d) with pH.

Soil	**b**	**K**	**k_d**
D	0.99**	0.92**	0.98**
NPK	-0.64	0.63	0.32
P	0.97**	0.99**	0.97**

**= significant at 0.1 level of probability while the others are not significant.

pH of the system at low initial phosphate concentration (Table 3). The pH was found to correlate positively with the sorption maxima, binding energy and distribution coefficient (Table 4). Conflicting results have been reported on the effect of pH on P sorption in variable charge soils. When 500 mg P kg^{-1} was added to the soil, there was no increase in the pH of the soil. This goes to show that phosphate treatment does not always alter the pH of the soil. Thus, pH rise is not a crucial variable as regard the increased adsorption of Cd in the presence of phosphate in this soil since it could not account for the increased adsorption of Cd at 500 mg P kg^{-1}. Increased P adsorption with increasing pH in weathered tropical soils has been attributed to polymerization of monomeric Al specie (Mokwunye, 1975; Haynes, 1983). However, savanna soils are dominated by Ca in the exchange sites, and it has been directly established by Sery et al. (1996) that Cd can occupy Ca crystallographic sites due to similarities in their chemistry, making it more difficult to effectively predict the mechanism of P-induced Cd retention in this soil. However, Cd may form a complex mineral with Ca minerals like tricalcium phosphate ($Cd_3(PO_4)_2$-β–$Ca_3(PO_4)_2$ and hydroxyl apatite ($Cd_3(PO_4)_2$–$Ca_5(PO_4)OH$) in the soil thereby reducing the solubility and availability of Cd; this merits further investigation. These Cd-Ca-P minerals ($Cd_3(PO_4)_2$-β–$Ca_3(PO_4)_2$ and ($Cd_3(PO_4)_2$–$Ca_5(PO_4)OH$) have been reported to control Cd activities in similar savanna soils in Northern Nigeria (Egwu and Agbenin, 2012).

Irrespective of fertilizer management history in the soil, the adsorption of Cd increased with increasing level of phosphate (Figure 1). The pH was found to correlate positively with the distribution coefficient, sorption maxima and binding energy of the Langmuir adsorption model (Table 4) except for the NPK soil where we observed weak correlation with all the sorption parameters. The slight rise in pH could be attributed to the increased Cd adsorption in this soil as a result of P amendment. The adsorption of Cd at 250 mg P kg^{-1} was found to be more than that at 500 mg P kg^{-1} at low initial Cd concentration (Figure 2). The high binding energy and distribution coefficient (Tables 1 and 2) suggested that the soil had high affinity for Cd at 250 mg P kg^{-1} which culminated in the increase in the proportion of Cd at specific adsorption sites with low-capacity and high affinity at low Cd concentration (Sposito, 2008); thus, the pH could not satisfactory explain the large Cd retention by the soil. The amount of Cd adsorbed increased with increasing organic matter content of the soils in the order D > NPK > P at all phosphate treatments. The only exception was at 250 mg P kg^{-1} in the NPK soil. This could probably be as a result of the increase in the proportion of Cd at specific adsorption sites at this level of phosphate treatment.

The increased adsorption of Cd for the soils could probably be as a result of the formation of bridging complex whereby anionic or polar functional group (for example, carboxylates or carbonyls) become bound to the Cd^{2+} adsorbed by phosphate (Sposito, 2008).

Conclusion

The results of this study indicated that Cd adsorption is higher in the presence of phosphate. The result suggested that the increased Cd adsorption in the presence of phosphate may be a consequence of Cd acting as a bridging element between phosphate and soil organic matter in the soil. Therefore, soils with high organic matter content have greater ability to immobilize Cd in the presence of phosphate. Further investigation should aim at studying the effect of clay and sesquioxides on P-Cd interaction.

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