



Immobilization of toxic metal cations on goethite-amended soils: a remediation strategy

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ABSTRACT: The study investigates a simple and viable option to reduce toxic metals mobility and availability in four surface (0–30cm) soils with varying physicochemical properties amended by different percentages of goethite. Batch sorption experiments carried out to study the effectiveness of immobilizing Pb²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ ions on these soils showed that goethite played vital role in the metals adsorption (≥10% increase in adsorption). Removal of soil iron oxides caused reduced Pb²⁺ adsorption on soils with high organic matter (≤10% decrease in adsorption) with no significant increase in adsorption upon amendment, while soils having low organic matter had enhanced adsorption with amendment. Cu²⁺ and Cd²⁺ adsorptions were not enhanced even at 10% goethite amendment. However, Zn²⁺ adsorption was interestingly different: the soils showed ≥55 % increases upon removal of inherent soil iron oxides without goethite amendment. Goethite amendments further enhanced Zn²⁺ adsorption on these soils. Generally, both whole and amended soils showed higher preference for Pb²⁺; the sorption trend is – Pb²⁺ > Cu²⁺ > Zn²⁺ > Cd²⁺. Goethite amendment of these soils improved Pb²⁺ and Zn²⁺ adsorption. Hence, goethite amendment may be an effective method for immobilizing Pb²⁺ and Zn²⁺ on these soils and thus reducing their availability to biota. The quantity of goethite required by a soil to attain maximum immobilization varies depending on the metal and the soil's physicochemical properties; however, Cu²⁺ and Cd²⁺ may not be effectively immobilized using goethite amendment. © JASEM

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Introduction

Toxic metals are important environmental pollutants threatening the health of the natural ecosystems due to their persistence and accumulation in the environment (Asiagwu *et al.*, 2012; Owamah, 2014). The severity of the environmental problems posed by the accumulation of these metals depends on their availability and mobility in soils, which are in turn dependent on their particular sorption reactions with soil colloids. The sorption behavior of toxic pollutants varies among soil types and is a function of one or more soil properties which can either enhance or reduce the adsorption capacity of the soil (Diagboya *et al.*, 2015; 2016).

Reducing metals solubility and bioavailability without removing them from contaminated soils is a viable method of reducing the detrimental impacts of toxic metals on the environment (Usman *et al.*, 2006). This

can be done by enhancing soil metal sorption capacity usually by soil amendment. Several soil properties affect and regulate the solubility and retention of toxic metals. Of these properties, soil pH, hydrous oxides content, mineralogy, organic matter content, and cation exchange capacity are critical to metal solubility and retention (Agbenin, 2010; Diagboya *et al.*, 2015). Amendment of these soil properties to improve soil metal sorption behavior has been used severally by the application of natural and synthetic additives like alkaline materials, phosphate minerals, zeolite, sewage sludge, Fe and Mn oxides, aluminosilicates, biomass, and coal fly ash (Usman *et al.*, 2006; Olu-Owolabi *et al.*, 2016), with the aim reducing metal availability in soil water and hence availability to biota.

Soils in the tropics are especially rich in hydrous iron oxides (haematite, goethite, gibbsite and ferrihydrite)

minerals; goethite which is responsible for the yellowish brown colour of many soils is the commonest of these hydrous iron oxides (Olu-Owolabi *et al.*, 2015). Surface chemistry of goethite is well understood and found to be responsible for the adsorption, remobilization and distribution of potentially toxic metals (Mustafa *et al.*, 2004). The chemical nature and high specific surface area of iron oxides as discrete particles and coatings on other minerals make these oxides efficient sinks for many contaminants (Mckenzie, 1980; Fu *et al.*, 1991; Mench *et al.*, 1994; Diagboya *et al.*, 2015). Thus, considering the good metal sorption property of goethite, it was used as an immobilizing agent in this study. Immobilization prevents the metals mobility into the soil water environment, and hence the aquifer by reducing its solubility and, consequently toxicity.

The aim of this investigation is to study four potentially toxic metal cations (Cd^{2+} , Zn^{2+} , Cu^{2+} and Pb^{2+}) associated with several agricultural chemicals. These metal cations have been reported to be toxic to biota at higher than the permissible limit in the environment, and can cause kidney and blood diseases among other organ dysfunctions in humans (Serrano *et al.*, 2005; Tiwari *et al.*, 2007; Gupta and Bhattacharyya, 2006). Since goethite has been recognized as having good metal sorption capacity, the objective of this work was to study the effectiveness of immobilizing the above cations on iron oxide-depleted soils using goethite amendment.

MATERIALS AND METHODS

Soil Sampling, pretreatment and characterization: Four surface soils (0–30cm) were obtained from three Nigerian sites in Adamawa State (12°30'E; 9°20'N)–Yola Metropolis (AD1), along the River Benue bank (AD2), Girei Local Government Area (AD3); and New Bussa (NB) (4°31'E; 9°53'N). Samples were air-dried, crushed gently and sieved through a 230-mesh size sieve, and the fine fraction retained for the studies.

The soils' pH values were determined in de-ionized water and 1.0 M KCl (ratio 1:1). Particle size determination was by the hydrometer method (Day, 1965). Organic carbon was determined by the Walkley-Black wet digestion method (Walkley and Black, 1934). The exchangeable bases (Na, K, Ca and Mg) were determined by the 1.0 M ammonium acetate (NH_4OAc) method at pH 7.0, while the exchange acidities were determined by titration (Chapman, 1965; Bower *et al.*, 1952). The cation exchange capacity (CEC) of each soil was obtained by summation of the exchangeable bases and the exchange acidity. Extractable micronutrients and heavy metals (Fe, Mn, Cu, Zn) were obtained by acid extraction and determined by Buck Scientific 205

Atomic Absorption Spectrometer (AAS) with air-acetylene flame on absorbance mode.

Synthesis of Goethite: Goethite was prepared using the method of Schwertmann and Cornell (1991) and Juang and Chung (2004). All chemicals were stored in polyethylene flasks and the experiments were carried out in polyethylene vessels to avoid possible contamination by silica. The water used throughout the experiments was distilled and deionized. After slow and drop-wise addition of 180 cm³ of 5 M KOH to 100 cm³ of 1 M $\text{Fe}(\text{NO}_3)_3$, the solution was diluted with water to 2 dm³ (pH 12). It was aged for 60 hours at 60 °C. During this period, the solution was agitated three times for 2 min each. After aging, a compact, brown precipitate of the goethite was formed. The resulting suspension was centrifuged and filtered, and the cake was washed with water until the solution was neutral. The iron oxide was dried at 60 °C for 24 h and finally stored in a dessicator. Prior to use, goethite was ground and sieved.

Removal of iron oxides in soil and preparation of goethite amended samples: 200 g of each sample was weighed into separate 1L beakers. 150ml each of citrate-bicarbonate buffer was added to the beakers, stirred, and 20 g of sodium hydrosulfite (dithionite - $\text{Na}_2\text{S}_2\text{O}_4$) was gradually added to stop frothing. The beakers were put in a water bath at 80°C, stirred for 20 minutes and then decanted. The above steps were repeated until the brown colour of the samples was fully removed (McKeague, 1978). The samples were then washed several times with deionized water until the filtrate was colourless. The samples were placed in an oven overnight at 105 °C and cooled in a dessicator. These were the iron oxide-free soils.

Amount of goethite used to amend the iron oxide-free soils were varied from 0 to 10%. This was achieved by weighing and dissolving appropriate quantity of goethite in 2 ml 0.1 M NaOH solution, followed by mixing with the corresponding mass of iron oxide-free soil to make a slurry. The slurry was incubated for 5 days before it was air dried, ground, sieved, and used for the sorption experiment.

Sorption studies: Equilibrium sorption study (Diagboya *et al.*, 2015) was carried out on the whole (untreated) soils by agitating 20mL single metal solutions containing 1.0 g of the soils for 24 h. Metal concentrations used were in the range of 25-500 mg/L. The experiments were done at ambient soil pH and room temperature (26 ± 1 °C) using 0.01M NaNO_3 as indifferent electrolyte in 50mL capped polyethylene bottles agitated in a mechanical shaker at 75 rpm.

Sorption study was also carried out on the goethite amended soils by weighing 1.0 g each of all percentages (0, 2, 4, 6, 8 and 10%) of amended soils into four series of polyethylene bottles representing each soil. Single metal solutions (20mL) of specific concentration (Pb– 500ppm; Cu and Zn– 200ppm; and Cd– 50ppm) were added to respective polyethylene bottles followed by incubation for 24 h in a mechanical shaker set at 75 rpm. All experiments were carried out in duplicate at ambient soils' pH and room temperature using 0.01M NaNO₃ at indifferent electrolyte. Samples were withdrawn after 24 h, filtered, and the amount of metal ion left in the filtrate determined using Buck Scientific 205 Atomic Absorption Spectrometer (AAS) with air-acetylene flame on absorbance mode.

Sorption data treatment: The amounts of metal ions sorbed by the soils were calculated from the initial and final metal concentrations of the solution after the incubation using equation 1:

$$q_e = \frac{(C_o - C_e)V}{m} \quad 1$$

Where q_e is the amount of metal adsorbed (mg/g), C_o and C_e are the initial and equilibrium metal concentrations in the solution (mg/L), respectively. V (mL) and m (g), respectively, are the volume of solution and mass of soil used for the experiment.

The Langmuir (1916) (Equation 2) and Freundlich (1906) (Equation 3) isotherms in their linear forms were tested in describing the adsorption data. Owamah et al. (2013) had used both isotherm models to study the removal of dye from aqueous solution using yam peels. The equations used are as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad 2,$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad 3$$

where Q_o (mg/g) is the Langmuir maximum adsorption capacity, b , K_f and n are isotherm constants obtained from the slopes and intercepts.

RESULTS AND DISCUSSION

Soil Properties: The results of the physicochemical characteristics of the soils samples are shown in Table 1. The results were compared with those of soils from several parts of Nigeria (Olu-Owolabi *et al.*, 2014). It was observed that the soils' pH were neutral except for AD3 which was slightly acidic in 1.0N KCl. The soils organic carbon contents were relatively low for AD1 and AD3 soils while it was high for AD2 and NB soils. The general order of organic carbon increase is AD2 > NB > AD3 > AD1. The higher organic matter content of AD2 and NB maybe attributed to the dumping of organic materials on both sampling vicinities due to the wave action from the Rivers Benue and Niger, respectively. Ca and Mg are the major contributors to the soils' exchangeable bases while Na and K in these soils were low; the predominance of Ca and Mg maybe a common feature of most Nigerian soils (Fagbami and Shogunle, 1995; Olu-Owolabi *et al.*, 2010). The CEC of the soils are very low. The soils' particle size distributions showed that the textural classes for AD1 and AD3 are loamy sand, while AD2 and NB are sandy loam and sandy clay loam, respectively. The order of abundance of clay fraction is NB > AD2 > AD3 > AD1. The level of exchangeable micronutrients and heavy metals (Table 2) in these soils are within the range found in typical Nigerian mineral soils (Olu-Owolabi *et al.*, 2010; Igwe *et al.*, 1999).

Table 1: Physico-chemical properties of the soil samples

Sample	pH		Org.C	Exchangeable Bases (mg/100g)				CEC	Base saturation	Particle size Analysis (%)		
	KCl	H ₂ O	%	Ca	Mg	Na	K	Meq/100g	%	Sand	Silt	Clay
AD1	6.7	7.4	1.2	1.48	0.69	0.09	0.17	3.03	80.20	85.2	9.4	5.4
AD2	6.6	7.6	3.8	1.50	0.76	0.11	0.18	3.55	71.83	51.2	31.4	17.4
AD3	5.7	6.7	1.2	1.57	0.74	0.10	0.18	3.59	72.15	81.2	11.4	7.4
NB	6.5	7.4	2.8	1.43	0.66	0.08	0.15	2.92	79.45	53.2	27.4	19.2

Org. C- Organic Carbon; T.N.- Total Nitrogen; CEC- Cation Exchange Capacity.

Table 2: Physico-chemical Properties of the soil samples

Sample	Exchangeable micronutrients/heavy metals					
	Mn	Fe	Cu	Zn	Cd	Pb
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
AD1	102.28	67.15	10.11	25.94	0.200	0.425
AD2	87.48	52.96	0.79	19.83	0.250	0.525
AD3	113.36	70.14	13.05	30.36	0.250	0.500
NB	98.56	67.59	11.15	26.75	0.175	0.475

BD- Bulk Density; HC- Hydraulic conductivity; EC- Electrical conductivity.

Cations Sorption Study

Equilibrium metal sorption on untreated soils

Fig. 1 shows the equilibrium metal sorption trend as metal concentration increased on all untreated soils. It was observed that increasing the initial metal concentrations of Pb^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} in solution led to increase in amount of metals adsorbed by the soils, indicating that sorption was progressively initial

concentration dependent. Olu-Owolabi *et al.* (2016) attributed similar trend to the fact that when the transport of metals between the soil's external surface film and internal pores are equal, the trans-boundary movement of metals will not be significantly permissible; however, increasing concentration will re-initiate the trans-boundary movement and hence, the process will be concentration dependent

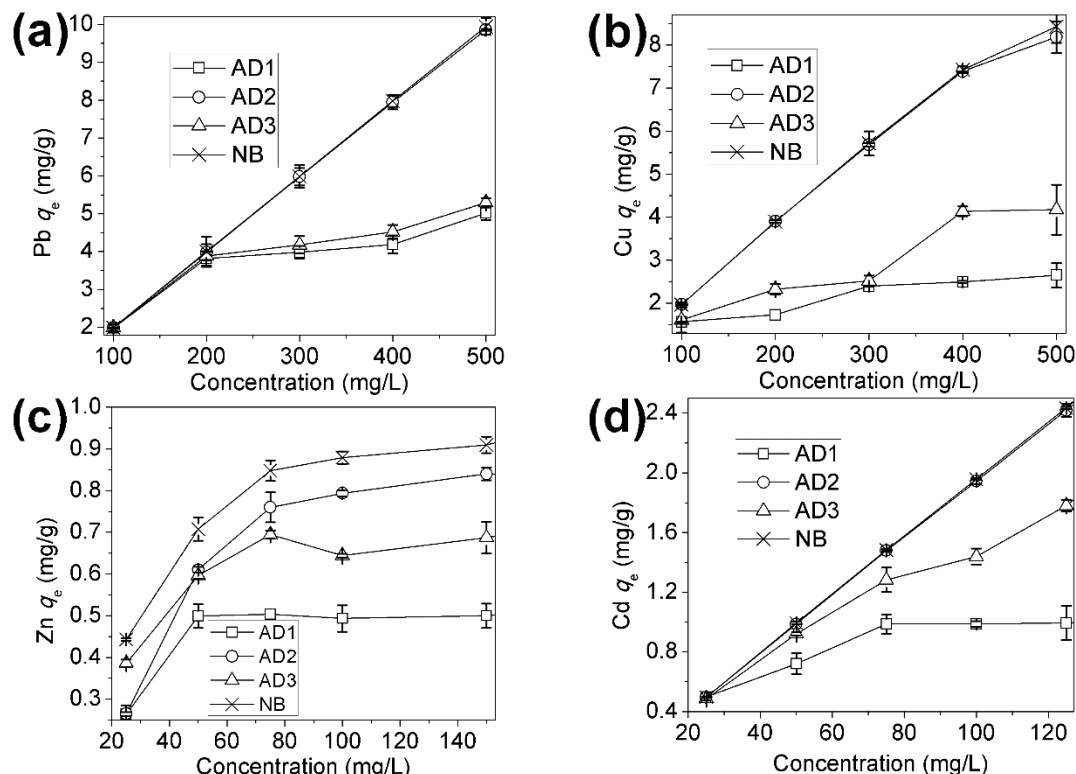


Fig. 1. Effect of metal concentration on metal adsorption on the various whole (untreated) soils for (a) Pb^{2+} , (b) Cu^{2+} , (c) Zn^{2+} and (d) Cd^{2+}

The trend may also be due to competition between the metals in solution and other sorbates hitherto on the soils adsorption sites; at low concentrations the ratio of the available metals in solution to the surface adsorption sites is low, and competition for adsorption sites from protons and other occupying molecules (cations) are higher than competition from the metals.

This results in the metals being adsorbed without the sites reaching saturation. With subsequently higher initial concentrations, the metals in solution to surface adsorption sites ratio progressively increases resulting in corresponding increase in competition for adsorption sites. The sheer number of the metals in solution forces the displacement of the protons and

other hitherto occupying molecules from the adsorption sites, and hence the increased adsorption recorded (Weber *et al.*, 1992). This increase in metals sorption was higher in the AD2 and NB soils which are in agreement with the high organic matter contents of both soils. The general trend is $AD2 \geq NB > AD3 \geq AD1$. Stronger preference for Pb^{2+} than other metals was shown by these soils. Similar preference has been reported in literature (Diagboya *et al.*, 2015; Olu-

Owolabi *et al.*, 2016; Pardo, 2000) and this has been attributed to Pb^{2+} smaller hydrated radius in comparison to other cations, the greater affinity of Pb^{2+} for most functional groups in organic matter, as well as its higher electronegativity; making it a better candidate for electrostatic and inner-sphere surface complexation reactions (Nightingale, 1959; Usman, 2008).

Table 3: Langmuir and Freundlich isotherm parameters for the untreated soils

Soil	Metal	*Exp. Q_o	Langmuir			Freundlich		
			Q_o	B	r^2	K_f	n	r^2
AD1	Pb	4.19	4.74	0.20	0.983	1.83	5.74	0.679
	Cu	2.50	2.82	0.08	0.897	1.05	5.21	0.668
	Zn	0.50	0.54	0.14	0.996	4.90	5.00	0.585
	Cd	0.99	1.04	0.41	0.997	1.40	13.70	0.896
AD2	Pb	8.90	10.00	10.00	0.996	4.06	13.33	0.020
	Cu	7.45	8.52	0.23	0.994	1.48	2.27	0.893
	Zn	0.80	0.93	0.07	0.979	6.24	2.76	0.660
	Cd	2.62	3.00	1.75	0.960	1.41	2.27	0.919
AD3	Pb	4.91	5.05	0.21	0.986	2.17	6.90	0.584
	Cu	4.15	4.24	0.03	0.850	1.10	4.13	0.880
	Zn	0.69	0.75	0.16	0.995	3.15	5.71	0.832
	Cd	1.83	2.11	0.19	0.908	1.76	3.01	0.953
NB	Pb	8.96	10.10	30.94	0.999	3.66	15.15	0.021
	Cu	7.93	0.07	0.51	0.742	1.37	2.08	0.919
	Zn	0.91	1.00	0.21	0.995	2.43	5.25	0.812
	Cd	2.67	3.02	1.72	0.940	1.64	2.35	0.971

* Experimental Q_o

The sorption data was fitted to the linear forms of the Langmuir and Freundlich adsorption isotherm models (equations 2 and 3) and the isotherm parameters are shown on Table 3. It was observed that the data fitted the Langmuir adsorption isotherm model ($r^2 \geq 0.897$) better than the Freundlich ($r^2 \leq 0.832$) with the exception of Cd^{2+} sorption on all soils and Cu^{2+} on AD2 and AD3 which fitted both models ($r^2 \geq 0.850$). The Langmuir maximum adsorption capacity (Q_o) was close to the experimental Q_o values (Tables). According to the Langmuir isotherm model assumption, the good fit of these data to the isotherm implies that sorption occurred on sites having equal affinity for the metals with formation of adsorbate (metal) monolayer on the soil surfaces at equilibrium. The good fits of Cu^{2+} and Cu^{2+} data to both models may not be out of place because a combination of several Langmuir type adsorption isotherm models occurring simultaneously have been shown to give a good approximation to the Freundlich type isotherm model (Olu-Owolabi *et al.*, 2016).

Effect of Goethite Amendment on Sorption: Fig. 2 shows the metals sorption trend by the various percentages goethite-amended soils. It was observed that as the percentage of goethite in each soil increased from 2 to 10%, there was corresponding increases in metal adsorption. This implies that the amount of iron oxides in the soils plays vital role in the soil's metal adsorption.

Comparing the amounts of Pb^{2+} adsorbed by the whole (Fig. 1) and goethite amended (Fig. 2) soils, it was observed that that removal of inherent iron oxides in AD2 and NB soils without goethite amendment (0% goethite) did not cause any significant reduction ($\leq 9\%$) in Pb^{2+} adsorbed when compared with the whole soils. Even increasing goethite content (up to 10%) had no significantly effect on the amount of Pb^{2+} adsorbed on both soils (Fig. 2a). For the AD1 and AD3 soils, removal of soil iron oxides without amendment (0% goethite) led to reduced Pb^{2+} adsorption of 34 and 11%, respectively. However, significant increases in adsorption were observed for both soils starting from the 2% goethite content. By 6% goethite content,

$\geq 46\%$ increases in Pb^{2+} adsorption were recorded. This suggests that adding exogenous goethite to AD1 and

AD3 may be a viable way to immobilize Pb^{2+} on these soils.

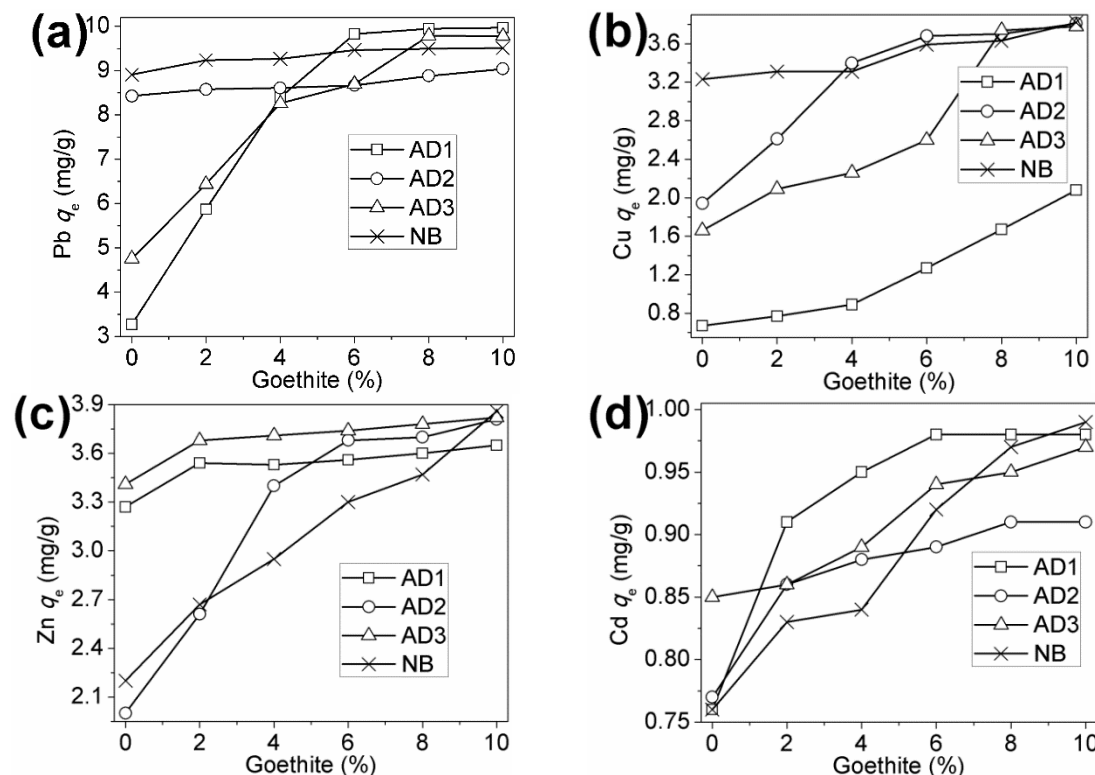


Fig. 2. Adsorption trend as percentage goethite increased on the treated soils for (a) Pb^{2+} , (b) Cu^{2+} , (c) Zn^{2+} and (d) Cd^{2+}

Fig. 2b showed that all soils exhibited lower Cu^{2+} adsorption ($\geq 60\%$) on removal of the inherent iron oxides on the soils. Goethite amendment (even up to 10%) did not significantly improve Cu^{2+} adsorption on these soils as 10% goethite amendment was not enough to achieve experimental maximum adsorption observed on whole soils (Fig. 1). Similarly, these soils exhibited lower Cd^{2+} adsorption (Fig. 2d) after removal of inherent soil iron oxides and goethite amendments also did not enhance the Cd^{2+} adsorption.

Zn^{2+} adsorption (Fig. 2c) exhibited a rather interestingly slightly different phenomenon. Removal of inherent soil iron oxides without goethite amendment, led to significant increases in adsorption in all soils in comparison to whole soils. For instance, 85, 60, 79, and 55 % increases in Zn^{2+} adsorption was observed for AD1, AD2, AD3 and NB, respectively. Goethite amendments (up to 4%) of AD1 and AD3 led further corresponding 8 and 11% increases, but no significant adsorption was observed beyond this goethite percentage. However, goethite amendment ($\geq 6\%$) in AD2 and NB led to significant Zn^{2+} adsorption enhancement of 47 and 44 %, respectively. This suggests that goethite amendment may be more

beneficial in Zn^{2+} immobilization in soils which are rich in organic matter such as AD2 and NB.

Fig. 2 also shows the contribution of goethite to the metals adsorption process. The degree of steepness of a curve indicates the extent of goethite contribution. Curve steepness implies that the bulk of metals adsorbed by the soils were on adsorption sites created by the exogenous goethite. This adsorption pattern was observed (Fig. 2) in Pb^{2+} adsorption on AD1 and AD3, Cu^{2+} adsorption in AD1, AD2 and AD3, Zn^{2+} adsorption in AD2 and NB, and Cd^{2+} adsorption in all soils. The soils exhibited similar metals adsorption preference for both treated and untreated soils – $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. The percentage of goethite needed for each soil to attain maximum adsorption varies depending on the metal and the soil physicochemical properties.

Conclusion: The study showed that goethite played vital role in immobilizing Pb^{2+} and Zn^{2+} ions on these soils. Adsorption of Cu^{2+} and Cd^{2+} ions were reduced on amendment of soil with goethite. Interestingly Zn^{2+} adsorption was enhanced ($\geq 55\%$) on removal of inherent soil iron oxides prior to goethite amendment.

Goethite amendments further enhanced Zn^{2+} adsorption on these soils. In general, goethite amendment of these soils improved Pb^{2+} and Zn^{2+} adsorption. Thus, goethite amendment may be an effective method for immobilizing Pb^{2+} and Zn^{2+} on these soils and thus reducing their availability to biota. The quantity of goethite required by a soil to attain maximum immobilization varies depending on the metal and the soil's physicochemical properties; however, Cu^{2+} and Cd^{2+} may not be effectively immobilized using goethite amendment.

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