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Removal of Heavy Metals (Cd and Pb) from Contaminated Soil by Amorphous Al and Fe Hydroxides

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Abstract. The sorption/desorption properties of heavy metals (Cd and Pb) on synthetically prepared amorphous Al and Fe hydroxide in the absence and presence of low (citrate) and high (tannate) molecular weight organic ligands from heavy metal-polluted soils were investigated in this work. The sorption kinetics and desorption of Cd and Pb have also been investigated. Four soil samples were collected from contaminated locations in Egypt: Abo-Rawash and El-Gabal El-Asfer, Mostorod and Shubra. The depth of collected samples is (0-30) cm. According to the results, all of the immobilizing agents tested have a cation exchange capacity of 31.3 to 67.8 C mol(c)Kg. In addition, the prepared amorphous hydroxides demonstrated Cd and Pb adsorption capability and retention of the adsorbed metal. The tested immobilizing agents (Fe–citrate and Al–tannate) show a high adsorption capability for Cd. The highest adsorption capacities of Al-tan and Fe-cit were 2.269 and 5.665 g/Kg, respectively. The tested immobilizing agents might be grouped in descending order based on their maximum adsorption capacity: Fe-cit. > Al-tin. The adsorption affinity (binding energy) between immobilizing agents and Cd ranged from 0.062 to 0.063. Fe-cit received the highest value (0.063), while Al-tan received the lowest one (0.062). Immobilizing agents (Fe-cit. and Al-tan.) have maximal adsorption capacity for Pb ranging from 2.5 to 5.0 g/Kg. Fe-Cit., like Cd, had the highest maximal adsorption capabilities, whereas Al-tan had the lowest. The tested immobilizing agents could be grouped in the following order, descending in Pb maximum adsorption capacity: Fe-cit. > Al-tan.

Keywords: soil contamination, heavy metals, chemical remediation, immobilization, metal oxides, organic ligands

Introduction

The rapid and extensive spread of contaminants like heavy metals in agricultural land has considerably raised the load on terrestrial ecosystems and communities (Alloway, 2013; Al Obaidy and Al Mashhadi, 2013; Grimm *et al*., 2008). One of the major responsibilities of soil contaminants is heavy metals, which pose serious hazards and negative health effects and are the most common toxins in soil (Johnson *et al*., 2023; Zahra *et al*., 2017; Al-Anbari *et al*., 2015).

Many different remediation technologies have been developed around the world for soil cleanup (Stegmann *et al*., 2001; Iskandar and Adriano 1997) such as thermal remediation for Hg (Hseu *et al*., 2014), soil washing for As (Ko *et al*., 2006), chemical leaching for Cd (Makino *et al*., 2007), solidification/stabilization for Zn (Al-Wabel *et al*., 2014) and phytore (Smith *et al*., 2023; Babu *et al*., 2013).

Sources of heavy metals in soils are from both lithogenic sources and different anthropogenic sources (Johnson *et al*., 2023; Al-Anbari *et al*., 2015; Rahi *et al*., 2014). Naturally, the heavy metals occur from soil parent materials, while present in the form unsuitable for plant uptake chiefly. Industrial sites generally expose soil to a variety of heavy metal contaminants, which vary by industry (raw materials and products). Due to traffic, paint and other non-specific urban sources, soils in all metropolitan contexts are typically contaminated with various metal species (such as Cd, Cu, Pb and Zn) (Tchounwou *et al*., 2012). The most frequent metals found in polluted areas are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu) and mercury (Hg) (Smith *et al*., 2022; Al Lami *et al*., 2021; Amin *et al*., 2018).

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Chemical remediation includes the application of additives in polluted media to remove or stabilize contaminants. Chemical remediation techniques include leaching (soil washing) and immobilization (solidification/stabilization, vitrification and electrokinetic approach) (Garcia *et al*., 2023; Ou-Yang *et al*., 2010; Tampouris *et al*., 2001). Immobilization techniques (chemical fixation) mean applying reagents or chemicals to the contaminated soil to produce insoluble or scarcely mobile, low-toxic compounds, thus reducing the migration of heavy metals to water, plants and other environmental media. Simplicity and rapidity can be accomplished if the soil immobilization technique is used. Pollutant activation, on the other hand, happens when soil physico-chemical parameters change since in situ immobilization is only a temporary fix (contaminants are still in the environment) (Davis *et al*., 2023; Zhou *et al*., 2004). The vitrification process, which depends on the electrokinetic methodology (Luo *et al*., 2004), specifically calls for the application of voltage on both sides of the soil to create an electric field gradient (Khandaker and Rinklebe, 2022; FRTR, 1999). Direct electrokinetic remediation, however which has poor treatment quality and cannot control the soil system's pH value. It was also shown that electrokinetic remediation takes to complete. It has been demonstrated that electrodialytic remediation can be effective when applied to stationary, water-saturated soils (*in-situ*) or suspended soil (*ex-situ*) (Khandaker and Rinklebe, 2022; Ottosen *et al*., 2012).

Metal oxides (such as Fe, Al, Ti and Mn) are important players in soil metal geochemistry. Through a special sort of sorption, co-precipitation and inner sphere complex formation, Fe metal oxides can strongly bind metals. The characteristics of soil's organic and inorganic ligands and their metal complexity significantly hinder their ability to bind to oxides, which affects the effectiveness of stabilization (Smith *et al*., 2023b; Zhu *et al*., 2011a and b; Zaman *et al*., 2009). The removal of heavy metals (As, Cd, Cu, Pb and Zn) from polluted soils uses nanosized metal oxides (NMOs) such as ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides, cerium oxides, due to their high efficiency and wide surface areas (Hua *et al*., 2012; Agrawal and Sahu, 2006). Due to environmentally safe elemental iron, nanosized iron oxides (NFeOs) have a low danger of secondary pollution when utilized in polluted media (Deliyanni *et al*., 2004).

The goal of this work was to examine the sorption and desorption properties of heavy metals (Cd and Pb) on synthetically created amorphous Al and Fe hydroxide in the absence and presence of organic ligands with low molecular weights (citrate) and high molecular weights (tannate). The kinetics and desorption of sorption of Cd and Pb have also been investigated. Amorphous Al and Fe hydroxides were chosen for this investigation due to their frequent occurrence in an environment with organic ligands (Cornell and Schwertmann, 1979). Also, have a larger surface area and higher anion adsorption reactivity than their corresponding phases of crystalline minerals (Bohn and O'Connor, 1979). Citrate and tannate ligands were chosen for this investigation because the soil rhizosphere contains a lot of them (Guo and Yan, 2019; Fox and Comerford, 1999; Robert and Berthelin, 1986). However, the tannate ligand was chosen to compare organic ligands with low and high molecular weights.

Materials and Methods

Study sites. ***Sample collection***. Four soil samples were collected from polluted sites in Egypt, Abo-Rawash, El-Gabal El-Asfer, Mostorod and Shubra. These four sites were polluted by the discharge of industrial residues and by heavy metals, respectively (polluted site of vehicle exhausts). The depth of collecting samples is (0-30) cm. In the labouratory, the samples were dried (under room temperature), sieved (< 2 mm) after the removal of gravels and roots and stored before carrying out the experiments.

Total Cd concentrations in the surface layers of the soils in the Fayoum District of Egypt ranged from 15.5 to 215, with a mean value of 40.8 mg/Kg soil, according to Abd El-Gawad *et al*. (2007). The average of 18.89 mg/Kg soil, corresponding values for the sub-surface start range from 2.3 to 38.5. The top 60 cm layer's total mean concentration was 29.73 mg/Kg soil. In the top 30 cm of soil, DTPA-extractable Cd concentrations range from 0.06 to 2.40 mg/Kg, with a mean value of 0.25 mg/Kg soil. Values varied from 0.02 to 0.30, averaging 0.11 mg/Kg soil in the sub-surface (30–60 cm). The top 60 cm layer's total mean value was 0.18 mg/Kg soil. According to Abdel-Hamid *et al*. (2012), surface soil samples (0–25 cm) taken from the east Rosetta Estuary in Egypt contained 5 and 20 mg/Kg of total Cd and 1.0 and 2.6 mg/Kg of Cd recovered using DTPA. The background levels of DTPA-extractable Cd in the alluvial soils of Egypt range greatly from non-detectable values to 0.06 mg/Kg soil, with an average of 0.018-0.002 mg/Kg soil, according to Aboulroos *et al*. (1996).

Preparation of amorphous hydroxides. ***Preparation of amorphous Al (III) hydroxides.*** In order to achieve pH 7.0, a solution of 0.001 M $AlCl_3$ was titrated with 0.1 M NaOH in either the lack or presence of citrate and tannate ligands. Tannate ligands were introduced in citrate form with tannate acid at a concentration of 0.001 M. The Al molar ratio of the ligands was 0.1 citrate. The final suspensions were centrifuged at room temperature (23-0.5 °C) at 10,000 rpm, equilibrated for 24 h and then rinsed with deionized water until clear of Cl^- before being freeze-dried. Al-OH, which formed in the absence of organic ligands and Al-cit and Al-tan, which were changed by co-precipitation of citrate and tannate ligands, respectively, which were both soluble in acid ammonium oxalate (pH=3), 1M HCl and showing that there is little to no crystallization (Kinniburgh *et al*., 1975).

Preparation of amorphous Fe (III) hydroxides. A stock solution of iron gel was made by quickly neutralizing reagent grade $Fe(NO_3)_3.9H_2O$ with NaOH at pH 7.0 in the presence or absence of citrate or tannate ligands at a ligand/Fe molar ratio of 0.1. This was done in a polypropylene beaker. At 133.32 g of $Fe(NO_3)_3.9H_2O$ crystal, weights of 6.34 and 56.14 g of citrate and tannic acid were added and thoroughly combined. The suspension was built upto a volume of 100 mL after being maintained at pH 7.0 for an hour, resulting in final concentrations of 0.30 and 0.033 M for Fe and ligands, respectively. Aging at room temperature took 30 min at (23±0.5 °C). The phase, as mentioned earlier with Al, was introduced (Kinniburgh *et al*., 1975).

Cation exchange capacity (CEC). The ammonium acetate technique was used to ascertain the cation exchange capacity (CEC) of Al and Fe, according to Page *et al*. (1982).

Immobilization technique. The treated soil samples were utilized to investigate amorphous Al and Fe (III) hydroxides. The amorphous Al and Fe (III) hydroxides were applied to heavy metal-polluted soils at three different rates of 0.1, 0.5 and 1.0%. Each soil sample was transported to a 250 mL glass bottle weighing around 100 g. Each container received 100 mL of deionized water that was pre-mixed with the necessary quantity of amorphous Al and Fe (III) hydroxides. The treated soils were allowed to dry naturally for a week before being alternately wetted with 50 cc of de-ionized water and allowed to dry. The treated soils are put through eight soaking and air drying cycles, one cycle each week, for eight weeks while also being chemically analyzed. The soils' Cd and Pb concentrations, as extracted by diethylene triamine penta acetate, were measured (DTPA).

Adsorption/desorption of Cd and Pb on amorphous Fe (III) and Al (III) hydroxides. ***Adsorption.*** A wide solid: solution ratio of (1:500), comparatively low Cd and Pb concentrations and a 24 h equilibrium duration were used in the adsorption experiment. Portions of 0.1g tested Amorphous Al and Fe (III) gently shaken hydroxides with 50 mL 0.01 M $CaCl_2$ containing 1.0, 5.0, 10, 20, 50 and 100/mg Cd or Pb concentrations for 24 h at (25±1 °C). At pH 7.0, the solution was adjusted using 0.1 NHCl or NaOH before applying it to the adsorbents. The suspensions were then readjusted after the addition.

The finished suspension is centrifuged for 10 min at 5000 rpm, and the clear filtrate is used to measure the amounts of Cd and Pb using an atomic absorption spectrophotometer (UNICAM 969). The difference in the equilibrium solution between the starting and final concentrations of the adsorbed Cd and Pb amounts was calculated.

Desorption. A solution of 1.0 M $MgCl_2$, pH 7.0 is employed similarly to the solution used for the adsorption experiment for the desorption of the previously sorbed Cd and Pb at a solid: solution ratio. After a response time of two hours, the suspension was gently shaken at (25 1 °C). Following centrifugation, the clear solution's Cd and Pb concentrations were assessed, as previously described.

Adsorption models. The applicability of the Cd and Pb adsorption data to the linear form of the Freundlich and Langmuir models was evaluated. Affinity (binding energy) and maximum adsorption capacity (quantities) were also calculated.

Freundlich model. To describe the soils in this study, modified Freundlich was used as follows:

$$\log X/m = \log K + n \log C$$

where:

C is the equilibrium concentration of metal in the reacted solution (mg/L), K and n are constants that denote the affinity of metal to the adsorbent and maximum adsorption capacity, respectively. x/m is the quantity of metal adsorbed per unit mass of adsorbent (mg/Kg).

Langmuir model. The Langmuir model that was applied to determine adsorption is:

$$\frac{C}{\frac{x}{m}} = \frac{1}{kb} + \frac{C}{b}$$

where:

x/m and C were previously indicated, k refers to the binding energy of the metal to the adsorbent, and b is the maximal capacity of metal ions for adsorption on the adsorbent.

Analytical procedures. *Total contents of Cd and Pb.* The Cd and Pb concentrations were determined using the Aqua-Regia method, as described by Cottenie *et al.* (1982). One gram of soil was sampled in the lab and 100 mL Pyrex digestion tubes were used. Next, 3 mL of distilled water were added to create the slurry. The digestion tube was then, after applying 5 mL of 3:1 mixture (2.5 mL of 70% HNO_3 and 7.5 mL of 37% HCl), sealed and left overnight. The suspension was then digested in a reflux condenser at 130 °C for 2 h. The suspension collected was then filtered through a Whatman filter paper (1 mm) and diluted to 25 mL with 0.5 mol :1 HNO_3 and deposited for analysis in a polyethylene container at 4 °C. Using an atomic absorption spectrophotometer, the extract's cadmium and lead concentrations were determined (APHA, 1989).

Statistical analysis. All data in this study were analyzed using a randomized complete block design with three replicates. According to Snedecor and Cochran, the least significant difference (LSD) test was used to compare the treatment means (Snedecor and Cochran, 1994). The specialized statistical application "Assistat" performed the statistical analysis (Silva and Azevedo, 2009).

Results and Discussion

Characteristics of amorphous hydroxides. *Cation exchange capacity (CEC).* Using 1M ammonium acetate at pH 7, Table (1) displays the cation exchange capacity (CEC) of immobilizing agents. The results indicate that all of the immobilizing agents examined have a CEC of between 31.3 and 67.8 Cmol(c)/Kg. The highest value (67.8 Cmol(c)/Kg) was recorded for Fe-tann, whereas the lowest one was recorded for Al-OH (31.3 Cmol(c)/Kg). Fe-OH has substantially higher CEC values than Al-OH, which is what they correspond to those of Fe-Oxal and Fe-cit which are marginally greater than those of Al-Oxal and Al-cit, respectively. Saha *et al.* (2002). The early variations in the reactivity proton dissociation of surface inorganic (OH and OH_2) groups may be the cause of the significant variances in CEC values between Fe-OH and Al-OH, Helal (2006).

Contents of Cd and Pb. The results shown in Table indicate that both immobilizing agents are almost devoid of Cd and Pb (1). Extracted by using DTPA and the total contents of Cd and Pb in immobilizing agents and their quantities were determined.

Adsorption isotherms of Cd and Pb. We employed a 24 h equilibrium period, a wide solid: solution ratio of (1:500) and comparatively low Cd and Pb contents (Sposito, 2008). The amounts adsorbed on tested amorphous hydroxides are represented against the equilibrium concentrations in Fig. 1, which shows the adsorption isotherms of Cd. According to the obtained isotherms, Cd (approximately 1865 and 865 mg/Kg) is adsorbed on Fe-citrate and Al-tannate, respectively.

The Fe-citrate adsorption curve was close to the L-curve, indicating that precise adsorption is the process responsible for Cd elimination. The curve obtained for Al-tannate, on the other hand, was similar to C-curve. The immobilizing agents for all the tested might be descending according to the Cd amounts that adsorbed on the tested agents: Fe-citrate > Al-tannate.

The collected isotherms show that Fe-citrate and Al-tannate have adsorbed bout 2505 and 2500 mg Pb/Kg, respectively. The Fe-citrate adsorption curve was close to the L-curve, suggesting that particular adsorption is the process responsible for Pb elimination. The measured

Table 1. General characteristics of the studied immobilizing agents

Reagent	CEC (Cmol (C)/Kg)	Cd (μ/g)		Pb (μ/g)	
		Aqua regia	DTPA-extractable	Aqua regia	DTPA-extractable
Al-OH	31.3	Nd	nd	nd	nd
Fe-OH	60.7	Nd	nd	nd	nd
Al-Cit.	59.7	Nd	nd	nd	nd
Al-Tann.	66.3	Nd	nd	nd	nd
Fe-Cit.	63.6	Nd	nd	nd	nd
Fe-Tann.	67.8	Nd	nd	nd	nd

*Cit. = citrate; Tann. = tannate; nd = not detectable.

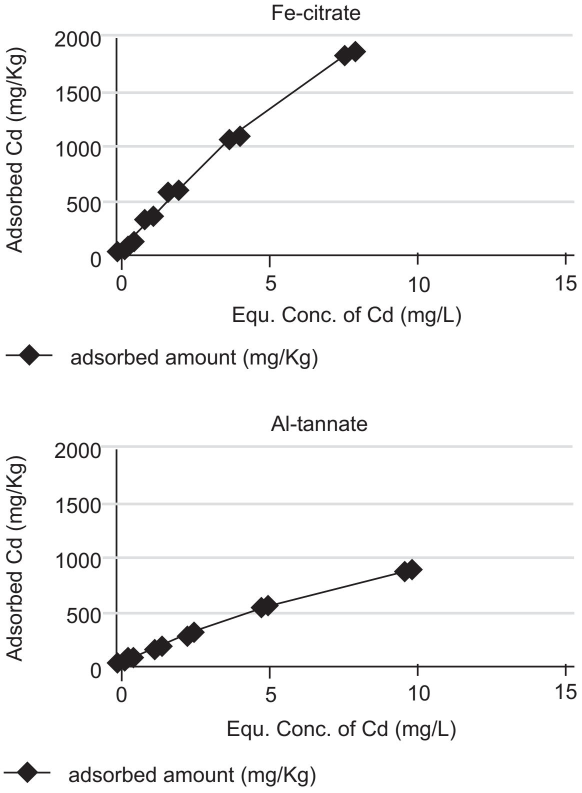

Fig. 1. Adsorption isotherms of Cd on Fe-cit., Al-tann.

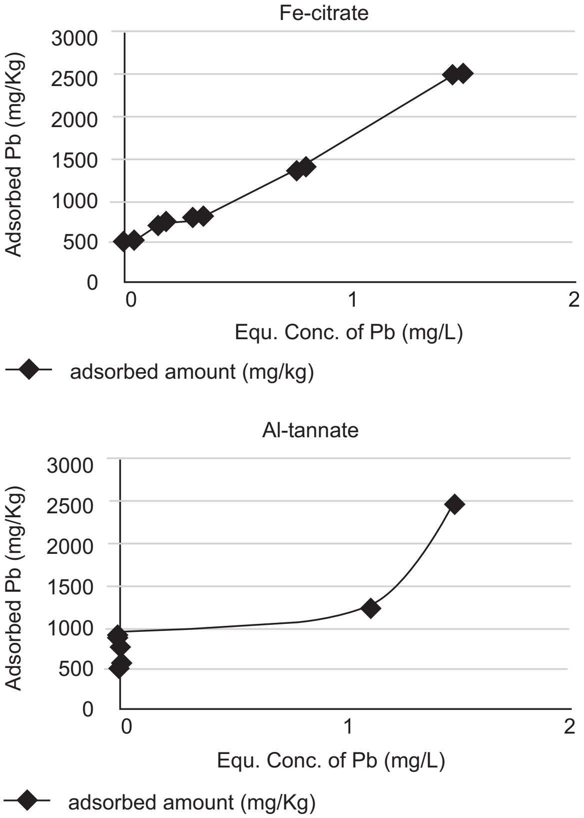

Fig. 2. Adsorption isotherms of Pb on Fe-cit., Al-tann.

immobilizing agents could be arranged as follows (descending), in order of the quantity of Pb adsorbed on the tested agents: Fe-citrate > Al-tannate.

The amount of Cd adsorbed on amorphous hydroxides is usually much lower than their Pb equivalents, meaning that these materials have a high capacity to adsorb Pb rather than Cd. Also, unlike Cd, the property of the Pb product causes it is to be isolated from the solution by electrostatic attraction to negatively charged sites, causing it to remain as exchangeable cations. Lead is derived from solution by forming chemical bonds (covalent and coordinate covalent) with surface functional groups, a property that not all surfaces which is such as negatively charged sites, share.

Adsorption models. It was looked into if the Cd and Pb adsorption data could be applied to linear Freundlich and Langmuir models. Langmuir models were also used to measure maximal adsorption capability and affinity (binding energy) quantities. Both Freundlich and Langmuir equations were found to match cadmium and lead adsorption data. High correlation coefficients (R2 ranging from 0.948-0.955 and 0.714-0.804, respectively) were found for the Cd and Pb Langmuir isotherms. The corresponding Freundlich (R2) values for Cd and Pb were 0.0.99-0.99 and 0.787-0.743, respectively.

The Langmuir linear forms for Cd and Pb adsorption on immobilizing agents are seen in Fig. 3-4. According to the linear Langmuir form the Table 2 shows maximal adsorption capacity and binding energy (affinity) for Cd and Pb. The findings show that the immobilizing agents (Fe-cit. and Al-tan.) have a high capacity to adsorb Cd. The highest adsorption capacity ranged from 2.269 to 5.665 g Cd/Kg. The maximum adsorption capacity value was found in Fe-citrate, while the lowest was found in Al-tannate. According to Wang *et al*. (2014), the maximum adsorption capacity of NZVI–RGO with As (III) and As (V) are 35.83 and 29.04 mg/Kg. These values are in the middle range found in the current study.

The measured materials' maximum adsorption capacities are approximately in the range of most maximum adsorption capacities recorded in the literature for many adsorbents; 3.37 mg/g for activated carbon (An *et al*., 2001), 4.94 mg/g for hematite (Singh *et al*., 1998), 48.3 mg/g for orange waste (Perez-Marin *et al*., 2007), 64.1 mg/g for bone char (Cheung *et al*., 2001), 204.1 mg/g for activated sludge (Soltani *et al*., 2009) and 229.3 mg/g for biogenic Mn oxides (Meng *et al*., 2009).

Table 2 reveals that the tested immobilizing agents (Fe-cit. and Al-tan) have a high capacity to adsorb Cd.

Table 2. Maximum Cd and Pb adsorption capacity and affinity on the immobilizing agent

Agents	Cd		Pb	
	Maximum adsorption gCd/Kg(b)	Affinity (K L/g)	Maximum adsorption gPb/Kg(b)	Affinity (K L/g)
Al-cit.	-	-	-	-
Al-tann.	2.269	0.062	2.500	0.056
Fe-cit.	5.665	0.063	5.00	0.071
Fe-tann.	-	-	-	-

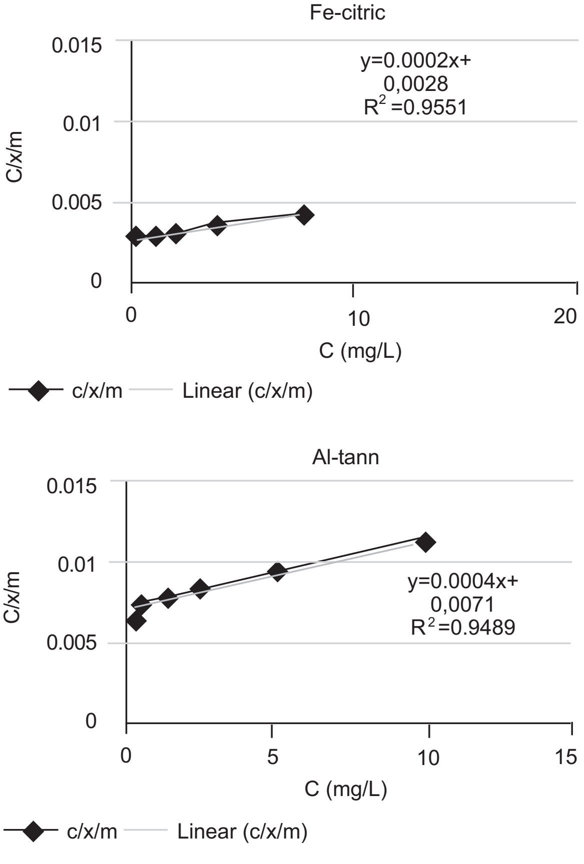

Fig. 3. The linear form of the Langmuir model for Cd adsorbed on the immobilizing agent.

Al-tan and Fe-cit had maximum adsorption capacities of 2.269 and 5.665 g/Kg, respectively. According to their maximum adsorption capacity, the tested immobilizing agents could be arranged in descending order as follows: Fe-cit. > Al-tann.

Between immobilizing agents and Cd, the adsorption affinity (binding energy) varied from 0.062 to 0.063. Fe-cit received the highest value (0.063), while Al-tann received the lowest one (0.062).

The maximum adsorption capacity of immobilizing agents (Fe-cit. and Al-tan) for Pb, on the other hand, ranged from 2.5 to 5.0 g/Kg (Table 2). Fe-cit which had the highest maximum adsorption capacities, similar to Cd. In contrast, Al-tan had the lowest.

The tested immobilizing agents could be grouped in the following order, descending in Pb maximum adsorption capacity: Fe-cit. > Al-tann.

The range of Pb's affinity for the adsorbents was 0.056-0.071. The results showed that Fe-cit had the highest value and Al-tann had the lowest.

The linear forms of Freundlich for Cd and Pb adsorption on immobilizing agents are seen in (Fig. 5-6), showing

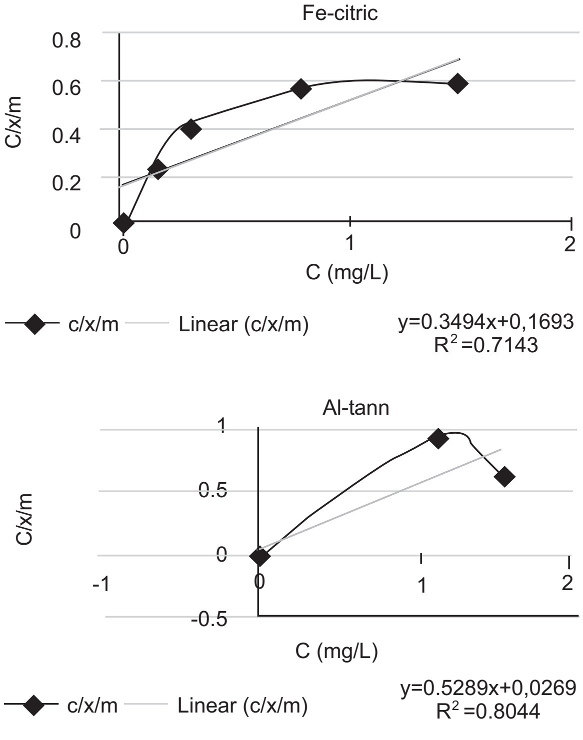

Fig. 4. The linear form of the Langmuir model for Pb adsorbed on the immobilizing agent.

the validity of the collected data to the Freundlich isotherm. The linear form constants of the Freundlich model, on the other hand, have not been determined because they are irrelevant.

Desorption of Cd and Pb. Figure 7 represents the amounts of Cd desorbed from previously adsorbed ones. The results showed that small amounts of Cd were desorbed from the previously adsorbed ones. Table 3 indicates the desorbed amounts were discovered to be just low percentages of the previously adsorbed ones. Fe-cit had the lowest percentage (6.32-24.77%), while Al-tann had the highest percentage (31.2-85.0%). The potential release of adsorbed Cd decreased as the desorbed percentages decreased, raising the material's effectiveness in immobilizing Cd in contaminated soils. The projected release of adsorbed Cd declined as the desorbed percentage decreased, implying that the material's effectiveness in controlling contaminants increased, implying that the emission abatement mechanism is undeniable.

Table 3. Adsorption/desorption of Cd on the immobilizing agent (Fe-cit., Al-tann.)

Agents	Adsorbed amount (mg/Kg)	Desorbed amount (mg/Kg)	Des./Ads. (%)
Al-Cit.	-	-	-
Al-Tann.	20-865	17-276	31.2-85
Fe-Cit.	35-1865	6.8-462	6.32-24.77
Fe-Tann.	-	-	-

Figure (8) shows the amounts of Pb desorbed from the previously adsorbed on (Fe-citrate and Al-tannate). The results showed that only small amounts of Pb were desorbed from the previously adsorbed ones. The desorbed amounts were discovered to be just a small portion of the previously adsorbed ones (Table 4). The lowest percentages were found in Fe-cit (3.15-15.01%), while the highest percentages were found in Al-tann (1.11-15.81%). The potential release of adsorbed Pb decreased as the desorbed percentages decreased, increasing the material's effectiveness in immobilizing Pb in contaminated soils.

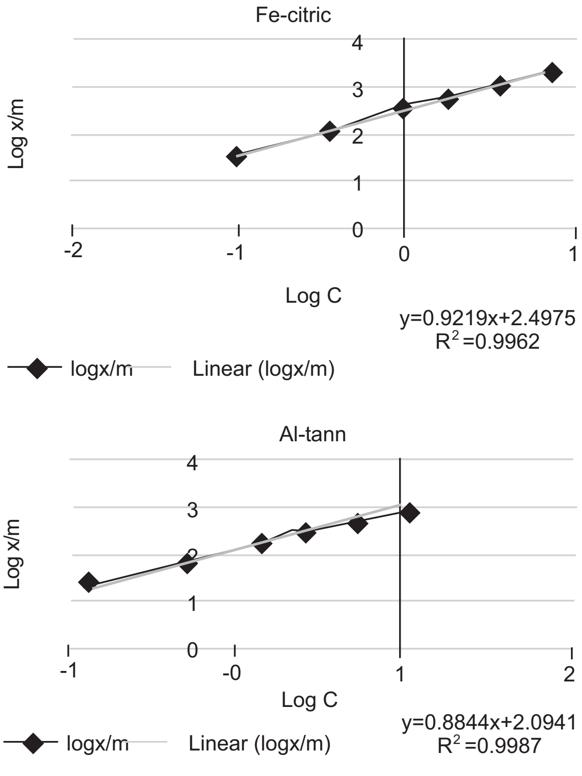

Fig. 5. The linear form of the Freundlich model for Cd adsorbed on the immobilizing agent.

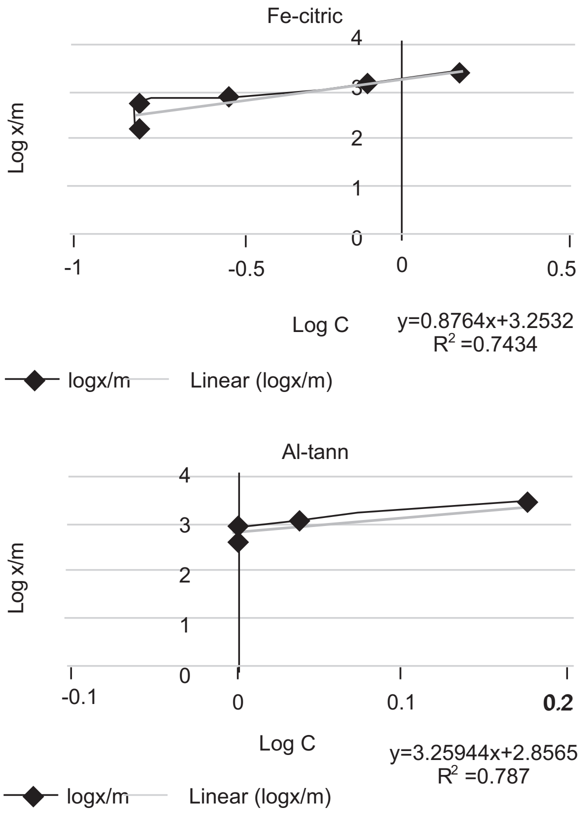

Fig. 6. The linear form of the Freundlich model for Pb adsorbed on the immobilizing agent.

Immobilization of Cd and Pb in polluted soil. ***DTPA extractable Cd and Pb in soil.*** The Mostord (S1, S2), Abo-Rawash (S3, S4), Shubra (S5) and El-Gabal El-Asfer (S6) soil samples were used in this investigation. The initial contents of plant-available Cd and Pb in these samples differed substantially in their first forms (Table 5-6). In these soils, DTPA extractable-Cd and Pb ranged from 3.16-12.77 and 3.97-15.36 mg/Kg, respectively. Additionally, the sources of the Cd and Pb contaminants in the soil samples examined varied (domestic sewage, industrial waste and vehicle exhausts). Fe-citrate and Al-tannate were applied to all soils in three concentrations, 0.1, 0.5 and 1.0% and incubated for 60 days at 30 °C.

Table 4. Adsorption/Desorption of Pb on the immobilizing agent (Fe-cit., Al-tann.).

Agents	Adsorbed amount (mg/Kg)	Desorbed amount (mg/Kg)	Des./Ads. (%)
Al-cit.	-	-	-
Al-tann.	455-2505	10-396	1.11-15.81
Fe-cit.	455-2505	14-376	3.15-15.01
Fe-tann.	-	-	-

Tables 5 and 6 show the DTPA extractable Cd and Pb levels in the soils before and after incubation. The immobilizing agents were able to lower the levels of DTPA extractable Cd and Pb in all soils, according to the results. The amount of a drop, however, varied according to the kind of immobilizing substance and the rate at which it was applied. The amount of DTPA extractable Cd and Pb in the soil was reduced for all agents when the application rate was increased from 0.1 to 1.0%.

Particularly in soils 1 and 3, Fe-citrate and Al-tannate were the most efficient immobilizing agents. (soils with moderate pollution and 3.16 to 3.66 mg/Kg DTPA extractable Cd). By adding 1% of aluminum citrate,

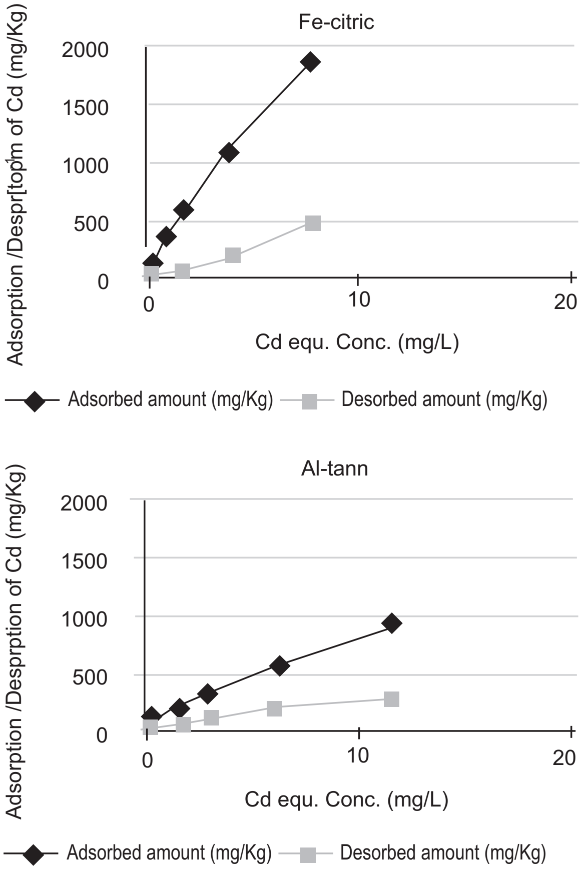

Fig. 7. Adsorption/desorption of Cd adsorbed on (Fe-citrate and Al-tannate).

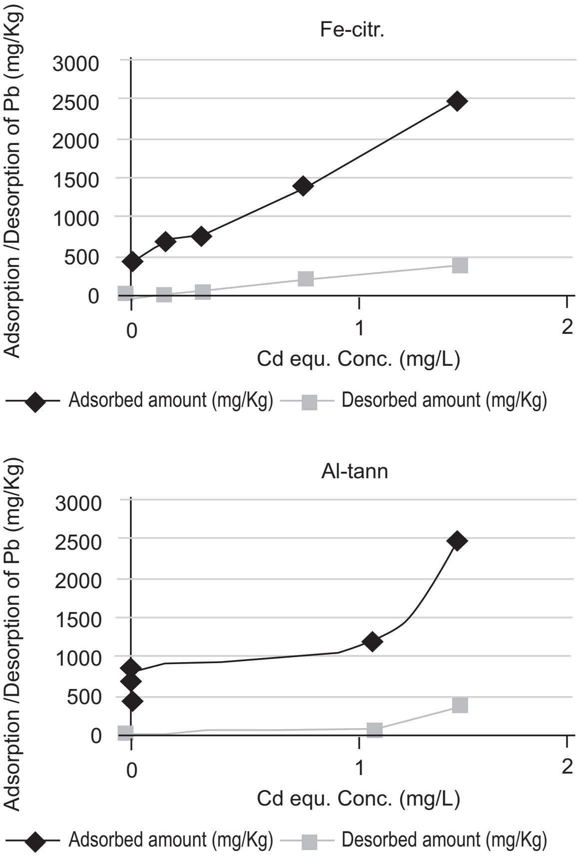

Fig. 8. Adsorption/desorption of Pb adsorbed on (Fe-citrate and Al-tannate).

Table 5. DTPA extractable – Cd (mg/Kg) of the studied soil samples before and after treating the soils with three rates of four immobilizing agents

Treatment	Addition rate (%)	DTPA- extractable Cd (mg/Kg) (soil)				Mean
		1	2	3	4	
Al-cit.	Initial	3.16	12.77	3.66	7.53	6.78
	0.1	1.59	6.28	1.95	4.66	3.62
	0.5	1.16	6.03	1.78	3.34	3.08
	1	0.83	4.86	1.65	1.34	2.17
Mean		1.69	7.49	2.26	4.22	3.91
Al-tann.	0.1	1.71	7.28	1.65	4.52	3.79
	0.5	1.28	6.16	0.77	1.74	2.49
	1	0.93	5.28	0.48	0.99	1.92
Mean	1.31	6.24	0.97	2.42	2.73	
Fe-cit.	0.1	1.14	5.6	1.73	4.32	3.20
	0.5	0.87	5.34	1.52	2.67	2.60
	1	0.66	4.4	0.65	1.84	1.89
Mean	0.89	5.11	1.30	2.94	2.56	
Fe-tann.	0.1	1.61	6.13	0.89	4.62	3.31
	0.5	0.98	5.47	0.8	3.53	2.70
	1	0.78	4.63	0.72	0.59	1.68
Mean	1.12	5.41	0.80	2.91	2.56	
	1	3.16	12.77	3.66	7.53	6.78
	2	1.51	6.32	1.56	4.53	3.48
	3	1.07	5.75	1.22	2.82	2.72
	4	0.80	4.79	0.88	1.19	1.91
Mean	1.64	7.41	1.83	4.02		

LSD value at 0.05 = rate 0.037; Treat = 0.037; Soils = 0.037; Interactions = 0.064.

aluminum tann, iron citrate and iron tann, the DTPA extractable-Cd of soils 1 and 3 was lowered to low values between 0.48 and 1.65 mg/Kg. These findings are slightly greater than the amount of DTPA extractable Cd in Egypt's unpolluted soils, which is 0.06 mg/Kg with an average of 0.018 0.002 mg/Kg Cd, according to Aboulroos *et al*. (1996).

Al-cit, Al-tann, Fe-cit and Fe-tann were able to reduce the amount of DTPA extractable Cd in highly polluted soils from 12.77 to 4.68, 5.28, 4.4 and 4.63 mg/Kg in soil (2) and from 7.53 to 1.34, 0.99, 1.84 and 0.59 mg/Kg in soil (4), respectively. Al-tannate was less effective at reducing Cd than other compounds, especially in the case of heavily polluted soil.

The effect of various agents on DTPA extractable-Pb is seen in Fig. 8 as a percentage of the initial values of the studied soils (S1, S2, S3 and S4). In soil 1 and 3 (moderately polluted soil), the level of DTPA extractable Pb decreased by 73.7, 70.57, 79.11 and 75.3% and 86.88, 82.24 and 80.31%, respectively, when the soil was treated with Al-citrate, Al-tann, Fe-cit and Fe-tann at concentrations of 1.0 %. Soil 2 and 4 (heavily polluted soils) had corresponding values of 63.35, 58.65, 65.55 and 63.74% and 82.2, 86.85, 75.56 and 92.16%, respectively.

Conclusion

- The obtained results show that all tested amorphous Al and Fe hydroxide has a high capacity to adsorb Cd.
- Fe-citrate and Al-tannate, the evaluated immobilizing agents, exhibited the greatest retention affinity for the adsorbate element.
- In the case of Pb, all of the immobilizing agents tested exhibited a high adsorption capacity for Pb, although their adsorption capabilities were lower than those reported for Cd.
- Fe-citrate is the finest immobilizing agent that is advised for use in the treatment of Cd and Pb-polluted soils. In addition, Fe-citrate is inexpensive and simple to make.

Table 6. DTPA extractable – Pb (mg/Kg) of the studied soil samples before and after treating the soils with three rates of four immobilizing agents

Treatment		Addition rate (%)	DTPA- extractable Pb (mg/Kg) (Soil)						Mean
			1	2	3	4	5	6	
Al-cit		Initial	6.24	6.45	6.27	5.68	15.36	3.97	7.33
		0.1	3.23	2.71	3.84	3.34	9.32	2.47	4.15
		0.5	2.91	2.54	3.56	2.9	7.77	1.86	3.59
		1	2.61	2.15	2.88	2.73	7.32	1.53	3.20
	Mean	3.75	3.46	4.14	3.66	9.94	2.46	4.57	
Al-tann		0.1	3.77	3.21	3.8	3.04	9.44	2.43	4.28
		0.5	3.52	2.71	3.61	2.9	8.76	2	3.92
		1	2.69	2.54	3.12	2.66	7.87	1.64	3.42
	Mean	3.33	2.82	3.51	2.87	8.69	2.02	3.87	
Fe-cit		0.1	2.72	2.46	3.73	3.31	9.44	2.03	3.95
		0.5	2.75	2.38	3.02	2.82	8.2	1.93	3.52
		1	2.14	2.27	2.68	2.1	7.35	1.8	3.06
	Mean	2.54	2.37	3.14	2.74	8.33	1.92	3.51	
Fe-tann		0.1	3.54	2.41	3.93	3.12	9.62	2.49	4.19
		0.5	2.69	2.32	2.89	2.98	9.38	2.08	3.72
		1	2.67	2.05	2.72	2.56	7.32	1.6	3.15
	Mean	2.97	2.26	3.18	2.89	8.77	2.06	3.69	
		1	6.24	6.45	6.27	5.68	15.36	3.97	7.33
		2	3.32	2.70	3.83	3.20	9.46	2.36	4.14
		3	2.97	2.49	3.27	2.90	8.53	1.97	3.69
		4	2.53	2.25	2.85	2.51	7.47	1.64	3.21
	Mean		3.76	3.47	4.05	3.57	10.20	2.48	

LSD value at 0.05; Rate = 0.015; Treat = 0.015; Soils = 0.017; Interactions = 0.03.

- These amorphous Al and Fe hydroxides might also be recommended for the treatment of Cd and Pb-polluted wastewater.

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