

Lead and Cadmium Removal from Aqueous Solution by Rock phosphate, Hydroxyapatite and Compost

Nasseem, M.G.; M.A.Hussein; W.H.Mohmed and J. Elgosni

Soil and Agricultural Chemistry Department, Faculty of Agriculture, Saba Basha, Alexandria University, Egypt,

Keywords : rock phosphate(RP); hydroxyapatite (HA); compost; Cadmium; lead; removal; sorption; low-cost materials

ABSTRACT

This study compares the abilities of rock phosphate (RP), hydroxyapatite (HA) and compost materials to remove lead and cadmium from synthetic single aqueous solutions. Effects of sorbent amount and initial concentration of metal ions were studied. The experimental data of the removal equilibrium were correlated, either by the Langmuir and/or Freundlich equations. The results proved that Langmuir model gave a better and acceptable fitting to the experimental data of cadmium than Freundlich equation within the used concentration range studied. To the contrary of Cd trend, Freundlich equation imposed a better fitting to the experimental data of lead than Langmuir. Results have shown that high cadmium and lead sorption were clearly manifested observed by the tested materials. The data also indicated that compost was more creative to remove cadmium ions with a maximum sorption (removal) capacity (83.33 mg/g) followed by hydroxyapatite (43.48) and rock phosphate (24.39 mg/g). For lead, the highest sorption capacity was observed by compost followed by rock phosphate and hydroxyapatite. The rock phosphate (RP) and compost as a low cost materials were able to reduce lead and cadmium concentrations in aqueous solutions, suggesting that rock phosphate (RP) and compost could be used as a cost-effective option to remediate heavy metals contaminated waters and soils.

INTRODUCTION

The presence of heavy metals in our environment represents a serious problem due to industrial pollution of the atmosphere, waterways, soils and sediments. Natural waters are contaminated with several heavy metals arising from mining waters and industrial discharges. The heavy metals are of special concern because they are non-degradable and therefore persistent. Commonly encountered metals of concern include Pb^{2+} , Cd^{2+} , and Zn^{2+} . These metals are toxic in both their chemically combined forms as well as the elemental form. Exposure of these contaminants were presented, even at the low concentration level were considered to be harmful to animals, humans and aquatic life.

In order to solve heavy metal pollution problem in the environment, it is important to bring applicable solutions. In this regard, the available

treatments of heavy metals removal from aqueous solutions are being directed to chemical precipitation, ions exchange, coagulation, bioremediation and sorption/adsorption (Sims *et al.*, 1986). The adsorption at solid substrate is preferred because of its high efficiency, easy handling and cost effectiveness as well as availability of different adsorbents (Mohammad and Mohammad, 1997). Several studies have shown that synthetic hydroxyapatite (HA) have potential for remediation because it can immobilize a great number of heavy metals (Ma *et al.*, 1993; Chen *et al.*, 1997) from aqueous media by forming new low soluble phosphates phases. However, the use of synthetic HA is only feasible when a small quantity of material is used because HA preparation is rather expensive. For this reason, low cost materials like phosphate rocks (PR) have been proposed and tested for heavy metal removal from contaminated waste and soils (Prasad *et al.*, 2000; Prasad *et al.*, 2001). Several authors showed that PR was very effective in retaining Pb and less effective in the removal of Cd from aqueous solutions (Chen *et al.*, 1997; Saxena, S., D'Souza, 2006). The Pb²⁺ immobilization was mainly controlled by apatite dissolution and the precipitation of a carbonated fluoropyromorphite (Ma *et al.*, 1995; Ma and Rao, 1999; Elena *et al.*, 2004).

Adsorption of metals by agricultural materials is a relatively recent method for recovery of metals from industrial liquid waste products. Various kinds of agricultural by- products have been tested for this purpose. As examples of agricultural absorbents, Marshall and Champagne (1995) used soybean hulls, cottonseed hulls, rice straw and sugarcane bagasse to remove Co²⁺, Cr³⁺, Ni²⁺ and Zn²⁺ from aqueous solutions and Sameer and Zdravko (1999) used canola meal for the removal of Cd²⁺, Zn²⁺ and Ni²⁺. In recent years, there has been increased focus on composting animal manure and agricultural waste as a part of sustainable agricultural practices. A new compost technology, known as compost bioremediation, is currently being used to restore contaminated soils, manage storm water, control odors, and degrade volatile organic compounds (EPA, 1997).

The objective of the current investigation is the overview of the comparative studies of the effectiveness of low grade and cost rock phosphate mineral, synthetic hydroxyapatite and compost as sorbents for remediating lead and cadmium from aqueous solutions.

MATERIAL AND METHODS

MATERIALS:

Three different sorbent materials were used in this study. The first one was a low-grade rock phosphate (RP) sample, originated from a

sedimentary phosphate rock deposits, supplied as row mining ore, after grinding to a fine powder to pass through a 400 mesh standard sieve by Al Ahram mining and natural fertilizer company in Egypt. The second sorbent is a pure reagent grade synthetic hydroxyapatite; HA [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$]. Chemical analysis of RP and HA materials were carried out according to the methods described by Jackson (1973) and given in Table 1.

Table 1 . Chemical analysis of RP and HA samples

(RP)		(HA)	
Constituents	Concentration, %	Constituents	Concentration, %
P	10.863	P	18.51
Ca	28.123	Assay of Ca	36-40
Si	6.071	As	0.0002
Cd	1.053	Cd	0.0001
Pb	4.021	Pb	0.0002
Na	0.668	Cu	0.0020
Fe	0.871	Fe	0.0400
K	0.108	Zn	0.0020
Mn	0.036	F	0.0050
Cl	0.570	Cl	0.1500
L.O.I.	16.560	L.O.I.	8.0000

L.O.I. =loss on ignition

The third selected sorbent was the organic compost, originated from the available plant residuals that are commonly prevailed in Egypt. The chemical and physical properties of the tested compost are presented in Table 2.

Table 2 . Chemical analysis of the compost sample

Character	Value
PH (1 : 5)	8.14
EC (1 : 5), dSm ⁻¹	6.50
O.M, %	51.20
P (Available), mg kg ⁻¹	0.13
N (Available), mg kg ⁻¹	0.27
Soluble Cations and Anions, meq L⁻¹	
Ca ²⁺	38.10
Mg ²⁺	0.02
Na ⁺	0.54
K ⁺	0.23
Cl ⁻	0.00
HCO ₃ ⁻	0.00
SO ₄ ²⁻	0.24
Available microelements, mg Kg⁻¹	
Fe	11.86
Mn	0.44
Zn	1.10
Cu	0.45
Cd	0.02
Pb	0.23

Batch sorption experiments

Stock solution (1000 mg/L) of lead and Cadmium ions (Pb²⁺, Cd²⁺) were prepared from analytical grade Lead nitrate (Pb (NO₃)₂) and Cadmium sulphate (CdSO₄) using distilled water and serially diluted to prepare solutions of varying initial concentration for experimental work. To study the effect of sorbent amount on sorption percent, 0.23 g to 3.68 g of each sorbent was equilibrated with 200 ml. of solution containing 100 mg/L of individual Pb²⁺ and /or Cd²⁺ ions

To study the effect of initial concentration of metal ions on adsorption behavior of Pb²⁺ and Cd²⁺, initial concentration of 10, 50, 100, 300, and 500 mg/L was equilibrated with fixed sorbent dose of 0.92 g of each sorbent . The suspensions were adjusted to pH of 5.0 by adding 0.01 M of NaOH or HNO₃ solutions. The mixtures were agitated on a shaker at room temperature for two hours, and then filtrated, to detect the Pb and Cd metal concentrations using atomic adsorption spectrophotometer. Each

experiment was carried out in duplicate and the average results are presented.

The Langmuir and Freundlich adsorption isotherms were used for modeling the sorption characteristics of Pb^{2+} and Cd^{2+} for each sorbent. The linear form of the Langmuir model is given as the following equation:

$$C/X = 1/(bX_m) + C/X_m$$

And Freundlich nonlinear and linear equations are given as the following equations:

$$q = K_f C^{1/n}$$

$$\text{Log } q = \text{log } K_f + 1/n \text{ log } C$$

were as : q (mg/g) is the equilibrium concentration of Pb and Cd ions on the tested sorbents, K_f and n are coefficients, C is the equilibrium concentration of Cd or Pb ions remaining in the solution (mg/L), X is the amount of Cd and Pb ions retained per gram of the sorbent (mg/g), X_m is the maximum amount of Cd and Pb ions (mg/g) that can be sorbed (adsorption capacity) and b is a constant related to the energy of sorption.

RESULTS AND DISCUSSION

Effect of sorbent amount

The variations in removal percentage of Pb and Cd ions by amount of sorbent for the three different sorbents are shown in Figure 1. The amounts of sorbent varied from 0.23 g to 3.68 g at pH 5. It is clear that as the amount of adsorbent increases, the percentage removal of Cd ion also increases steadily but only up to certain values. For RP, the percentage removal increased from 95.34% to 99.94% for Pb ion and from 11.0 to 88.53% for Cd ion. The comparable values for HA were quite different, ranging, from 88.15 to 98.12% for Pb ion and from 40.50 to 99.66 % for Cd ion. The respective values for compost averaged 96.90 to 99.51% for Pb ion and from 60.11 to 97.43 % for Cd ions when sorbent amount increased from 0.23 g to 3.68 g.

The increase of metal removal yield observed with increasing the amount of sorbent gradually decreased and can be described a typical saturation curve. This observation is consistent with Langmuir hypothesis of increasing competition among the adsorbent particles for organic substances with increase in the number of adsorbent particles per unit (Conveerti *et al.*, 1992). Comparing these results, it can be noted that the order of the metal ion sorption was $Pb > Cd$, using the three tested sorbents. Also it can be observed that the order of sorbents efficiency was $\text{compost} > \text{HA} > \text{RP}$ for Cd ion removal and $\text{PR} > \text{compost} > \text{HA}$ for Pb ion removal. The average values of removal percentage over the different

amounts of sorbents for Cd ion were 86.16, 81.52 and 66.34 for compost, HA and RP respectively. For Pb ion, the corresponding average removal percentage values were 98.97, 95.63 and 98.19 for RP, HA and compost respectively.

The reaction mechanism responsible for removal of metal ion by rock phosphate/apatite is still unknown. It has been shown that the primary mechanism of metal ion removal by rock phosphate (RP) is governed by its dissolution in acidic environment followed by subsequent precipitation. The recently evidences support the concept of dissolution-precipitation mechanism. In addition, to the above hypothesis, where P in the form of $H_2PO_4^-$ helps in precipitating metal ions in aqueous solutions, the possibility of exchange of Ca^{2+} by interpreted that the dissolution of apatites also provides Ca^{2+} , which exchanges with the aqueous metal leading to the precipitation of corresponding mineral phase. There are different theories such as free energy, rates of complex formation, ionic radius, are being proposed to explain the binding of metal ions onto a given adsorbent, which provide insights into the factors governing the complex formation and ion exchange. It has been reported (Christopher *et al.*, 2002) that in ion exchange process, larger multivalent ions are more effectively removed in comparison to smaller ones. There is in fact isomorphic substitution of calcium with divalent ions, which is correlated to their ionic radius and electro negativity (Perrone *et al.*, 2001). The hydrated radius of an ion is a function of charge and ionic radius, which dictates the removal of Pb^{2+} having high electro negativity and ionic radius of 1.20 \AA is attributed to the fact that the ionic radius of Pb^{2+} is very close to the ionic radius of Ca^{2+} (0.99 \AA). The cadmium ion (ionic radius 0.97 \AA) having smaller ionic radius than Ca^{2+} . Hence, higher removal of Pb^{2+} may be attributed to the fact that the ionic radius of Cd^{2+} is smaller than the ionic radius of Ca^{2+} and Pb^{2+} . This result corroborates the observations of earlier investigators (Le Geros and Le Geros, 1984; Yuping *et al.*, 1994).

Effect of Pb and Cd initial concentrations

To evaluate the effect of metal ion concentration on sorption process of Pb^{2+} and Cd^{2+} in single solution, studies were conducted with initial concentration of 10, 50, 100, 300 and 500 mg/L with fixed sorbent dose of 0.92 g. It is clear from Figure 2 that when the initial concentration of metal ions was increased from 10 to 500 mg/L, the amount of metal removal per unit weight of the sorbent was progressively increased. The extent of Pb ions sorption (removal) increased from 2.16 mg/g to 106.69 mg/g for HA and 2.12 mg/g to 108.48 mg/g for compost when the initial concentration

was increased from 10 mg/L to 500 mg/L. The corresponding values for Cd ions removal were 2.12 mg/g to 24.57 mg/g, 2.12 mg/g to 43.48 mg/g and 2.16 mg/g to 75.71 mg/g. The results also showed that the removal of Pb or Cd ions is highly concentration dependent. On other hand, the removal percentage decreased only for Cd²⁺ with the tested sorbents (Fig.3). This can be explained in terms of relatively lesser number of active sites at higher concentration of metal ions. Similar trends were also observed by other investigators who used RP for the removal of Pb²⁺ and Cd²⁺ (Ma *et al.*, 1995; Chen *et al.*, 1997; Saxena and D'souza, 2006) and agricultural by-products for the Cd²⁺ removal (Bhattacharya and Venkobchar, 1984; Marshall and Champagne, 1995). Also, adsorption isotherms for Pb and Cd ions on the tested sorbents are presented in Figure 4 for Pb and Cd ions, which is characteristic for chemical interactions.

To quantify the sorption capacity of the tested sorbents in relation to the Cd and Pb ions, the experimental data were fitted to the Langmuir linear equation and Freundlich nonlinear and linear equations. The Figure 5 shows the straight lines obtained by plotting C/X versus C for Cd ions using the RP, HA and Compost sorbents.

According to the linear form of freundlich isotherm, the Freundlich parameters are listed in Table 3. It is worthy to point out that the quantity 1/n is less than unity for Cd ions which indicates adsorption isotherm is favorable for adsorptive removal of Cd ions. For Pb ions, the 1/n values are slightly higher than unity which indicates that adsorption isotherm of Pb ions is less favorable for sorption (removal) than Cd.

The results for Pb²⁺ and Cd²⁺ were clearly manifested by the linearized Freundlich isotherms model, using the three tested sorbents. When the Langmuir isotherm model was applied to the data of the two metals, a reasonable fit was achieved, only for the equilibrium data of Cd²⁺ (Fig.5). When applied to the equilibrium data of Pb ions, the Langmuir model exhibited wider deviation from experimental data and unreasonable values of R² for RP. Suitability of the Freundlich model in representing the equilibrium data of both metals and Langmuir model in representing the equilibrium data for Cd²⁺ revealed that there was a formation of a monolayer of metal ions was formed on the surface of the tested sorbents.

According to the linear form of Langmuir adsorption isotherms, Figure 5 represents the Langmuir plots for the sorption of Cd ions on the tested sorbets. The points are experimental data and straight lines represent the best fitness as assessed by determination coefficient (Table 3). Langmuir and Freundlich isotherms both adequately predicted cadmium sorption on the tested sorbents but Langmuir equation yielded greater coefficients for RP and HA implying that there is monolayer coverage of the sorbate

species on sorbent surface. For compost, the R^2 value was lower than that of Freundlich equation. The values of X_m and b were determined for Cd ion sorption from the slope and intercept of plot C/x versus C (Table 3) . A value of 83.33 mg/g has been obtained as the batch studies. This means that one gram of compost could absorb or remove 83.33 mg/g of Cd ions from aqueous solutions under our experimental conditions. The sorption capacities of RP and HA have been found to be 24.39 mg/g and 43.48 mg/g respectively. A comparison of these values reveals that compost exhibits quite a good capacity for removing Cd ions from aqueous solution followed by HA and RP. From these results, high maximum Cd ions sorption capacities were noted with these materials and the highest removal of Cd ions is obtained with compost.

In conclusion, the obtained results proved that the low-cost materials (RP and compost) can remove lead and cadmium ions from aqueous solution. The sorption performances are strongly affected by parameters such as, initial lead or cadmium concentrations and sorbent material type. The amount of lead or cadmium sorbed by these materials was increased with the increase of the initial ions concentration. From these data, high maximum lead or cadmium sorption (removal) are realized with these materials. The highest removal of lead or cadmium ions was detected with compost. Additional works are still needed to determine the sorption of other metal ions to optimize the overall process and to identify the different functional groups responsible for the metal ion binding.

Table 3 .Characteristic, parameters and determination coefficient of the experimental data for Pb and Cd ions removal according to the degree of correlation Langmuir and Freundlich.

Metal type	Sorbent material	Freundlich parameters			Langmuir parameters		
		1/n	K_f	R^2	X_m (mg/g)	b (L/mg)	R^2
Pb	RP	2.04	18.03	0.926	-22.73	-31.425	0.279
	HA	1.484	3.917	0.950	-45.45	-0.079	0.372
	Compost	1.435	48.641	0.789	-26.315	-0.633	0.365
Cd	RP	0.305	4.666	0.884	24.390	0.087	0.987
	HA	0.376	5.794	0.907	43.478	0.073	0.981
	Compost	0.475	6.577	0.997	83.333	0.042	0.940

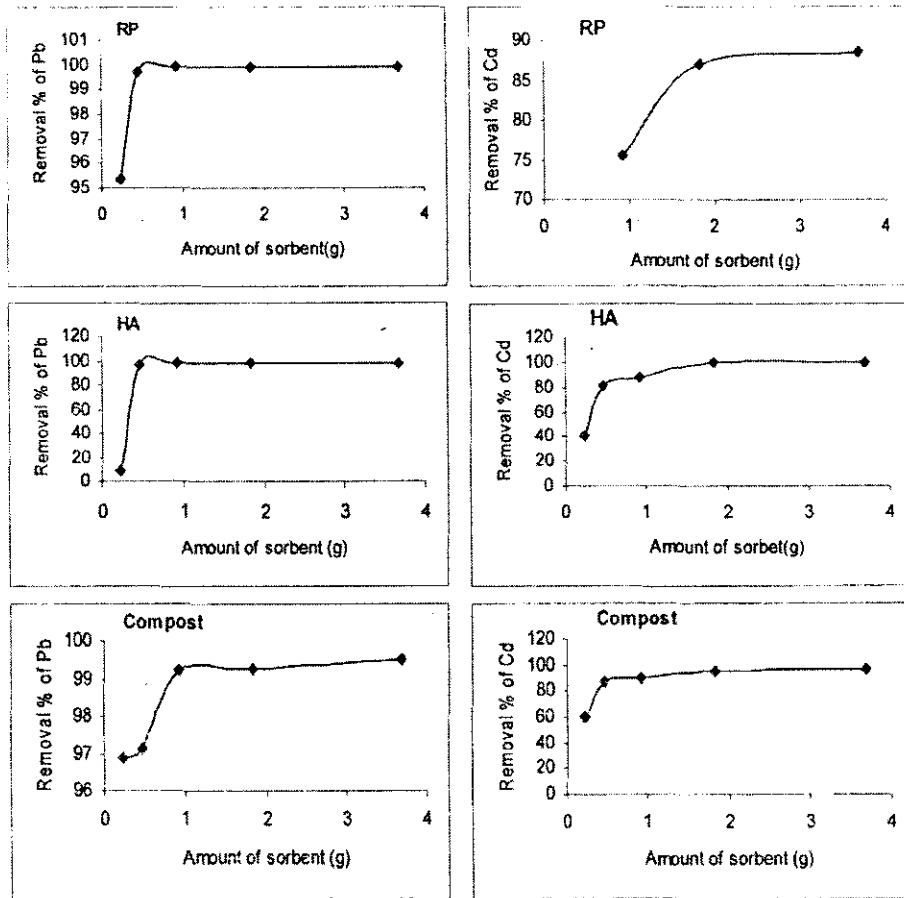


Fig. 1 : Effect of the amount of sorbent on removal percent of Pb and Cd ions by three sorbent materials.

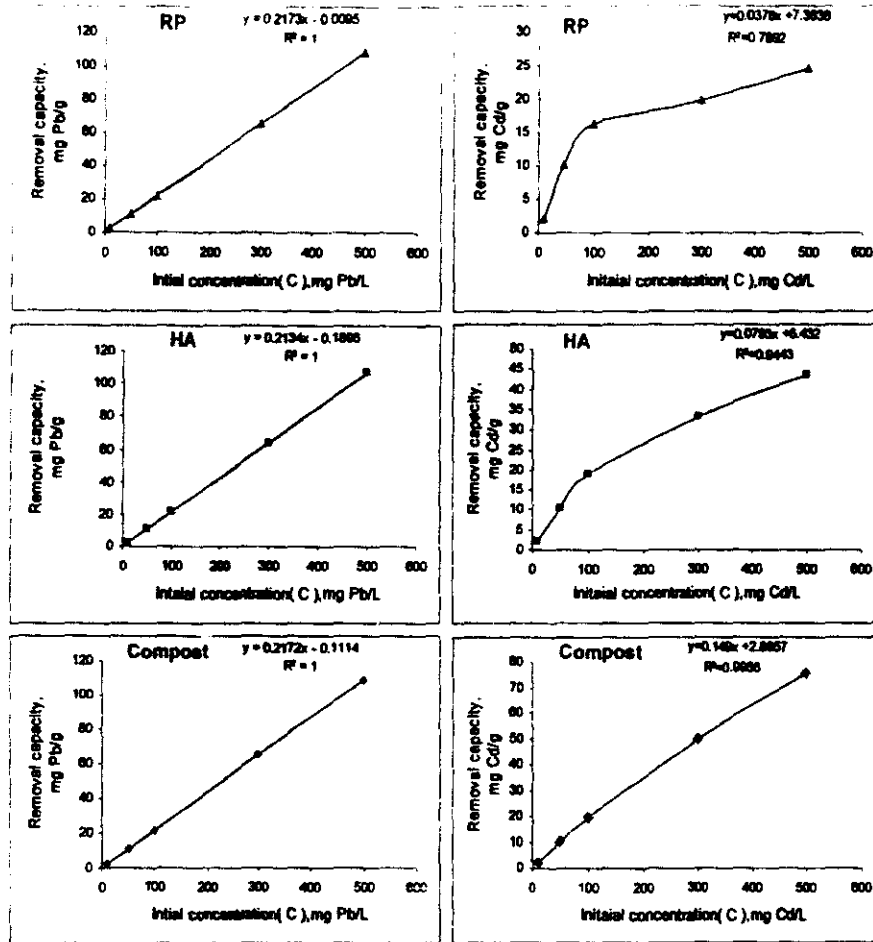


Fig. 2 : Effect of initial concentration on the removal capacity of Pb and Cd ions by three sorbent materials

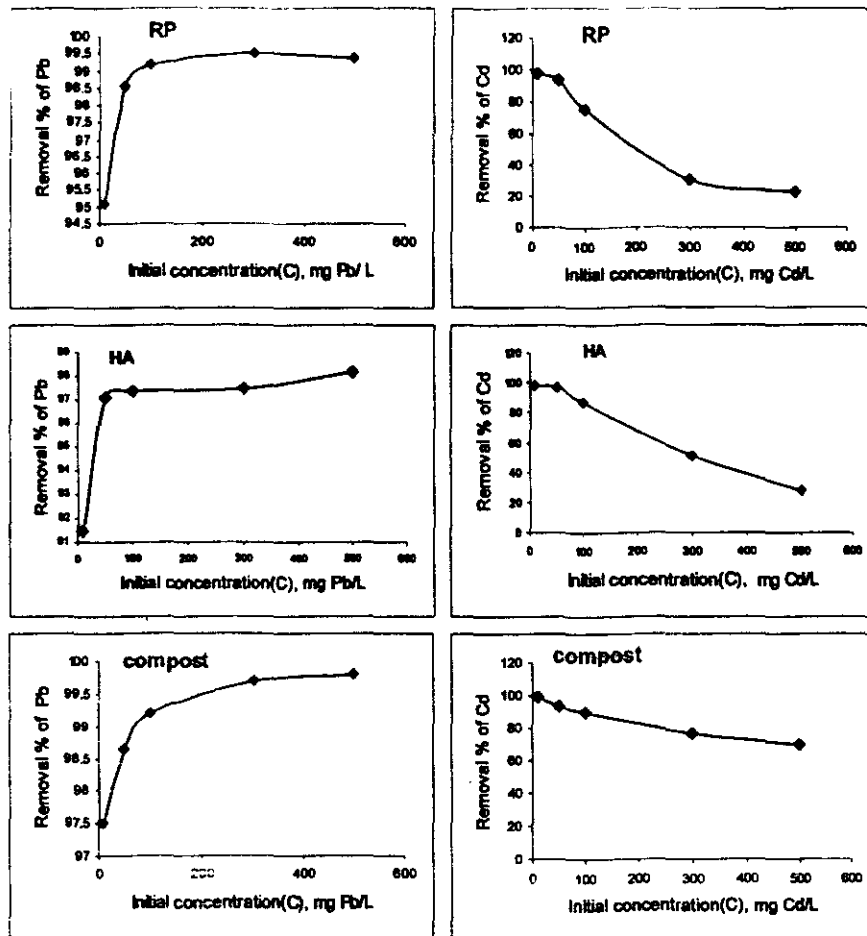


Fig. 3: Effect of initial concentration of Pb and Cd ions on removal percentage of Pb and Cd ions by three sorbent materials.

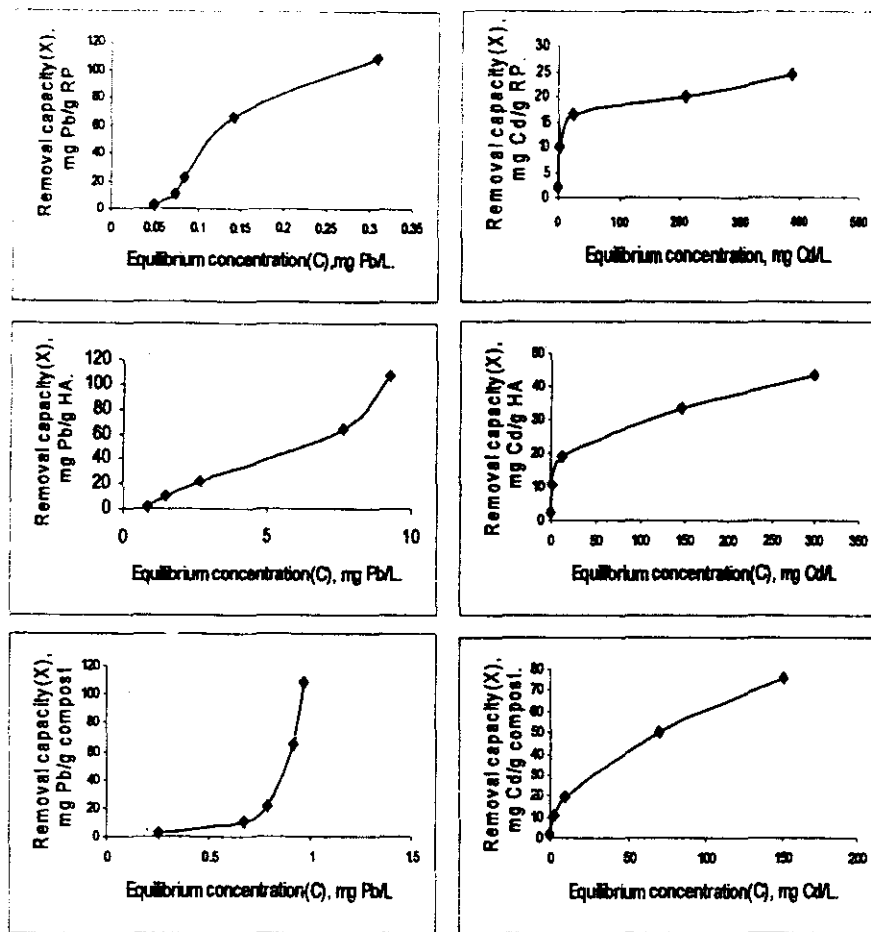


Fig. 4: Isotherms of Pb and Cd ions sorption by three sorbent materials.

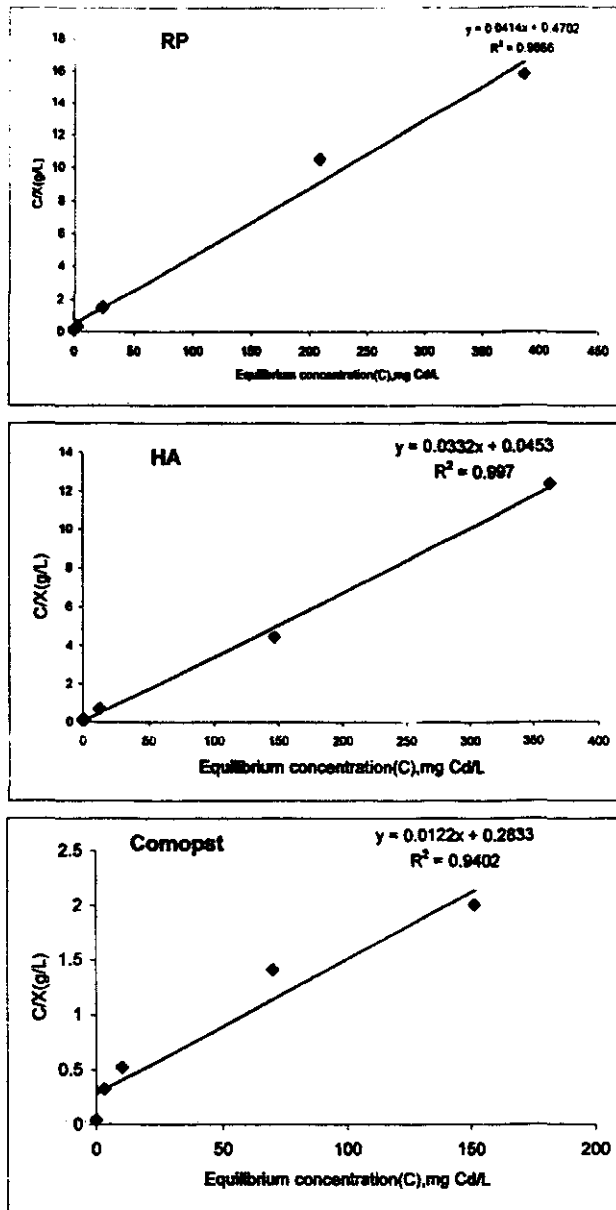


Fig. 5 : Langmuir plots for Cd ions sorption by three sorbent materials.

REFERENCES

- Bhattacharya A.K. and Venkobachar C. (1984).** Removal of cadmium by low cost adsorbent, *J. Am. Civ. Engg.*, 110, 110-116.
- Chen, V.J.Wright, L.J.Conca and L.M.Peurrung. (1997).** Evaluation of heavy metal remediation using mineral apatite. *Water, Air Soil Poll.*, 98, 57.
- Christopher, J.G.; Tran, Tri D.; Suffet Meu, H.I.(2002).** Electrosorption of inorganic salts from aqueous solutions using carbon aero gels. *Environ. Sci. Technol.* 30:10-3019;
- Conveerti,M.D.,Borgi,M.L.,Ferraiolo,g.,and Zillin (1992).** Fly ash as sorbent for COD suspended solid abatement from industrial waste waters.*Chem.Biochem.Eng. Q.* 16:195-200.
- Jackson, M.L. (1973).** "Soil Chemical Analysis". Prentice-Hall Englewood Califfs, New Jersey.
- Le Geros, R.Z.; LeGeros J.P. (1984).** Phosphate minerals in human tissues. In *Phospahte Minerals*; Nriagu J.O., Moore P.B. Eds.; Springer-Verlag; B-
- M.Elena, C.C.Nilce, C.M.Josino, M.R.Alexandre, M.C.And´ea, C.M.Josino and S.Marcelo.(2004).** Studies on the Mechanisms of Lead Immobilization by Hydroxyapatite. *Environ. Sci. Technol.*, 36 (7), pp 1625–1629.
- Ma LQ, Rao GN.(1999).** Aqueous Pb reduction in Pb-contaminated soils by Florida phosphate rocks. *Water Air Soil Pollut*; 110(1–2):1– 16.
- Ma, Q.Y., Traina, S.J., Logan, T.J., Ryan, J.A. (1993).** In situ lead immobilization by apatite. *Environ. Sci. Technol.* 27, 1803–1810.
- Ma, Q.Y., Logan, T.J., Traina, S.J. (1995).** Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. *Environ. Sci. Technol.*, 29:1118- 1126.
- Marshall, W.E., Champagne, E.T. (1995).** Agricultural by-products as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater. *J. Environ. Sci. Health A30, 2, 241-261.*
- Mohammad A.; Mohamed, N.P.A. (1997).** Physico-chemical adsorption treatments for minimization of heavy metal contents in water and wastewaters. *J. Sci. Ind. Res.*, 56:523-539;
- Perrone, J.; Fourest, B.; Giffaut, E. (2001).** Sorption of nickel on carbonate fluoroapatites. *J. Colloid Interface Sci.* 239: 303-313;.

- Prasad, M., Amritphale, S.S., Saxena, S., Chandra, N., Rao, T.C. (2000).** Attenuation of heavy metal ions by lean grade phosphorite. Miner. Eng. 13, 1301–1305
- Prasad, M., Saxena, S., Amritphale, S.S., Chandra, N.(2001).** Detoxification of aqueous zinc using fluorapatite-bearing lean grade rock phosphate. Environ. Technol. 22, 367–371.
- R.; Jurinak, J.; Wagner, K. (1986).** Contaminated surface soils in-place treatment techniques; Noyes Publications: Park Ridge,
- Sameer , A. and Zdravko , D. (1999).** Sorption of heavy metals by canola meal. Water Air Soil Pollut 114:251-276.1999.
- Sims, R.; Sorensen, D.; Sims, J.; McLean, J.; Mahmood, R.; Dupont, Sona Saxena and S.F. D'Souza.(2006).** Heavy Metal Pollution Abatement Using Rock Phosphate Mineral,. Environ.Int.32 (32), 199-202.
- USEPA. (1997).** Innovative uses of compost: disease control for plants and animals. Solid Waste and Emergency Response (5306W) EPA530-F-97-044. 4 pp.
- Yuping, X.; Schwartz, F.; Traina, S.F. (1994).** Sorption of Zn^{2+} and Cd^{2+} on hydroxy- apatite surface. Environ. Sci. Technol. 28; 1472-14580:.

الملخص العربي

إزالة الرصاص والكاديوم من المحلول المائي بالصخر الفوسفاتي والهيدروكسي أباتايت والكمبوست

ا.د. ماهر جورجى نسيم، ا.د. ماجدة أبوالمجد حسين، د. وفاء حسن محمد ، جمال الفصني
قسم الأراضي والكيمياء الزراعية - كلية الزراعة (سابا باشا) جامعة الإسكندرية.

تقوم هذه الدراسة على المقارنة بين قدرة الصخر الفوسفاتي، الهيدروكسي اباتيت و الكمبوست على ازالة كل من الرصاص والكاديوم من المحاليل المائية المحضرة فردية العنصر، حيث تمت دراسة تأثير كمية المواد الماصة والتركيز الأولي لهذه المعادن. وقد تم عمل ارتباط بين البيانات التجريبية لإتزان الإزالة لأيونات هذه المعادن وكل من معادلة لانجمير أو معادلة فريندليخ. وقد أشارت النتائج الى أن نموذج لانجمير قد أعطى أفضل تفسيراً ملائماً للبيانات التجريبية للكاديوم عن معادلة فريندليخ وكان ذلك

ضمن مدى التركيز المدروس. ومن ناحية أخرى أعطت معادلة فريندلخ أحسن تفسيراً للبيانات التحريبية للرصاص عن معادلة لانجمير. وقد لوحظ وجود إرتفاع في إمتصاص كل من الرصاص والكاديوم بواسطة المواد المختبرة. و كان الكمبوست الأكثر فعالية في إزالة ايونات الكاديوم مع أقصى إمتصاص (إزالة) بسعة (٣٣،٨٣ جم/جم) يليه الهيدروكسي أباتيت بسعة (٤٨،٤٣) جم/جم والصخر الفوسفاتي بسعة (٣٩،٢٤) جم/جم). أما بالنسبة للرصاص فقد لوحظ أن اعلى سعة إمتصاص كان بواسطة الكمبوست يليه الصخر الفوسفاتي و الهيدروكسي أباتيت. ويعتبر الصخر الفوسفاتي و الكمبوست كمواد منخفضة التكاليف ذات كفاءة عالية على خفض تركيزات كل من الرصاص والكاديوم في المحاليل المائية الملوثة، وبذلك يمكن الإقتراح بأنه يمكننا إستخدام الكمبوست والصخر الفوسفاتي كخيار فعال من حيث التكلفة لمعالجة التربة والعياء الملوثة بهذه المعادن.