

## Treatment of polluted water by clay minerals to eliminate the heavy metals

\*Wahba, M. M.; \*\*Sherine, M. Shehata and \*A. M. Zaghloul

\*Soils & Water Use Department, National Research Centre, Dokki, Cairo

\*Soil Chemical and Physical Dept., Desert Research Centre, Mataria

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### Abstract

The main objective of this research work is using some clay minerals as adsorbed material of the heavy metals from contaminated water with heavy metals.

In this laboratory experiment montmorillonite (Mont.), kaolinite (Kaol.) and mixture of them, with or without treatment of potassium dihydrogen phosphate were applied to evaluate the adsorption capacity of lead (Pb) cadmium (Cd) and zinc (Zn) from the contaminated water. The kinetic study was performed using Electrical Stirred Flow Unit (ESFU) at reaction times ranging between 1-120 min in each treatment.

The obtained results indicate that after 2 hours and at 2000ppm concentration, all heavy metals content in the polluted water were decreased, the removal order of the applied heavy minerals was :

Mont+P> Mont+ Kaol> Kaol+P > Mont+Kaol+P> Mont.> Kaol

Increasing the concentration of heavy metals to 6000ppm resulted in the same trend. Treatment of montmorillonite with potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) have significantly increased the adsorbed heavy metals. The rate constants and capacity factors of Modified Freundlich and Elovich are found to be the best kinetic models beside the distribution coefficient  $K_d$ . The retention of heavy metals by both pure and treated clay minerals have the order  $\text{Pb}>\text{Cd}>\text{Zn}$ .

The results of this experiment emphasize these treatments to minimize the application of the harmful impact of heavy metals in the contaminated water.

**Key words:** contaminated water- heavy metals-clay minerals-kinetic models

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Corresponding Author: monier morad <moniermorad@ yahoo.com>

### Introduction

Heavy metals are harmful for living organisms because of their stability, toxicity and tendency to accumulating in the environment. The industrial wastewaters are considered to be the main source of heavy metal impurities. Their purification prior to discharge into a recipient is, therefore, necessary. Various chemical and physico-chemical methods for heavy metal removal are followed such as chemical precipitation, sorption, solvent extraction, ultra filtration and ion exchange according to Vaca et al 2001 and Peri et al 2004. One of the most serious environmental problems concerning heavy metals is the disposal of metal-finishing- industry liquid effluents that have hazard, but relatively low Cr, Ni, Zn, Cu and Cd concentrations of tens to hundreds of mg/L. The problem is a serious one, due to both the number of enterprises involved in this sector and their geographical distribution.

Persistent heavy metal ions in trace quantities are difficult to remove from aqueous solution. Sorption is a promising technique for regulating mobility of chemical species and their geochemical cycles in the environment. The process has the additional advantages of applicability at very low concentrations, suitable for batch and continuous processes, ease of operation, little sludge generation, possibility of regeneration and reuse, and low capital cost as mentioned by Mohanty et al 2006. Thus, sorption becomes a preferred method for removal, recovery and recycling of toxic heavy metals from wastewater. Different types of

adsorbents are used for removing metal ions from aqueous solutions, **Gupta and Sharma 2002 and Alvarez and Nugteren 2005**.

**An et al (2001) and Li et al (2002)** referred that Lead is attracting wide attention of environmentalists as one of the most toxic heavy metals. The sources of lead release into the environment by waste streams are battery manufacturing, acid metal plating and finishing, ammunition, tetraethyl lead manufacturing, ceramic and glass industries printing, painting, dying, and other industries. Lead has been well recognized for its negative effect on the environment where it accumulates readily in living systems. Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead has been associated with sterility, abortion, stillbirths and neo-natal deaths, **Geol et al 2005**.

According to **Erdem et al (2004)**, Among various available treatment processes for the removal of heavy metals, such as precipitation, phytoextraction, ultra filtration and reverse osmosis, ion exchange is considered to be a cost effective method provided that low cost ion exchangers, such as zeolites and clays, are used Clay linings have been used as barriers to prevent contamination of groundwater and subsoil by leach containing metals. So ion exchange and sorption mechanisms of clay and clay minerals are utilized to remove different types of pollutants, for example, Zeolites and bentonite are naturally occurring structured and phyllosilicate minerals respectively, with high cation exchange and ion sorption capacity. Another chemical/mineralogical method of rendering metals immobile and non-bioavailability in situ has been suggested by **Ma et al. 1993; Cotter-Howells and Caporn, 1996**. These methods focus on converting the metals present in the soil into metal phosphates. However, many of these technologies are costly (e.g. excavation of contaminated material and chemical/physical treatment) or do not achieve a permanent or aesthetic solution. An alternative approach is to form insoluble heavy metal compounds thereby immobilizing the metal and reducing their ecological bioavailability. The prediction of the fate and transport of contaminants such as Pb in the environment, it is commonly rely on distribution coefficients and maximum adsorption levels that are obtained from experiments in which it is assumed that the reaction is at equilibrium. However, reactions in the environment are rarely at equilibrium, but instead are in a state of continuous change because of the dynamic processes occurring (**Sparks, 1995**).

The present work was undertaken to explore the feasibility of using kaolinite and montmorillonite, individually, the mixture of both and the modification of those natural materials for removal of Pb(II), Cd(II) and Zn(II) in single batch system from aqueous solution. In this study, the authors also evaluated the kinetic approach as a decision maker technique of remediation for pollutants in low quality of irrigation water

## 2. Materials and Methods

### 2.1 Treatment of clay minerals

Twenty grams of the montmorillonite, kaolinite minerals or mixture of both by 1:1 ratio clay was added to 500 ml of 200 mg/l of potassium dihydrogen phosphate 1-l vessels. The suspensions were stirred on a magnetic stirrer for 6 h after which they were centrifuged. The supernatant was discarded, and the treated samples were washed with distilled deionized water until test for phosphate was negative. They were then dried in the oven at 343 K. These treated samples were dissolved in 500 ml of 0.1 M of CaCl<sub>2</sub> solutions and stirred for 3 h in a magnetic stirrer. The suspensions were again centrifuged and supernatant discarded. The samples obtained were washed several times with distilled deionized water to get rid of Ca<sup>2+</sup>.

They were all dried in an oven at 343 K. The dried samples were gently crushed and packed into plastic containers for further use.

## 2-2. Solutions

Heavy-metals acetate of ( $\text{PbSO}_4$ ,  $\text{CdSO}_4$  and  $\text{ZnSO}_4$ ) were used to obtain three aqua solutions of single component i.e. Pb, Cd and Zn at fixed concentrations of 2000 and 6000  $\text{mg L}^{-1}$  pH =5.5 prepared from these cations and kept for sorption study.

## 2-3. Kinetic experiment

Experiments were carried out using Electrical stirred Flow unit (ESFU) method for all clay minerals and for different incubation times i.e. 2, 8 and 16 weeks. About 30 ml of the standardized metal ion solutions ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ) of concentrations 2000 and 6000  $\text{mg L}^{-1}$  was added to 0.5 g of each clay mineral. The dispersions were placed on a rotary shaker for 24 h. The metal concentrations in the eluates were determined by atomic sorption.

The supernatants obtained after centrifugation were analyzed by Atomic Absorption Spectrophotometry (AAS 200A Buck Scientific Model). The amount adsorbed was calculated from the concentration difference.

A Diagram of ESFU used in this paper, the modification of the new set up and mechanism of kinetic were previously mentioned in more details (Zaghloul, 2002). The system was vigorously shaken and the solution samples were received after different periods ranged between 1 to 120 min. at  $25^\circ\text{C} \pm 2^\circ\text{C}$  and analyzed for their concentrations of heavy metals using atomic absorption( Cottenie, et.al 1982).

## 2-4. Kinetic Models

In order to investigate the mechanism of sorption and potential rate controlling heavy metals transport and chemical reaction processes, both theoretical and empirical widely used kinetic models have been applied to test the experimental data. These kinetic models included:

- Horel's equation in the form :

$$q = at^b e^{(C*t)}$$

- Fractional power or modified Freundlich equation ( MFE) in the form :

$$q = bk^a$$

the linear transformation is:  $\log q = \log b + a (\log t)$

- Elovich equation in the form :

$$q = b + (1/a) \ln t$$

where:

$q_e$  : sorption capacity at equilibrium

$q_t$  : sorption capacity at time t

t : time (min)

$Q_t$  : quantity of diffusing substance

$Q_\infty$  : is the corresponding quantity after infinite time

r : radius of the cylinder

a, b,  $k_2$ ,  $\beta$ ,  $\alpha$ : constants

In this experiment, regression analysis was applied to test the conformity of HM adsorbed on used clay minerals to specific model(s) and testing for significant differences in rate coefficients and cumulative quantity of HM adsorbed was done using regression SAS software (SAS institute, 1985). The conventionality of HM sorption study was based on higher coefficient of determination ( $R^2$ ) and lower standard error (SE) values (Sparks, 1989 and 1998).

## 2.4 Distribution coefficient

The partition (or distribution) coefficient values, DC were used to measure sorption of contaminants to clay minerals; it is the simplest, yet least robust model available. The  $K_d$  model originates from thermodynamic chemistry and is defined as the ratio of the quantity of the adsorbate per gram of solid to the amount of the adsorbate remaining in solution at equilibrium. For the reaction

$$A = C_i = A_i$$

The mass action expression is the partition coefficient ( $K_d$ , ml/g):

$$K_d = A_i/C_i$$

Where:

$A$  = concentration of free or unoccupied surface sorption site on a solid phase (mol/ml),

$A_i$  = concentration of adsorbate on the solid at equilibrium (mol/g or  $\mu\text{g/g}$ ).

$C_i$  = total dissolved adsorbate concentration remaining in solution at equilibrium (mol/ml or  $\mu\text{g/ml}$ ), and  $A \% C_i$

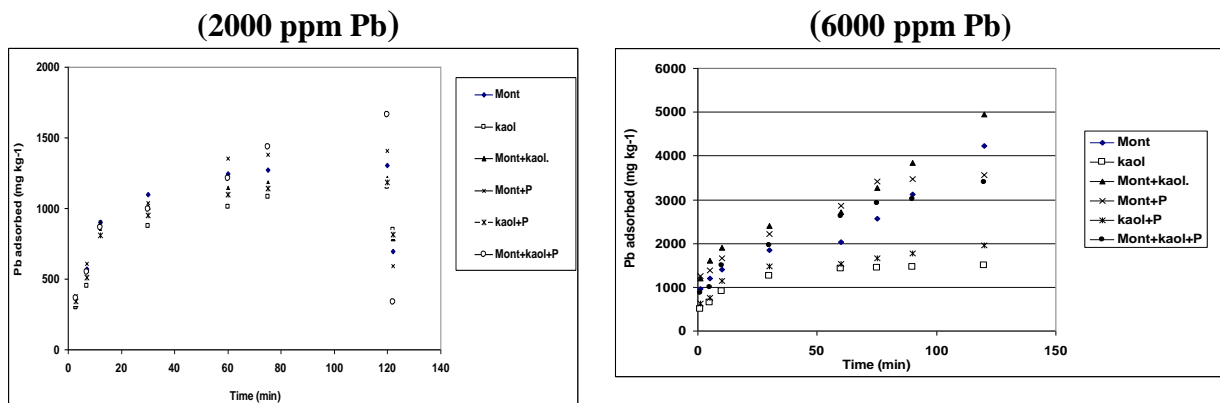
## 4. Results and Discussion

### 4.1 Rate of potential Toxic Elements (PTE) removal from polluted water

Recently, more research efforts have been focused on the beneficial utilization of natural materials or industrial by-products as effective adsorption of heavy for metals in polluted water

Figures 1, 2 and 3 represent the rate process of Pb, Cd and Zn adsorbed on the applied natural and treated clay mineral. As shown in these figures, regardless the concentrations of pollutants in the water, the rate of all HM adsorbed divided into three reaction periods. In the 1<sup>st</sup> one (0-30 min), fast sorption reaction started randomly for all pollutants, followed by medium speed reaction at time ranged between (30-90 min) and almost steady state reaction condition in the 3<sup>rd</sup> period of reaction.

The 3<sup>rd</sup> period, however, takes the rest of the reaction time (about 60 min) and characterized by almost stability or light increase in the rate of sorption (slow step) regardless the type of HM.



**Fig. (1) Rate of Pb adsorption on different natural and treated clay minerals**

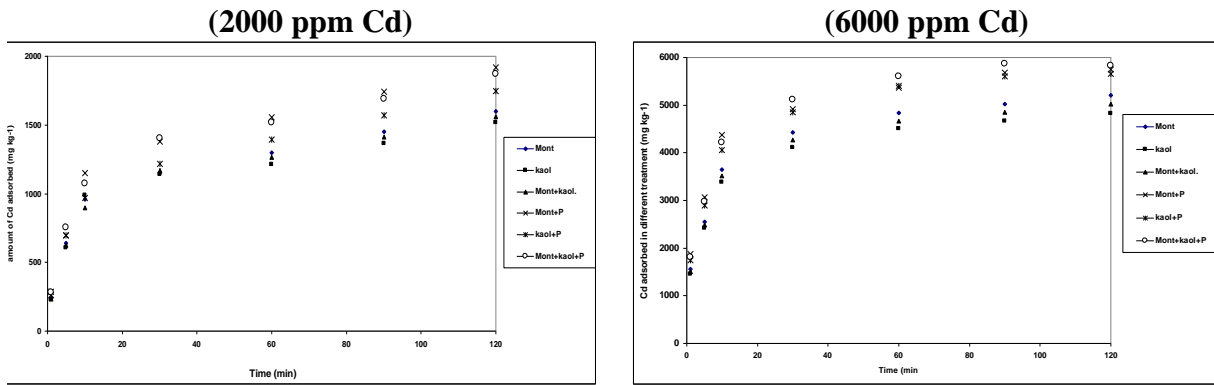


Fig. (2) Rate of Cd adsorption on different natural clay and treated clay minerals

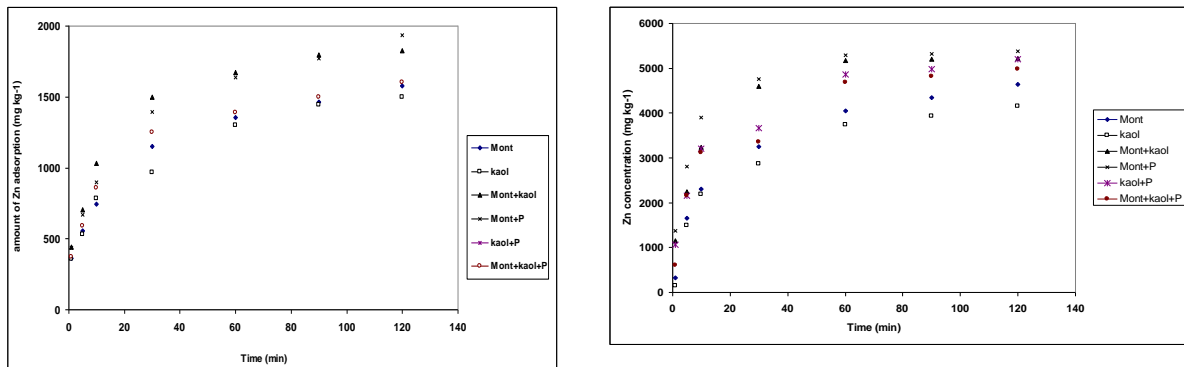


Fig. (3) Rate of Zn adsorption on different natural clay and treated clay minerals

Concerning the pollutants adsorbed, in the 1st period, almost no remarkable differences were observed between different treatments applied for Pb, Cd and Zn. However in the 2nd and 3rd periods, the variations were clearly observed with high rate of sorption detected in Zn followed by Cd and for less extend Pb.

Although the increase of HM concentration in solutions to (6000 ppm) gave the same trend in their arrangement of adsorption on the clay minerals especially in 1:1 (kaolinite) which gave the lesser sorption capacity. In other words, at 6000 ppm concentration of heavy metal solution, high Zn content was adsorbed on different clay minerals (about ~ 75-89% of total), followed by Cd (about 65-85% of total), and the amount adsorbed of Pb gave the minimum value compared with other HM (about 25-85 % of total).

#### 4.2 The kinetic models:

Table (1) represents the kinetic removal of Pb, Cd and Zn from aqua solutions as a function of applied clay minerals. According to  $R^2$  values, the three models used showed high and significant correlation which indicated that different mechanisms took place in sorption of such pollutants on tested materials.

Generally, according to MFE, data showed that Pb removal from solution was higher than Cd and followed by Zn. For example, the  $k_d$  value which represents the rate of Pb removal from contaminated water as affected by applying mixture of Mont+ Kaol used was  $2.81 \text{ mgkg}^{-1} \text{ min}^{-1}$  and montmorillonite treated by P was  $2.83 \text{ mgkg}^{-1} \text{ min}^{-1}$  for Cd was  $0.36, 0.37 \text{ mgkg}^{-1} \text{ min}^{-1}$  and Zn values were  $0.32$  and  $0.33 \text{ mgkg}^{-1} \text{ min}^{-1}$  respectively.

**Table (1) Rate constants of Kinetic models describe PTE's adsorption from contaminated water by clay minerals and treated clay minerals at 2000 ppm**

Treatments	Pb			Cd			Zn		
	K <sub>d</sub>	R <sup>2</sup>	SE	K <sub>d</sub>	R <sup>2</sup>	SE	K <sub>d</sub>	R <sup>2</sup>	SE
<b>Modified Freundlich equation( MFE)</b>									
<b>Mont.</b>	2.69	0.95***	0.05	0.35	0.93***	0.08	0.31	0.98***	0.03
<b>Kaol.</b>	2.65	0.94***	0.06	0.33	0.95***	0.09	0.30	0.99***	0.02
<b>Mon+Kaol.</b>	2.81	0.96***	0.05	0.36	0.96***	0.07	0.32	0.99***	0.02
<b>Mont. +P</b>	2.83	0.97***	0.02	0.37	0.93***	0.04	0.33	0.98***	0.03
<b>Kaol. +P</b>	2.68	0.96***	0.04	0.35	0.97***	0.07	0.31	0.98***	0.02
<b>Mont.+Kaol.+P</b>	2.70	0.99***	0.03	0.36	0.98***	0.02	0.32	0.99***	0.01
<b>Horel's Model</b>									
<b>Mont.</b>	1.45	0.98***	0.02	1.64	0.97***	0.08	1.40	0.99***	0.01
<b>Kaol.</b>	1.41	0.96***	0.06	1.60	0.96***	0.12	1.37	0.99***	0.02
<b>Mont+Kaol.</b>	1.44	0.97***	0.02	1.64	0.97***	0.02	1.45	0.99***	0.01
<b>Mont. +P</b>	1.48	0.98***	0.03	1.68	0.97***	0.08	1.48	0.99***	0.01
<b>Kaol. +P</b>	1.42	0.97***	0.03	1.62	0.97***	0.07	1.26	0.99***	0.02
<b>Mont.+Kaol.+P</b>	1.46	0.99***	0.02	1.66	0.99***	0.02	1.41	0.99***	0.01
<b>Elovich equation</b>									
<b>Mont.</b>	2.70	0.95***	0.05	0.34	0.93***	0.08	0.32	0.90***	0.06
<b>Kaol.</b>	2.66	0.94***	0.06	0.31	0.95***	0.09	0.24	0.83***	0.23
<b>Mon+Kaol.</b>	2.81	0.96***	0.05	0.36	0.96***	0.07	0.41	0.89***	0.12
<b>Mont. +P</b>	2.83	0.97***	0.02	0.37	0.93***	0.04	0.64	0.93***	0.05
<b>Kaol. +P</b>	2.68	0.96***	0.04	0.35	0.97***	0.07	0.27	0.89***	0.27
<b>Mont.+Kaol.+P</b>	2.71	0.99***	0.03	0.36	0.98***	0.02	0.35	0.95***	0.12

Changes occurred in the rate constants R<sup>2</sup> indicated that kaolinite + montmorillonite with phosphate were the highest treatments in the adsorption of the Pb, Cd and Zn. The same trend was in Horel's Model and Elovich equation.

Results also indicated that modification of montmorillonite with phosphate was the best treatment in minimizing the concentration of Pb and Cd in polluted water and mixture Mont+Kaol+P is better than applying clay mineral individual.

Data of MFE in table 2 showed that increasing the concentration of Cd from 2000 to 6000 ppm, led to increase the rate of sorption on montmorillonite from 0.35, 0.31 mgkg<sup>-1</sup>min<sup>-1</sup> to 5.61 and 9.01 mgkg<sup>-1</sup>min<sup>-1</sup> in Cd and Zn respectively, the same trend was observed in Pb.

Also data in table 2 indicated that according to kinetics models montmorillonite treated with phosphate was the best treatment in minimizing the concentration of Pb, Cd and Zn in solution through the sorption phenomenon.

**Table (2) Rate constants of Kinetic models describe PTE adsorption from contaminated water by clay mineral and treated clay mineral at 6000 ppm**

Treatments	Pb			Cd			Zn		
	K <sub>d</sub>	R <sup>2</sup>	SE	K <sub>d</sub>	R <sup>2</sup>	SE	K <sub>d</sub>	R <sup>2</sup>	SE
<b>MFE</b>									
<b>Mont. (T1)</b>	2.61	0.97***	0.83	5.61	<b>0.98***</b>	<b>0.11</b>	9.01	0.98***	0.23
<b>Kaol. (T2)</b>	2.30	0.95***	0.88	5.22	0.97***	0.17	8.78	0.95***	0.36
<b>Mont+Kaol. (T3)</b>	2.41	0.98***	0.64	6.12	0.99***	0.11	10.42	0.97***	0.29
<b>Mont. +P (t4)</b>	2.84	0.97***	0.91	6.85	0.98***	0.65	10.82	0.98***	0.28
<b>Kaol. +P (T5)</b>	2.37	0.97***	0.71	5.54	0.99***	0.11	9.06	0.96***	0.42
<b>Mont.+Kaol.+P (T6)</b>	2.70	0.97***	0.82	6.61	0.99***	0.16	10.97	0.97***	0.36
<b>Horel Model</b>									
<b>Mont.</b>	1.17	0.98***	0.03	1.38	0.99***	0.01	2.27	0.99***	0.004
<b>Kaol.</b>	1.11	0.97***	0.02	1.26	0.98***	0.01	1.99	0.93***	0.712
<b>Mont+Kaol</b>	1.25	0.99***	0.02	1.40	0.99***	0.01	2.33	0.97***	0.101
<b>Mont. +P</b>	1.33	0.99***	0.01	1.48	0.99***	0.02	2.48	0.99***	0.011
<b>Kaol. +P</b>	1.17	0.96***	0.04	1.34	0.99***	0.01	2.11	0.92***	0.072
<b>Mont.+Kaol+P</b>	1.23	0.98***	0.04	1.41	0.99***	0.01	2.29	0.94***	0.017
<b>Elovich equation</b>									
<b>Mont.</b>	0.25	0.96***	3.13	16.38	0.98***	4.26	29.94	0.99***	1.79
<b>Kaol.</b>	0.09	0.79**	2.67	15.12	0.98***	3.69	26.84	0.99***	3.53
<b>Mont+Kaol</b>	0.34	0.97***	3.01	17.89	0.98***	3.97	30.95	0.99***	5.81
<b>Mont. +P</b>	0.37	0.99***	1.66	19.66	0.98***	5.11	32.77	0.98***	7.78
<b>Kaol. +P</b>	0.12	0.86***	2.56	15.77	0.98***	4.95	27.34	0.99***	6.14
<b>Mont.+Kaol+P</b>	0.29	0.98***	2.24	18.50	0.97***	5.51	30.29	0.96***	1.23

It can be concluded that all soil minerals tended to adsorb Pb followed by Cd and Zn at low and high concentrations, according to the type of sorption and bonding mechanism. The high radius number takes a reverse order of the above arrangement i.e. Pb ( $1.81 \times 10^{-10}$  m) > Cd ( $1.71 \times 10^{-10}$  m) > Zn ( $1.53 \times 10^{-10}$  m). Since the greater atomic radius related with the higher adsorption capacity, this may explain the higher adsorption capacity of Pb over Cd and Zn. Moreover the electro-negativity of these metals takes, the order of atomic radius i.e. Pb (2.33 Pauling) > Cd (1.69 Pauling) > Zn (1.65 Pauling).



## Conclusion

There are several approaches for the removal of hazardous heavy metals from aqueous solutions, such as precipitation, phytoextraction ultra filtration and reverse osmosis. Ion exchange and sorption mechanisms of natural clay minerals are an effective and low cost method.

The experimental work which was carried revealed that there was three rates of adsorption for Pb, Cd and Zn on natural and mixtures of clay minerals, according to time (0-120min).

i.e fast, medium and steady.

The kinetic model of Modified Freundlich equation showed that mixture of montmorillonite and kaolinite has higher adsorption for Pb than Cd and Zn.

Treating montmorillonite with K-phosphate was the best to minimize the content of Pb, Cd and Zn in the polluted water at high concentration of 6000ppm, according to MFE.

The adsorption capacity of various heavy metals depends on two main factor 1- The 2:1 layer silicates as montmorillonite has high surface charges, as a result of isomorphous substitution, compared to 1:1 layered kaolinite. 2- The radius number of the heavy metal has great influence on its adsorption capacity; Pb ( $1.81 \times 10^{-10}$ m) > Cd ( $1.71 \times 10^{-10}$ m) > Zn ( $1.53 \times 10^{-10}$ m).

Therefore, the application of montmorillonite treated with K-phosphate to increase the sorption capacity is considered a convenient method in treating the polluted water with heavy metals.

## 5. Reference

- Alvarez, A. E. and Nugteren, H.W.(2005). Purification of chromium (VI) finishing wastewaters using calcined and uncalcined Mg–Al– CO<sub>3</sub>–hydrotalcite. *Water Res.* 39, 2535–2542.
- Aly, R. and Wada, K. (1981). Adsorption of lead, copper, zinc, cobalt and cadmium by soils that differ in cation exchange materials. *Journal of Soil Science* 32, 271– 283.
- An, H.K., Park, B.Y. and Kim. D.S. (2001). Crab shell for the removal of heavy metals from aqueous solution, *Water Res.* 35,3551–3556.
- Chiron, N., Guilet, R. and Deydier, E.(2003). Adsorption of Cu(II) and Pb (II) onto a grafted silica: isotherms and kinetic models. *Water Res.* 37, 3079–3086.
- Erdem, E., Karapinar, N. and Donat, R. (2004).The removal of heavy metal cations by natural zeolites, *J. Colloid Interface Sci.*, 280, 309–314.
- Goel, J., Kadirvelu, K., Rajagopal, C. and Garg. V.K. (2005).Removal of lead(II) by adsorption using treated granular activated carbon: batch and column studies, *J. Hazard. Mater.* B125 ,211–220.
- Gupta, V.K. and Ali, I.(2004). Removal of lead and chromium from wastewater using bagasse fly ash — a sugar industry wastes. *J. Colloid Interface Sci.* 271, 321–328.
- Gupta, V.K. and Sharma, S. (2002). Removal of cadmium and zinc from aqueous solutions using red mud. *Environ. Sci. Technol.* 36, 3612–3617.
- Gupta, V.K., Jain, C.K., Ali, I., Sharma, M. and Saini, V.K. (2003). Removal of cadmium and nickel from wastewater using bagasse fly ash — a sugar industry wastes. *Water Res.* 37, 4038–4044.
- Li, Y.H., Wang, S.G., Wei, J.Q., Zhang, X.F., Xu, C.L. Luan, . Z.K., Wu, D.H. and Wei. B.Q. (2002). Lead adsorption on carbon nanotubes. *Chem. Phys. Lett.* 357, 263–266.
- Mohan, D., Gupta, V.K., Srivastava, S.K. and Chander, S. (2001). Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste. *Colloids Surf. A: Physicochem. Eng. Asp.* 177, 169–181.



- Mohanty, K., Das, D. and Biswas, M.N.(2006). Preparation and characterization of activated carbons from Sterculia alata nutshell by chemical activation with zinc chloride to remove phenol from wastewater. Adsorption 12, 119–132.
- Peri. J., Trgo. C.M. and Vukojevi, N. (2004). Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms, Water Res. 38 (7), 893–1899.
- Peric, J., Trgo, M. and Medvidovic, N.V.(2004). Removal of zinc, copper and lead by natural zeolites — a comparison of adsorption isotherms. Water Res. 38, 1893–1899.
- Vaca. M. R., Callejas, R., Gehr, B.E., Jimenez, C.and Alvarez.P. (2001). Heavy metal removal with Mexican clinoptilolite: multicomponentionic exchange, Water Res. 35 (2), 373–378.
- Zaghloul, A.M. (2002) Kinetics of potassium adsorption in some soils of Egypt using Electrical Stirred Flow unit (ESFU). Egyptian Jou. Of soil Sci., 42, 463 – 471.