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REMOVAL OF LEAD FROM POLLUTED WATER BY USING CLAY MINERALS

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ABSTRACT: Clay minerals or natural materials such as zeolite play an important role in reducing the potential hazards of toxic elements. They cannot completely destroy heavy metals but can only be transformed from a single phase oxidation or organic compound to another. In this study clay minerals used to reduce the hazardous of lead on aqueous solutions. The used minerals were zeolite, bentonite and montmorillonite. Each mineral was applied at the rates of 1, 3 and 5% (*W/V*) of waste water. The concentrations used of lead were 60, 120 and 180ppm. The results observed that wherever increased the rate of the clay minerals added to the contaminated liquid has increased the amount adsorbed of lead. Therefore, the highest amount adsorbed of lead was obtained with 5% of soil minerals in all cases. The highest amount of lead adsorbed was obtained with zeolite at the rate of 5% (177 ppm) followed by montmorillonite and bentonite (165 and 145 ppm), respectively. There is a positive relationship with both the amount adsorbed of lead and the rate of soil mineral added to the solution of contaminated. On the other hand, the highest lead removal efficiency was found as about 98.7% with the rate of 5% zeolite mineral. Whereas, the lowest lead removal efficiency was found as about 39% with the rate of 1% bentonite mineral. The arrangement of the soil minerals ability to adsorb lead was followed this order: zeolite > montmorillonite > bentonite. This study suggests that using of available natural materials could be an economic and promising alternative solution in contaminated water to minimize hazards of heavy metals. The clay minerals are suitable materials for heavy metal removal from the industrial waste water.

Key words: Heavy metals, lead, adsorption, zeolite, montmorillonite, bentonite.

INTRODUCTION

Removing heavy metals demands high energy or advanced operational requirements. A number of conventional technologies such as coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction, biosorption, and adsorption have been considered for the treatment of contaminated waste water (Kwon *et al.,* 2010; Wang and Peng, 2010). In the last few years many researchers have studied new techniques to remove contaminants from soils (Saber *et al.,* 2012). In other words, Mojiri *et al.* (2015) reported that, for heavy metals removal from landfill leachate and domestic waste water, employing the powdered zeolite method was more effective than the application of the traditional activated carbon.

For the importance role of zeolite in reducing harmful hazarded of lead, Hasanabadi *et al.* (2015) indicated that zeolite was able to decrease the amount of uptake and transmission of lead and cadmium in plant and with decreasing the harmful effects of these elements cause to increase the growth traits, protein and uptake of nutrient in plant. So, zeolite can be used in order to decrease heavy metals uptake

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such as lead and cadmium and also improvement of growth of plants in polluted areas. Marzieh (2014) stressed on the bentonite play an important role in the adsorbent of the heavy metals, due to the high density and berry color properties and adsorption played an important role in clarifying water and the addition of natural zeolite will reduce, significantly heavy metal pollution.

In this point, Esmaeilpour *et al.* (2015) studied the effects of adsorbent minerals (bentonite, zeolite and sepiolite) on transfer of some heavy metals (*i.e.*, Pb, Zn and Cd) from soil to tissues of sunflower. Treatments included: Non-polluted soil, HM-polluted soil, polluted soil + bentonite, polluted soil + zeolite, and polluted soil + sepiolite. Zeolite addition decreased plant uptake of Zn and Cd by about 12 and 0.21 mg/kg, respectively, while bentonite addition reduced Pb uptake by about 3.05 mg/kg, without any significant difference for the other treatments. On the other hand, Wahba *et al.* (2016a) reported that the numerical values of rate constants indicated that in natural materials, zeolite has a sorption capacity to studied PTE's (potential toxic elements) more than bentonite used. Also, according to the kinetic studies, the selectivity of pollutants to be sorbed on clay minerals take the order Zn^{+2}>Ni^{2+}>Pb^{2}.

The objective of this experiment was to compare three different soil minerals (zeolite, montmorillonite and bentonite) for their ability to remove hazard of heavy metals.

MATERIALS AND METHODS

To investigate sorption characteristics of lead onto three clay minerals (montmorillonite, bentonite and zeolite) at rates 1, 3 and 5% from aqueous solutions, have been done by using batch experiments technique. In three replicates, these clay minerals were weighed into 50 ml centrifuge tubes containing 25 ml of prepared solutions of Pb^{+2} (60, 120 and 180 mg l^{-1}). The suspensions were shaken mechanically for 24 hr. After equilibration, the suspension was centrifuge at 3000-5000 rpm for 10-20 min. Equilibrium concentration of heavy metal (Ce) was determined in 1 ml of supernatant using Atomic Absorption Spectroscopy (AAS). The differences between Ci "initial concentration of heavy metal" and Ce are assumed to be adsorbed on adsorption materials. The concentration of HMs adsorbed on clay minerals, Cs (mmol l^{-1}) is expressed by equation: Cs = Ci − Ce. Sorption isotherms curves were obtained by plotting (Cs = conc. of heavy metal adsorbed on clay mineral in mg kg^{-1} clay) versus Ce = mg per liter).

Heavy Metals

The stock solutions of metal ions, having concentrations of 1000 mg l^{-1} were prepared from lead nitrate $Pb(NO_3)_2$ in1 mM HNO_3 acid. Lead concentration was determined by atomic absorption (Perkin Elmer-AAnalyst 400) as described by Cottenie *et al.* (1982).

Clay Minerals

Three types of clay minerals namely; bentonite, montmorillonite and zeolite (clinoptilolite) from ALIX zeolite Company were used in batch experiments. The data in Tables 1, 2 and 3 represent some physic-chemical properties of these clay materials.

RESULTS AND DISCUSSION

The laboratory experiment which was conducted to evaluate the impact of some natural minerals on the adsorption of heavy metals to overcome their hazard on contaminated water had resulted in valuable data useful in formations.

Concerning the effect of clay minerals type, results in Table 4 indicate that decreasing order of rate of lead element desorbed was more pronounced in zeolite mineral compared to montmorillonite and bentonite, respectively. It is noteworthy that whenever zeolite rate increased the adsorption amount of lead increased. It's found that the amount adsorbed of lead increased by about 98.7% at the rate of 5% zeolite compared to the rate of 1% at high concentration of lead.

On the other hand, results in Table 4 show that increasing the concentration of lead from 60 to 180 mg l^{-1}, on 5% of zeolite increased the rate of sorption from 57.2 to 177 mg l^{-1}. In other words, wherever lead concentration increased the adsorption amount of lead increased. Fig. 1 represents the rate process of Pb adsorbed on clay mineral (zeolite). It shows the highest amount of lead adsorption which was 177 mg l^{-1} with 5% of zeolite and the least amount of adsorption which was 44.7 mg l^{-1} with 1% of zeolite.

Table 1. Selected chemical analyses of zeolite mineral used in the study

CEC Cmolc Kg-1	Surface area (m^2 g^{-1})	pH 1:2.5	K_2O	Na_2O	Elements oxides (%)			
					SiO_2	Al_2O_3	Fe_2O_3	CaO
220	89.82	6.8	3.27	0.78	62.220	11.096	4.033	3.583

Table 2. Particle size distribution and some chemical properties of bentonite

Particle size distribution (%)					pH 1:2.5	EC dS/m	$CaCO_3$ g Kg^{-1}	CEC cmolc Kg^{-1}
C.sand	F.sand	Silt	Clay	Text.class				
1.1	3.8	5.3	89.8	Clay	8.3	4.10	27.3	53.2

Table 3. Selected chemical analyses of montmorillonite mineral used in the study

Color	Purity (%)	pH 1:2.5	Maximum moisture (%)	CEC cmolc Kg^{-1}	Chemical structure
Off white	> 98	6.8	89.82	116	Natural montmorillonite MMT M+y (Al2-y Mgy) (Si4) O10$(OH)_2$ nH_2O

Table 4. Amount of lead removed from aqueous solutions by clay minerals

Clay mineral	Rate of applied mineral (*W/V*)	Concentration of the applied Pb (mg/l)		
		60	120	180
	1%	44	88	151
Zeolite	3%	51	100	162
	5%	57	117	177
	1%	35	82	144
Montmorillonite	3%	40	93	157
	5%	45	101	165
	1%	23	61	125
Bentonite	3%	32	75	133
	5%	41	92	145

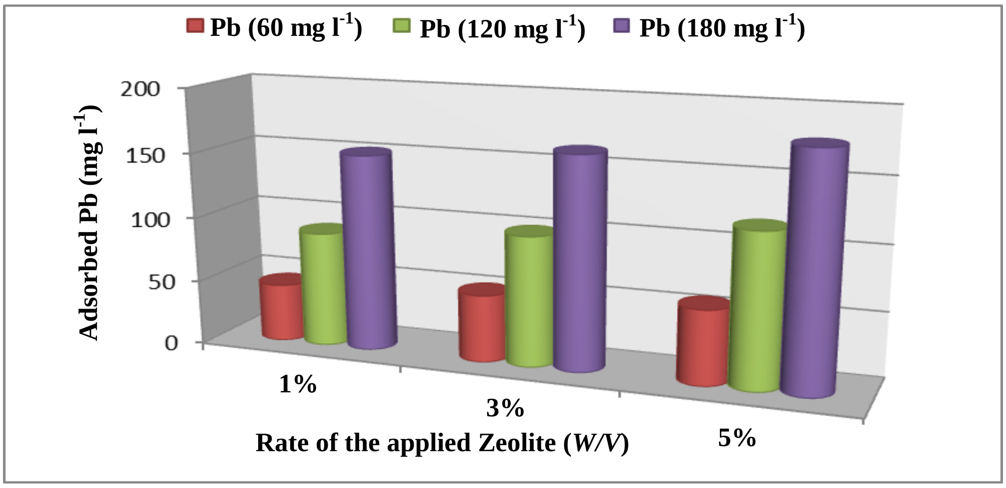

Fig. 1. Lead removal (mg l^{-1}) by diffrent rates of zeolite from aqueous solutions containing different lead levels

For the montmorillonite, results in Table 4 presents that the highest percentage of lead absorption was 80.7% with the rate of 5% montmorillonite, while the lowest one was 58.6% with the rate of 1% montmorillonite. In the case of increasing the concentration of lead from 60 to 180 mg l^{-1}, the adsorbed amount of lead increased.

Fig. 2 illustrated that the highest amount of lead adsorption was 165 mg l^{-1} with 5% of montmorillonite and the least amount of adsorption was 35 mg l^{-1} with 1% of montmorillonite. These results are in agreement with Wahba *et al.* (2012) who found that the adsorption capacity of various heavy metals depends on two main factors 1- The 2 : 1 layer silicates as montmorillonite has high surface charges, as a result of isomorphism substitution, compared to 1:1 layered kaolinate. 2- The radius number of the heavy metal has great influence on its adsorption capacity; Pb (1.81*10-10m)

For the applying of bentonite mineral with lead, Table 4 reveals that the highest adsorption ratio was 91.7% with 5% of bentonite at concentration 180 ppm of lead. On the other hand, the lowest adsorption ratio was 39% with 1% of clay mineral at concentration 60 mg l^{-1} of lead.

Fig. 3 illustrated the quantity of lead adsorbed at different ratios of bentonite with different concentrations of lead. It is noteworthy that wherever bentonite ratio increased the adsorption amount of lead increased. The highest amount of lead adsorbed was 145 mg l^{-1} with 5% of bentonite at concentration 180 mg l^{-1} of lead, while the lowest amount adsorbed of lead was 23.4 mg l^{-1} with 1% of bentonite at concentration 60 mg l^{-1} of lead. These results are in agreement with Wahba *et al.* (2016b) recorded that bentonite has certain properties as its ability to form thixotrophic gels with water and relatively high cation exchange capacity which allowed the adsorption of heavy metals and reduced their release in soils.

Regarding the effect of zeolite, montmorillonite and bentonite addition on the adsorption of Pb^{2+} added to water, the adsorption with zeolite was obviously higher than montmorillonite and bentonite, respectively. The results proved that the highest amount adsorbed of lead was 178 mg l^{-1} with zeolite followed by montmorillonite and bentonite (165, 145 mg l^{-1}), respectively.

Regarding the effect of zeolite, montmorillonite and bentonite addition on the adsorption of Pb^{2+} added to water, the adsorption with zeolite was obviously higher than montmorillonite and bentonite, respectively. The results proved that the highest amount adsorbed of lead was178 mg l^{-1} with zeolite followed by montmorillonite and bentonite (165, 145 mg l^{-1}), respectively.

For example, Fig. 4 represented the comparison between quantity of lead desorbed from liquid polluted as affected by zeolite, montmorillonite and bentonite application at three rates.

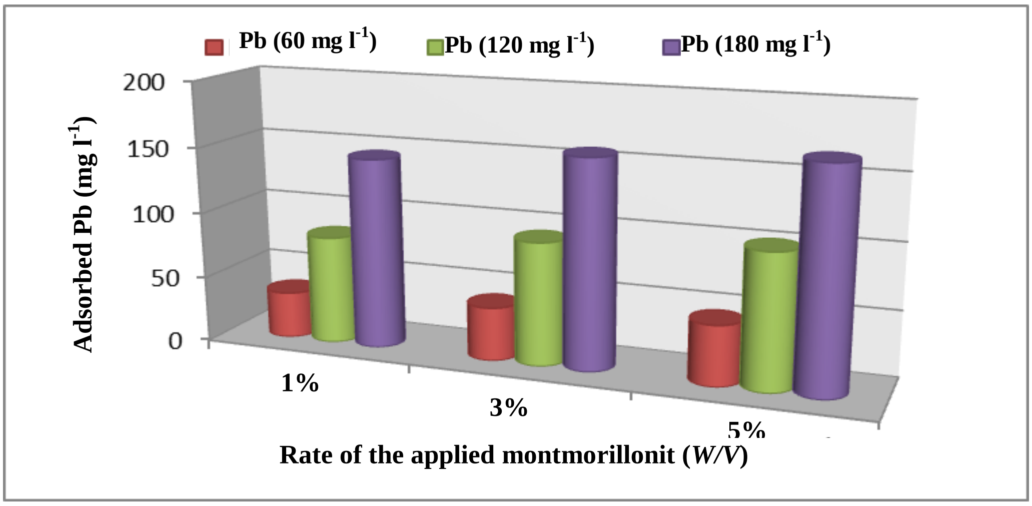

Fig. 2. Lead removal (mg l^{-1}) by diffrent rates of montmorillonite from aqueous solutions containing different lead levels

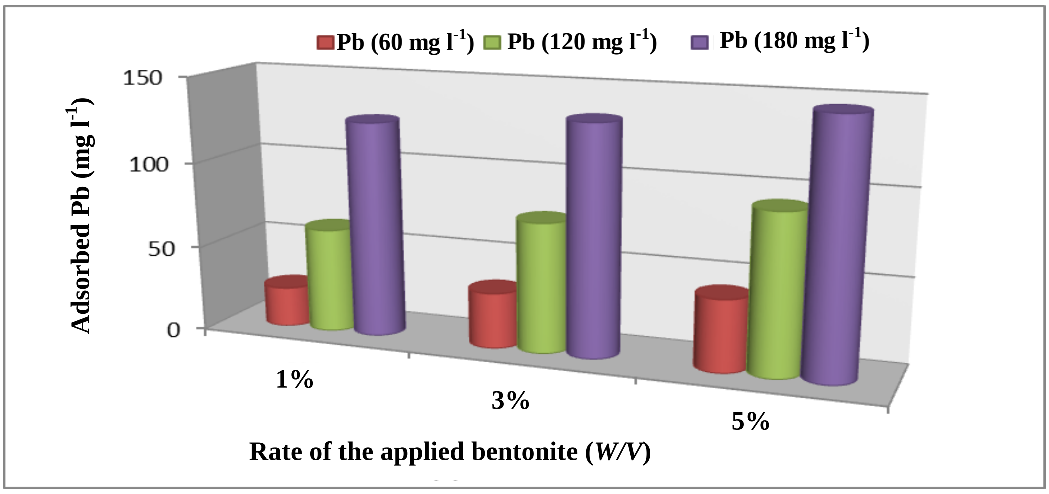

Fig. 3. Lead removal (mg l^{-1}) by different rates of bentonite from aqueous solutions containing different lead levels

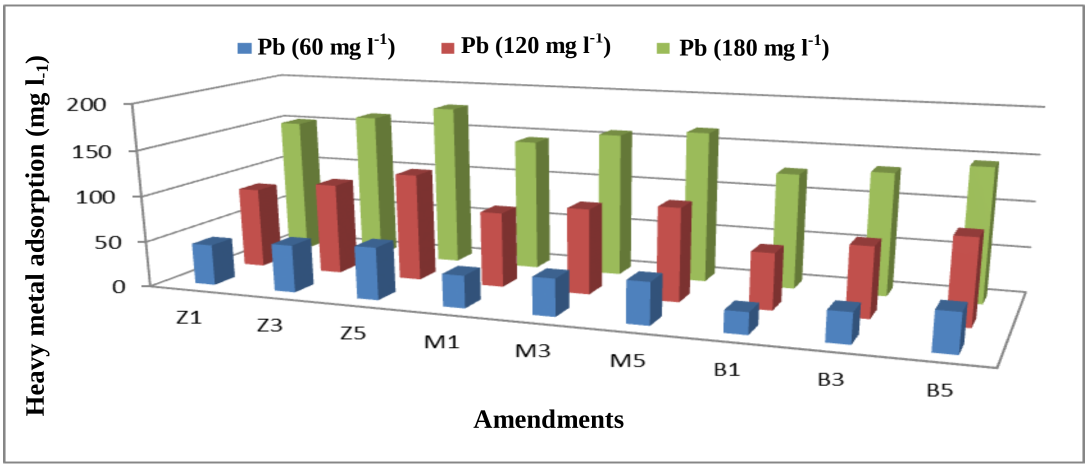

Fig. 4. Lead removal from aqueous solutions containing different lead levels at different rates of zeolite (Z), montmorillonite (M) and bentonite (B)

The highest amount of lead adsorbed was found with zeolite followed by montmorilonite and bentonite, respectively. These results are in agreement with Wahba *et al.* (2016a) reported that the role of zeolite was more pronouncing in enhancing the adsorption of the heavy metals more than bentonite due its specific molecular structure and high surface area. Therefore it recommended to be applied as a remediation material in polluted soils by heavy metals.

On the other hand, Fig. 4 illustrate the concentration of element adsorbed from water as affected by three rates of zeolite, montmorillonite and bentonite (1, 3 and 5%). wherever increased the rate of clay minerals increased the amount adsorbed of lead.

Conclusions

The contribution of the conducted experiment to evaluate the role of zeolite, montmorillonite and bentonite to eliminate the hazard of lead on contaminated water, had led to important scientific information which can be outlined in the following points:

- The role of zeolite, as a remediation material, was more effective on the adsorption of heavy metals than montmorillonite and bentonite, respectively. This was related to the specific structure of zeolite high cation exchange capacity and large surface area. However, montmorillonite and bentonite had certain properties as its ability to form thixotrophic gels with water and relatively high cation exchange capacity which allow the adsorption of heavy metals and reduce their release in liquid.
- The clay minerals are significantly minimized the rate of heavy metals release. It was obvious from the obtained results that the ability of zeolite in reducing the heavy metals release was more pronounced than montmorillonite and bentonite.
- According to results reported in this study, lead adsorption mechanisms by clay minerals may be explained as follows:

1. Vander-walls and hydrogen binding of lead with hydroxyl group of zeolite, montmorillonite and bentonite surfaces.
2. Ion exchange between Pb(II) ions and exchangeable cations (Na, K *etc.*) which balance negative charge of aluminum atoms.

Summarily, all these experimental results showed that clay minerals are suitable adsorbent for removal of heavy metals.

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إزالـــــــة الــرصــــــاص مــــــن الميــــاه المــلــوثـــــة باســــــتخـــدام معــــــــادن الطيـــــــن

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يهدف هذا البحث إلى دراسة استخدام معادن الطين مثل المونتملليورنيت والبنتونيت والزيوليت فى إزالة الرصاص من المياه الملوثة به، لذلك استخدمت المعادن الثلاثة السابق ذكرها كل على حدا بتركيزات ١، ٣، ٥ % (وزنية/حجمية) مع تركيزات مختلفة من الرصاص وهى ٦٠، ١٢٠، ١٨٠ملليجرام/لتر، وأوضحت النتائج أنه كلما زاد تركيز معدن الطين كلما زادت الكمية المدمصة من الرصاص حيث كانت أعلى كمية ادمصاص من الرصاص كانت مع تركيز ٥% من الزيوليت يليه المونتملليورنيت ثم البنتونيت وكانت الكميات كالأتي: ١٧٨، ١٦٥، ١٤٥ ملليجرام/لتر على التوالى، على صعيد أخر من حيث قدرة أدمصاص المعادن أكدت النتائج على أن أعلى كميات أدمصاص من الرصاص كانت مع الزيوليت يليه المونتملليورنيت ثم البنتونيت وهذا يرجع للقطر الأيوني للرصاص وملائمته للبناء البلورى للزيوليت أكثر من كل من المونتملليورنيت والبنتونيت، لذلك نوصى باستخدام معادن الطين فى معالجة المياه الملوثة بالرصاص حيث تعتبر من الطرق الاقتصادية للمعالجة علاوة على أنها طريقة أمنة أفضل من الطرق الكيماوية التى تسبب ضررا للطبيعة والإنسان والحيوان.

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