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REMOVAL OF LEAD (Pb^{2+}) FROM AQUEOUS SOLUTIONS BY NATURAL BENTONITE

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Abstract

The aim of the present work is to investigate the ability of natural bentonite (untreated) from Pacitan, East Java to remove lead ions from aqueous solution. The bentonite has specific surface area and cation exchange capacity of 27.52 $m^2\ g^{-1}$ and 65.20 meq/100 gr of bentonite, respectively. Towards this aim, batch adsorption experiments were carried out and the effect of various parameters on this removal process has been investigated. The effects of pH, grain size of bentonite, adsorption time and lead ion concentration on the adsorption process were examined. The optimum pH for adsorption was found to be 9, with the finer grain size of bentonite is more effective. In adsorption studies, residual lead ions concentration reached equilibrium in a duration of 24 hours. Adsorption of lead on bentonite appeared to follow Freundlich isotherm. Our results demonstrate that the adsorption process was mostly dominated by ion exchange process.
Keywords: *Removal, lead, aqueous solution, natural bentonite, adsorption.*

1 Introduction

The removal of metal ions from wastewaters by different adsorbents is always of great challenge (Emin and Dursun, 2008). Almost all of wastewaters contain considerable amounts of metal ions that would be harmful for public health and the environment if discharged without treatment. High concentrations of the metals in water affect humans, animals and vegetation. The pollution of water and soil with heavy metals ion increases proportionally with the expansion of industrial activities (Aydin *et al*, 2008). In order to minimize a treatment costs for the industrial wastewaters, most of the last investigations have focused on the use of low cost adsorbents (Meena *et al*, 2008).

In the last decade, utilization of geologic material as adsorbent is more applicable (Wilopo *et al*, 2012; Wilopo *et al*, 2011; Wilopo *et al*, 2010). One of geologic materials is clay minerals which applied to control the pollution due to the effluents polluted with heavy metal ions. Bentonite is one type of clay minerals which has ion-exchange capability to remove unwanted metal ions and this property makes bentonite favorable for wastewater treatment. Therefore, bentonite clay has been studied as ion exchanger and/or adsorbent due to its framework (Sajidu *et al*, 2008). Beside this, price of bentonite is considered very cheap and easy to find in our surrounding area (Zhu *et al*, 2007). The objective of this research is to evaluate the capability of bentonite from Pacitan, East Java for removing of lead from aqueous solution.

2 Experimental

2.1 Material

The adsorbent is a natural bentonite from Pacitan, East Java Province. The bentonite was grinded become sand size and directly used without any activation. The specific surface

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area of bentonite was determined by applying the BET (Brunauer, Emmet, Teller) equation. The resulted surface area of bentonite is 27.52 $m^2\ g^{-1}$. These values are lower than those expected for montmorillonite (Hillel, 1998), but it may be due to the lack of treatment. In fact, Bourg *et al* (2007) and Goldberg (2002) have measured, for a montmorillonite without pretreatment, specific surface areas of 23.9 and 18.6 $m^2\ g^{-1}$. It is possible that N_2 molecules can not penetrate easily the interlayer regions between the layer sheets, involving an underestimation of specific surface areas (Dékány and Nagy, 1991). Cation exchange capacity (CEC) of bentonite value is 65,20 meq/100 gr bentonite without any pretreatment. Based on the XRD (Figure 1) of bentonite consist montmorilonite, smectite and hematite. The composition of elements in bentonite was characterized using XRF shown the dominant elements consist of Al (9.3 wt.%), Fe (4.88 wt.%), Ca (2.05 wt.%) and Mg (1.7 wt.%). Therefore, bentonite from Pacitan is categorized as Ca-Mg bentonite (Meunier, 2003).

2.2 Batch Experiments

Several batch tests were performed to determine the capability of bentonite to remove Pb^{2+} in solution. Five grams of bentonite was used to find the sorption isotherm of Pb onto bentonite using 0.25 dm^{-3} solutions containing different concentrations of Pb^{2+} with initial pH 7. The pH of the solution was adjusted by using a dilute NaOH and HCl solutions. All solutions of Pb^{2+} were prepared using PbO special grade from Merck KGaA Germany. All solutions were shaken at 120 rpm and 25°C until sorption equilibrium was attained. Lead concentration was determined by Atomic Absorption Spectrophotometer (AAS).

3 Result and Discussion

The raw data for sorption isotherm of Pb^{2+} onto Bentonite at 25°C was presented in Figure 4a. It shows that the sorption equilibrium was achieved after 24 hour. The equilibrium pHs of the solutions from bentonite are 7.9–8.2, all of them are higher than the initial pH as shown in Figure 4b). As can be seen from this figure, increase in the final suspension pH after lead adsorption may be attributed to the replacement of alkaline and alkaline earth metals (Na^+, K^+, Ca^{2+}, Mg^{2+}) located in the exchange sites of bentonite with lead ions existed in the solutions.

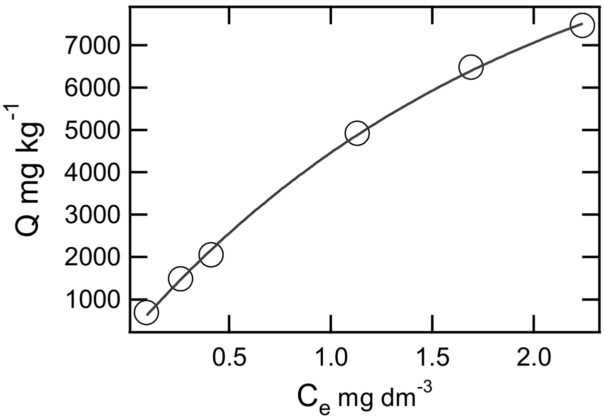

Figure 3: Adsorption isotherm of Cu^{2+} ion on lignite.

Adsorption isotherm for lead on the bentonite is presented in Figure 3. This isotherm is generally L type according to the Giles Classification. Type L represents the Langmurian adsorption isotherm, which is characteristic for strong chemical reaction. To quantify the adsorption capacity of lignite in relation to the lead ion, the experimental data were fitted to the Langmuir linear equation:

$$C/Q_e = 1/\,(b\,Q_{max}) + C/Q_{max} \qquad (1)$$

and Freundlich nonlinear and linear equations:

$$Q = K_f\,C^{1/n} \qquad (2)$$

$$q = \log K_f + 1/n\ \log C \qquad (3)$$

Where: q (mg/kg) is the equilibrium concentration of lead, C is in the equilibrium concentration of lead remaining in the solution. Q_e is the amount of lead retained per kilogram of lignite. Q_{max} is the maximum amount of lead that can be adsorbed in a monolayer (adsorption capacity) and b is a constant related to the energy of adsorption (Yavuz *et al*, 2007).

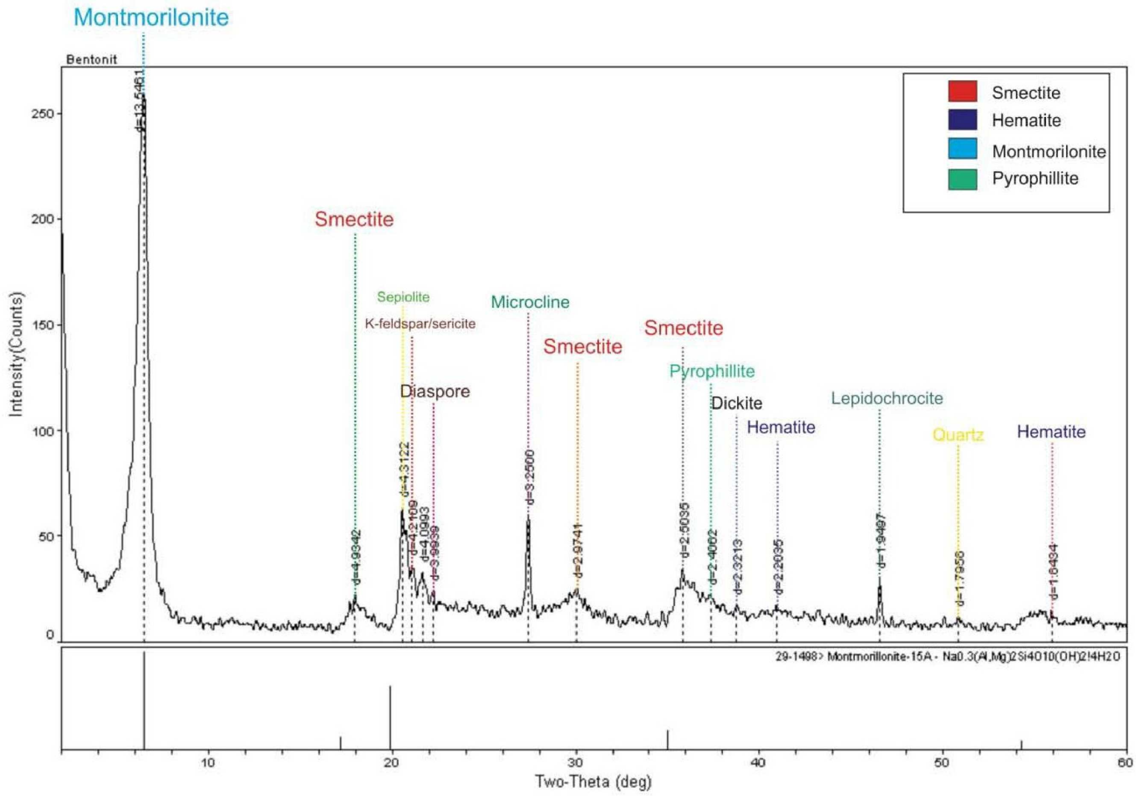

Figure 1: X-ray diffraction analysis of Bentonite showing the presence of montmorilonite, smectite and hematite.

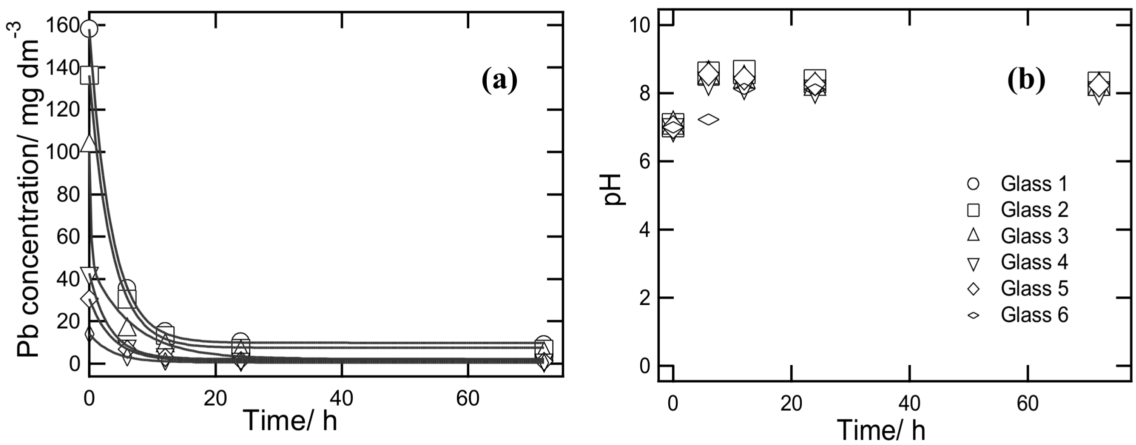

Figure 2: (a) Sorption of Pb onto Bentonite at initial pH 7 and 25°C; (b) pH of Pb solution during the batch experiment.

Table 1: Characteristic, parameters and determination coeeficient of the experimental data according to the degree of correlation Langmuir and Freundlich.

Langmuir Parameters			Freundlich Parametere		
Qm (mg/kg)	B (L/mg)	R^2	Kf	n	R^2
5000	400	0.95	0.11	0.56	0.99

Table 2: Concentration of Ca^{2+} and Mg^{2+} in the initial and after reach equilibrium.

Glass Number	Cations			
	Ca^{2+}		Mg^{2+}	
	Initial (mg dm^{-3})	After 72 hours (mg dm^{-3})	Initial (mg dm^{-3})	After 72 Hours (mg dm^{-3})
Glass 1	5.94	169.30	1.19	5.94
Glass 2	2.97	162.36	1.19	3.56
Glass 3	1.98	158.40	1.19	15.44
Glass 4	1.98	93.06	1.19	33.26
Glass 5	1.98	42.57	1.19	4.75
Glass 6	1.98	38.61	1.19	4.75

Figure **??**a shows the straight lines of Langmuir isotherm obtained plotting C/Q_e versus C_e for lead on bentonite samples studied, correlation coefficients being in this cases greater than 0.94. Q_{max} and b parameters were calculated from the least squares method applied to the straight lines in Figure **??**a. The Langmuir characteristic parameters and the degree of correlation of the adsorption data with respect to this equation are given in Table 1. Figure **??**b shows the Fruendlich isotherm with their parameters in Table 1. The degree of correlation of Fruendlich isotherm is better than Langmuir isotherm, it means that this reaction more favorable to follow the Fruendlich assumption.

Analysis of cations concentration before the experiment and after reach the equilibrium shows that mostly of cations concentration after reach the equilibrium were higher than before the experiment especially for Calcium (Table 22). This data indicate that the mechanism of lead removal onto bentonite not only by physical sorption due to high surface area but also mostly by cation exchange process with calcium.

The effect of grain size was also studied using bentonite with mesh number 18, 115 and 270. It shows that the bentonite with fine grain size (mesh 115) is more effective than coarse grain size due to increase of surface of bentonite. Therefore lead solution is easier to react with bentonite surface as shown in Figure 5.

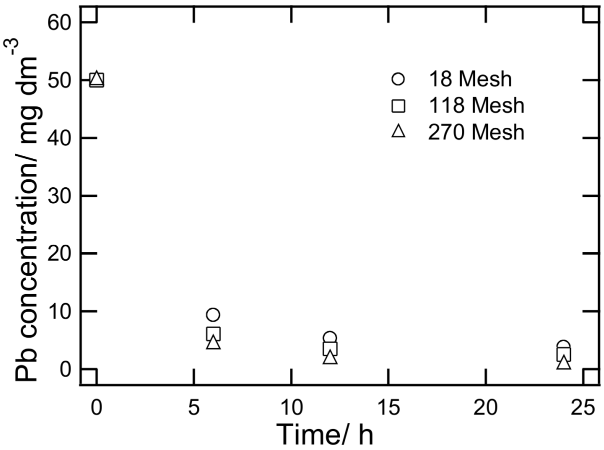

Figure 5: The effect of grain size in the Pb removal by bentonite.

The pH dependence of Pb^{2+} sorption onto Bentonite is shown in Figure 6. Experiments were carried out using Pb^{2+} ion concentrations 100 mg dm^{-3} at different pH values. As it is seen in Figure **??**, adsorbed amount of lead is low at low pH values. The value of adsorbed amount of lead is increased by increasing the pH value. It is apparent that using solutions at pH values 9 gives the highest adsorbed amount of lead values. The surface charge of bentonite is a strong function of the pH. Therefore at low pH, the exchange sites on the bentonite particle become positive, the lead cations compete with the H^+ ions in the solution for the active sites and consequently lower adsorption (Srivastava *et al*, 2006). At high pH values, surface of the bentonite has a higher negative charge which results in higher attraction of Pb^{2+} cations. These data are in agreement with the results obtained by several earlier workers for metal adsorption on different adsorbent (Bhattacharya *et al*, 2006; Chakir *et al*, 2002)

4 Conclusions

The Pacitan bentonite has characteristic with specific surface area and cation exchange capacity of 27.52 m^2 g^{-1} and 65.20 meq/100 gr of bentonite, respectively. According to the experiment showed that bentonite are good sorbent

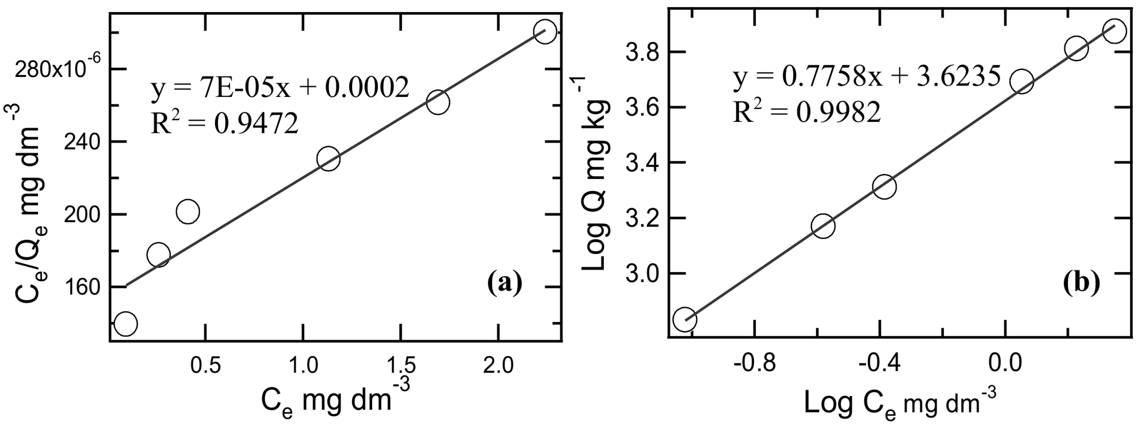

Figure 4: (a) The langmuir isotherms of Pb^{2+} ion on bentonite; (b) The Fruendlich isotherm of Pb^{2+} ion on bentonite.

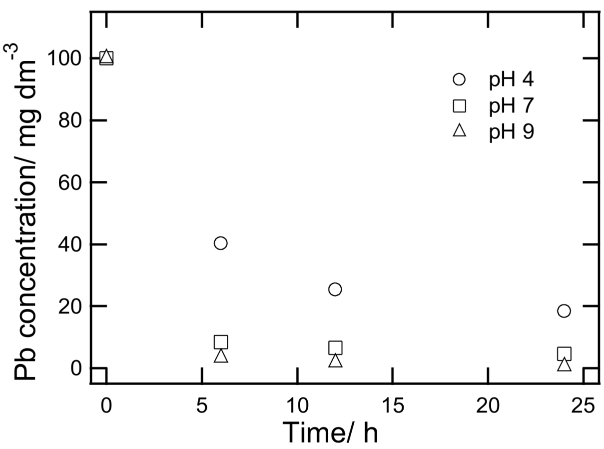

Figure 6: Removal of lead in the different of pH solution.

of lead. The adsorption isotherm analysis was favorable to follow the Freundlich isotherms for single metal system. The maximum lead removal was estimated 5 g kg^{-1} of bentonite according to the Langmuir equation. Smaller grain size of bentonite and high pH of lead solution makes more effective of lead removal by bentonite. The mechanism of lead removal onto bentonite is mainly by cations exchange process.

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