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# Effect of Manganese Coating on the Sorption Performance of Pyrolusite for Lead in Aqueous Conditions

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**Abstract.** A process to modify the property of pyrolusite, a natural form of manganese dioxide, was done in order to get a better adsorption performance. Modification was executed by coating the mineral with manganese solution (KMnO<sub>4</sub>, 0.05 M). Characterization analysis with XRF described significant change on Mn and MnO components, which was higher on the coated material compared to the ore. Meanwhile, although has not perfectly homogenous, it was identified that the distribution of pore diameter reduced from 2.23 – 4.08  $\mu\text{m}$  to 0.65 – 1.07  $\mu\text{m}$ . Another important result from this study was that  $\text{pH}_{\text{pzc}}$  of pyrolusite shifted from 4.2 to 1.9, giving a wider range on pH working solution for the adsorption performance. Manganese coated pyrolusite performed very well in 4 different pH conditions, providing overall removal efficiency above 90% for Lead. Furthermore, from a series of adsorption batch experiments it has been known that the adsorption mechanism of modified pyrolusite for Lead was better explained with Langmuir equation and the kinetics reaction was best modelled by pseudo-second order.

## 1. Introduction

Pyrolusite, ore form of manganese dioxide, can be enormously found in Indonesia especially in East Nusa Tenggara area. This mineral has been widely known as an important agent for several purposes, such as glass decolorizing, drying paints, coloring ceramics and battery making process. Beside those functions, with its oxides based content pyrolusite also has effective capability to adsorb trace metals in soil and water system. Several researchers have previously investigated the use of natural pyrolusite to eliminate several contaminants in water system. For heavy metals, natural manganese oxide has been reported successfully reduce Copper, Cadmium and Lead as much as 54.35, 6.80 and 98.00 mg/g respectively [1, 2]. Another study provided information that pyrolusite was able to adsorb phosphate in aqueous solution. The maximum adsorption capacity in eliminating phosphate following Langmuir model was as high as 11.40 mg/g [3]. The adsorption capacity of pyrolusite was considered higher if compared to industrial by-products (coal dust, sludge, coal fly ash and lignin) proving that mineral oxides still more effective than any other materials (industrial by-products and/or agricultural/fishing waste) [4]. However, as a common problem for mineral oxides, the poor crystalline morphology of pyrolusite is indicated as barrier for its best adsorption performance [5, 6]. To deal with this problem, several studies proposed modification onto the surface of material and one of the popular methods is by coating process. Coating process is able to create more homogenous surface that may result in smaller pore diameter distribution. In addition, coating compounds (mostly iron or manganese) will enhance



the active site of material so that the adsorption capacity can be lifted. Based on those considerations, in this study, modification by applying manganese-coating material onto pyrolusite was carried out. The intention of modification was to upgrade the morphology structure; while manganese substance was chosen to increase the active sites of mineral. The performance of modified pyrolusite was then tested in a series of batch experiments for Lead (Pb) in aqueous solutions. In order to evaluate the adsorption mechanism of coated pyrolusite several variables were applied, such as pH and temperature of solution and initial concentration of Lead.

## 2. Experimental Set Up

### 2.1. Coating process

Materials used in this study, including  $\text{Pb}(\text{NO}_3)_2$ , HCl, NaOH,  $\text{MnCl}_2$ ,  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4$  and KCl were in analytical grade and pyrolusite was supplied by a private company in Surabaya (ECOME). Coating process was done by preparing 50 g of pyrolusite (40 mesh) into conical flask with 250 mL of  $\text{MnCl}_2$  0.05M in it. The mixture was then shaken carefully in water bath shaker with temperature maintained at 60-70°C. In constant temperature, 200 mL of  $\text{KMnO}_4$  0.05M was added slowly to the mixture. Shaking of the mixture was continued for 24 hours and after that the solution was decanted and the material was stored in furnace with temperature of 160°C for 5 hours. Coated material was rinsed with demineralized water prior to characterization analysis and adsorption batch experiment.

### 2.2. Adsorption experiments

Adsorption experiments were done in batch condition involving several variables such as pH, initial concentration of Lead and temperature. In order to investigate the effect of pH on the adsorption performance of coated pyrolusite, 200 mL of Lead with initial concentration of 10 mg/L was prepared into conical flask prior to the addition of 2.5 g/L adsorbent. The desired pH value (3, 4, 5, 6) was adjust by adding either HCl or NaOH (0.1M). The flask was then mixed constantly at 160 rpm and until the process reached equilibrium condition interval sampling was taken. Measurement of metal concentration was conducted with UV – Spectrometer (HP series 8453). Removal efficiency (%) and adsorption capacity ( $q_e$ ) were defined by equation (1) and (2).

$$\text{Removal efficiency (\%)} : \quad R = \frac{C_0 - C_e}{C_0} * 100\% \quad (1)$$

$$\text{Adsorption capacity } (q_e, \text{mg/g}) : \quad q_e = \frac{(C_0 - C_e)}{m} * V \quad (2)$$

Where  $C_0$  is the initial concentration of Lead (mg/L),  $C_e$  is the concentration of Lead at equilibrium condition (mg/L),  $q_e$  (mg/g) is Lead adsorbed at given mass of adsorbent in the working volume (L). The collected data of equilibrium concentrations for each initial concentration of Lead were analysed using two adsorption models, Langmuir and Freundlich.

$$\text{Langmuir} : \quad q_e = \frac{b q_{max} C_e}{1 + b C_e} \quad (3) \quad \text{Freundlich} : \quad q_e = k_f C_e^n \quad (4)$$

where  $C_e$  is the heavy metal concentration in the solution at equilibrium (mg/L),  $b$  is Langmuir constant related to the affinity of binding sites (L/mg),  $q_{max}$  is the maximum adsorption capacity (mg/g),  $k_f$  is a Freundlich constant related to roughly adsorption capacity (mg/L),  $n$  is the constant related to adsorption density. Meanwhile, kinetics reaction was defined by applying pseudo first order (5) and pseudo second order equations (6).

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (5) \quad \frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (6)$$

Another series of batch experiments in four different temperatures (298K, 308K, 318K and 328K) were carried out to evaluate the effect of temperature. Thermodynamic data expressed as values of standard enthalpy change ( $\Delta H^\circ$ ), standard entropy change ( $\Delta S^\circ$ ) and Gibb's free energy ( $\Delta G^\circ$ ). Those values can be determined by applying these equations:

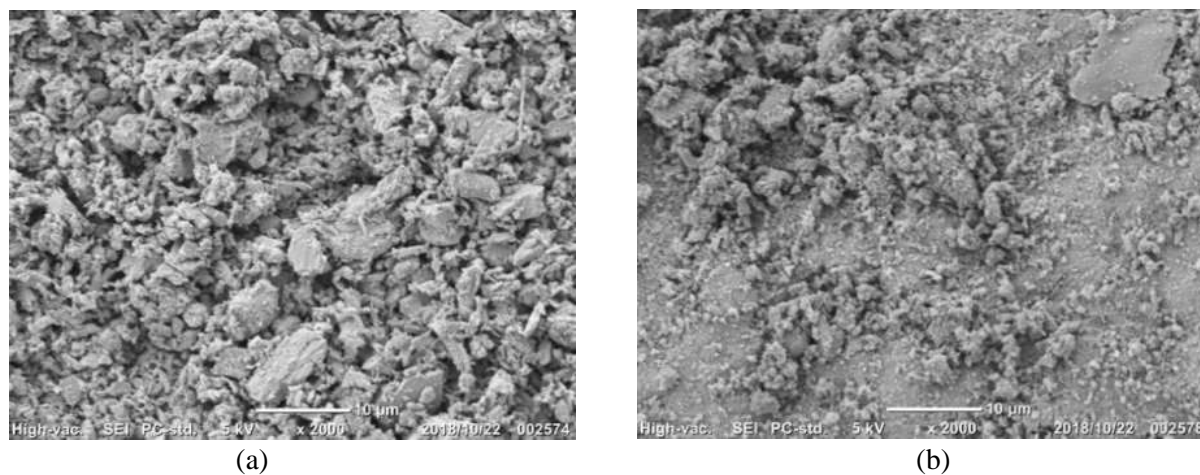
$$K_d = \frac{C_s}{C_e} \quad (7); \quad \ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8); \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

where  $C_s$  and  $C_e$  are the removed and remaining concentrations of Lead respectively.  $R$  ( $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ) is the ideal gas constant,  $T$  is temperature in Kelvin. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined from the slope and y-intercept on the plot between  $\ln K_d$  versus  $1/T$ .

### 3. Results and Discussion

#### 3.1. Characterization of Coated Pyrolusite

Morphology transition of pyrolusite was identified by SEM analysis with 2000 magnifications. Figure 1(a) shows the surface of uncoated pyrolusite that are rough with uneven pores, meanwhile the image of coated pyrolusite (Fig 1(b)) displays a smoother surface with coverage of manganese coat. However the SEM images provide indication that manganese layer has not homogenously cover the material, suggesting either more concentrate of coated compound or more intense mixing during the coating process. Nevertheless, coating process improved the elemental properties of material as proven from XRF analysis. Table 1 describes that Mn and MnO elements in the coated mineral was higher compared to the raw one, this is important for the uplifting of adsorption performance.



**Figure 1.** (a) SEM image of raw pyrolusite; (b) SEM image of coated pyrolusite

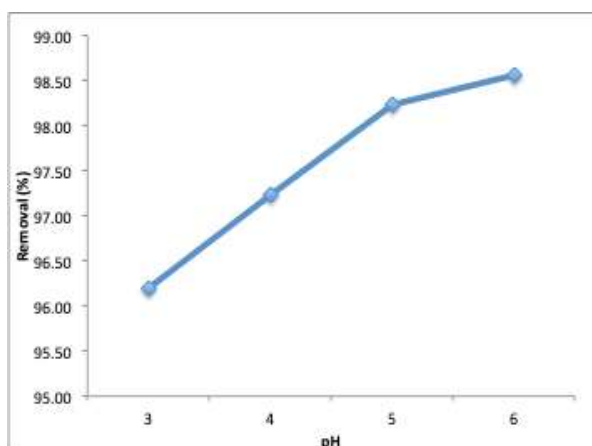
**Table 1.** Elements of Pyrolusite from XRF Helium Analysis

Elements	Percentage (%)	
	Raw Pyrolusite	Coated Pyrolusite
Mn	93.1	96.8
Si	1.56	1.18
K	0.199	0.274
Ti	0.18	0.1
MnO	88.4	93.6
SiO <sub>2</sub>	2.85	2.16

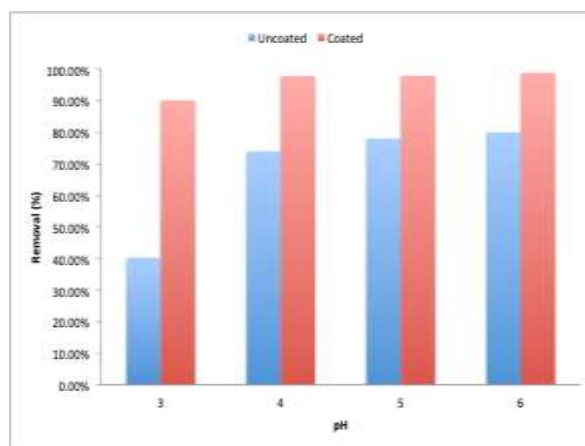
### 3.2. Adsorption Experiments

#### 3.2.1. Effect of pH

pH is a crucial factor in determining the nature of attachment between adsorbate and adsorbent in aqueous condition [7]. There were four different pH (3, 4, 5, 6) applied in adsorption experiments, in alkali condition (pH above 6) Lead started to form precipitate therefore pH variation above this value was neglected. Interestingly, among those four pH values total removal for Lead was not significantly different, putting them in the range of 96.20% to 98.55% as can be seen in Fig. 2. This result was unlikely when applying raw pyrolusite, in which the notable gap existed between total removal of Lead in low and high pH value. Comparison between total removal of Lead by using raw and coated pyrolusite in different pH is presented in Fig.3. A plausible explanation for this phenomenon could be related to the  $pH_{pzc}$  (point of zero charge) of pyrolusite. Previous study reported that  $pH_{pzc}$  of pyrolusite was 4.2 [8], thus if the pH solution is above 4.2 the surface of material will be lack of hydrogen ions resulted in negatively charge [9]. This mean the adsorption performance of pyrolusite will be effective if the working pH solution is above 4.2, expecting a favourable interaction between negative surface charge of the material and positive charge of metal ions. In this study,  $pH_{pzc}$  of coated pyrolusite was found at 1.9, shifting from the value of uncoated one, which were 4.2. By that, when the pH solution is gradually increase (above 1.9), the surface charge of coated pyrolusite will tend to be more negative resulting a less electrostatic repulsion to the metal ion. A wider range of pH working solution is very important especially for the implementation of modified pyrolusite in field scale.



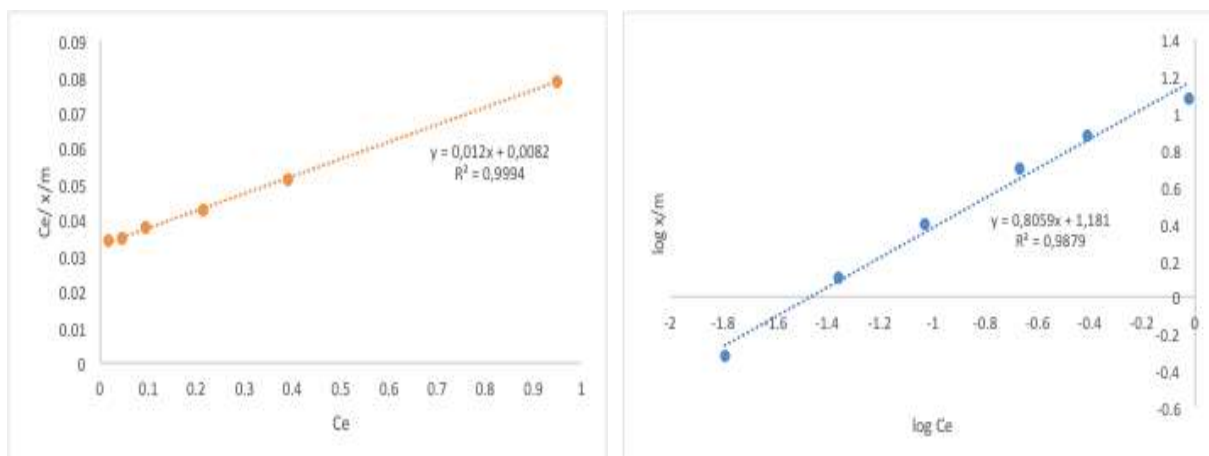
**Figure 2.** Removal of Lead with Coated Pyrolusite



**Figure 3.** Comparison of Lead removal in various pH values

#### 3.2.2. Adsorption Isotherms

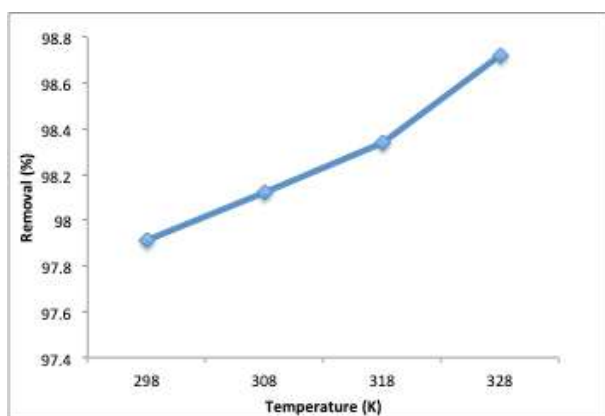
Collected data of equilibrium concentration ( $C_e$ ) for every initial concentration of Lead were plotted following the Langmuir (3) and Freundlich (4) equations. The results, as displayed in Fig. 4 (a) and (b), propose that the interaction between modified pyrolusite and Lead fit better to Langmuir model. By following Langmuir model, it is indicated that the adsorption is driven by chemical reaction (chemisorption) rather than physical process. Lead is adsorbed creating a smooth monolayer all around the homogenous surface of collector. In addition to that, data analysis with Langmuir equation came up with the information on maximum adsorption capacity of coated pyrolusite which was 221 mg/g, higher than the capacity of the raw one which was 123.45 mg/g.



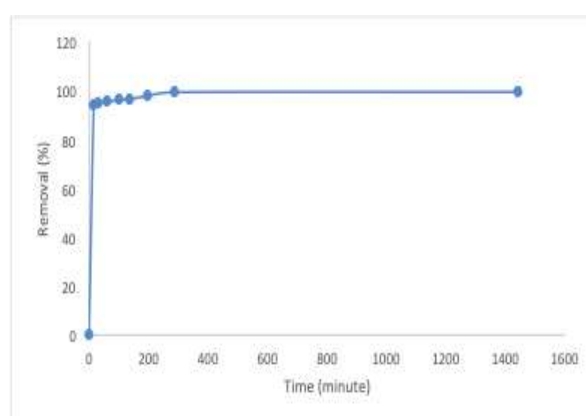
**Figure 4.** (a) Linear Plot – Langmuir ; (b) Linear Plot - Freundlich

### 3.2.3. Effect of Temperature

The effect of temperature on process sorption was evaluated by conducting batch experiments in four different temperatures (298K, 308K, 318K and 328K). Figure 5 depicts that the total removal of Lead increases along with the hotter condition of the solution, giving the biggest removal of 98.72% at the highest temperature (328K). Thermodynamic data (Table 2) reveals several important information regarding the adsorption mechanism. The positive value of  $\Delta H^\circ$  suggests that the adsorption process is endothermic and because the value is bigger than 4200 J/mol it is also indicated that the process determined by chemical reaction [10]. Meanwhile the positive value of  $\Delta S^\circ$  explains the progress of structural change in the surface of collector when the interaction with Lead occurred. Finally, the negative value of  $\Delta G^\circ$  proposes a spontaneous reaction between coated pyrolusite and Lead. The lower value of  $\Delta G^\circ$  in higher temperature describes that the adsorption process is more spontant when the temperature of solution increases [11].



**Figure 5.** Removal of Pb in different temperature



**Figure 6.** Adsorption rate of Pb

**Table 2.** Thermodynamic data of Pb onto Coated Pyrolusite

Temp (K)	$\Delta H^\circ$ (J/mol)	$\Delta S^\circ$ (J/mol.K)	$\Delta G^\circ$ (J/mol)
298	13,003	69.547	-7,821
308	13,003	69.547	-8,378
318	13,003	69.547	-8,963

328

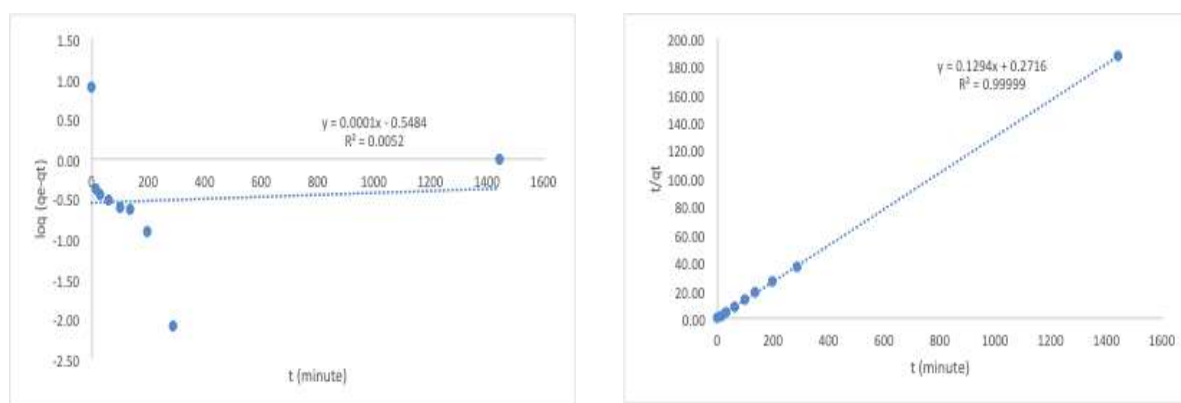
13,003

69,547

-9,958

### 3.2.4. Adsorption Kinetic

The spontaneity of adsorption process onto the modified pyrolusite was confirmed by the kinetic study analysis. Figure 6 portrays that the interaction between Lead and collector surface took place in the very beginning of reaction, just after 15 minutes about 95% of Lead was absorbed. Kinetics reaction of the process was evaluated by applying pseudo-first order and pseudo-second order models, the plotting result for both model is presented in Fig. 7 (a) and (b). Based on  $R^2$  value, it is obvious that the pseudo-second order model fit very well to the adsorption process. This model elaborates that both active sites on the collector surface and metal concentration actively determine the adsorption rate [7].



**Figure 7.** (a) Pseudo-first order and (b) Pseudo-second order model for Pb

## 4. Conclusions

Modification on pyrolusite by manganese coating gave significant impact on the adsorption performance of the material. The shifting of  $pH_{pzc}$  not only expanded the pH working solutions but also increased the adsorption capacity. The adsorption isotherm of Lead onto coated pyrolusite was best modelled by Langmuir equation, indicating a complete monolayer formation. Adsorption process was endothermic, spontaneous and followed the pseudo-second order.

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