Adsorption Cadmium and Lead Onto Natural Manganese Dioxide

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The utilization of natural material as an adsorbent to eliminate contaminants in the water is of great interest. Natural material can be directly used without further treatment which may lead to higher environmental impact. In this study, natural manganese dioxide (pyrolusite) which is immensely available in Indonesia, especially in East Nusa tenggara, were used to adsorb Cadmium (Cd) and Lead (Pb) in single and simultaneous condition. Several operational parameters such as initial concentration, pH and temperature were applied in order to elaborate the sorption mechanism and to determine the adsorption capacity. Meanwhile, simultaneous condition was set to identify the effect of coexistence ion on adsorption process. The amount of absorbed Cd and Pb were increased at a higher pH and reached the optimum condition at pH 7 for both. The adsorption isotherm for both adsorbate were best modeled following The Langmuir equation, giving an adsorption capacity as high as 108.70 mg/g and 123.45 mg/g for Cd and Pb respectively. Thermodynamics data showed that the adsorption process in this study was endothermic process. Additionally, in simultaneous condition, the presence of coexistence ion reduced the adsorbed amount of targetted ion. In this case the adsorption of Pb were less impacted compared to the adsorption of Cd.

1. Introduction

The excessive heavy metals in aquatic ecosystem are mostly derived from industrial activities. Cadmium (Cd) and Lead (Pb) are commonly found in bivalent cations form in water system. Those two metals have been known as significant elements in the manufacture of batteray, cable, paint, pesticide and in electroplating process. Although wastewater as a common source has been treated to an acceptable level, following national or international standard, continuous discharge practice will lead into accumulation. The presence of Cd and Pb in the water will then enter the food-chain cycle resulting in a harmful effect to human as the top consumer. There are several serious effects have been reported because of Cd and/or Pb contamination, such as necrosis, proteinuria, gastrointestinal and neurology problem, even lead to malformation and cancer in worst case (Zhao et al., 2010). Considering the damaging effect, World Health Organization (WHO) has published the maximum tolerable concentrations of Cd and Pb to human which are 0.007 mg/Kg weight and 0.05 mg/Kg weight respectively. Therefore, continual effort to find the most feasible technique in order to eliminate Cd and Pb from contaminated water. Chemical precipitation, by adjusting pH of the solution or after coagulation – flocculation process, are considered as the easiest method to remove heavy metals. However, this treatment produces excessive sludge that need to be further treated (Fransiscus et al., 2018). Filtration, including membrane and ultra-membrane system; reverse osmosis and electro-dialysis are other systems, but less effective in term of operational simpleness and economic perspective (Lima et al., 2017). Meanwhile, the application of the biological approach is still ongoing process as stability on the performance need to be improved. Adsorption has been widely used in different scale because of its simplicity in operation and high efficiency over a wide range of concentration (Qin et al., 2011). Currently, there are many researches focus on the investigating and/or modifying adsorbent materials in order to find ones that have high adsorption capacity (Kow, et al., 2017). Assorted materials encompassing natural minerals (soils), industrial by-products (eg. fly ash, steel slag), agricultural products (e.g. rice husk, sawdust, peanut shells), fishing waste (e.g. Shrimp and crab shells) have been reported to have high adsorption capacity. Among those materials, natural minerals

(soils) with oxides based content such as Iron and Manganese oxides are highly preferred. Oxides based minerals usually found with poor crystalline structure and known as a potent scavenger of trace metals in soil, sediment and water (Zhao et al., 2010)). One of the most important Manganese oxide minerals is pyrolusite, which is massively available in Indonesia especially in East Nusa Tenggara. For this particular mineral, single chains of edge-sharing $Mn(IV)O_6$ octahedral share corner with other chains to build a framework structure accommodating tunnels of square cross sections that are one octahedron by one octahedron (Post, 1999). This composition reflecting the poor crystalline morphology as commonly observed in other minerals. Pyrolusite is an essential material used as an oxidant in organic synthesis and for industrial batteray, however information on its potential function in wastewater or water treatment area is still limited. The utilization of manganese (di)oxides as adsorbent for water contaminants have been reported by several papers. Manganese oxide in synthetic form (AMO – amorphous manganese oxide and MOF - manganese dioxide formed in situ) were used to remove Cu, Cd, Pb and Zn (Puppa et al., 2013 and Qin et al., 2011). Meanwhile, the application of beta manganese dioxide (ß-MnO2) to eliminate Pb(II) in single condition was successfully presented by considering several parameters (Zhao et al., 2010). In spite of existing information, further investigation is still needed in order to have a better understanding on the performance of pyrolusite as adsorbent for heavy metals. Based on that consideration, a set of batch experiments was conducted to evaluate the effectivity of pyrolusite to adsorb Cd and Pb in aqueous solutions. In this study, adsorption process was done in independent condition (each for Cd and Pb) with pH, initial concentrations and temperature as working variables and in simultaneous condition in which Cd and Pb were together in the solutions. Independent condition was set to elucidate the adsorption process mechanism and determine the adsorption capacity, while simultaneous condition was conducted to learn about competitiveness.

2. Materials and Methods

2.1 Materials

The entire chemicals used in this study, including $Pb(NO_3)_2$, $CdNO_3$, HCl, NaOH, $KMnO_4$, H_2SO_4 and Sodium oxalate were in analytical grade and no treatment needed prior to the utilization. Pyrolusite, an ore form of manganese dioxide was supplied by a private company in Surabaya. Characterization of pyrolusite were done by titration process to quantify the manganese oxides content, Fourier Transform Infra-red (FTIR, Shimadzu) to identify the surface functional groups and X-Ray diffraction (XRD) in order to determine the structural condition. The content of manganese oxides in pyrolusite was as high as 84.76% (w/w) as described in previous work (Fransiscus et al., 2018).
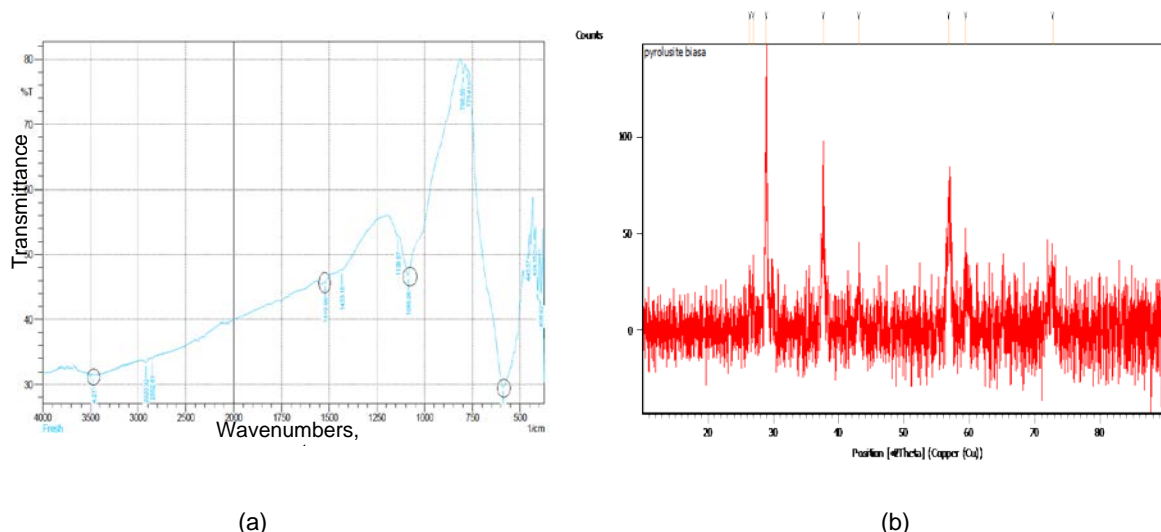

(a)   (b)

Figure 1 (a). FTIR spectra for pyrolusite; (b). XRD pattern for pyrolusite

As described in Figure1(a), the result of FTIR analysis indicating a stretching vibration of Mn-O and Mn-O-Mn bonds at the peak of 590cm^{-1}. Two other peaks, at 1085cm^{-1} expresses a vibration of hydroxyl groups that are joined to Mn atoms, and at 1519cm^{-1} reveals bending vibration of O-H and H_2O which insinuates that water molecule exists in nanostructure. In addition, the rise at peak of 3464cm^{-1} indicating stretching vibration on O-H bond and bending vibration of the absorbed water molecule in the lattice. XRD analysis was conducted with Cu Kœ radiation (1.544Å) and operated at the voltage of 40kV and tube current of 30mA. Figure 1(b) portrays

the peaks that appear (2Ø=28.8949°; 37.6337°; 43.0352°; 56.8375°; 59.4419°) are mostly reflection of manganese dioxide (except value at the peak of 2Ø=72.6963°), indicating a relatively high purity of the material.

2.2 Methods

All batch experiments in this study were conducted at temperature T=298K and under ambient condition. To evaluate the effect of pH in adsorption process, 200 mL of heavy metal solutions (Cd or Pb) with the initial concentration of 10 mg/L were prepared into conical flask, follow to that 2.5 g/L pyrolusite was added. The flask was put on thermo–shaker for mixing at 160 rpm, and at certain interval sampling were done until reaching equilibrium condition. Sample solutions were filtered using membrane filter 0.45 µm (Sartorius) prior to analysis with UV – Spectrometer (HP series 8453). The desired pH level (4, 5, 6, 7) for both metals solutions was set using either 0.1 M HCl or NaOH. The reduction of heavy metals concentration in aqueous solutions expressed as removal efficiency that can be calculated with equation (1). The adsorption capacity (q_e) was defined by equation (2) and also used in the determination of isotherm models.

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

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

Where C_0 is the initial concentration of Cd or Pb (mg/L), C_e is the concentration of heavy metals at equilibrium condition (mg/g), q_e is Cd or Pb adsorbed at given mass of adsorbent in the working volume (L). Adsorption isotherm models were developed by running batch experiments in different initial concentrations. The collected data of equilibrium concentrations for each metal were analysed using two adsorption models, Langmuir and Freundlich.

Langmuir :
$$q_e = \frac{b q_{max} C_e}{1 + b.C_e}$$
(3)

Freundlich :
$$q_e = k_f C_e^n$$
(4)

where C_e is the heavy metals 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. In order to have an understanding on the effect of temperature, another series of batch experiments in three different temperatures (298K, 308K and 318K) were carried out. Thermodynamic data expressed as values of standard enthalpy change (ΔH°), standard entropy change (ΔS°) and Gibb's free energy (ΔG^0). Those values can be determined by applying these equations:

$$K_d = \frac{C_s}{C_e}$$
(5)

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$
(6)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
(7)

where C_s and C_e are the removed and remaining concentrations of heavy metals, respectively. R (8.314 Jmol⁻¹K⁻¹) is the ideal gas constant, T is temperature in Kelvin. The values of ΔH^0 and ΔS^0 were defined from the slope and y-intercept on the plot between $\ln K_d$ versus $1/T$. As for simultaneous condition, two heavy metals with total volume of 200 mL were put together in conical flask. One metal as the reference was set at

the same initial concentration (10 mg/L) while the coexistent metal had the initial concentration between 1 to 10 mg/L. Operational conditions on this experiments were identical as the previous.

3. Results and Discussion

3.1 Effect of pH

The pH value of solution plays a significant role in determining attachment process of metal ions onto the adsorbent. The change on pH value will affect the distribution of metal ions species and the active site of the adsorbent through the dissociation of functional groups and change of surface charge, leading to the increasing or decreasing amount of adsorbed metals. Fig.2(a) depicts the transition of Pb and Cd removal from the aqueous solutions in different pH. The trends are similar for both metals, initially steep at pH 4 to 6 then the change is relatively flat at the pH of 6 to 7. In all pH condition, the removal of Pb is higher than Cd. At acid condition (pH < 7), the main species of Pb and Cd are Pb^{2+} and Cd^{2+}, thus the removal is mainly driven by adsorption process. The surface charge of pyrolusite will then very crucial in determining the portion of the adsorbed metals. Several papers mentioned that pyrolusite (MnO_2) have a net charge of zero at the pH of 1.4 to 4.5 (Tripathy et al., 2006; Zhang et al., 2008; Liu et al., 2009), known as pH_{pzc} (point of zero charge). Lately from a deeper investigation Zhao et al., 2010 confirmed that the pH_{pzc} of pyrolusite is 4.2. This mean that if the pH solution is above 4.2 the surface charge of pyrolusite will tend to be negative due to deprotonation process (Chaudry et al., 2016), in which hydrogen ions leave the sites. This phenomenon causes the de creasing of electrostatic repulsion between the adsorbent and metal ions, as consequence the interaction will be more intense since electrostatic attraction being dominant. Minor change in the portion of metals removed at pH 6 to 7 can be explained from the speciation of Pb and Cd, at pH 6.69 – 7 for Pb and 9.03 for Cd the solubility of both metals decrease significantly and tend to precipitate, this instability diminishes the adsorption process.
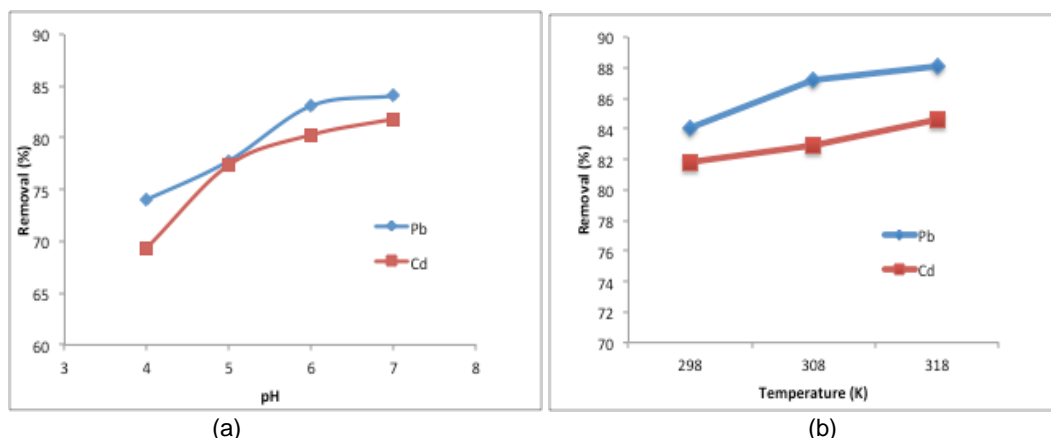
(a)	(b)

Figure 2 (a). Removal of Pb and Cd in different pH value; (b) Removal of Pb and Cd in different temperature

Table 1: Thermodynamic Data of the adsorption of Pb and Cd

T (K)	C_0 (mg/L)	ΔS^O (J/mol.K)	ΔH^o (J/mol)	ΔG^o (J/mol)
Pb				
298	10	72.18	13335.66	-8173.98
308	10	72.18	13335.66	-8895.78
318	10	72.18	13335.66	-9617.58
Cd				
298	10	52.15	7851.74	-7688.96
308	10	52.15	7851.74	-8210.46
318	10	52.15	7851.74	-8731.96

3.2 Effect of temperature

The removal of Pb and Cd through adsorption process in three different temperature is presented in Figure 2(b). For both metals, the highest removal is achieved at 318K indicating that the adsorption process of Pb and Cd onto pyrolusite is more favorable at higher temperature. A plausible elucidation for this is that

dissolved metals need to destroy the hydration sheaths prior to the adsorption process. The destruction process needs energy, while the adsorption process of metals onto pyrolusite emits energy. The need of energy seems to be more than the available source, thus in higher temperature the elimination of heavy metal ions is more effective. Adsorption mechanism of Pb and Cd on pyrolusite can be evaluated from thermodynamic data. The positive value of standard enthalpy (ΔH^o) relates to the information that the adsorption process is endothermic. The low value of ΔH^o in this experiment is similar to that found by Zhao et al., 2010 confirming that the adsorption process of Pb onto pyrolusite is weak, which is also apply for Cd. The value of ΔG^o reflects the spontaneity process, at higher temperature the process is more spontant. The positive value of ΔS^o suggests structural changes in adsorbate and adsorbent creating disorder-ness of the solid-liquid system (Ajmal et al., 2003).

3.3 Adsorption isotherms

In this study two models, Langmuir and Freundlich were applied to identify the isotherms adsorption that can be used to describe the distribution of adsorbate in liquid and solid phase. The result of analysis provides information that for both metals, Langmuir model fit better than Freundlich model to elaborate adsorption process onto pyrolusite (Figure 3 and 4). The finding that Langmuir model is more suitable to the adsorption data indicates that pyrolusite has homogenous surface and as the result creating identical adsorption activity. Pb and Cd are adsorbed by forming a complete monolayer all around the surface of adsorbate. By that, assumption of interaction between adsorbate following the formation of monolayer as suggested by Freundlich model is negligible. In fact, pyrolusite has limited adsorption capacity as can be calculated better with Langmuir equation (Table 2).
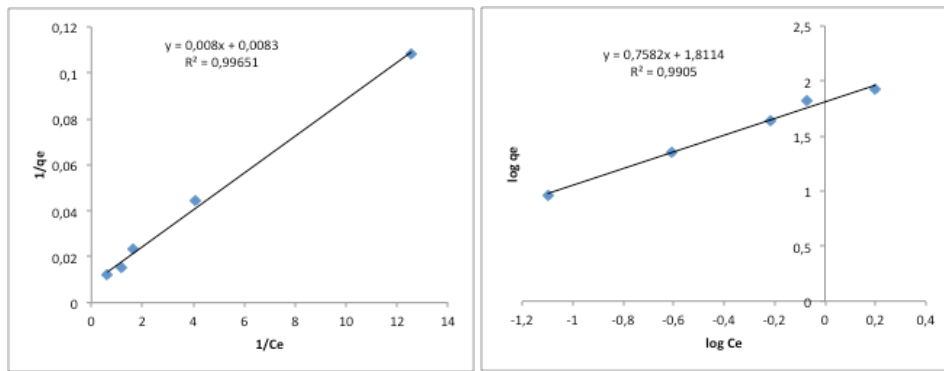

| (a) | (b) |
Figure 3 (a). Linear plot of Langmuir for Pb; (b) Linier plot of Freundlich for Pb
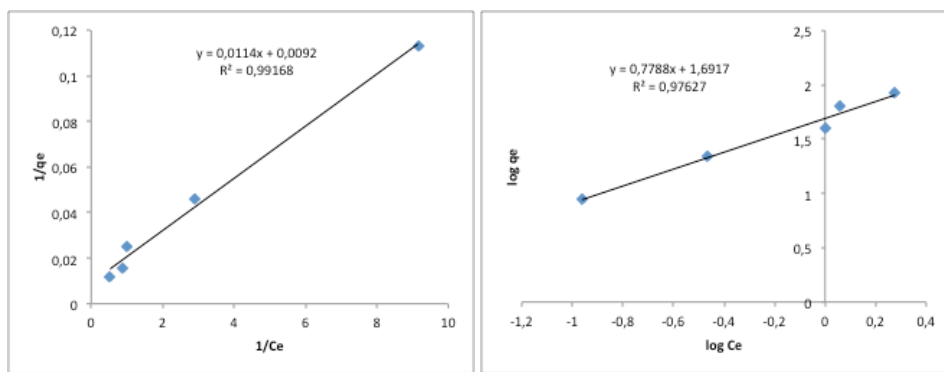

| (a) | (b) |
Figure 4 (a). Linear plot of Langmuir for Cd; (b) Linier plot of Freundlich for Cd

Table 2: Langmuir and Freundlich isotherm parameters for Pb and Cd

Model	Parameter	Pb	Cd
Langmuir	b (L/mg)	1.01	0.88
	q_{max} (mg/g)	123.45	108.70

Freundlich	K_f (mg/g)	64.71	49.09
	n	0.76	0.78

3.4 Adsorption in simultaneous condition

Experiments in simultaneous condition elaborate that the attachment process of metal ion onto pyrolusite strongly influenced by the existence of other ions. Figure 5 portrays the removal efficiency of Pb and Cd decreases gradually by the increase of coexistence ion's concentration. By adding competing ion with concentration as high as 10 mg/L, the removal of Pb lessens from 84.06% to 49.09% while for Cd drops from 81.67% to 25.91%. The affinity of Pb is bigger than Cd, this will cause a more favorable interaction with the active site of pyrolusite, besides that the radius is indicated as another factor in determining the amount of adsorbed ions. In this case, Pb has the smaller radius (0.084 nm) than Cd (0.097 nm) results in more suitable with the pore size of adsorbent.
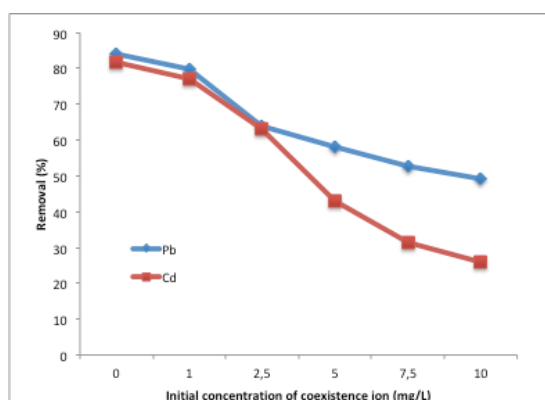

Figure 5. Removal of pb and Cd in simultaneous condition

4. Conclusions

This study concludes that (1) pyrolusite, a natural manganese dioxide is an effective adsorbent for Pb and Cd with adsorption capacity as high as 123.45 mg/g and 108.70 mg/g respectively, (2) the adsorption of both metals is pH dependent and the mechanism can be described by following Langmuir isotherm model, (3) thermodynamic parameters demonstrate that the adsorption process is endothermic and at high affinity, and lastly (4) the presence of coexistence ion alters the removal of Pb and Cd, in this case Pb is less affected than Cd.

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