A PRELIMINARY STUDY OF HEAVY METALS REMOVAL FROM SYNTHETIC RAINWATER BY NATURAL MINERAL ADSORBENTS

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ABSTRACT: *Rainwater harvesting system has many advantages to citizens. The low concentration of contaminants in harvested rainwater is the primary benefits to transform it as an alternative source for drinking water. However, the presence of heavy metals such as iron and manganese in drinking water may cause illness to the users. Therefore, further treatment is necessary for the harvested rainwater to reduce the content of these heavy metals. Many treatments have been applied in order to treat rainwater, such as UV disinfection, reverse osmosis, and ion exchange. In this study, adsorption process was chosen as a treatment for the rainwater. The performance of natural mineral adsorbents such as zeolite, limestone, and laterite soil in removing the low concentration of heavy metals in rainwater is investigated. The natural mineral adsorbents were washed thoroughly with distilled water and were then oven dried at 105^0C for 24 hours. The synthetic rainwater was prepared separately by diluting 1000mg/L of stock solution for iron and manganese to obtain the desired concentration of 1mg/L for each heavy metal. The experimental work in this research was carried out by applying different dosage of the natural adsorbents into 100mL of the synthetic rainwater and were shaken at 200 rpm for 60 minutes. The obtained results were then analysed by developing Langmuir and Freundlich adsorption isotherm model. The analysis shows that the removal of iron and manganese by different types of adsorbents is fitted Langmuir isotherm model, suggesting the adsorption process is monolayer. The obtained results show that limestone provides the maximum adsorption capacity of iron followed by laterite soil and zeolite. However, the removal of manganese shows a different result with the sequence of maximum adsorption capacity of manganese is laterite soil > limestone > zeolite.*

Keywords:adsorption, heavy metals, zeolite, limestone, laterite soil

1.   INTRODUCTION

Malaysia receives about 990 billion m^3 of rainfall. The huge amount of the abundant rainfall is partially evaporated, dissipated into the groundwater, or flows as surface runoff [1]. Therefore, rainwater harvesting system has potential in developing a new source of potable water by fully utilizing the abundant rainfall [2]. However, the presence of toxic heavy metals such as lead, copper, zinc, cadmium, chromium, and iron i n rainwater may affect human health by consuming the rainwater as drinking water without any treatment [3]. Most of the heavy metals are not biodegradable and tends to accumulate in organism, causing diseases and disorders [4].

Adsorption process has been widely demonstrated in water treatments. Generally, it is defined as a mass transfer operation, which a compound can be transferred from liquid phase to solid phase. The substance removed from liquid phase at the interface is described as adsorbate, while adsorbent is the medium which the adsorbate accumulated with in the form of solid, liquid, or gas phase [5]. Many types of low cost adsorbents such as zeolite, limestone, and laterite soil have been studied and applied in adsorption process. These adsorbents have the ability in removing organic and inorganic pollutants [6-8].

Natural zeolites able to remove heavy metal ions by utilizing the ion exchange [9]. It is an inorganic substance that contains of aluminosilicates substance and non - metallic minerals with high surface area [7]. The zeolite framework structure encloses cavities occupied by large ions and water molecules that are movable and allow ion exchange [10]. These characteristics are the main contributions in the adsorption of heavy metals.

Numerous studies have shown that the usage of limestone in water treatment removes heavy metals. Limestone contains calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$) and some impurities. The removal of heavy metals is due to the surface charge of limestone. It is proven that heavy metals with a surface charge of 2^+ ions are highly adsorbed by limestone as it contains of $CaCO_3$ [11]. The formation of chemical precipitation such as metal carbonate and metal hydroxide is a key factor in removing heavy metals with limestone [12].

Laterite soil formed from the intensive chemical weathering in tropical and subtropical environments under strong oxidizing conditions. The colour of the soil represents the iron compound in the laterite soil [13]. The chemical composition of laterite soil consists of silica, alumina, and metal oxides that remove inorganic pollutants from water . Therefore, removal of pollutants by laterite soils due to the high content of silica compound [14].

The characteristics of natural adsorbents such as zeolite, limestone, and laterite soil have the potential to remove heavy metals. Hence, the aim of this study is to investigate the performance of natural mineral adsorbents in order to remove the low concentration of heavy metals such as iron and manganese from synthetic rainwater.

2.   EXPERIMENTAL DETAILS

Preparation of Synthetic Rainwater

A stock solution of 1000mg/L of manganese and iron was prepared by dissolving an appropriate amount of $MnSO_4.H_2O$ and $FeCl_2.H_2O$ into 1000mL deionised water. The synthetic rainwater was prepared by diluting the stock solutions to obtain the desired concentration of 1mg/L for each heavy metal.

Preparation of Materials

High quality limestone and zeolite were sieved to obtain the size of 2.00mm mesh. The adsorbents were then washed with distilled water for several times in order to remove dust and other impurities. After that, the adsorbents were dried in the oven at 105^oC for 24 hours. On the other hand, the laterite soil was washed by adding 100g of laterite soil into 1000mL of deionised water and were stirred with 250 rpm for 30 minutes. The mixture was then filtered to collect the treated laterite soil and was oven dried at 105^oC for 24 hours [8]. Then, the washed laterite soil was sieved and the sample that retained at 630μm were used for the adsorption process [15].

Experimental Work

A batch adsorption study was conducted in determining the optimum adsorbent dosage and adsorption isotherm models. The experiments were carried out with two series of experimental works consist of thirty units of 250mL conical flasks contained of 100mL synthetic rainwater for iron and manganese with the adsorbent. The adsorbent dosages for zeolite and laterite soil were in the range of 0.5 to 5.0g. Meanwhile, the adsorbent dosages for limestone is in the range of 5 to 50g. The conical flasks were placed on the orbital shaker at 200rpm for 60 minutes. After that, the conical flasks were left for 120 minutes for the settling time.

Analytical Method

The chemical compositions of adsorbents were determined by X-ray Diffraction Test (XRD). The heavy metals concentration in the samples of synthetic rainwater was determined by using Inductively Coupled Plasma - OES (ICP- OES).

Adsorption Equilibrium

Adsorption isotherm is a function of the concentration of adsorbate at constant temperature in order to determine the amount of material adsorbed. The adsorbent phase concentration can be computed by Equation (1) below [5]:

$$q_e = \frac{(C_o - C_e)V}{m}$$

(1)

Where;

q_e = adsorbent phase concentration after equilibrium, mg/g adsorbent

C_o = initial concentration of adsorbate, mg/L

C_e = final equilibrium concentration of adsorbate after adsorption has occurred, mg/L

V = volume of liquid in the reactor, L

m = mass of adsorbent, g

In this study, the chosen adsorption isotherms were Langmuir isotherm model and Freundlich isotherm model. These isotherms were chosen in order to determine the efficiency of adsorption process.

Langmuir Isotherm Model

Langmuir isotherm model assumes a fixed number of sites and only one solute molecule per site of adsorbent and suggest the monolayer adsorption on a homogeneous surface [5, 7, 8]. The Langmuir isotherm relates with q_e (mg of adsorbate adsorbed per gram of adsorbent media) and C_e (the equilibrium adsorbate concentration in solution) as shown in Equation 2 [16]:

$$q_e = \frac{Q_m b C_e}{(1 + bC_e)}$$

(2)

Where;

Q_m = maximum adsorption capacity, mg/g

b = Langmuir constant, L/mg

The constant in Langmuir isotherm can be determined by plotting graphs of Ce/cue against Ce which can be rewritten as shown in Equation (3):

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q}$$

(3)

Based on the Langmuir isotherm model equation, a dimensionless constant that indicates the nature of the monolayer adsorption can be determined. It is expressed in terms of equilibrium parameter, R_L as shown in Equation (4):

$$R_L = \frac{1}{1+(1+bC_o)}$$

(4)

Where,

R_L = equilibrium parameter

b = Langmuir constant (L/g)

Co = initial concentration of heavy metals (mg/L)

The R_L value determine the monolayer adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$ [7, 8].

Freundlich Isotherm Model

On the other hands, Freundlich isotherm model assumes the uptake of adsorbate occurs on a heterogeneous surface by multilayer adsorption and the amount of adsorbate adsorbed increases infinitely with an increase in concentration [5, 7]. The Freundlich isotherm can be expressed as shown in Equation (5) [8]:

$$q_e = K_F C_e^{1/n}$$

(5)

Where;

K_F = indicator of the adsorption capacity

1/n = adsorption intensity

The value of K_F and $1/n$ can be determined by plotting the graph in linear form of the Freundlich expression as shown in Equation (6), which K_f can be determined fro he intercept of the graph while $1/n$ can be determined by the slope of the graph.

$$log\ q_e = log\ K_F + \frac{1}{n}\ log\ C_e$$

(6)

3.   RESULTS AND DISCUSSIONS

Batch Equilibrium Study

Figure 1 shows the removal of heavy metals against the weight of zeolite, limestone, and laterite soil at 1mg/L metals concentrations. Based on Figure 1(a), the removal of manganese and iron for zeolite reached optimum at dosage of 1.0g. The optimum of the percentage removal of iron and manganese by zeolite is 79% and 94%, respectively.

Meanwhile, Figure 1(b) depicted the removal of iron and manganese by limestone. Based on the figure, the optimum dosage of limestone for the removal of iron and manganese is 5g (95% percentage removal) and 15g (96% percentage removal), respectively. Figure 1(c) indicated that the highest percentage removal of iron and manganese by laterite soil at dosage 0.5g for both heavy metals.

The obtained results in Figure 1 indicated the efficiency of removal increases by increasing the mass of adsorbent and become plateau after reached the optimum dosage of the adsorbents due to the introduction of more binding sites and surface area. The removals became almost constant due to the saturation of the binding sites [17]. The heavy metals removal by zeolite occurs due the ion exchange process. During the process, metal ions moved through the pores of zeolite mass, the channel of the lattice and replace the exchangeable cations [18]. On the other hands, the removal of heavy metals from synthetic rainwater by limestone was due to the reaction of calcium carbonate in limestone, causing the formation of metal carbonate precipitate from the synthetic rainwater [12]. Meanwhile, the heavy metals adsorption takes place in laterite soil due to the formation

of stable complex of proton bearing surface functional group in the adsorbent [19].
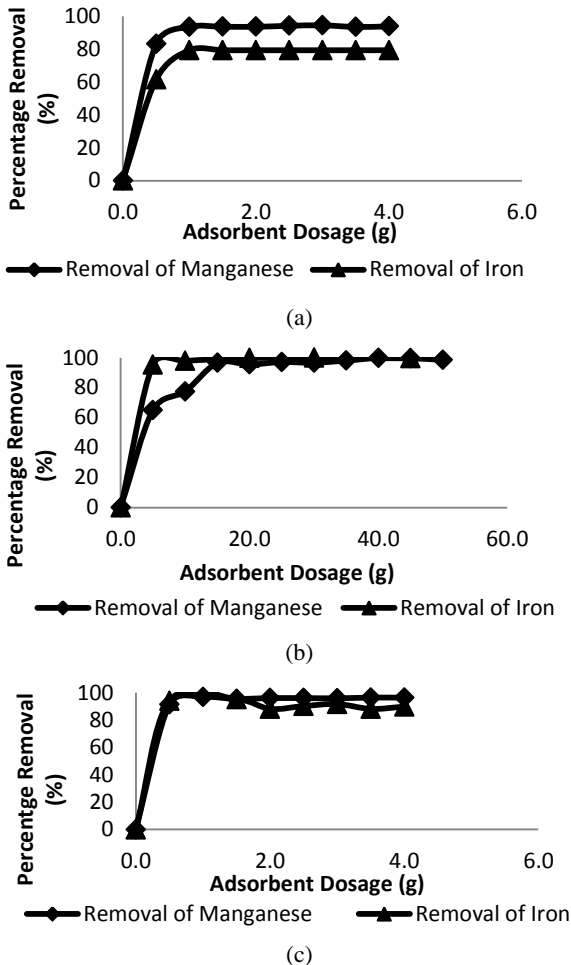

Figure 1 Percentage Removals of Manganese and Iron by Different Adsorbents (a) Zeolite (b) Limestone (c) Laterite Soil

Adsorption Isotherm

The adsorption of iron and manganese from the synthetic rainwater by zeolite, limestone, and laterite soil was analyzed by Langmuir and Freundlich Isotherm as shown in Table 1. Based on the table, Langmuir Isotherm model gave a better fit compared to Freundlich Isotherm Model for both heavy metals and the adsorbents. The values of R_L of iron and manganese for zeolite, laterite soil, and limestone are in the range of $0 < R_L < 1$, indicating the adsorption process was favourable. Therefore, in this study, the adsorption process in removing iron and manganese by zeolite, laterite soil, and limestone was monolayer adsorption as the process was fitted the Langmuir isotherm model.

According to the Langmuir isotherm model, the maximum adsorption capacities of iron by the adsorbents follow the sequence: limestone > laterite soil > zeolite. However, the removal of manganese showed a different results, which the sequence of maximum adsorption capacity of manganese was laterite soil > limestone > zeolite.

The different adsorption capacity may be influenced by the properties of the adsorbents [6]. Besides, the properties of heavy metals would also contribute to the adsorption capacity due to the ionic radius, hydrated radius, and electronegativity of the heavy metals [4]. Based on the obtained result of XRD test as shown in Table 2, the major component zeolite and laterite soil contained clinoptilolite

and kaolinite, respectively. The presence of alumina (Al_2O_3) and silica (SiO_2) in both components contributed to the removal of iron and manganese. The cage structure of aluminosilicate mineral in zeolite offers large internal and external surface for ion exchange. The net negative structural charge of clinoptilolite caused a strong affinity for transition of heavy metals [18]. On the other hand, kaolinite was found in laterite soil, which consisted of alumina and silica layered structure. The net negative charge of the component is small causing it as the least reactive material to allow substitution from other ions [20]. However, in this study, the obtained results demonstrated the use of laterite soil in removing iron and manganese is more efficiency than zeolite. In this research work, the grain size of laterite soil is much smaller than zeolite; enhancing the higher capacity of heavy metals to be adsorbed due the larger surface area compared to particle of zeolite [21]. The other adsorbent used in removing iron and manganese from synthetic rainwater is limestone. The main component in the limestone is calcium carbonate ($CaCO_3$). The adsorption mechanism involved between limestone and heavy metals was the formation of metal precipitates in the form of metal oxide or metal carbonate [12]. The rough surface of the limestone gives a solid contact, causing chemisorptions of metal ions at low concentration [16].

Based on the obtained results, the sequence adsorption capacity of iron and manganese by zeolite and laterite soil is: manganese > iron, while the sequence for limestone is iron > manganese. The difference in adsorption capacity of the heavy metals to the adsorbents may be due to the properties of heavy metal cations. The properties of iron and manganese were summarised in Table 3. According to Erdem and his co researchers, the smallest particles should ideally be adsorbed faster and in larger quantities compared to larger particles due to the ability of the smaller particles to pass through the micropores and channels of the adsorbent with ease [18]. Therefore, ions with the higher charge and the smaller hydrated radius have higher affinity; greater polarization facilitates electrostatic ion exchange [22]. Besides that, energy hydration of cations is one of the contributions of heavy metal removals. It was justified by Amarasinghe and Williams that the stronger hydration energy the less it can interact with the adsorbents [23]. Hence, the sequence of heavy metal removals due to hydration radii and energy is iron > manganese.

4. CONCLUSION

In this study, the optimum dosage of zeolite, limestone, and laterite soil in removing heavy metals were determined. Langmuir and Freundlich isotherm model were developed in order to determine the mechanism of adsorption in this study. The obtained results showed that the removal of iron and manganese by different types of adsorbents fitted Langmuir isotherm model, suggesting the adsorption process is monolayer. The equilibrium parameter of Langmuir isotherm, R_L indicated that the nature of the adsorption process was favourable. The results showed that the sequence of the maximum adsorption capacity of iron by the adsorbents follows the sequence: limestone > laterite soil > zeolite. However, the removal of manganese showed a different result, which the sequence of the maximum adsorption capacity of manganese is laterite soil > limestone > zeolite. The obtained maximum capacities of the heavy metals were influenced by the properties of adsorbents such as chemical compositions and grain size.

Table 1 Summary of Adsorption Isotherm Model

Removal of Iron			
	Zeolite	**Laterite Soil**	**Limestone**
Langmuir Isotherm Model			
Linear form	$\frac{C_e}{q_e}=26.96C_e - 3.035$	$\frac{C_e}{q_e}=12.411C_e - 0.114$	$\frac{C_e}{q_e}=10.485C_e - 0.002$
R^2	0.9833	0.9981	0.9999
Q_m (mg/g)	0.0371	0.0806	0.0954
R_L	0.0919	0.0091	0.0001
Final Equation	$q_e=\frac{0.330\,C_e}{1+8.845C_e}$	$q_e=\frac{8.741\,C_e}{1+108.488C_e}$	$q_e=\frac{666.67\,C_e}{1+6990C_e}$
Freundlich Isotherm Model			
Linear form	y = 2.0218x - 0.0696	y = 1.0491x - 1.5124	y = 17.34x - 2.4852
R^2	0.4887	0.0304	0.8648
K_f	1.0721	4.5376	12.0035
1/n	2.0218	1.0491	17.3400
n	0.4946	0.9532	0.0577
Final Equation	$q_e= 1.0721C_e^{2.0218}$	$q_e=4.5376C_e^{1.0491}$	$q_e=12.0035C_e^{17.34}$
Removal of Manganese			
Langmuir Isotherm Model			
Linear form	y = 12.807x - 0.1341	y = 10.797x - 0.0151	y = 12.597x - 0.0037
R^2	1	1	0.9998
Q_m (mg/g)	0.0781	0.0926	0.0794
R_L	0.0103	0.0014	0.0003
Final Equation	$q_e=\frac{7.457\,C_e}{1+95.50C_e}$	$q_e=\frac{66.225\,C_e}{1+715.03C_e}$	$q_e=\frac{270.270\,C_e}{1+3404.59C_e}$
Freundlich Isotherm Model			
Equation	y = 1.4256x + 0.3461	y = 12.384x - 1.8328	y = 8.8349x - 2.7686
R^2	0.591	0.519	0.6432
K_f	1.4135	6.2514	15.9363
n	0.7015	0.0807	0.1132
Final Equation	$q_e= 1.4135C_e^{1.4256}$	$q_e=6.2514C_e^{12.384}$	$q_e=15.9363C_e^{8.8349}$

Table 2 Chemical Composition of Adsorbents

	Zeolite	**Limestone**	**Laterite Soil**
Chemical Composition	Clinoptilolite (89.1%) Impurities (10.9%)	Calcium Carbonate (87%) Impurities (13%)	Kaolinite (86%) Impurities (14%)

Table 3 Properties of Iron and Manganese [24].

Properties	**Iron (Fe)**	**Manganese (Mn)**
Hydration Radius (Å)	4.28	4.38
Hydration Energy (kJ/mol)	-1946	-1841
Pauling Electronegativity	1.83	1.55

The natural adsorbents showed its capabilities in removing low concentration of heavy metals in rainwater. Therefore, further study is necessary to determine the potentials of these adsorbents as a medium in a simple treatment to develop new alternative source of drinking water.

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REFERENCES

[1]   NAHRIM. *Malaysian Research Experience in Rainwater Harvesting [Presentation]*. (2007).
[2]   Cain, N.L., "A Different Path: The Global Water Crisis and Rainwater Harvesting". *Consilience-The Journal of Sustainable Development,* **3:** 187-196 (2010).
[3]   Wilbers, G.-J., Sebesvari, Z., Rechenburg, A., and Renaud, F.G., "Effects of local and spatial conditions on the quality of harvested rainwater in the Mekong Delta, Vietnam". *Environmental Pollution,* **182:** 225-232 (2013).
[4]   Kragović, M., Daković, A., Sekulić, Ž., Trgo, M., Ugrina, M., Perić, J., and Gatta, G.D., "Removal of lead from aqueous solutions by using the natural and Fe (III)-modified zeolite". *Applied Surface Science,* **258:** 3667-3673 (2012).
[5]   Tchobanoglous, G.B., Franklin L; Stensel, H David. , "Wastewater engineering: treatment and reuse." Fourth Edition. (2003).
[6]   Aziz, H.A., Yusoff, M.S., Adlan, M.N., Adnan, N.H., and Alias, S., "Physico-chemical removal of iron from semi-aerobic landfill leachate by limestone filter". *Waste Management,* **24:** 353-358 (2004).
[7]   Halim, A.A., Aziz, H.A., Johari, M.A.M., and Ariffin, K.S., "Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment". *Desalination,* **262:** 31-35 (2010).
[8]   Rout, P.R., Bhunia, P., and Dash, R.R., "A mechanistic approach to evaluate the effectiveness of red soil as a natural adsorbent for phosphate removal from wastewater". *Desalination and Water Treatment,* **54:** 358-373 (2014).
[9]   Perić, J., Trgo, M., and Medvidović, V.N., "Removal of zinc, copper and lead by natural

zeolite — A comparison of adsorption isotherms". *Water Research,* **38:** 1893-1899 (2004).

[10] Deer, W.A., Howie, R.A., and Zussman, J., "An introduction to the rock-forming minerals." **Vol. 2**. (1992).

[11] Wang, Y., Sikora S Fau - Townsend, T.G., and Townsend, T.G., "Ferrous iron removal by limestone and crushed concrete in dynamic flow columns". **124:** 165-171 (2013).

[12] Reddy, K.R., Xie, T., and Dastgheibi, S., "Removal of heavy metals from urban stormwater runoff using different filter materials". *Journal of Environmental Chemical Engineering,* **2:** 282-292 (2014).

[13] Volkoff, B., "Red and lateritic soils: World scenario". *Red & Lateritic Soils,* **1:** 57 (1998).

[14] Lau, Y.-Y., Wong, Y.-S., Teng, T.-T., Morad, N., Rafatullah, M., and Ong, S.-A., "Coagulation-flocculation of azo dye Acid Orange 7 with green refined laterite soil". *Chemical Engineering Journal,* **246:** 383-390 (2014).

[15] Maiti, A., Thakur, B.K., Basu, J.K., and De, S., "Comparison of treated laterite as arsenic adsorbent from different locations and performance of best filter under field conditions". *Journal of Hazardous Materials,* **262:** 1176-1186 (2013).

[16] Aziz, H.A., Adlan, M.N., and Ariffin, K.S., "Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: Post treatment by high quality limestone". *Bioresource Technology,* **99:** 1578-1583 (2008).

[17] Shavandi, M.A., Haddadian, Z., Ismail, M.H.S., Abdullah, N., and Abidin, Z.Z., "Removal of Fe(III), Mn(II) and Zn(II) from palm oil mill effluent (POME) by natural zeolite". *Journal of the Taiwan Institute of Chemical Engineers,* **43:** 750-759 (2012).

[18] Erdem, E., Karapinar, N., and Donat, R., "The removal of heavy metal cations by natural zeolites". *Journal of Colloid and Interface Science,* **280:** 309-314 (2004).

[19] Yavuz, Ö., Altunkaynak, Y., and Güzel, F., "Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite". *Water Research,* **37:** 948-952 (2003).

[20] Bhattacharyya, K.G. and Gupta, S.S., "Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review". *Advances in Colloid and Interface Science,* **140:** 114-131 (2008).

[21] Tan, Y., Bond, W.J., and Griffin, D., "Transport of bacteria during unsteady unsaturated soil water flow". *Soil Science Society of America Journal,* **56:** 1331-1340 (1992).

[22] Perez Holmberg, J., "Competitive Adsorption and Displacement Behaviour of Heavy Metals on Peat". (2006).

[23] Amarasinghe, B.M.W.P.K. and Williams, R.A., "Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater". *Chemical Engineering Journal,* **132:** 299-309 (2007).

[24] Shaheen, S.M., Derbalah, A.S., and Moghanm, F.S., "Removal of heavy metals from aqueous solution by zeolite in competitive sorption system". *Int J Environ Sci Dev,* **3:** 362-7 (2012).