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Competitive adsorption of metals on volcanic ash active sites from multi-metal solutions

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GRAPHICAL ABSTRACT
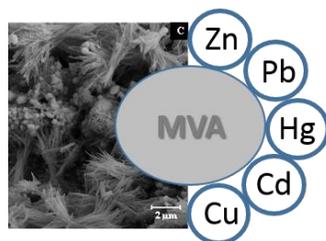
ABSTRACT

Merapi Volcanic Ash (MVA) was used to study the competitive adsorption of several metal cations (Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+}) from multi-metal ions solution within various experimental conditions. The properties of adsorbent were characterized with XRD, FESEM-EDX and FT-IR. The influence of pre-treatment condition, contact time, pH of solution, adsorbent dosage, initial metal concentration and temperature on multi-metals adsorption were investigated. The characterization results showed that the MVA exhibited the presence of aluminate, quarts and maghematite. The maximum adsorption capacities for all metal ions were observed at pH 6 and adsorbent dosage of 0.1 g L^{-1}. The adsorption reached equilibrium within 120 minutes. Adsorption equilibrium study showed that Freundlich isotherm model fitted very well with the Zn, Pb, Cd and Cu while adsorption on Hg was best fitted with Langmuir isotherm model. The kinetic of adsorption on multi-metal ions were best described by pseudo-second order kinetic model. The thermodynamic properties confirmed that the adsorption of multi-metal ions onto MVA was spontaneous and endothermic in nature. The activation energy, E_a of the adsorption process showed that it was a chemisorption process. The results showed that MVA could be used as a low-cost material for the adsorption of multi-metals in water treatment.

Keywords: *Competitive adsorption; Volcanic ash; Isotherm; Kinetic; Low-cost*

1. INTRODUCTION

Removal of heavy metal from waste water is an important issue due to the concern to environment and health problems. The acceptable concentration heavy metal in water as defined by World Health Organization (WHO) for Zn is 3 mg L^{-1}, Pb is 0.01 mg L^{-1}, Hg is 0.001 mg L^{-1}, Cd is 0.003 mg L^{-1} and Cu is 2 mg L^{-1}. Many countries like Bangladesh, United State and Argentina are affected by heavy metal water contamination in their water resources. Long term exposure of heavy metals can results in many health problem such as cancer, muscular dystrophy and common allergies [1].

There were many studies focusing on removing heavy metals by using membrane filtration, chemical precipitation, ion exchange, and adsorption. However, many of them are having disadvantages such as incomplete metal removal, formation of sludge, high energy requirement of reactant and expensive [2-5]. Among the technique proposed, adsorption by far is most widely used due to its high effectiveness. Yet, the efficiency of adsorption depends very much on the characteristics of the metals and environment. In previous years, activated carbon is traditionally used to adsorb heavy metal ions from aqueous solution. However, major constraint especially in having very high cost operation has caused new research on low-

cost, effective new material such as agricultural waste, fly ash and biosorbent [6]. Recent studies have shown that mesoporous powder materials based on silica, such as MCM-41, SBA-15, FSM, and HMS, which have a large surface area and a meso-scale pore size, promise a high adsorption capacity for removal of toxic compounds and/or heavy metals from aqueous solutions [4]. Nevertheless, these materials possess a neutral framework that limits their application as a catalyst, support, and adsorbent. Recently, efforts have been made to modify the mesoporous molecular sieve in order to increase the active sites for catalysis or adsorption and to enhance their practicability. Several studies have been reported on the modification of mesoporous silica with organic compounds, such as amino groups and organosulfur for the removal of heavy metals.

In this study, volcanic ash has been chosen due to easy availability and thus making it very cheap. Merapi volcanic ash (MVA) from Gunung Merapi, Central Java, Indonesia has been used and modified by chemical pre-treatment to enhance its adsorption capacity towards heavy metals ions of Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+} [7]. The presence of Si and other type of metal and metal oxides in the MVA promises the high adsorption capacity of MVA due to the ability of providing silanol and hydroxyl groups

or generating charges which acts as active sites in the heavy metals adsorption processes.

2. EXPERIMENTAL

2.1 Adsorbent Preparation

Natural volcanic ash was collected from Gunung Merapi, Central Java, Indonesia. The Merapi Volcanic Ash (MVA, Fig. 1) was calcined at 573 K for 3 h, followed by treatment with 0.1 M H_2SO_4 for an hour. Distilled water was added to the solution until the pH reached 6. MVA was then soaked in 0.1 M NaOH for 12 h and dried at 383 K in an oven for 12 h followed by calcination at 573 K for 3 h. Characterization of the treated and untreated MVA was done using X-ray Diffraction (XRD), Field-Emission Scanning Electron equipped with Energy Dispersion X-Ray Spectrometer (FESEM-EDX) and Fourier Transform Infrared (FT-IR) to study the properties of MVA.
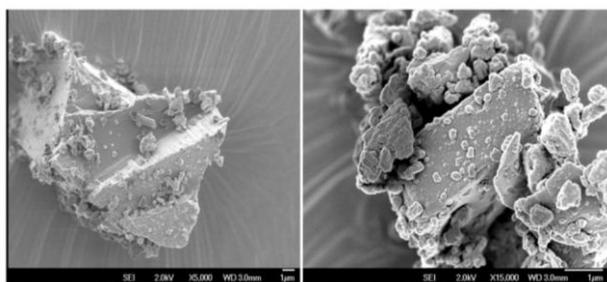

Fig. 1 SEM images of raw MVA

2.2. Adsorption Experiment

Metals stock solution was prepared by dissolving of $N_2O_6Zn \cdot 6H_2O$, $(CH_3COO)_2Pb \cdot 3H_2O$, $(CH_3COO)_2Cu \cdot H_2O$, $(CH_3COO)_2Cd \cdot 2H_2O$ and $HgCl_2$ in a double distilled water. Batch adsorption experiments were conducted by placing 0.02 g of MVA in 250 mL conical flask containing 200 mL of various concentrations of metal ions. Prior to the adsorption, MVA was activated in vacuo-heat at 673 K for 1 h unless otherwise specified. The pH of the solution was adjusted to the desired value with 0.1 M NaOH and 0.1 M HCl. The sample was stirred at 300 rpm using a magnetic stirrer to reach equilibrium. Adsorption isotherms were studied under various metal ions solution concentration ranging from 10-150 mg L^{-1}. Kinetics and thermodynamic studies were performed at different time ranging from 0-120 minutes at different temperatures (303-323 K).

2.3. Metal ions concentration and Adsorption Capacity

The concentration of metal ions was determined by using Microwave Plasma-Atomic Emission Spectrometer (MP-AES). A linear calibration graph was plotted with the concentration-adsorption profile to obtain calibration curve. The adsorption capacity on each metal was calculated as follows:

$$q_e = \frac{[(c_i - c_f)V]}{m} \qquad (1)$$

where q_e is the equilibrium adsorption capacity (mg g^{-1}), C_i and C_f are the initial and equilibrium concentration (mg L^{-1}) respectively, m is the MVA dry weight (g) and V is the volume of multi-metal ions aqueous solution (L).

3. RESULTS AND DISCUSSION

Fig. 2A illustrates the crystallinity of untreated and treated MVA samples examined by XRD. Both treated and untreated MVA showed highly crystalline structures showing the presence of aluminate, quartz and maghemite [8]. The functional groups of MVA were investigated using FT-IR analysis. Fig. 2B shows the FT-IR spectra of untreated and treated MVA. The absorbance band observed at 3100 cm^{-1} for both treated and untreated MVA are corresponded to the O-H groups. While peaks at 1300-1010 cm^{-1} and 950 cm^{-1} belong to Si-O-Si and Si-OH groups, respectively [9]. The unresolved peaks below 1000 cm^{-1} may be correspond to the presence of Al-O and Fe-O.
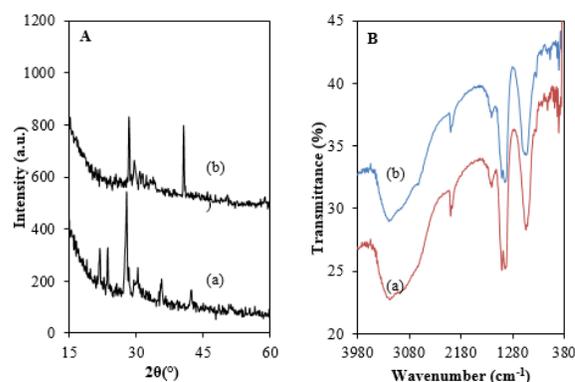

Fig. 2 A) XRD pattern and B) FTIR spectra of (a) untreated MVA and (b) treated MVA

The morphology and elemental properties of adsorbent examined by FESEM-EDX are shown in Fig. 3. The untreated and treated MVA showed irregular and rough structure of materials. This may be indicated good possibilities for metal adsorption as more active sites or defect sites (silanol and hydroxyl groups) for ion exchange process (Fig. 3A and 2B). On the other hand, Fig. 3C shows treated MVA after adsorption. The adsorbent exhibited fibrous-like structure which most probably because of the presence of metal ions adsorbed. To identify the elements adsorbed on the MVA, EDX analysis was carried out and is tabulated in Table 1.

Similar with almost mineral in volcanic ash, MVA has a higher proportion of silica dioxide (SiO_2) [10]. The percentage of Potassium (K) has increased from 0.91 to 35.12 % after pre-treatment on MVA most probably because of the acid and base treatment has destruct the nature of the volcanic ash, thus exposing more K. The presence of Zn, Pb,

Hg, Cd and Cu in used MVA indicating that all metals were successfully adsorbed onto MVA.

Fig. 4 shows the effect of contact time on the adsorption capacity of untreated MVA and treated MVA. The results showed that the treatment increased adsorption capacity of the MVA towards all heavy metals. Acid treatment has caused some changes on the adsorbent surface. It varnished impurities and eliminated water molecules, thus increase the exposure active sites or defect sites (silanol and hydroxyl groups) on the surface [11]. It is also clearly shown that the highest adsorption capacity was obtained within the first 15 minutes. This is because, competitive adsorption occur very rapidly when there are plenty of free active sites. However, the adsorption rate started to decrease and reached equilibrium after 60 minutes due to less free active sites available for adsorption.
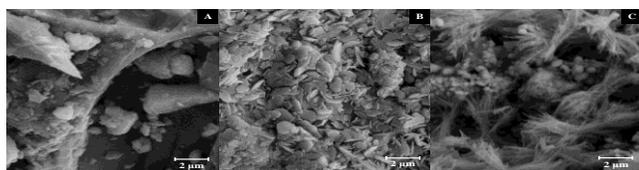

Fig. 3 FESEM images of (a) untreated MVA (b) treated MVA and (c) treated MVA after adsorption of multi-metals.

Table 1 Percentage of elements presence in MVA

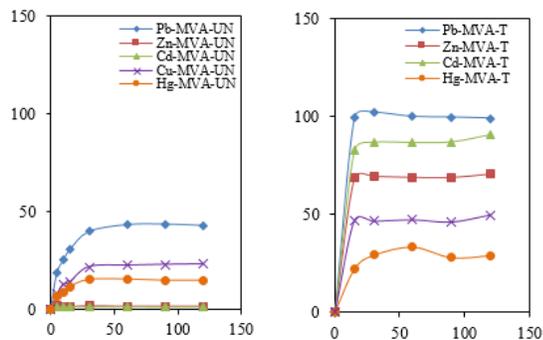| Type/ Element	O (%)	Si (%)	Al (%)	K (%)	Zn (%)	Pb (%)	Hg (%)	Cd (%)	Cu (%)
Untreated MVA	47.56	22.64	13.56	0.91	-	-	-	-	-
Treated MVA	49.49	2.22	0.13	35.12	-	-	-	-	-
Used MVA	33.39	7.82	0.87	0.07	2.50	24.01	2.01	1.42	21.64

Fig. 4 Adsorption capacity of a) MVA-untreated and b) MVA-treated on multimetal adsorption (Pb, Zn, Cd, Cu, Hg)

The effect of the pH solutions is clearly shown in Fig. 5A. The highest adsorption of most metal ions was observed at pH 6. At high pH, the presence of hydroxide (OH⁻) ions will lead to the formation of metal hydroxide, $M(OH)_2$. This will cause the metal ions to exist in aqueous form as it hardens the adsorption process [12]. The other parameter that also affects the adsorption capacity of MVA is the adsorbent dosage. The effect of adsorbent dosage onto treated MVA is shown in Fig. 5B. From the graph, it is understood by increasing the adsorbent dosage has increased the adsorption capacity. This is because as more adsorbent is added, more active sites are present for metal ions adsorption. However, the adsorption capacity started to

decrease beyond 0.1 g L^{-1} due to the overlapping of adsorption sites as a result of overcrowding of adsorbent particle [13].

Table 2 shows the non-linear isotherms of the adsorption of multi-metal ions onto treated MVA. Two commonly used isotherm models, Langmuir and Freundlich were used to describe the equilibrium of the metal ions adsorbed onto treated MVA. From the isotherm, it has been found that the maximum adsorption capacities of multi-metals onto treated MVA are in the order of Pb > Zn > Cd > Hg > Cu. According to Huan and Chung, the adsorption capacity of metal ions should be proportional to the ionic radii [14]. However, adsorption capacity of Zn was found to be higher than Hg even though Zn ionic radius is smaller than Hg. This may be due to the competitive environment among these ions which has caused some alterations in their affinities. Table 2 shows the parameters of isotherm study for the multi-metal adsorption onto treated MVA. Based on the correlation coefficient values (R^2), the experimental equilibrium adsorption data for Pb, Zn, Cd and Cu were best fitted to Freundlich isotherm model while adsorption of Hg was best described by Langmuir isotherm model. The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules present on the adsorbent surface. The experimental data of Hg adsorption was fitted very well with Langmuir model indicating monolayer surface adsorption taken place in the adsorption while, the other heavy metals adsorption was fitted with Freundlich isotherm model showing the adsorption has occurred not restricted to the formation of monolayer.
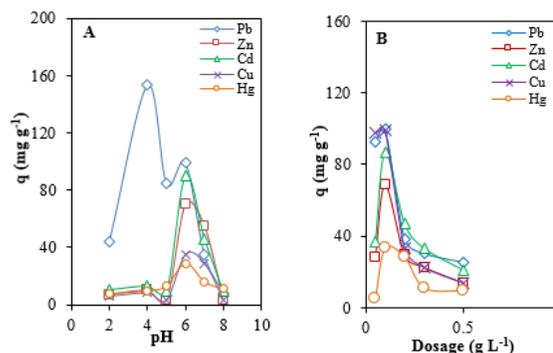

Fig. 5 Effect of A) pH and B) adsorbent dosage on the adsorption of multi-metal ions onto treated MVA.

Table 2 Parameters of isotherm study for the multi-metal adsorption on MVA-treated at different metals initial concentration

Isotherm	Parameter				
	Zn	Pb	Hg	Cd	Cu
Langmuir	q_m: 256.7	q_m: 333.2	q_m: 151.8	q_m: 172.9	q_m: 76.1
	R_L: 0.761	R_L: 0.981	R_L: 0.818	R_L: 0.498	R_L: 0.257
	R^2: 0.831	R^2: 0.846	R^2: 0.974	R^2: 0.681	R^2: 0.852
Freundlich	n: 0.739	n: 0.584	n: 0.359	n: 1.2	n: 1.9
	K_F: 19.2	K_F: 8.8	K_F: 4.5	K_F: 7.4	K_F: 3.7
	R^2: 0.868	R^2: 0.967	R^2: 0.933	R^2: 0.931	R^2: 0.854

In order to clarify the adsorption kinetics of the metal ions onto MVA, two kinetic models were applied to the

experimental data. The summary of the models used at three different temperatures and the kinetic information obtained from the pseudo-first and pseudo-second order are presented in Table 3. In all conditions studied, the values of R^2 for the pseudo-second-order models were greater than the pseudo-first-order model for almost every metal ion. In addition, the theoretical equilibrium adsorption capacity, $q_{e,calc}$ values were closer to experimental equilibrium adsorption capacity, $q_{e,exp}$ in pseudo-second-order model. These results proved that pseudo-second-order model fit more precisely for kinetic data in order to represent the adsorption kinetic of the metal ions onto MVA.

Table 3 Parameters of kinetic study for the adsorption of Zn, Pb, Hg, Cd and Cu onto treated MVA at different temperatures.

Metal	Temp (K)	$q_{e,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
			k_1 (min^{-1})	$q_{e,calc}$ (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e,calc}$ (mg/g)	R^2
Zn	303	250.9	0.102	315.4	0.997	0.00049	284.2	0.999
	313	845.5	0.18	827.1	0.998	0.00051	870	0.995
	323	1434.7	0.079	1449	0.973	0.0050	1707	0.980
Pb	303	271.4	0.158	271.9	0.998	0.001	292	0.991
	313	1124.4	0.170	1093	0.986	0.0004	1153	0.992
	323	1757.2	0.083	1768	0.981	0.0006	2066	0.988
Hg	303	119.2	0.135	119.4	0.978	0.0018	130.9	0.969
	313	304.2	0.180	1054	0.980	0.0002	359	0.985
	323	825.4	0.083	834.5	0.977	0.00011	975.2	0.981
Cd	303	187.5	0.204	181.4	0.996	0.00284	190.7	0.996
	313	673.3	0.263	655.1	0.983	0.00293	660.4	0.989
	323	1171.7	0.096	1165	0.962	0.000102	1321	0.984
Cu	303	76	0.0362	91.4	0.944	0.0002	133.7	0.935
	313	252.6	0.0744	244.2	0.969	0.0003	288.2	0.984
	323	391.5	0.0945	358.7	0.943	0.0165	361.3	0.943

Adsorption process strongly relies on adsorption temperature. For an endothermic reaction, rate of reaction will be proportional to temperature. By studying the effect of temperature, one can measure the adsorption enthalpy (ΔH^0), entropy (ΔS^0), Gibbs free energy (ΔG^0) by using the Van't Hoff equation. Table 4 shows the thermodynamic parameters for the adsorption of multi-metals at different temperatures. These values are calculated from Van't Hoff plot of $1/T$ versus $\ln K_c$ and Arrhenius plot of $1/T$ versus $\ln k_2$.

A positive enthalpy of adsorption was found, implying that the adsorption process was endothermic, suggesting a chemisorption process. The positive ΔH^0 value might be explained by assuming that when metal ions were brought into contact with surface, their solvating water molecules, were stripped off. This dehydration process requires energy and presumably it exceeded the exothermicity of the metal ions attaching to the surface. The ΔS^0 was also positive signified that the adsorption reaction of these metal ions onto MVA was random and disordered state. The water molecules were separated from metal ions before they are trapped at the active sites of the adsorbent. This eventually increased the randomness of the process [15-17]. ΔG^0 value of every metal ion decreased with the increase of the adsorption temperature. This meant that as temperature increased, the reaction was favored to the product formation. At temperature 303 K, most adsorption

still required energy to carry out the adsorption. However, some of the metal ions like Zn, Pb and Cd reached a negative value of ΔG^0 at 323 K. These results indicated that the reaction is a spontaneous, feasible and favourable at high temperature (323 K).

The activation energy for the adsorption of Zn, Pb, Hg, Cd and Cu were found to be 93.17, 21.35, 114.37, 133.82 and 177.911 kJ mol^{-1}. For all metals, their E_a values were > 40 kJ mol^{-1}, confirming the chemisorptive nature of the adsorption processes. Therefore, the thermodynamic, kinetics and equilibrium isotherm studies all verified that the adsorption of multi-metals onto MVA occurred through a chemisorption process.

Table 4 Thermodynamic parameters for the adsorption of multi-metals at different temperatures

Metal	T (K)	q_e (mg g^{-1})	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	E_a (kJ mol^{-1})
Zn	303	250.9	3.366	95.13	0.0264	93.17
	313	845.5	0.562			
	323	1434.7	-2.695			
Pb	303	271.4	3.174	100.93	0.0265	21.35
	313	1124.4	0.284			
	323	1757.2	-3.285			
Hg	303	119.2	6.033	77.44	0.0252	114.37
	313	304.2	4.710			
	323	825.4	1.297			
Cd	303	187.5	4.044	93.57	0.0263	133.82
	313	673.3	1.087			
	323	1171.7	-1.864			
Cu	303	76	6.730	61.69	0.0248	177.91
	313	252.6	2.251			
	323	391.5	3.162			

4. CONCLUSION

This study demonstrated the utilization of Merapi volcanic ash (MVA) as a low cost adsorbent for multi-metals (Pb, Zn, Hg, Cd and Cu) adsorption. MVA possessed rough and irregular form/surface before and after pre-treatment. After chemical treatment, the adsorption capacity of MVA increased to 99, 49, 28.9, 90 and 70 mg g^{-1} for Pb, Cu, Hg, Cd and Zn, respectively. The experimental equilibrium adsorption data for Pb, Zn, Cd and Cu were best fitted to Freundlich isotherm model while adsorption of Hg was best described by Langmuir isotherm model. The kinetics adsorption for all metals follow pseudo-second-order model with the activation energy > 40 kJ mol^{-1} indicating the adsorption is controlled by a chemisorption process. The thermodynamic properties confirmed that the adsorption of multi-metal ions onto MVA was spontaneous and endothermic in nature. Results from this study recommend that MVA is a very suitable and cost effective adsorbent for multi-metals removal.

ACKNOWLEDGEMENT

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