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Performance Evaluation of Coal Fly Ash Based Zeolite A for Heavy Metal Ions Adsorption of Wastewater

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Abstract. One of the environmental characteristics of chemical industries is producing wastewater effluent that containing heavy metals, which are hazardous to the aquatic life and the human health. The purpose of this research is to evaluate the use of zeolite A as a sorbent for the heavy metal ions removal from wastewater. Zeolite A was synthesized from coal fly ash by fusion-hydrothermal method by the authors contains cation exchange capacity of 5.05 meq/g. This study used a series of artificial wastewater containing one and mixed heavy metal ions (Cu (II) and Zn (II)). The result showed that wastewater containing one heavy metal ion was almost fully adsorbed, for instance percentage sorption of Cu (II) and Zn (II) ions were 95.61 % and 92.15 %. On the other hand, for binary system, the percentage sorption slightly decreased becoming 91.51 % with the increase the amount of Zn (II) ion in solution. Based on kinetic data, sorption of Cu (II) and Zn (II) ions is controlled by pseudo-second order. In addition, adsorption isotherm follows Langmuir model. From this study, it is confirmed that zeolite A has a good possibility to be used as sorbent of heavy metal ions removal in wastewater.

1. Introduction

Coal fly ash is a by-product produced in large quantities from combustion of coal-based thermal power plants and is generally considered as waste product [1]. However, only 20-30% of the coal fly ash was utilized on worldwide in 2015, while the remainder was disposed of in landfills [2]. Therefore, it is necessary to develop potential alternatives in the sustainable use of coal fly ash. Several papers by other authors show coal fly ash can be applied for mixed material of cement and concrete production, mine reclamation [3], as well as there is evidence that it can also be applied directly for the removal of pollutants, such as heavy metals.

Heavy metals ions are the abundant pollutants in many industrial wastewater such as in electroplating facilities, mining operation, the production of battery, the manufacture of paints and pigments, and ceramic and glass industries [4]. Wastewater streams of these industries commonly contain Sb, Cr, Cu, Pb, Zn, Co, Ni, etc. which may be found in high concentrations even up to 500 mg l⁻¹ [5]. Heavy metal ions are not biodegradable and can cause various diseases and disorders in living organisms [6].

However, the direct use of coal fly ash as sorbent of heavy metals is not effective due to the variability in physical and chemical properties of different coal fly ash [7]. In addition, the sorption capacity is relatively low [8]. Coal fly ash is suitable as precursor for synthesizing zeolite with enhanced surface area and sorption characteristics, due to contents of silica and alumina.

Zeolite is a crystalline material composed aluminosilicates with a three-dimensional network of silicon and aluminium tetrahedral linked by oxygen atoms [9]. In comparison with all types of synthetic



zeolites, zeolite A has high cation exchange capacity (CEC) due to substitution of Si (IV) by Al (III) in its framework, high porosity and specific surface area, as well as high affinity towards polar molecules [10].

In this study, coal fly ash was specifically converted into zeolite A by alkaline fusion followed by hydrothermal method. Furthermore, zeolite A was used as sorbent for sorption of heavy metal ion. Cu (II) and Zn (II) ions were chosen as heavy metal ions sorbed. Moreover, the work was conducted to investigate the selectivity of mixed heavy metal ions.

2. Experimental section

Coal fly ash was obtained from PT YTL Paiton East Java, Indonesia. Before synthesis process, coal fly ash was pre-treated using hydrochloric acid technical grade. Sodium hydroxide and sodium aluminate was used in zeolite synthesis. Two heavy metal ion solutions were prepared using analytical grade of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. For pH adjusting purpose, 2 % HNO_3 solution and 0.1 M NaOH solution were prepared.

The experiments were conducted in three steps including pre-treatment of coal fly ash, zeolite synthesis, and batch sorption. In pre-treatment step, coal fly ash was heated at 850°C for 2 h. Then, it was mixed with 10% of hydrochloric acid solution (ratio of 1 g : 25 ml) in a 500 ml three-neck flask. The mixture was heated at 80°C for 1 h and stirred constantly at 300 rpm. After that, pre-treated coal fly ash was recovered by filtration, repeatedly washed with distilled water, and dried at 100°C for 24 h. The zeolite synthesis process consists of fusion, aging, and hydrothermal. In fusion process, 10 g of pre-treated coal fly ash was mixed with 12 g of sodium hydroxide. The mixture was put into crucible nickel and left to fuse at 550°C for 1 h. The sintered granules of fused coal fly ash were cooled down, grinded, and added sodium aluminate solution. Furthermore, the mixture was shaken at 30°C for 16 h in incubator shaker for aging process and subsequently heated to temperature of 100°C during 1 h for hydrothermal process. After hydrothermal step was complete, the suspension was filtered and zeolite was washed repeatedly until pH of solution of 9-10. Then, zeolite was dried at 105°C for 16 h.

In batch sorption step, Cu (II) and Zn (II) metal ion solutions were separately prepared. The sorption experiments were performed under following conditions: temperature of 30°C , stirring of 150 rpm, synthetic zeolite A mass/solution ratio of 0.125 g/50 ml. Kinetic experiments were conducted at constant metal ions concentration of 200 mg l^{-1} with different time intervals (from 5 to 480 min). Furthermore, sorption capacity experiments were conducted in various initial metal ion concentrations of 200-645.26 mg l^{-1} for 480 min. For binary metal ion sorption experiments were carried out in various concentrations of Cu (II) and Zn (II) ion for 480 min. After the batch sorption step, the supernatants were recovered by filtration and final concentration of heavy metal ions in the solution was determined using Atomic Adsorption Spectrophotometer (AAS). Percentage sorption was (%) calculated as:

$$\text{percentage sorption (\%)} = \frac{C_i - C_f}{C_i} \times 100\%$$

Where C_i and C_f are the concentrations of the heavy metal ions in the initial and final solutions, respectively.

The sorption capacity was calculated as:

$$\text{sorption capacity } (q_e) = \frac{C_i - C_e}{C_i} \times \frac{V}{m}$$

Where q_e is the sorption capacity at equilibrium time (mg g^{-1}); C_i is initial concentration of heavy metal ions (mg l^{-1}); C_e is equilibrium concentration of heavy metal ions (mg l^{-1}); V is volume of solution (l); and m is mass of sorbent (g).

3. Results

3.1. Characterization of zeolite A

The coal fly ash used in this study contains major components such as Fe_2O_3 40.2%, CaO 25.2%, SiO_2 18.6% and Al_2O_3 7.18%. However, significant amount of Fe_2O_3 and CaO would be inhibitor for zeolite

synthesis. In this work, the pre-treatment process of coal fly ash was conducted using hydrochloric acid solution and was found successfully to reduce the amount of Fe_2O_3 and CaO .

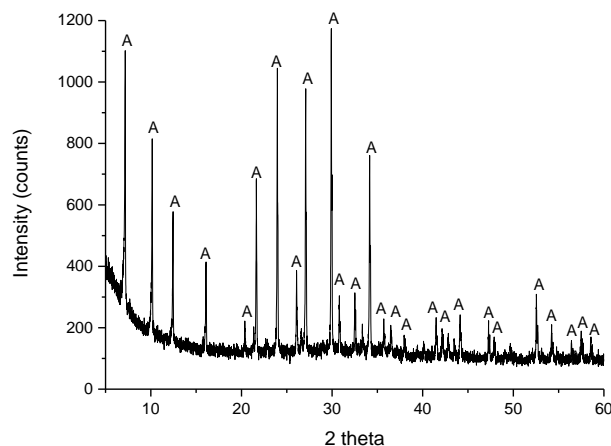


Figure 1. XRD pattern of zeolite A.

Figure 1 illustrates the XRD pattern of zeolite A obtained from pre-treated coal fly ash. According to XRD pattern obtained that there are no detected peaks of impurities such as hydroxysodalite and crystalline components of coal fly ash, indicating the formation of relatively pure zeolite A without hydroxysodalite and high conversion of coal fly ash to zeolite A. In addition, the cation exchange capacity of zeolite A is 5.05 meq/g. This cation exchange capacity is relatively high for the application of zeolite A in sorption of heavy metal ions based on ion exchange.

3.2. Effect of contact time

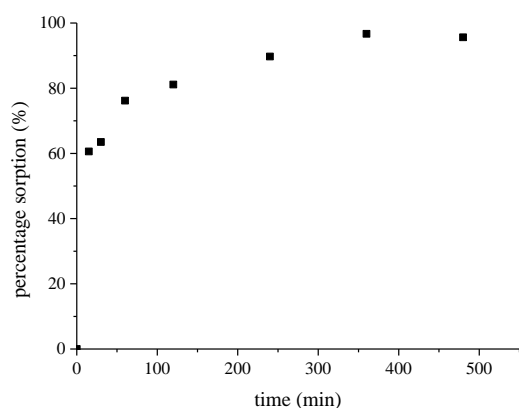


Figure 2. Percentage sorption of zeolite A for Cu (II) ion against contact time

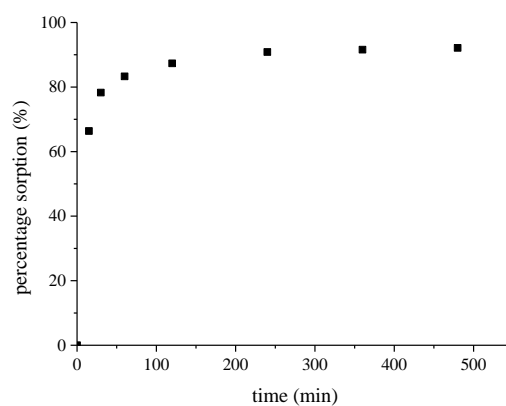


Figure 3. Percentage sorption of zeolite A for Zn (II) ion against contact time

The effect of contact time on the percentage sorption of Cu (II) and Zn (II) into zeolite A are shown in Figure 2 and Figure 3. These figure show that the sorption of Cu (II) and Zn (II) ions are quite fast initially followed by increase slightly to reach an equilibrium time of around 360 min for Cu (II) and 240 min for Zn (II). These tendency related to the fact that abundant of active sites are available in the initial process and heavy metal ions interact easily. In addition, the fast sorption initially corresponds to high driving force that can be seen from the high concentration difference between bulk solution and solid-liquid interface [6]. Furthermore, active sites become increasingly used up and the sorption rate

become slower [11]. The results showed that the percentage sorption at 200 mg l⁻¹ are 95.61 % for Cu (II) and 92.15 % for Zn (II).

3.3. Effect of initial metal concentration

The effect of initial metal ion concentrations on the percentage sorption of Cu (II) and Zn (II) ions by zeolite A are shown in Figure 4 and Figure 5. When the initial metal ion concentrations increase from 200 to 645.26 mg l⁻¹ for Cu (II) and 200 to 540.08 mg l⁻¹ for Zn (II), the percentage sorption gradually decrease. A decrease from 95.61% to 36.14% and from 92.15% to 42.13% for Cu (II) and Zn (II) respectively are obtained. These phenomenon occur due to the fixed number of active sites used in this study. Therefore, the active sites become saturated at high concentrations [12].

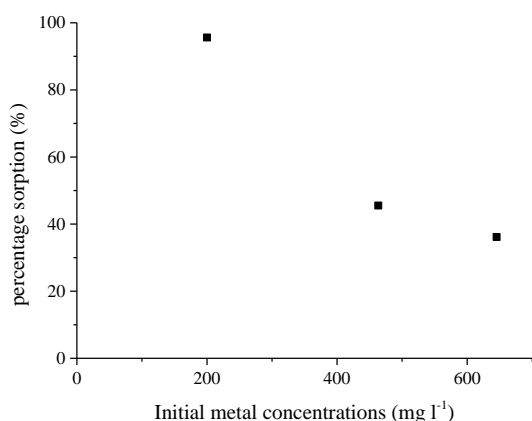


Figure 4. Percentage sorption of zeolite A for Cu (II) ion against initial metal concentration.

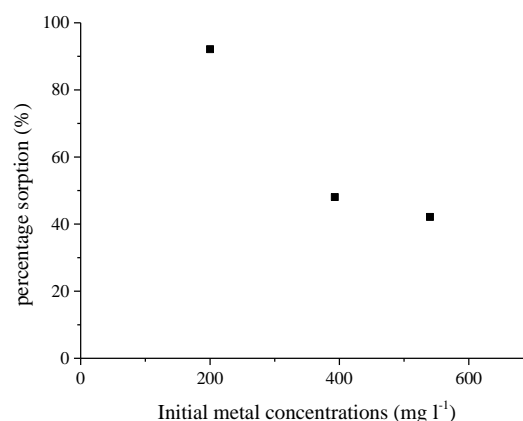


Figure 5. Percentage sorption of zeolite A for Zn (II) ion against initial metal concentration.

3.4. Kinetic sorption

In order to investigate the kinetic mechanism and rate law describing the Cu (II) and Zn (II) ions sorption with zeolite A, the data of effect of contact time on 200 mg l⁻¹ of Cu (II) and Zn (II) ions are analysed using two kinetic equations, the pseudo-first order and the pseudo-second order. The equation of pseudo-first order can be expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where q_e is the sorption capacity at equilibrium time (mg g⁻¹); q_t is the sorption capacity at time t (mg g⁻¹); and k_1 is the pseudo-first order rate constant (min⁻¹). Parameter k_1 can be determined from the slope of the $\ln(q_e - q_t)$ against t plots. Furthermore, the equation of pseudo-second order can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where k_2 is the pseudo-second order rate constant (g mg⁻¹.min⁻¹). Parameter k_2 can be determined from the intercept of the $\frac{t}{q_t}$ against t plots.

The values of kinetic parameters for each equation are given in Table 1. Based on the Table 1, pseudo-second order equation offers the best correlation both Cu (II) and Zn (II) ions. These results are in accordance with previous research by Hui et al. (2005) [5].

The pseudo-second order based on the assumption that sorption follows chemisorption, indicating the rate limiting step may be a chemical sorption occurred valance forces through sharing or exchange of electrons between zeolite A and heavy metal ions [13]. This assumption does not consider that diffusion as limiting step in the sorption process.

Table 1. The values of kinetic parameters of pseudo-first and second order in adsorption of Cu (II) and Zn (II).

Kinetic parameters	Cu (II)	Zn (II)
Pseudo-first order		
k_1 (min ⁻¹)	0.0092	0.0105
q_e calculation (mg g ⁻¹)	32.589	16.013
Correlation coefficient (R ²)	0.9815	0.968
Pseudo-second order		
k_2 (g mg ⁻¹ .min ⁻¹)	0.0009	0.00198
q_e calculation (mg g ⁻¹)	78.125	74.627
Correlation coefficient (R ²)	0.9978	1

3.5. Sorption isotherms

This section examines the values of sorption isotherm based on the Langmuir and Freundlich isotherm model. The Langmuir isotherm model can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{k_L q^*} + \frac{C_e}{q^*}$$

Where q_e is the sorption capacity at equilibrium time (mg g⁻¹); q^* is the monolayer sorption capacity (mg g⁻¹); C_e is equilibrium concentration of heavy metal ion (mg l⁻¹); and k_L is Langmuir constant. Parameter k_L and q^* can be determined from the slope and intercept of the $\frac{C_e}{q_e}$ against C_e plots. In addition, the Freundlich isotherm model can be expressed as:

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

Where k_f is the Freundlich constant (mg g⁻¹) and n is the constant indicative of the intensity of the sorption process. Parameter k_f and n can be determined from the intercept and slope of the $\log q_e$ against $\log C_e$ plots.

Table 2. The values of adsorption isotherm parameters of Cu (II) and Zn (II).

Adsorption Isotherm Parameters	Cu (II)	Zn (II)
Langmuir		
q^* (mg g ⁻¹)	92.5926	90.0901
k_L (mg l ⁻¹)	0.1166	0.0769
Correlation coefficient (R ²)	0.9947	0.9773
Freundlich		
Correlation coefficient (R ²)	0.8384	0.4751

Based on correlation coefficient on Table 2, it is obtained that the sorption of Cu (II) and Zn (II) ions by zeolite A are more appropriate following the Langmuir isotherm model, which is indicated from the correlation coefficient close to one. It could be assumed that maximum removal corresponds to interaction between solute molecules and the zeolite surface and results in monolayer coverage on zeolite surface [14].

According to q^* parameter, Cu (II) ion is sorbed more than Zn (II) ion onto zeolite A with value of 92.5926 and 90.0901 mg g⁻¹. Therefore, it could be concluded that the zeolite A is higher affinity towards Cu (II) ion than Zn (II) due to ion electronegativity and ionic radius. Ion electronegativity of Cu (II) and

Zn (II) ions are 1.93 and 1.63, while the ionic radius of Cu (II) and Zn (II) ions are 0.072 nm and 0.083 nm [15]. The smaller ions are easier to pass through the micropores and channels of zeolite A [6].

3.6. Metal ions removal in binary systems

The metal ions removal in binary systems represented by relatively zeolite A without hydroxysodalite are shown in Table 1. The concentration of heavy metal ions are adjusted at 200 mg l⁻¹. As mentioned in 3.2, the percentage sorption of Cu (II) and Zn (II) ions at 200 mg l⁻¹ are 95.61 % and 92.15 %. Compared with the single system, percentage sorption of binary system is slightly lower. The percentage sorption of binary system decrease from 94.04 % to 91.51 % with the increase of Zn (II) ion in solution. These results indicate that sorption selectivity of Cu (II) ion is higher that of Zn (II) ion and in good agreements with the results of sorption capacity.

Table 3. Heavy metal ions sorption of zeolite A in binary system.

Metal ions	c _o (mg l ⁻¹)	c _f (mg l ⁻¹)	Total percentage sorption (%)
Cu (II)	50	0.30	91.51
Zn (II)	150	16.68	
Cu (II)	100	2.66	93.25
Zn (II)	100	10.85	
Cu (II)	150	4.99	94.04
Zn (II)	50	6.93	

4. Conclusion

Kinetic sorption was analysed and was found that the rate limiting step for sorption of Cu (II) and Zn (II) ions follows chemical sorption which occurred valance forces through sharing or exchange of electrons between zeolite A and heavy metal ions. The sorption capacity was calculated from Langmuir model and was found that the sorption capacity of Cu (II) and Zn (II) ion are 92.5926 and 90.0901 mg g⁻¹. Therefore, zeolite A is higher affinity towards Cu (II) ion than Zn (II). At binary system, sorption selectivity of Cu (II) ion is higher that of Zn (II) ion. Overall, this study showed that zeolite A obtained from coal fly ash is possible to remove the heavy metal ions.

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