

COPPER (Cu^{2+}) REMOVAL FROM WATER USING NATURAL ZEOLITE FROM GEDANGSARI, GUNUNGGKIDUL, YOGYAKARTA

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Abstract

Development of industrialization and urbanization not only increase economic growth but also contribute to the environmental degradation, especially contamination of heavy metals in water. In other side, there are many geological materials have capability to immobilize heavy metals. Therefore, the objective of this research is to know the maximum capacity of natural zeolite from Trembono area, Gunung Kidul regency to immobilize copper (Cu^{2+}) from water and to understand their mechanism. This experiment was carry out by a batch test. The result showed that the maximum capacity of zeolite to immobilize Cu (q_{max}) is 63,69 mmolCu/kg Zeolite according to Langmuir adsorption equilibrium model. In addition, the capability to immobilize Cu will increases due to decreasing the grain size. The result of this research can be used as an alternative for waste water treatment, especially Cu.

Keywords: Removal, copper (Cu^{2+}), natural zeolite, Langmuir isotherm.

1 Introduction

Industrialization and urbanization have led to an increase in environmental problems. Water is particularly vulnerable to contaminate from discharge of waste-waters by various indus-

tries. The increasing presence of heavy metals such copper, zinc, cadmium and lead in rivers and streams is very problematic due to their great toxicity (Stum and Morgan, 1996). The recent development of new technologies for the decontamination of soils, sediments, mining residues and sewage sludge (municipal and industrial) has led to the production of heavy metal loaded leachates. The situation persists and it will continue to cause substantial loss of human lives unless it is seriously dealt with all levels. In the developing countries treatment plants are expensive, the ability to pay for services in minimal and skills as well as technology are scarce.

In order to alleviate the prevailing difficulties, approaches should focus on sustainable water treatments systems that are low cost, robust and require minimal maintenance and operator skills. Locally available materials can be used towards achieving sustainable safe portable water supply. Yogyakarta city is one of big cities in Indonesia that facing the problem about groundwater quality. There are many home industries like silver, leather and batik. These home industries produce liquid waste that contains some heavy metals. Recent study of heavy metals in groundwater at Yogyakarta City was conducted by Putra (2007), shows that the concentration of some heavy metals in groundwater more than the maximum Drinking Water Standard (WHO), were measured commonly in samples from urban-

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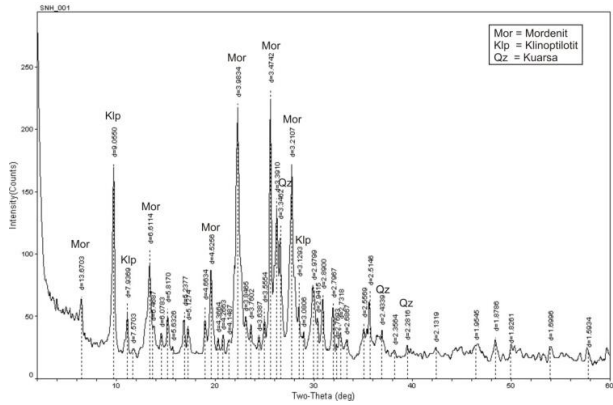


Figure 1: X-ray diffraction analysis of zeolite showing the presence of mineral phases, including zeolite minerals, mordenite (Mor) and clinoptilolite (Klp).

commercial/industrial areas such as canning factory, metal/machine industry, home industries of metal finishing workshops - jewellery craft, batik-textile painting, car/motorcycle workshops and bus station.

Therefore, the aim of this research is to immobilize copper (Cu^{2+}) in water using natural zeolite as an adsorbent.

2 Experimental

2.1 Material

The reactive material is a natural zeolite from Trembono, Gunungkidul, DIY. The natural zeolite was grinded become sand size and directly used without any activation. Analysis of surface area using Brunauer Emmet Teller (BET) method of natural zeolite is $75 \text{ m}^2\text{g}^{-1}$. It has also cation exchange value (CEC) is $67.37 \text{ mg Na}_2\text{O}/100 \text{ gr zeolite}$. Based on the XRD and SEM analyses (Figures 1 and 2) of zeolite consist zeolite minerals, mordenite (Mor) and clinoptilolite (Klp). Bulk-geochemistry of Gunungkidul zeolite are virtually identical, characterized by major oxides SiO_2 (72 wt.%), Al_2O_3 (9-11 wt.%), FeO (1.6 wt.%), MgO (0.8-1.2 wt.%), CaO (3.3-4.5 wt.%), Na_2O (1.1-1.5 wt.%), K_2O (0.7-1 wt.%) and H_2O (8 wt.%) (Idrus *et al.*, 2007).

According to the EDX from SEM in the Figure 3 and Tabel 1 showed that Si/Al ratio is

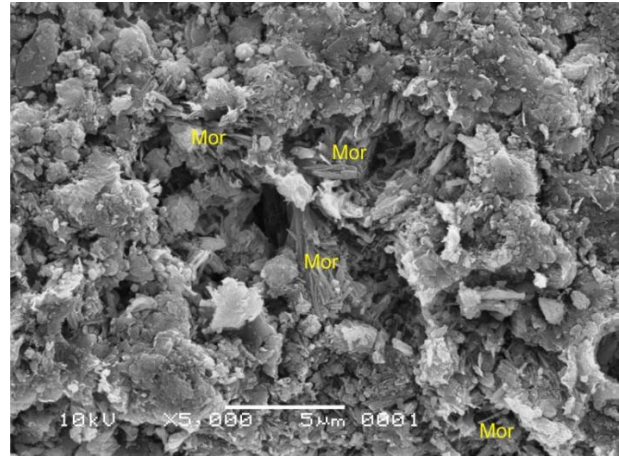


Figure 2: Scanning electron micrograph of mordenite needles/fibers [Mor] in zeolite.

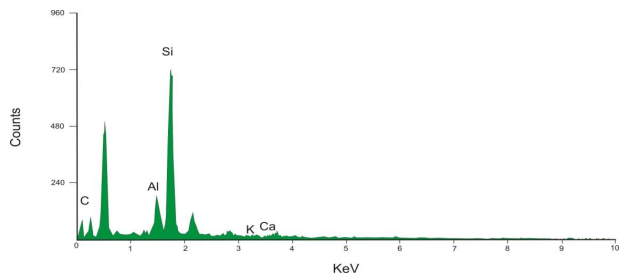


Figure 3: EDX peaks from SEM in Figure 2.

very high. This data support to the present of mordenite and clinoptilolite in the zeolite material because Si/Al ratio of mordenite and clinoptilolite are 4.5 to 5.5 and 4.5 to 5.2, respectively.

2.2 Batch Experiments

Several batch tests were performed to determine the capability of zeolite to remove Cu^{2+} in water. Five gram of zeolite was used to find the sorption isotherm of Cu onto zeolite

Table 1: Composition of Zeolite from EDX in Figure 2.

Element	KeV	Massa %	At%
O		45.31	
Al	1,486	6.41	6.42
Si	1,739	33.08	63.61
K	3,312	1.04	0.72
Ca	3,690	2.59	3.49

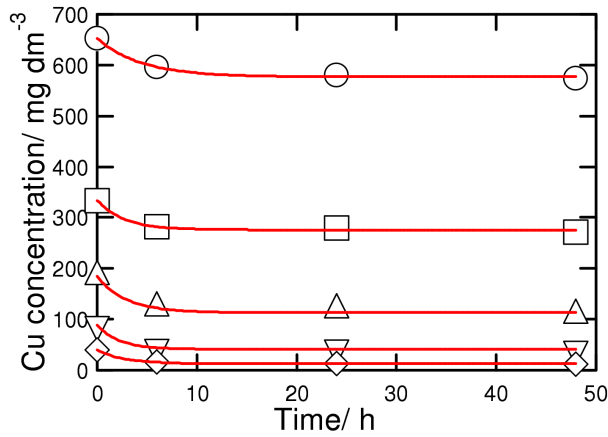


Figure 4: Sorption of Cu onto zeolite at initial pH 5 and 25°C.

using 0.3 dm³ solutions containing different concentrations of Cu²⁺ with initial pH 5. All solutions of Cu²⁺ were prepared using CuSO₄ special grade. All solutions were shaken at 100 rpm and 25°C until sorption equilibrium was attained. Copper concentration was determined by Atomic Absorption Spectrophotometer (AAS).

3 Result and Discussion

The raw data for sorption isotherm of Cu²⁺ onto zeolite at 25°C was presented in Figure 4. The equilibrium pHs of the solutions from zeolite are 5.5-6.8, all of them are higher than the initial pH. It shows that the sorption equilibrium was achieved after 24 hour. Figure 4. Sorption of Cu onto zeolite at initial pH 5 and 25°C. Langmuir isotherm model was fitted to the sorption isotherm data of Cu onto Zeolite following this equation:

$$Q = \frac{q_{\max}C_e}{(C_e + K_d)} \quad (1)$$

Where Q_{max} is the maximum of sorbed Cu per unit amount of sorbents (mmol kg⁻¹), K_d is the dissociation coefficient of the solute-adsorbent complex which represents the affinity between the solute and the adsorbent. The Langmuir model was fitted to the equilibrium data of Cu sorption onto Zeolite with R² is 0.99 as shown in Figures 5 and 6 following the eq.

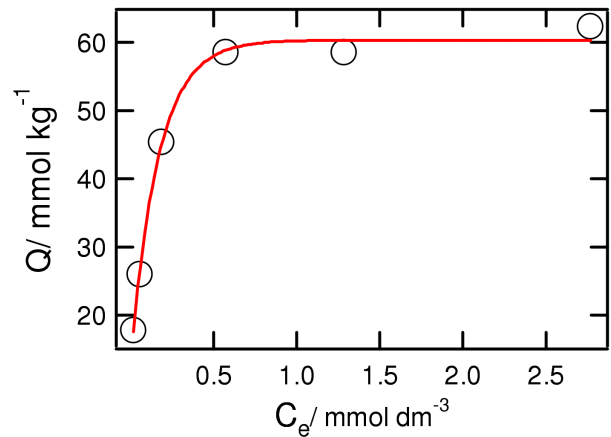


Figure 5: Plots for sorption of Zn onto zeolite showing Langmuir isotherm fits to the data.

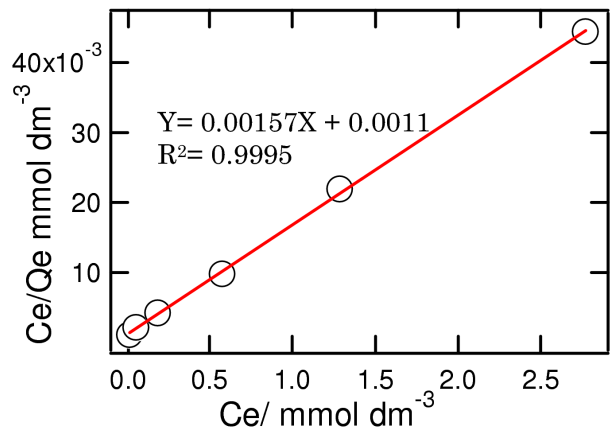


Figure 6: Plots for sorption of Cu onto zeolite showing linearized Langmuir isotherm fits to the data.

(2). The maximum capacity of zeolite to immobilize Cu is 63.69 mmol kg⁻¹ as shown in Table 2.

$$Q = \frac{63.69C_e}{(C_e + 13.33)} \quad (2)$$

The effect of zeolite grain size was also studied using zeolite with mesh number 5-8, 16 -25 and 60 – 115. It shows that the zeolite with fine grain size (mesh 60 – 115) is more effective than others due to increase of surface area of zeolite as shown in Figure 7.

Analysis of cations concentration before the experiment and after reach the equilibrium shows that mostly of cations concentration after reach the equilibrium were higher than

Table 2: Summary of Langmuir constants in sorption isotherm of Cu onto zeolite.

Sorbent	Q_{max} ($mmolkg^{-1}$)	K_l	R^2
Zeolite	63.69	14.27	0.99

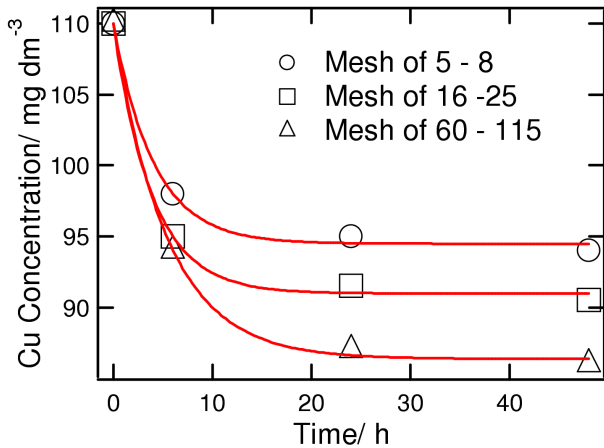


Figure 7: The effect of grain size in the Cu immobilization by zeolite.

before the experiment especially for Sodium (Table 3). This data indicate that the mechanism of Cu immobilization onto zeolite not only by physical sorption due to high surface area but also cation exchange.

4 CONCLUSIONS

From this study it is concluded that zeolite are good sorbent of Cu. The adsorption isotherm analysis using zeolite was found to follow the Langmuir for single metal system. The maximum Cu removal was estimated 63.69 mmol kg⁻¹ of zeolite according to the Langmuir equation. The mechanism of Cu immobilization onto zeolite is not only physical sorption due to high surface area of zeolite but also cations exchange.

Table 3: Cations concentration before and after the experiment.

Cation ($mg\ dm^{-3}$)	Before reaction (0 hours)			After reach equilibrium (48 hours)		
	Enl. 1	Enl. 3	Enl. 6	Enl. 1	Enl. 3	Enl. 6
Ca ²⁺	0	0	16.2	0	0	21
Na ²⁺	20	16	16	48	40	32

Acknowledgment

Financial supports were provided by the Research Grant for International Collaboration and International Publication from DP2M DIKTI.

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