

EFFECTIVITY OF DOLOMITE ADSORBENT IN PURIFICATION OF Mn AND Cu FROM ACID MINE DRAINAGE

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Abstract

The mining industry raises many environmental problems in the ecosystem, one of which is the emergence of acid mine drainage. Because of this issue, this study was conducted to see the performance of dolomite adsorbents in purifying acid mine drainage at iron ore mining in Aceh Besar, Indonesia. The adsorption of Cu²⁺ metal ions using dolomite adsorbents has the best equilibrium result at a contact time of 15 minutes, the efficiency at equilibrium reaches 92.97%, and the absorption capacity reaches 9.07 mg/g at an initial measured concentration of 19.5 mg/L with an adsorbent weight of 0.2 gr. On the other hand, Mn²⁺ has the best equilibrium in 30 minutes with an efficiency of 95.17% and an adsorption capacity of 0.92 mg/g at a measured concentration of 5.8 mg/L and an adsorbent weight of 0.6 gr. The obtained kinetic model is a pseudo second order.

Keywords: *Adsorption, Dolomite, Acid Mine Drainage, Copper, Manganese, Efficiency*

1. INTRODUCTION

Indonesia is one of the countries with an abundance of mineral resources. According to Ditjen Minerba ESDM, state mineral and coal sector revenues will reach 183.35 trillion in 2022, with 4,050 IUP licenses, 9 IUPK, 31 KK, and 60 PKP2B (ESDM, 2023). A majority of mining industries can have a positive impact in terms of employment and increased regional income, but it can also have a negative impact in terms of hazardous wastes such as acid mine drainage, the more significant part of which have a low pH and contain heavy metals which need to be addressed while not affecting the balance of the environmental eco-system.

Various conventional methods have been developed in the treatment of acid mine drainage, which are classified into passive systems and active systems that are used based on the need for the addition of chemicals, infrastructure, maintenance, and monitoring (Kaur et al., 2018), such as chemical precipitation (Hassas et al., 2020), filtration membrane (Wang et al., 2021), and electrodialysis (Malakootian et al., 2019). This wastewater treatment method requires high operational costs and long duration, complicated procedures, incomplete disposal, high energy requirements, and produces toxic sludge (Kushwaha et al., 2017)

As a result, using green technologies, such as adsorption methods, can be an alternative to effectively remove heavy metals from wastewater without negatively impacting the process (Rahman et al., 2021). Adsorption is one of the most common methods used for the treatment of wastewater contaminated with toxic ions because of its low cost, simplicity, high efficiency, non-toxic, and environmental sustainability by using natural and inexpensive materials (Yang et al., 2021). Many adsorption developments have been carried out which produce various types of adsorbents by utilizing materials such as activated carbon (Tran et al., 2020), zeolite and clay minerals (Ngulube et al., 2017), coal ash (Mahidin et al., 2017), and dolomite (Syah, 2022). Dolomite-based adsorbents have several significant advantages, such as the availability of abundant resources, simple application, low cost, utilization capability for a wide range of contaminants, and the ability to create selective adsorbents using various modification methods (Gruszecka-Kosowska et al., 2017; Khashbaatar et al., 2022; Shah et al., 2019).

This study will examine the effectiveness of using dolomite adsorbent on acid mine wastewater collected from iron ore mining reservoirs in Aceh Besar, Indonesia. Another comparison is the adsorbent concentration and the waste parameters to be adsorbed, such as heavy

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metal content, turbidity, BOD, and COD in acid mine drainage wastewater obtained from iron ore mining.

2. IMPLEMENTATION METHOD

Materials used in this study were activated dolomite adsorbents from Aceh Tamiang, Indonesia. The acid mine wastewater was collected from iron ore mining reservoirs located in Aceh Besar, Indonesia.

Adsorption of acid mine wastewater using activated dolomite adsorbent

The adsorption process in this study was carried out in batches by preparing and weighing 0.2, 0.4, and 0.6 gr of adsorbent. Dolomite nanoparticle size that has been activated as much as 0.2, 0.4, 0.6 gr is stirred with 100 mL of pure mine acid water at a speed of 300 rpm under a contact time of 5, 10, 15, 20, 25, and 30 min at room temperature. The examination is carried out on each sample before and after adsorption tests on pH and heavy metal concentrations using an Atomic Adsorption Spectrophotometer (AAS). The heavy metals tested in this adsorption process are copper (Cu^{2+}) and manganese (Mn^{2+}), where the presence of metal ions of copper (Cu^{2+}) and manganese (Mn^{2+}) is above environmental quality standards. While the content of COD, BOD, turbidity, and other heavy metal ions, namely metal iron (Fe^{2+}), zinc (Zn^{2+}), and lead (Pb^{2+}), their presence is below environmental quality standards. In this case, no tests were carried out on the waste parameters.

Atomic Adsorption Spectrophotometer Analysis

This analysis is carried out using an Atomic Absorption Spectrometer (AAS) brand Perkin Elmer to determine the concentration of copper (Cu^{2+}) and manganese (Mn^{2+}) ions contained in acid mine wastewater before and after the adsorption process using dolomite adsorbent.

pH Analysis

pH measurements were carried out using a pH meter (HACH EC 10 brand) at the Chemical Engineering Laboratory of Universitas Syiah Kuala to determine the pH in acid mine water before and after the adsorption process. The data obtained from the measurement results were then analyzed to determine the effect of dolomite adsorbent concentration on the pH value of acid mine water.

Determination of Adsorption Capacity

Calculation of the adsorption capacities of copper (Cu^{2+}) and manganese (Mn^{2+}) ions at equilibrium is calculated by the following equation :

$$q_e = \frac{(C_0 - C_e)V}{m} \dots\dots\dots(1)$$

Where, q_e is adsorption capacity (mg/g), C_0 is concentration parameters of the effluent prior to adsorption (mg/L), C_e is parameter concentration of effluent after adsorption (mg/L), V is sample solution volume (L), and m is the weight of the adsorbent (g).

Determination of Adsorption Kinetics

Adsorption kinetics of Copper (Cu^{2+}) and manganese (Mn^{2+}) is determined by using pseudo first order and second order by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \dots\dots\dots(2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \dots\dots\dots(3)$$

Where, q_t is adsorption capacity at time t (mg/g), q_e is adsorption capacity at equilibrium (mg/g), t is time (s), k_1 is the first order speed constant (min^{-1}), and k_2 is the second order speed constant ($\text{g.mg}^{-1}.\text{min}^{-1}$).

3. RESULTS AND DISCUSSION

Parameter composition of acid mine drainage

Preliminary tests on the composition of the resulting wastewater will determine the quality and characteristics of the acid mine drainage in the main iron ore mining reservoirs in Aceh Besar, Indonesia. Acid mine drainage was taken on January 4, 2023, at 11.16 WIB with clear weather conditions in the iron ore mining settling pond in Jantang Village, Lhoong District, Aceh Besar, Indonesia. The results of the parameter composition test of acid mine drainage wastewater are shown in Figure 1.

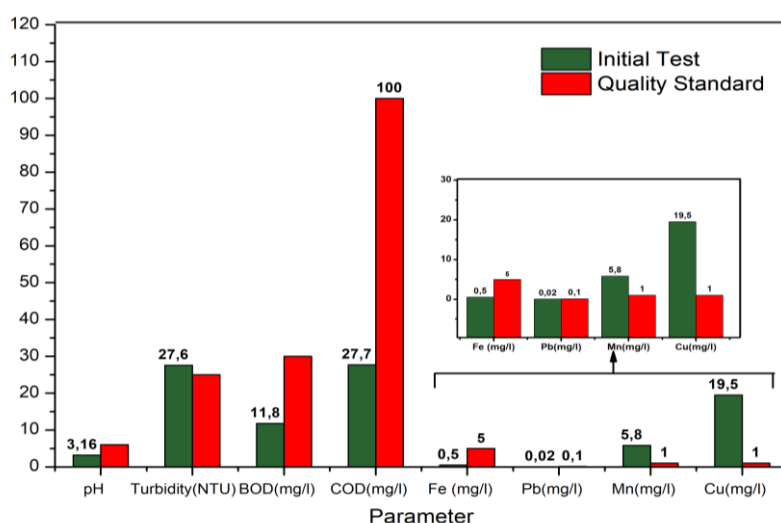


Figure 1. Comparison of test results for the composition of acid mine wastewater against environmental quality standards

It can be seen that the composition of acid mine drainage from iron ore mining in the Aceh Besar has mostly met the established quality standards. There are only two metal concentrations that are above environmental quality standards, which the presence of copper metal (Cu^{2+}) with a concentration of 19.5 mg/l and manganese metal (Mn^{2+}) of 5.8 mg/l, based on regulations stipulated by the Minister of Environment and Forestry of the Republic of Indonesia Number 5 of 2022 regarding the quality standards for metal ion concentrations of copper (Cu^{2+}) and manganese (Mn^{2+}) which are allowed each to be 1 mg/l (Kementrian Lingkungan Hidup dan Kehutanan, 2022).

Effect of contact time on the adsorption capacity (q_t) and efficiency

The effect of contact time on the capacity and absorption efficiency of copper and manganese metal ions in the purification of acid mine waste water from iron ore mining in Aceh Besar, an adsorption test of metal and metal Mn^{2+} was carried out with variations of time 5, 10, 15, 20, 25 and 30 min with 0.2 gr dolomite adsorbent. Changes in concentration at each contact time will be analyzed to obtain the value of each adsorbed metals capacity and absorption efficiency, which can be seen in Figure 2.

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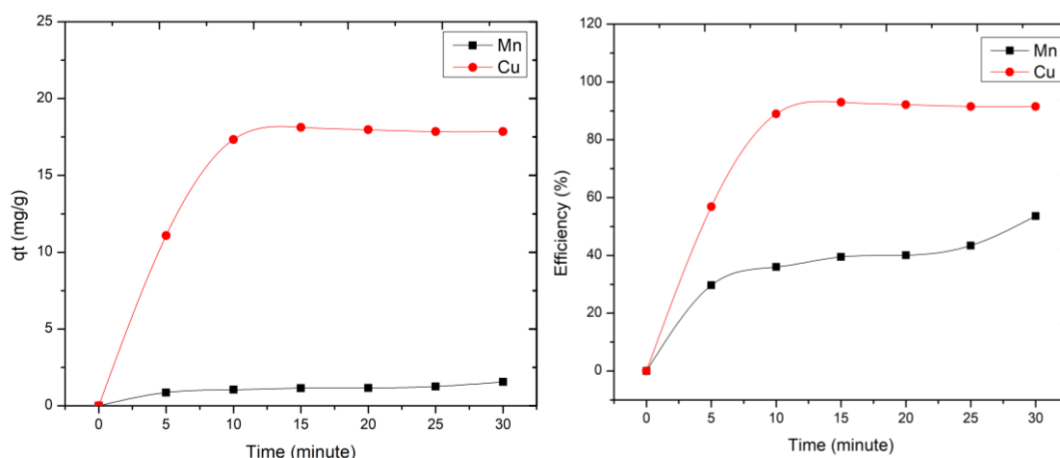


Figure 2. The relationship between contact time and (a) adsorption capacity and (b) efficiency in adsorbing Mn and Cu metals

Based on the results, the adsorption capacity and efficiency tend to increase with the length of contact time. The adsorption capacity and efficiency for manganese metal increased markedly at 30 minutes. (Cao et al., 2018) revealed that the adsorption equilibrium of copper ions using dolomite was reached in 30 minutes. Meanwhile, for copper metal, the adsorption capacity and efficiency increased sharply in the first 15 minutes due to the presence of large numbers of active sites on the adsorbent surface, which were still free and had not been accommodated by copper metal ions (Martini et al., 2018). Then the efficiency increases slowly from 20 to 30 minutes and tends to be constant. The result is because partial saturation has occurred on the surface of the adsorbent, which makes some active sites start to saturate and can no longer adsorb adsorbate ions (Vilela et al., 2019). The percentage of absorption efficiency for each metal can be seen in Table 1.

Table 1. Percentage of Metal Ion Absorption Using Dolomite Adsorbent

adsorbate	Adsorbent mass (gram)	acid mine waste volume (L)	Initial C measured (mg/L)	Adsorption Capacity (mg/g)	Efficiency (%)
Cu	0.2	0.1	19.5	9.07	92.97
Mn			5.8	1.56	53.62

Effect of adsorbent mass on the adsorption capacity (q_t) and efficiency

In this study, the mass variation of the adsorbent used was 0.2, 0.4, and 0.6 grams. The use of variations in the mass of the adsorbent was carried out to determine the effect of the mass of the adsorbent on the absorption efficiency and absorption capacity of Cu^{2+} metal ions and Mn^{2+} metal ions at the equilibrium time of each metal. The capacity and efficiency of each metal can be seen in Figure 3.

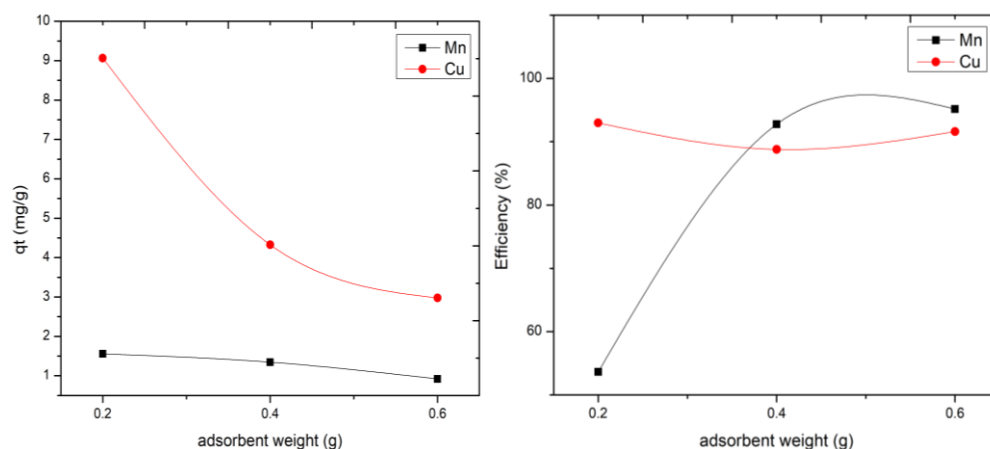


Figure 3. The relationship between the mass of the adsorbent and (a) absorption capacity (b) metal ion efficiency

Based on the result, the best capacity and efficiency of Mn are 0.92 mg/g and 95.17%, respectively with equilibrium in 30 minutes and adsorbent of 0.6 gram. It shows that Mn metal increases the mass of the adsorbent used and the higher the value of the efficiency of metal absorption Mn^{2+} . This result is similar with previous study, where the high absorption of manganese is consistent with using sufficient carbonate adsorbent mass in the system (Silva et al., 2012). The total mass of the adsorbent is equivalent to the number of metal ion exchange sites. If the mass of the adsorbent used increases, the ion exchange sites for the adsorption of Mn^{2+} ions would also increase. This is because the use of adsorbent mass in adsorption increases the availability of a more significant active site to interact with metal ions (Arida et al., 2016).

Meanwhile, as the mass of the adsorbent used increases, the absorption efficiency value of Cu^{2+} metal decreases. The best efficiency and capacity in adsorbing copper metal ions using a mass of 0.2 gram adsorbent, which is resulted in 92.97% and 9.07 mg/g, respectively. This decrease in efficiency is possible by copper, which have been absorbed at a contact time of 5 to 10 minutes and are released again when the contact time is 15 minutes or commonly called the desorption process (Rápó & Tonk, 2021).

Adsorption Kinetics

Adsorption kinetics expresses the absorption rate that occurs in the adsorbent against the adsorbate or the amount of Mn and Cu ions absorbed by the adsorbent per unit of time. The ion adsorption model for Mn and Cu metal ions uses two kinetic models: pseudo first order and pseudo second order. The optimal model to characterize the kinetics of each metal ion is determined by comparing the squared regression value (R^2), and it is constant (Harrache et al., 2019). The first order pseudo-kinetic model for each metal can be seen in Figure 4. A pseudo first order rate constant kinetic model that can be determined based on the slope of the linear plot of $\ln(q_e - q_t)$ versus t . The q_e and q_t are the amount of metal adsorbed at equilibrium for adsorption time.

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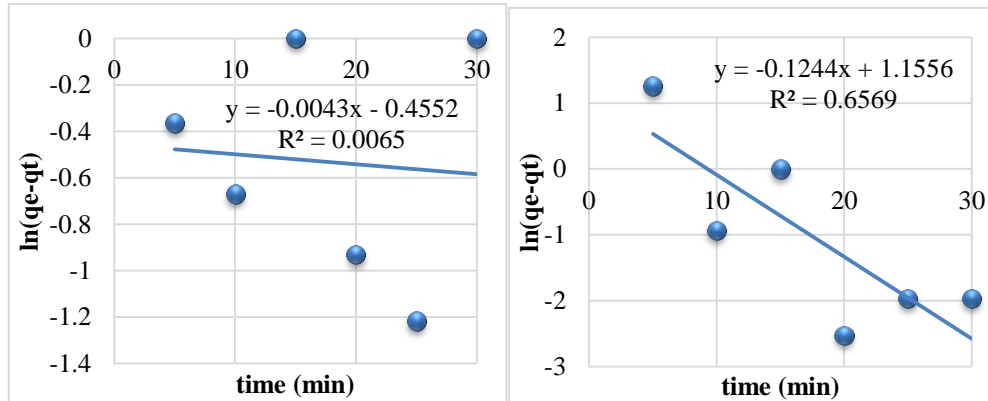


figure 4. First-order pseudo-kinetic model for (a) Mn metal (b) Cu metal

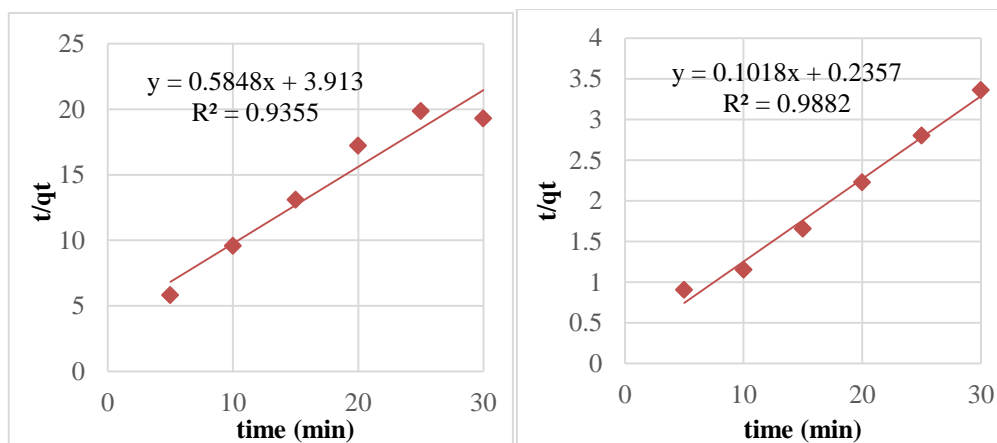


Figure 5. Second-order pseudo-kinetic model for (a) Mn metal (b) Cu metal

The second order pseudo-kinetic model can be seen in Figure 5. It shows that the pseudo-second order model correlates better with the kinetic data than the first-order pseudo marked with R^2 , which is closer to number 1 than the first-order pseudo. This is in accordance with research that has been conducted by (Harrache et al., 2019). The details of comparison between pseudo first-order and second-order kinetic models can be seen in Table 2.

Table 2. Comparison of Pseudo First Order and Pseudo Second Order Kinetic Models on Metal Adsorption

Sample	Concentration (mg/L)	Pseudo First Order			Pseudo Second Order		
		q_e	k_1	R^2	q_e	k_2	R^2
Mn	5.8	0.63	-0.0043	0.0065	1.71	0.0874	0.9355
Cu	19.5	3,18	-0.1244	0.6560	9,82	0.0439	0.9882

4. CONCLUSION

In conclusion the adsorption of Cu^{2+} metal ions using dolomite adsorbents has the best equilibrium result at a contact time of 15 minutes, the efficiency at equilibrium reaches 92.97%,

and the absorption capacity reaches 9.07 mg/g at an initial measured concentration of 19.5 mg/L with an adsorbent weight of 0.2 gram. On the other hand, Mn^{2+} has the best equilibrium in 30 minutes with an efficiency of 95.17% and an adsorption capacity of 0.92 mg/g at a measured concentration of 5.8 mg/L with and adsorbent weight of 0.6 gr. The obtained kinetic model is a pseudo second order.

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