

Performance Evaluation of Physically and Chemically Modified Pumice on Removal of Cu(II) from Aqueous Solution

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Abstract

Modification by physical and chemical treatments was evaluated to increase the adsorption capability of natural pumice in the removal of Cu(II) from aqueous solution. The treatments were heating at temperatures of 300, 450 and 600 °C for physical and soaking in acid solutions (HCl, H₂SO₄ and HNO₃) for chemical treatment. The adsorption was performed in the batch system at the optimum condition (5 of pH solution, < 63 μm of adsorbent diameter, 3 g/L of adsorbent dose, 5 mg/L of Cu(II) concentration and 30 min of contact time). The results showed the removal efficiency and Cu(II) uptake increased using modified pumice from 71.19 % and 1.19 mg/g to 84.45 % and 1.41 mg/g. The highest removal efficiency and Cu(II) uptake were obtained from 300°C of heating temperature and HCl for the acid solution. The application of physical and chemical treatments in modification has the potential to increase the removal efficiency and heavy metal uptake of the natural pumice.

Keywords: Adsorption, Cu, Modification, Pumice

Introduction

Industrial activities and technology development lead to a significant release of important quantities of heavy metal ions to the environment. As examples of industries releasing wastewaters charged with heavy metal ions, one can cite mining, electroplating, electronic equipment, battery manufacturing processes, etc. The wastewater commonly contains Cu, Ni, Cd, Cr and Pb which are not biodegradable and their accumulation in the ecological system can cause harmful effects to humans, animals and plants [1,2]. Copper (Cu) is a widely used metal in industries such as plating, mining, and smelting, brass manufacture, electroplating industries, petroleum refining, etc. [3], which produce much wastewater and sludge containing Cu(II) ions with various concentrations, which may have negative effects on the environment. High doses of copper can cause serious toxicological concerns since it can be deposited in the brain, skin, liver, and pancreas. It will then lead to nausea, vomiting, headache, diarrhea, respiratory difficulties, liver and kidney failure, and death [4]. The World Health Organization recommended a maximum acceptable concentration of Cu(II) in drinking water less than 1.5 mg/L [5].

Adsorption is the most common technique for metal removal because adsorption has a simple design, is low cost, easy to perform, and insensitive to toxic substances [6]. Adsorption onto activated carbon has been widely applied for removing metals from water and wastewater. However, adsorbent-grade activated carbon is expensive, and the regeneration of activated carbon for reuse increases the cost. Therefore, more interest has recently arisen in the investigation of low-cost adsorbents with a good sorption capacity to remove heavy metal ions from water and wastewater [7-9].

Geomaterials are low-cost adsorbent resources offering frequent applications to water and wastewater treatments. They are mostly available in the local sources and the requirement for processing them is minimal. Geomaterials such as fired clay [10], bentonite [11], diatomite [12], grey and red clay [13] as well as zeolites [14] were used as adsorbents. In the series of geomaterials, a porous and amorphous material that consists mainly of SiO₂ is pumice. Pumice is one of the natural pozzolan created by the release of gases during cooling and solidification of lava. Pumice has a low weight, porous structure, and a large surface area [15,16]. The utilization of pumice mainly is for structural applications such as aggregate in lightweight concrete, cement and filters. However, nowadays, pumice also has been used as an adsorbent for pollutant removal from water and wastewater [17]. The natural and modified

pumice were explored to be a better adsorbent for organic and inorganic water pollutants in recent years [18,25].

From some previous investigations, it was proved that naturally occurring materials have lower adsorption capacity. For that various methods have been evaluated for the modification of naturally occurring materials, and hence appropriate modification will improve natural adsorbent sorption capacity. Generally, modification of the adsorbent exhibits higher adsorption capacities than their unmodified forms due to change in the specific surface area, pore structure, and surface chemical functional groups of the adsorbent. Numerous techniques physically by heat treatment and chemically by using chemicals include mineral and organic acids, bases, oxidizing agents have been used for modification of the adsorbents [21].

The present study is aimed to evaluate the performance of natural and physical as well as chemically modified pumice on Cu(II) uptake from water. Pumice was obtained from Sungai Pasak, West Sumatera, Indonesia. This local mineral is available in great abundance, as a byproduct of the process of sand mining in that area. For this research, heat treatment is performed as a physical modification technique, while acid immersion for chemical treatment.

Materials and methods

Reagents

All used chemicals in this study were reagent grade from Merck (Germany). Cu(II) stock solutions were prepared by dissolving Cu(II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in distilled water. HCl, H_2SO_4 and HNO_3 were used for chemical treatment in the modification of the pumice.

Preparation and modification of pumice

The pumice stone was collected at the riverside of Sungai Pasak, West Sumatera, Indonesia. SiO_2 , Al_2O_3 and K_2O are the major components in natural pumice from Sungai Pasak, as shown in **Table 1** as determined by EDX. The chemical compositions of the pumice also indicate the absence of hazardous or carcinogenic substances; thus, the pumice is considered appropriate as an adsorbent to treat polluted water.

Table 1 Chemical components of natural pumice from Sungai Pasak, West Sumatra, Indonesia.

Oxide	% Weight
MgO	0,876
Al_2O_3	13,913
SiO_2	76,586
P_2O_5	0,822
K_2O	3,604
CaO	2,11
TiO_2	0,197
MnO	0,044
Fe_2O_3	1,485
ZnO	0,006

To remove any impurities, pumice was washed several times with distilled water before use and dried at laboratory temperature (25 ± 1 °C). Afterward, the stone was crushed and sieved to produce particle size fractions of < 63 μm . The obtained particles were prepared for physical and chemical treatments of modification. For physical treatment, pumice was given the heat treatment by burning it at 300, 450 and 600 °C for 3 h. For chemical treatment using an acid solution, pumice was immersed and stirred in HCl 1 M, H_2SO_4 1 M and HNO_3 1 M for 4 h and washed using distilled water, then dried at 130 °C for 3 h.

Batch adsorption experiments

Batch adsorption experiment was performed at laboratory temperature (25 ± 1 °C), pH 5; 3 g/L of adsorbent dose; < 63 μm of adsorbent diameters and 30 min of contact time. That condition was obtained as the optimum adsorption condition from the previous research. In each experiment, 100 mL of Cu(II) solutions of 5 mg/L of initial concentration were treated with 7 kinds of adsorbents in a set of erlenmeyer flasks and shaken with a shaker machine at a speed of 100 rpm. After 30 min of contact time, the adsorbents were separated from the metal solutions by filtered through a 0.45 μm membrane filter. A 10 mL of the supernatants were analyzed by atomic absorption spectrophotometer (Rayleigh WFX 320, China) for measurement of Cu(II) concentration. The amount of Cu(II) ions adsorbed by the pumice was obtained as the difference between the initial and final ion concentrations of the solutions. All experiments were repeated 3 times and the results presented are the averaged values of replicate tests, consequently.

The removal efficiency and the Cu(II) uptake (q_e , mg/g) on natural and modified pumice were calculated by the following equation;

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

where C_0 is the initial concentration of Cu(II) (mg/L), C_e is the equilibrium concentration of Cu(II) (mg/L), V is the volume of the solution (L), and m is the mass of the pumice (g).

Results and discussion

Physical treatment for modification of pumice

The removal efficiencies and Cu(II) uptakes of natural pumice and modified pumice by physical treatment are shown in **Figure 1**. Natural pumice had a removal efficiency of 71.19 %, while modified heating pumice at 300, 450 and 600 °C had 78.09, 73.31 and 71.46 % of removal efficiencies, respectively. The Cu(II) uptake of natural pumice was 1.19 mg/g, whereas by modified heating pumice were 1.30, 1.22 and 1.19 mg/g for 300, 450 and 600 °C of heating temperature, respectively. The experimental results indicated an increase in the removal efficiency and Cu(II) uptake by using modified pumice by heating at 300 and 450 °C compared to those of natural pumice.

Generally, physical modification results in the enhancement of physical characteristics (BET area and total pore volume). The thermal/heat treatment or calcining process leads to a change in the chemical composition of the surface and the porosity of the mineral. The product of heat or thermal processing also showed a significant increase in specific surface area and pore volume [26]. The heat treatment also can remove the water contained in the pores of the adsorbent, so the pores of the adsorbent are empty and may increase its adsorption ability. However, the higher temperature for heat treatment also may cause damage in the adsorbent structure which may affect the adsorption process, as obtained from the experiment with 600 °C of heating temperature. Its removal efficiency and Cu(II) uptake were lower than those of natural pumice.

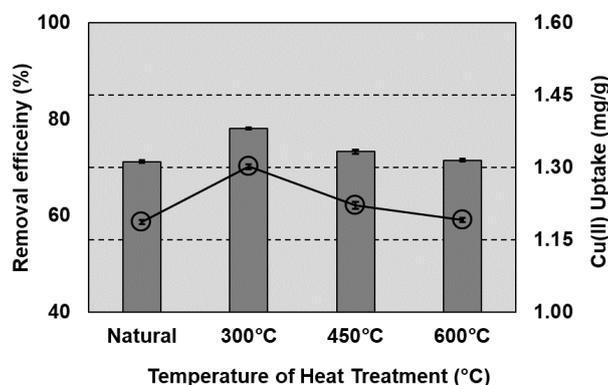


Figure 1 Removal efficiencies and Cu(II) uptakes of natural and modified pumice by physical treatment. (pH 5; 3 g/L of adsorbent dose; < 63 μm of adsorbent diameters; 30 min of contact time; 5 mg/L of initial concentration).

Figure 2 presents the SEM analysis results for natural and modified pumice by heat treatment. It is shown that the natural pumice (**Figure 2(a)**) has a relatively large number of pores, but the pores are covered by other compounds. Meanwhile, modified pumice heated at 300 and 450 °C is revealed to have more number open pores (**Figures 2(b)** and **2(c)**). These conditions lead to an increase in pore volume and surface area of the adsorbent, thereby increasing the adsorption capacity of the adsorbent. However, modified pumice by heating at 600 °C seem to have fewer pores, which may be due to damage in the structure of the adsorbent pores caused by overheating temperatures.

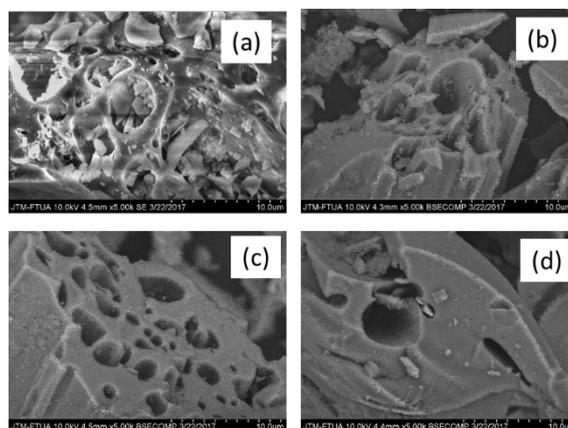


Figure 2 SEM images of natural pumice (a) and modified pumice by heat treatment at 300 °C (b), 450 °C (c) and 600 °C (d).

Chemical treatment for modification of pumice

An increase in removal efficiency by using modified pumice with acid immersion compared to the natural pumice is also obtained based on the experimental results, as shown in **Figure 3**. The Cu(II) removal efficiency was found 71.19 % by using the natural pumice, while with modified pumice by soaking in HNO₃, HCl and H₂SO₄ removal efficiencies achieved 79.75, 84.45 and 72.57%, respectively. Similar to the removal efficiencies, an increase in the Cu(II) uptake is obtained as well by using the modified pumice. The Cu(II) uptake of the adsorption using the natural pumice was 1.19 mg/g, increased to 1.33, 1.41 and 1.21 mg/g using modified pumice by soaking in HNO₃, HCl and H₂SO₄, respectively.

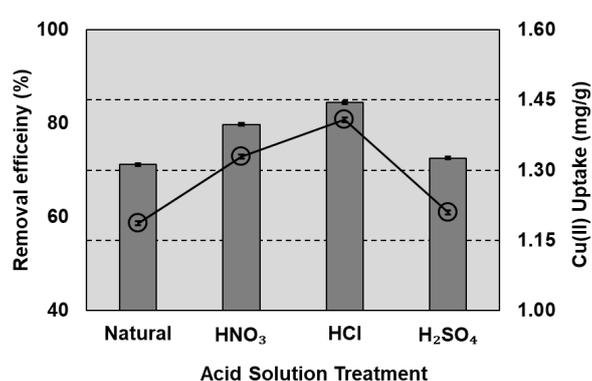


Figure 3 Removal efficiencies and Cu(II) uptakes of natural and modified pumice by chemical treatment. (pH 5; 3 g/L of adsorbent dose; < 63 μm of adsorbent diameters; 30 min of contact time; 5 mg/L of initial concentration).

For the removal of heavy metals from water, acidic functional groups on adsorbent surfaces have been examined and found to be highly favorable because metal ions tend to form metal complexes with the negatively charged acid groups. Moreover, soaking the adsorbent in acid solution may dissolve the impurity compound on the surface of the pores of the adsorbent, increasing surface area and adsorption capability of the adsorbent. Although acid modification decreased the organic content of adsorbent and increased porosity, positively charged surfaces with hydrogen ions prevented the extra increase of adsorption [27]. The results reveal the highest removal efficiency and Cu(II) uptake were obtained using

modified pumice by soaking in HCl 1 M. However, compared to H₂SO₄ and HNO₃ the removal efficiency and Cu(II) uptake were not much different may due to HNO₃, HCl and H₂SO₄ are strong acids and the concentrations used for soaking are similar. The increase in the amount of adsorption per mass unit of the adsorbent (q_e , mg/g) was also found in the adsorption of methylene blue dye from aqueous solutions by modified pumice using HCl 1 N. The dye uptake increased from 1.488 mg/g by natural pumice to 15.87 mg/g using the modified pumice [18-28].

The SEM images of natural and modified pumice by soaking in the acid solution; HCl, HNO₃ and H₂SO₄ was shown in **Figure 4**. As mentioned previously, the pores of natural pumice were largely in number but were covered by other compounds or impurities (**Figure 4(a)**). The surfaces of modified pumice by acid solution appear to be cleaner and the pores were uncovered by impurities (**Figures 4(b)** and **4(c)**).

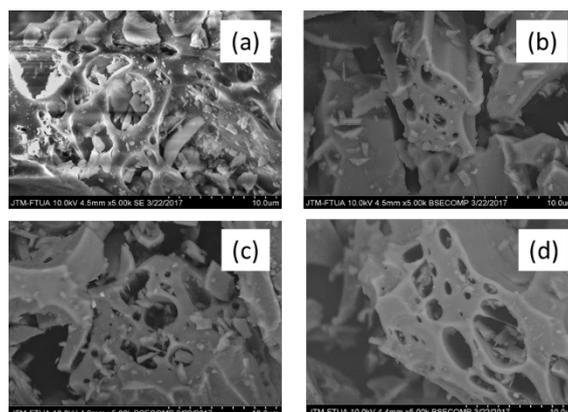


Figure 4 SEM images of natural pumice (a) and modified pumice by acid solution: HCl (b), HNO₃ (c) and H₂SO₄ (d).

Table 2 presents the comparison of removal efficiencies and Cu(II) uptakes of natural pumice and modified pumice by heating at 300 °C and soaking in HCl 1 M. These 2 latest conditions were chosen as the best condition which resulted in the highest removal efficiency and Cu(II) uptake in the batch adsorption experiment. It was revealed that the modification of pumice physically and chemically increased the removal efficiency and Cu(II) uptake. Changes in the surface area, pores and chemical functional groups on the adsorbent surfaces may occur caused by physical and chemical treatment. Finally, it was suggested that to increase the removal efficiency and metal uptake of the pumice, various treatments of modification may be applied. However, further investigations are still needed to explore various treatments and results of the modification of pumice.

Table 2 Comparison of removal efficiencies and Cu(II) uptake of natural pumice and modified pumice by physical and chemical treatment

Kind of adsorbent	Removal efficiency (%)	Cu(II) Uptake (mg/g)
Natural Pumice	68.83	1.15
Heating at 300 °C	78.09	1.30
Soaking in HCl 1M	84.45	1.41

The removal of Cu(II) using natural (water washed) and modified adsorbents, including this study is listed in **Table 3**. Generally, it can be recognized that the differences in Cu(II) removal were obtained from different adsorbents used depending on their physical natures and chemical compositions. However, in some studies, the capacity of adsorbent increases by using modification methods. The comparison showed that the Cu (II) removal using natural and modified pumice was relatively low compared to other adsorbents reported in the literature.

Table 3 Summary of previous work using different adsorbents for removal of Cu(II) and comparison with this study.

Adsorbents	Modification method	Cu(II) removal, %	References
Cellulose pulp waste	Water washed	80.00	[29]
Minced banana peel	Water washed	90.00	[30]
Watermelon shell	Water washed	84.00	[31]
Coconut shell	ZnCl ₂	71.26	[32]
Prosopis juliflora plant	HNO ₃	89.00	[33]
Sugarcane Bagasse	Water washed	88.90	[34]
Sugarcane Bagasse	Citric acid	96.90	[34]
Sugarcane Bagasse	NaOH	94.80	[34]
Pumice	Water washed	68.83	This study
Pumice	Heat treatment	78.09	This study
Pumice	HCl	84.45	This study

Conclusions

The performance of natural as well as physically and chemically modified pumice from Sungai Pasak, West Sumatra, Indonesia on removal efficiency and Cu(II) uptake were evaluated. The physical modification was performed by heat treatment at 300, 450 and 600°C and it was found that the highest removal efficiency and Cu(II) uptake were obtained by modified pumice by heating at 300 °C. For chemical modification, 3 kinds of acid solutions were evaluated: HCl, H₂SO₄ and HNO₃ with 1 M of concentration. The highest removal efficiency and Cu(II) uptake (84.45 % and 1.41 mg/g) were achieved using modified pumice by soaking in HCl 1 M. Physical and chemical treatment to pumice may modify the surface areas, pore structures, and chemical functional group on the surface of the pumice. Overall results were indicated that pumice from Sungai Pasak, West Sumatra, Indonesia has the potential to be an alternative low-cost adsorbent for Cu(II) removal from water and wastewater and modification by physical and chemical treatment may increase its adsorption capability.

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