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Utilization of Pumice from Sungai Pasak, West Sumatera, Indonesia as Low-Cost Adsorbent in Removal of Manganese from Aqueous Solution

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Abstract. Adsorption of manganese (Mn) from aqueous solution by using pumice from Sungai Pasak, West Sumatera, Indonesia as low-cost adsorbent was studied. Batch experiments were carried out at ambient temperature (25°C) and 100 rpm of agitation speed to examine the effect of various experimental parameters on the removal of Mn such as solution pH, dose of adsorbent, particle size of adsorbent, initial concentration and contact time. The Langmuir and Freundlich models were employed to characterize the adsorption isotherm of Mn by the pumice. The results revealed that the optimum condition of Mn removal by pumice were 0.3 g/L of adsorbent dose, 90 min of contact time of adsorption, <149 µm of particle size, 4 of pH solution and 6 mg/l of Mn concentration with 171 mg Mn/g pumice of adsorption capacity. The Freundlich model was found to better fitting of adsorption isotherm within the concentration range studied. This study indicated that pumice from Sungai Pasak, West Sumatera, Indonesia has potential for Mn removal from groundwater or other polluted waters.

INTRODUCTION

Contamination of ground water with metals poses dangerous environmental problem due to the fact that metals are not biodegradable, may accumulate throughout the food chain and, in turn, may cause harmful effects to organisms living in water and severe adverse effects on human health [1, 2, 3]. Some regions in Indonesia suffer from the contamination of ground water with high concentration of iron and manganese, which endanger human health and cause the chronic diseases. Manganese (Mn) is a common toxic metal that present in water supplies from natural processes like catchments and erosion as well as from the effluents of many industries [4,5]. In general, through oral or respiratory system, manganese can be absorbed by the human body. High amounts of manganese in human body can cause edema of the respiratory system, pneumonia, circulatory collapse and also damage the nervous system irreversibly [6]. On the other hand, high concentration of manganese in the drinking water can result in the discoloration of water and laundry, formation of oxide deposits in pipelines, and impart an unpleasant metallic taste. So, the determination of manganese concentration in is necessary for the environment and human health. In drinking water sources, the secondary maximum contaminant level (SMCL) for Mn(II) must not exceed 0.05 mg/L [7].

Currently, different treatment technologies have been applied to remove metals from water and wastewater and these include electrochemical, membrane filtration, chemical precipitation, chemical oxidation and reduction, ion exchange, phytoremediation and adsorption [8,9]. Among these technologies, adsorption is a most common technique since it has a simple design, easy to perform and insensitive to toxic substances. Adsorption is also seems to be more effective and environmental friendly if combined with appropriate adsorbent and regeneration steps. In

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last decade, one approach increasingly researched in removing metals is the use of various agricultural byproducts such as pine bark wastes [10], rice husk ash [11] and maize husk [12] as adsorbent. In addition, the potential the use of natural materials or local minerals such as zeolite [13, 14], bentonite [15], and pumice [16,17] for metal removal also have been widely considered in recent years. Pumice is one of natural pozzolan created by release of gases during cooling and solidification of lava. Pumice has low weight, porous structure and a large surface area [17,18]. The utilization of pumice mainly is for structural applications such as aggregate in light weight concrete, cements, and filters. However, nowadays, pumice also has been used as adsorbent for pollutant removal from water and wastewater [19].

The main objective of this study was to evaluate the ability of pumice from Sungai Pasak, West Sumatera, Indonesia which is available in a great abundance, as byproduct of the process of sand mining in that area, to remove manganese from aqueous solution under different experimental conditions. Batch experiment and isotherm studies were performed in a laboratory scale to determine the adsorption capacity of pumice. The parameters affecting the adsorption process such as dose of adsorbent, contact time, diameter of adsorbent, pH and initial concentration on removal of manganese were studied.

MATERIAL AND METHODS

Preparation of adsorbent

Pumice stone was collected at the riverside of Sungai Pasak, West Sumatera, Indonesia as byproduct of the process of sand mining in that area. It was washed with distilled water several times and dried out at room temperature. The stone was crushed and sieved in order to produce the desired particle size fractions. A scanning electron microscopy (SEM, model S-3400N, Hitachi, Japan) was used to observe the surface morphology of that pumice.

Preparation of reagents

All used chemicals in this study were reagent grade from Merck (Germany). Mn (II) stock solutions were prepared by dissolving manganese (II) sulfate ($MnSO_4.4H_2O$) in distilled water. Either NaOH or HNO_3 were used for adjusting pH of the solutions to the desired values.

Batch adsorption experiments

Batch adsorption experiment was carried out at room temperature (20-25°C) by varying dose of adsorbent, contact time, diameter of adsorbent, pH and initial concentration. In each experiment 100 ml of manganese solutions was contacted with pumice in an erlenmeyers and gently agitated at 100 rpm. After a period of time, the mixture was filtered by using Whatman's filter paper no 42 and the concentration of manganese in the filtrate was determined by atomic absorption spectrometry (Rayleigh WFX 320, China). The amount of Mn ion adsorbed by the pumice was obtained as the difference between the initial and final concentration of the solutions. All experiments were repeated three times, and results presented are consequently the averaged values of replicate tests. The adsorption capacity of manganese adsorbed (qt, mg/g) at any time, t or the Mn uptake on pumice was calculated by the following mass-balance equation:

$$qt = \frac{C_0 - C_t}{W} \times V \qquad (1)$$

where C_0 is the initial concentration of Mn (mg/L), C_t is the equilibrium concentration of Mn (mg/L), V is the volume of the solution (L), and W is the mass of the pumice (g).

RESULTS AND DISCUSSION

Pore structure of Pumice from Sungai Pasak, West Sumatra, Indonesia

Analysis of surface morphology on pumice from Sungai Pasak was conducted using SEM analysis. Figure 1. shows the SEM micrograph of pumice. The image indicated that the pumice had a highly porous, smooth surface, cellular and irregular texture with larger cavities, which provides suitable sites for adsorption.

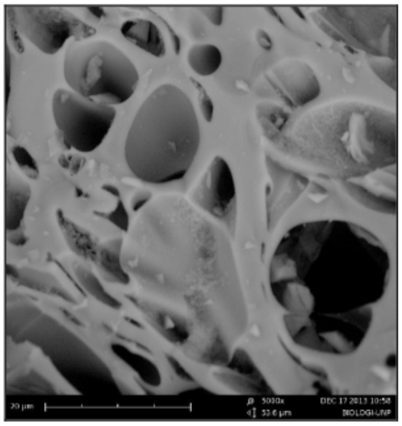

FIGURE 1. SEM micrograph of pumice from Sungai Pasak, West Sumatra, Indonesia

Effect of Adsorbent Dose

To obtain the optimum amount of pumice required for the removal of manganese, the study on the effect of adsorbent dose is needed. Figure 2 shows the effect of the pumice dose (0.3 – 30 g/L) on the adsorption of manganese from aqueous solution. The results revealed that the manganese uptake increased as the adsorbent dose decreased. The agglomeration of adsorbent particles may occur at high adsorbent dose that reducing the available external surface area, strong limitations of Mn species mobility in the adsorption medium and leaving some binding sites unsaturated [20-22]. A maximum adsorption uptake at equilibrium of 117 mg Mn/g was obtained for a pumice dose of 0.3 g/L. Therefore, 0.3 g/L of adsorbent dose was determined to be the optimum dose in this study and above all the following experiments were carried out with this dose.

Effect of Contact Time

The effect of contact time on manganese adsorption onto pumice is shown in Fig. 3. Since it may influence the adsorption process of metals in a medium, the contact time is one of the important factors in adsorption. It was observed that the Mn uptake increased with increase in contact time up to 90 min. At this time, Mn uptake reached 120 mg Mn/g. However, at 120 and 150 min of contact time, the Mn uptake decreased to 110 and 94 mg Mn/g. Therefore, the optimum contact time was selected as 90 min for further experiments. A large number of vacant surface sites of pumice that available for adsorption resulted the increasing Mn uptake during the initial stage of sorption. After an interval in time, due to repulsive forces between the solute molecules on the adsorbent surface and the bulk phase, the remaining vacant surface sites of pumice were occupied [23].

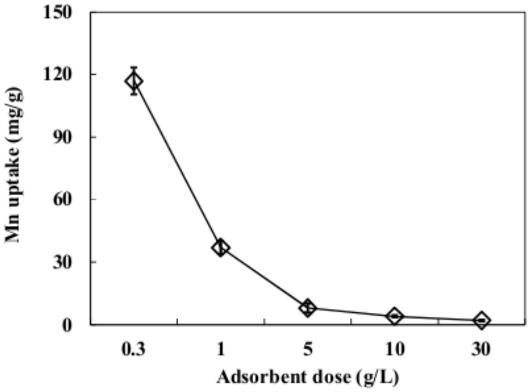

FIGURE 2. Effect of adsorbent dose on adsorption capacity of manganese onto pumice (manganese concentration: 5 mg/L; pH: 8; diameter of adsorbent: <149 µm; contact time: 30 min).

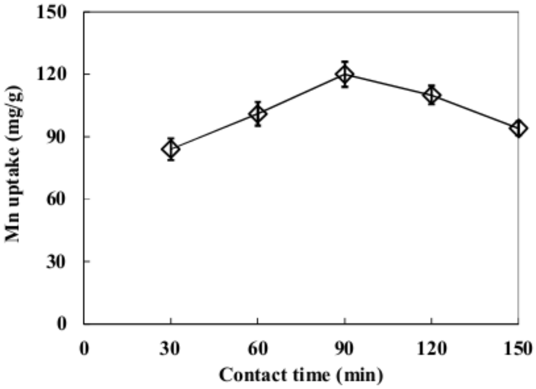

FIGURE 3. Effect of contact time on adsorption capacity of manganese onto pumice (manganese concentration: 5 mg/L; pH: 8; diameter of adsorbent: <149 µm; adsorbent dose: 0.3 g/L).

Effect of Diameter of Adsorbent

The particle sizes of adsorbent could be important factor to control the adsorption process. In this study, 5 variations of diameter of adsorbent representing the variation of particle size of adsorbent were applied to study their effect on the adsorption of manganese onto pumice. As shown in Fig. 4, the increasing in the diameter of adsorbent resulted the decreasing in Mn uptake. The Mn uptake was decrease from 136 to 95 mg Mn/g as diameter of adsorbent increase from <149 to 595-707 µm. It indicated that the adsorption capacity depends on the size of adsorbent; as the diameter of adsorbent decreases, the adsorption capacity increases due to the wider exchange surface provided for the adsorption of the manganese ions. The smallest diameter of the 5 variation, <149 µm was defined as the optimum diameter of adsorption and were applied for the further experiments.

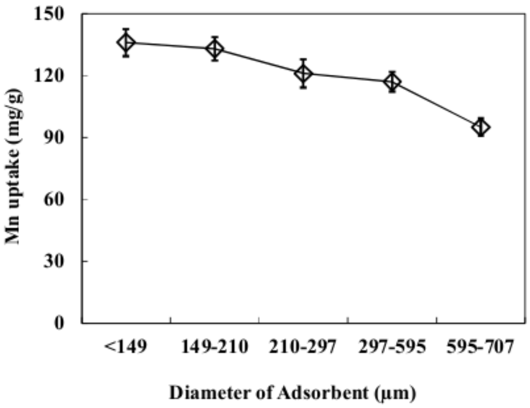

FIGURE 4. Effect of diameter of absorbent on adsorption capacity of manganese onto pumice (manganese concentration: 5 mg/L; pH: 8; adsorbent dose: 0.3 g/L; contact time; 90 min).

Effect of pH

pH of the initial solution is an important parameter to be identified in the adsorption process because it can affect the surface charge of adsorbent, the solubility of metal and the competition of metallic ions. Therefore, differences in initial pH directly may affect the competitive ability of hydrogen ions with metal ions for the active sites on the adsorbent surface [24]. In this study, the effect of pH on the adsorption of manganese onto pumice was studied at pH 4-8 and the results are given in Fig. 5. At the range of pH studied, the maximum uptake of Mn was obtained at pH 4 (143 mg Mn/g). The increasing of pH to 8 gradually decreased the Mn uptake to 124 mg Mn/g. Thus, the optimum pH for adsorption of Mn onto pumice was observed at pH 4. At acidic pH, maximum adsorption was obtained. An increase in H^+ ions on the pumice surface at low pH may result strong electrostatic attraction between positively charged pumice surface and manganese ions. However, with increasing pH, the partial hydrolysis of Mn(II) ions might be occurred and formed the complexes with OH^- such as $Mn(OH)^-$, $Mn(OH)_2$, $Mn_2(OH)_3^+$, $Mn_2OH_3^+$ and $Mn(OH)_4^{2-}$ species in solution [25]. Mn hydroxyl species may take part in the adsorption and/or precipitation onto the adsorbent structure. The maximum Mn uptake was found at pH 4 and accordingly it was taken as the optimal pH value for further experiments. Similar finding on pH trend has been reported in study of manganese removal from aqueous solutions by adsorption on activated carbon derived from *Ziziphus spina-christi seeds* [26].

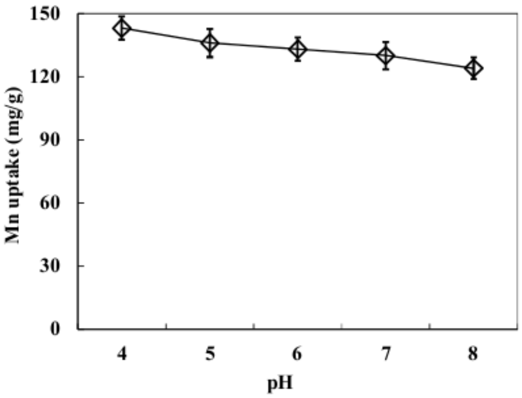

FIGURE 5. Effect of pH on adsorption capacity of manganese onto pumice (manganese concentration: 5 mg/L; adsorbent dose: 0.3 g/L; contact time: 90 min; diameter of adsorbent: <149 µm).

Effect of initial concentration

The initial concentration's effect on manganese adsorption onto pumice was investigated in the range 2-6 mg/L and is shown in Fig. 6. It was observed that as the initial concentration increased, the uptake of Mn also increased. As the concentration was increased from 2 to 6 mg/L, the Mn uptake increased from 52 to 171 mg Mn/g. The results indicated that higher initial concentration of manganese can enhance the adsorption process and the interaction between manganese and pumice as adsorbent, resulting to the higher adsorption capacity of manganese. This is due as the initial concentration increases, the driving force of concentration gradient will increase as well. The result is consistent with the finding by other researchers [11, 12, 26].

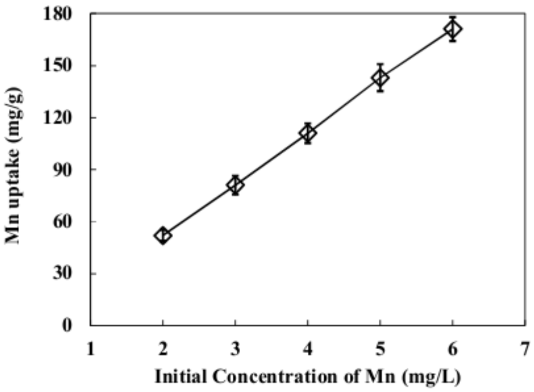

FIGURE 6. Effect of initial concentration on adsorption capacity of manganese onto pumice (adsorbent dose: 0.3 g/L; contact time: 90 min; diameter of adsorbent: <149 µm; pH: 4).

Adsorption Isotherm Models.

An adsorption isotherm describes the equilibrium relationship between the concentration of adsorbate on the adsorbent surface and its concentration in the liquid phase at a given concentration. The adsorption isotherm could give information on the maximum capacity of the adsorbent or the amount needed to remove a unit mass of pollutant under the system conditions. In this study, Freundlich and Langmuir adsorption isotherm models were used to describe the obtained equilibrium data. Those models were applied to study of the adsorption isotherms of manganese onto pumice.

The Freundlich model assumes a heterogeneous adsorption surface and active sites with different energy [28]. Freundlich model is represented by the following equation:

$$q_e = K_F C_e^{1/n} \tag{2}$$

The linearized logarithmic form of the equation is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

Where K_F is the Freundlich constant that interprets the relative adsorption capacity of the adsorbent and the empirical parameter $1/n$ implies the adsorption intensity. Stronger interaction between the adsorbent and heavy metal was defined by smaller value of $1/n$, while $1/n$ values exist between 0 and 1 showing the identical adsorption process and adsorption energies for all sites.

For the Langmuir model, the adsorption assumes to occur on a homogenous surface and the atoms or ions form a monolayer on the adsorbent surface without any interaction between adsorbed ions [27]. This model is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \tag{4}$$

where C_e is the equilibrium concentration of Mn solutions (mg/L), q_e is the equilibrium concentration of Mn on the adsorbent (mg/g), q_{max} is the maximum adsorption capacity of the adsorbent (mg/g), and K_L is the Langmuir adsorption constant (L/mg).

To evaluate whether an adsorption process is a thermodynamically favorable process or not, the value of essential characteristics of the Langmuir isotherm (R_L), which is a dimensionless constant, is often used. If $R_L > 1$, the adsorption is an unfavorable; when $R_L = 1$, the adsorption is a linear; when $0 < R_L < 1$, the adsorption is a favorable and when $R_L = 0$, it should be an irreversible adsorption. The R_L is measured by using the equation (5) as below:

$$R_L = \frac{1}{1+K_L C_0} \quad (5)$$

Figure 4a shows the Freundlich isotherm model which was found by plotting log q_e against log C_e values. From this plot the values of the correlation coefficient (R^2) was obtained to be 0.975 for manganese adsorption onto pumice. For the Langmuir isotherm which was generated by plotting C_e/q_e against C_e values, the R^2 was 0.879 (Fig. 4b). The values of R^2 are considered a measure of the goodness of-fit of the experimental data to the isotherm models. The result showed that the Frendlich isotherm model fitted well with the equilibrium data as it presents higher R^2 value than that of the Langmuir isotherm. It indicated that the adsorption of manganese onto pumice is multilayer sorption and the adsorption occurred on the heterogeneous surface of pumice and the active sites of pumice have different energy, as the Freundlich isotherm model's assumption. Data in Table 1 show that from the both isotherm model calculation, for the Langmuir model, the maximal value of adsorption qmax was negative, which reflects the inadequacy of this model for explaining the adsorption process [29]. From the Freundlich isotherm model, the adsorption of manganese onto pumice from Sungai Pasak resulted 232.65 mg Mn/g of K_F as adsorption capacity and 0.559 of $1/n$ indicating stronger interaction between the pumice and manganese, while $1/n$ values exist between 0 and 1 suggesting the identical adsorption process and adsorption energies for all sites.

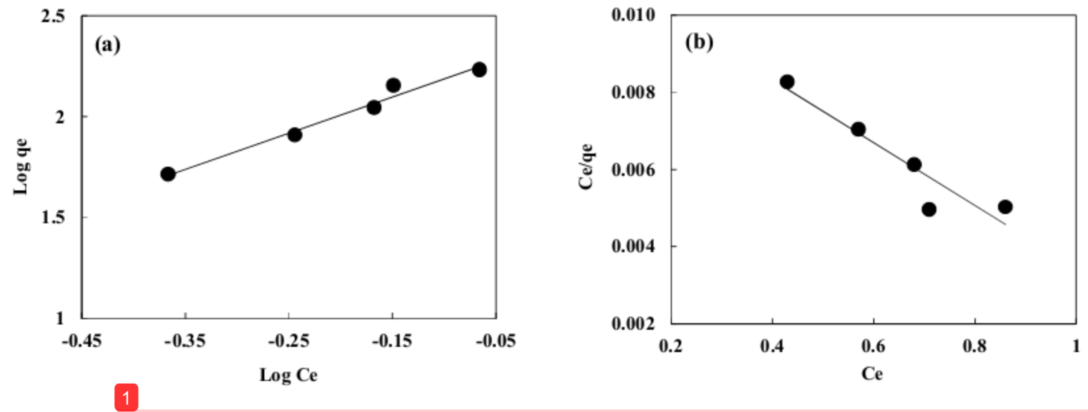

FIGURE 7. Freundlich (a) and Langmuir (b) isotherm plots for the adsorption of iron onto maize husk (iron concentration: 1-10 g/L; adsorbent dose: 20 g/L; contact time: 60 min; pH: 4)

TABLE 1. Parameters of the Freundlich and Langmuir models for adsorption of manganese onto pumice

Freundlich isotherm model			Langmuir isotherm model		
K_F (L/g)	$1/n$	R^2	K_L	q_{max} (mg/g)	R^2
232.65	0.559	0.975	-0.707	-121.95	0.879

CONCLUSION

Pumice from Sungai Pasak, West Sumatra, Indonesia, which is available in a great abundance, as byproduct of the process of sand mining in that area, was demonstrated to become an alternative low-cost adsorbent for the removal of manganese in water. The pumice had a highly porous, smooth surface, cellular and irregular texture with larger cavities, which provides suitable sites for adsorption. In batch mode studies, adsorption was dependent on adsorbent dose, contact time, diameter of adsorbent, pH and initial manganese concentration. The optimum condition of manganese removal by pumice were 0.3 g/L of adsorbent dose, 90 min of contact time of adsorption, <149 µm of particle size, 4 of pH solution and 6 mg/l of Mn concentration with 171 mg Mn/g pumice of adsorption capacity. The result revealed that the Freundlich isotherm model fitted well with the equilibrium data within the concentration range studied as it presents higher R^2 value than that of the Langmuir isotherm. It indicated that the adsorption of manganese onto pumice is multilayer sorption and resulted 232.65 mg Mn/g of K_F as adsorption capacity and 0.559 of $1/n$ indicating stronger interaction between the pumice and manganese. Overall study revealed that pumice from Sungai Pasak may be a promising adsorbent for manganese removal from groundwater or other polluted waters.

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