

Dynamic Removal of Toxic Metals from Wastewater using Perlite as Sorbent

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Expanded perlite has been used as an adsorbent for the effective removal of chromium, cadmium, copper and zinc from laboratory wastewater. The percent removal of toxic metals investigated at pH 6 were in the range of 75-90 % for Cr(III), Cu(II) and Zn(II). While Cd(II) could be removed from aqueous solution around 75 % at pH 7-8. Diverse metal ions, *i.e.* Cr(III), Zn(II) and Cd(II) could significantly reduce the Cu removal at concentration ratio 1:4 for Cu:Cr, 1:6 for Cu:Zn and Cu:Cd. Sorption capacities are 29.7, 23.5, 27.3 and 24.7 mg/g perlite for Cr(III), Zn(II), Cu(II) and Cd(II), respectively. Desorption of metal ions from adsorbent were in the range of 83-99 % at pH 1. All the metal ions concentration was measured using atomic absorption spectrophotometric detection. Application of the proposed method was successfully demonstrated using the laboratory wastewater.

Key Words: Adsorbent, Toxic metal, Wastewater, Perlite.

INTRODUCTION

Toxic metals are now-days amount among the most important pollutant in source and treated waters had been subject of research in environmental sciences¹. Heavy metals contained wastes resulting from the industrial and mining activities may be deemed to pose a hazard to human health and the quality of the environmental it self².

To remove toxic heavy metals pollution from wastewater, processes for wastewater treatment need to be developed. Chemical precipitation and liquid-phase sorption has been shown to be an effective technique for removing toxic metals from aqueous stream. However, metals removal in the precipitation-coagulation system does not generally allow strict regulating requirement to be met. In the last few years, adsorption technique has been shown to be an economically feasible alternative method for removing and pre-concentration trace heavy metals from wastewater and other waters^{3,4} and or synthetic ion-exchanger resin are effective for treatment of wastewater and have been the most used adsorbent because of its have a high capacity for the adsorption of toxic pollutants⁵⁻⁷. However, its use is limited due to it is relatively high costs. This has led to the investigation of alternative technologies, which consider

low cost beside their abilities as adsorption material^{4,8,9}. For this purposes, biosorbent from biological materials have been tried with varying success for toxic pollutant removal¹⁰⁻¹².

The potential geosorbent such as perlite was received many attentions for the industrial purposes. Perlite is inexpensive and easily available in West Sumatra Province, Indonesia, This could make it a viable candidate as an economical adsorbent for removing heavy metals from wastewaters.

Perlite is a glassy volcanic rock, commonly light gray, with a rhyolitic composition and 2 to 5 % combined water. When heated quickly at temperature ranges from 800 to 1,100 °C will expand or “pop” up to 30 times of its original volume, forming a lightweight frothy material. The uses of expanded perlite are many and varied based primarily upon its physical and chemical properties. The main function of perlite are used for aggregate plasters, insulate storage vessels for liquefied gas, rooting medium and soil conditioner, carrier for herbicides, insecticides and chemical fertilizers, food processing and pharmaceutical manufacturer, filler or extender in paints, enamels, glazes, plastics, resins, rubber and agent in mixture for oil well cementing¹³⁻¹⁵. As most of perlite have a high silica contain *i.e.*, 71-80 % and adsorptive, perlite are chemically inert in many environments and hence are excellent material for adsorption of toxic metals in waste water. Unfortunately, few articles^{16,17} are cited for the use of perlite as an adsorbent in the literature. The present work describes the capabilities of the expanded perlite to remove toxic heavy metals present in wastewater.

EXPERIMENTAL

Obsidian ore is collected from Lubuk Basung district of West Sumatra Province, Indonesia. The ore is collected from obsidian mining. The ore collected was then washed with water, milled and grinded. Fine particles of obsidian ore was then introduced into a furnace, that rapidly heats the ore to yield expanded perlite. The expansion process produces a material that can weight as little as 30 kg/m³, has high surface area and white colour. The expanded perlite was then ground and screened to particle size of within the range of 150-450 µm using octagon 200 screen.

All reagents employed in this work were of analytical reagent grade or better, and obtained from E. Merck (Darmstadt, Germany), unless otherwise noted. Activated carbon is used for the validation of metal ions sorbed by present geo-material. Aqueous standard solution of metal chlorides, namely Cr(III), Zn(II), Cd(II) and Cu(II) were prepared from the stock solution containing 1,000 mg/L of each metal and obtained from Wako Pure Chemical Co. (Osaka, Japan). Cr(VI) was in form of K₂Cr₂O₇. Column experiments were conducted in glass tube (10 mm × 150 mm). All metal ions concentration was analyzed by using atomic absorption spectrophotometer (Model Alpha 4, Ana lab, England).

Absorption behaviour: 2 g of expanded perlite was inserted into the column made of glass tube (10 mm × 150 mm). Water was then slowly added to wet the

packing and then conditioned with the eluent to appropriate of pH. The heavy metal solution having a 10 mg/L concentration of metal ion was passed through the column at the optimal pH. The initial and final concentration of heavy metal ion is determined.

The procedure for the investigation of diverse metal ions area as follows: 10 mg of Cu(II) ion is mixed with each metal ions interfere at concentration ratio 1:0 to 1:10. 10 mL of mixed solution was then flowing to the column as described above.

Desorption behaviour: After the sorption process was completed, the adsorbed metal ions were desorpted with diluted mineral acid at various pH. The metal ions concentration is determined as describe above.

RESULTS AND DISCUSSION

Effect of particle size on the sorption efficiencies: The chemical composition of Indonesian perlite is given mainly composed of silica as SiO_2 (72.2-76.7 %), aluminium as Al_2O_3 (13.5-16.9 %), potassium as K_2O (3.7-5.8 %) and sodium as Na_2O (3.2-4.8 %). Varying amounts of other minor oxides and few elements made up remaining composition. Expanded perlite is inert, non-combustible and has low moisture absorption characteristics. The surface of hydroxyl groups on perlite namely hydrous metal oxides contribute for its adsorption capacity. Since the major element of perlite is silica and alumina, it is useful to review the surface of silica and alumina hydroxyl on the perlite. The silicon atoms at the surface tend to maintain their tetrahedral coordination with oxygen. They complete this coordination at room temperature by attachment to monovalent hydroxyl groups, forming silanol groups. Therefore, it is possible to use a pattern in which on silicon atom bears two or three hydroxyl groups, yielding silanediol and silanetriol groups, respectively.

The type of silanol groups are: silanol groups, $-\text{SiOH}$; silanediol groups, $-\text{Si}(\text{OH})_2$ and silanetriol groups, $-\text{Si}(\text{OH})_3$. Moreover, the hydrous oxide surface groups in alumina^{13,18} are as follows : $-\text{Al-OH}$ or $\text{Al}-(\text{OH})_2$.

The ion exchange capacities much depends on the surface activity, in particular specific surface area available for solute-surface interaction, which is accessible to solute. Consequently, it is expected that the ion-exchange capacity increase with increasing surface area of adsorbent. The rate of exchange is generally controlled by the rate of ion diffusion within the particle and this is related to the size of particles. In the previous experiment¹⁹, it was found that porous silica gel having a small pore size, *i.e.*, 3 nm with the specific surface area 704 m^2/g , gave the best resolution for the separation of cations. As expanded perlite has a big portion of silica content (72.2-76.7 %), it was assumed that the ion-exchanged much depends on silica, *i.e.* silanol groups. The effect of particle size on the sorption capacities has been carried out by using various sizes *viz.*, 150, 180, 250 and 425 μm . The result is shown in Fig. 1. From the figure it seen, that for all metal ions examined, the increase of particle size will decrease the percentage of metal uptake of metal ions investigated, namely Cr(III), Zn(II), Cd(II) and Cu(II) from 85 % to almost 92 %, except for Cr(VI) ion, where the sorption decreased from 25 to 14 %. For this, 150 μm of the particle size was selected for the experiment described below.

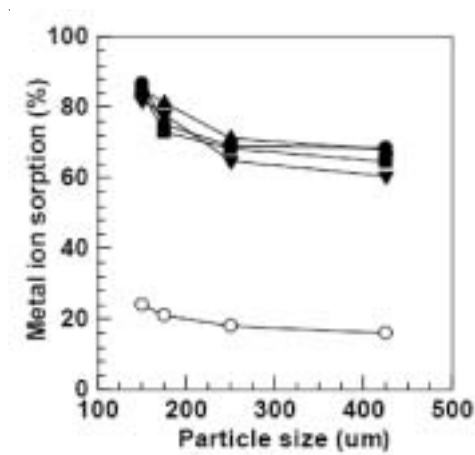


Fig. 1. Effect of particle size of expanded perlite on metal ion sorption. Initial concentration of metal ions sorbed = 10 mg/L, mass of expanded perlite used = 2 g, solution of pH = 6. ○ = Cr(VI), ● = Cr(III), ▲ = Cu(II), ▼ = Cd(II) and ■ = Zn(II)

Effect of pH on metal ions sorption: It is well known that sorption of metal ions by solid substrates much depends on pH medium. As the perlite sorbent has highly silica contents, it seems that the sorption activity much depends on the silanol site of silica. The acidic properties of silica depend strongly on the nature of the surrounding liquid, while water and aqueous solutions reduce the activity and acidity of the surface sites.

It is expected that owing to the weak acidic properties of the silanol groups, the cation exchange capacity should be a function of the solution of pH. The pH markedly influences not only the dissociation state of the surface groups, but also the hydrolysis of the species to be exchanged. Depending on the pH, metal ions may exist in their non-hydrolyzed or their hydrolyzed form. The ionic strength of the eluent also affects the capacity. The effect of pH on the adsorption of cations on perlite may be explained on the basis of aqua complex formation of the oxides present in the perlite. A positive charge develops on the surface of the oxides of perlite in an acidic medium. A lowering of cation adsorption at low pH is due to the fact that surface charge, thus, developed is not suitable for metal ion adsorption. In an alkaline medium the surface of the perlite becomes negatively charged and thus, favours the adsorption of metal ions.

Fig. 2 shows that increasing of pH, increases the removal of metal ions examined. Metal ions uptake by perlite increases up to around 75-80% for Cr(III), Cu(II) and Zn(II) at pH 6. On the other hand, Cd(II) ion sorption by perlite raises to around 85% at pH 5 and 81% at pH 6. In the present study, an optimum pH of 6.0 was selected for metal ions-perlite system. Moreover, Cr(VI) ion sorption by perlite remains constant, ca. 25% at pH 3 to 7. This may be because the Cr(VI) examined in the form of anion, *viz.*, $\text{Cr}_2\text{O}_7^{2-}$.

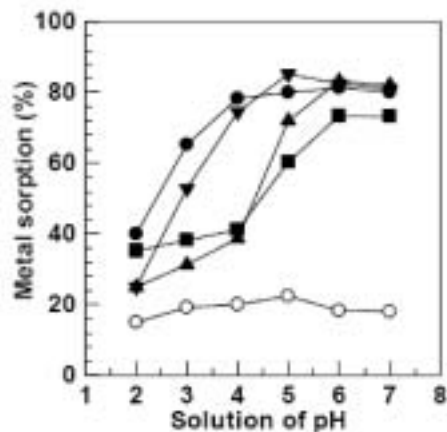


Fig. 2. Effect of the solution of pH on metal ion sorption. Particle size of expanded perlite = 150 μm . Other conditions and symbol as in Fig. 1 except for the solution of pH

Effect of initial concentration of toxic metal ions on the perlite sorption capacities: The initial concentration of Cr(III), Cu(II), Zn(II) and Cd(II) provides the necessary driving force to overcome all mass-transfer resistance of metals between the aqueous and solid phases. Hence, a higher initial metal concentration will have a benefit effect on the perlite sorption capacity. Such an effect is clearly shown in Fig. 3. From the figure it seen that the equilibrium sorption capacity seems to increase essentially linearly with an increases in the initial metals concentration. In this case, the distribution of the solute, *i.e.*, Cr(III), Cu(II), Zn(II) and Cd(II) metal ions between the liquid phase and solid phase can be described by several mathematical relationships such as the standard Langmuir model^{20,21}. The Langmuir model assumes mono layered coverage and constant sorption energy without interaction between sorbed molecules. The Langmuir isotherm can be represented as:

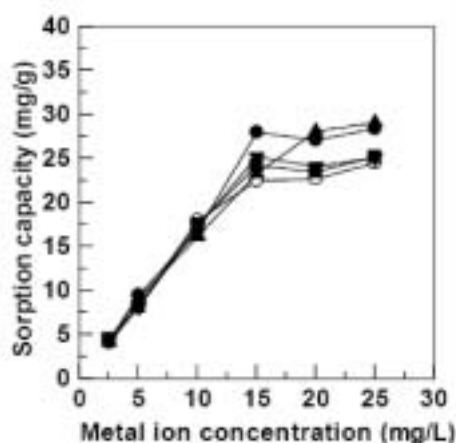


Fig. 3. Effect of metal ion concentration on metal ion sorption. Particle size of expanded perlite = 150 μm . Other conditions as in Fig. 1 except for the metal ion concentrations

$$Ce/Ne = 1/N^*b + Ce/N^*$$

where C_e is the concentration of metal ion (mg/L) at equilibrium, N_e is the amount (mg/g) of metal ion sorbed by perlite at equilibrium, N^* is the asymptotic maximum sorption of the metal ion-perlite system and b the Langmuir constant related to the energy of sorption (L/mg). Linear plot of C_e/Ne vs. C_e yielded the parameters N^* and b . From the experimental data for binding metal ions-perlite system, fit the Langmuir isotherm, where the maximum sorption capacities for metal-perlite system is 29.7 mg for Cr(III), 23.5 mg for Zn(II), 27.3 mg for Cu(II) and 24.7 mg for Cd(II) per g perlite.

Effect of diverse metal ions on sorption behaviour: The effect of diverse metal ions on the sorption behaviour was investigated. Different metal ions have the different ionic strength on the binding site competition, which can affect the sorption behavior of metal ion target. For this experiment Cu(II) metal ion was chosen as the model, while other metal ions, *i.e.*, Cr(III), Zn(II) and Cd(II) as the ion interference. In this case the Cu(II) concentration and the solution of pH were kept constant at 10 mg/L and 6, respectively. While other metal ions interfere were varied with the ratio between Cu(II) and metal ion interfere from 1:1 to 1:10. The result showed in Fig. 4. From the figure, it is seen that no metal ions interference on the binding site competition with Cu(II) up to the concentration ratio 1:2 for all metal ions interferences. On the other hand, at concentration ratio 1:4 for Cr(II) and 1:6 for Zn(II) and Cd(II), the Cu(II) ion removal from solution was reduced significantly, *i.e.*, 20, 15 and 17 % for Cu(II), Cd(II) and Zn(II) ions, respectively. These results suggest that the metal ions having the same affinity class will have the similar type of binding sites at the perlite surface. However, the strength of binding may differs depended on their atomic weight, concentration, medium of pH, electronegativity and type of binding, which can affect the metal ion sorption competition.

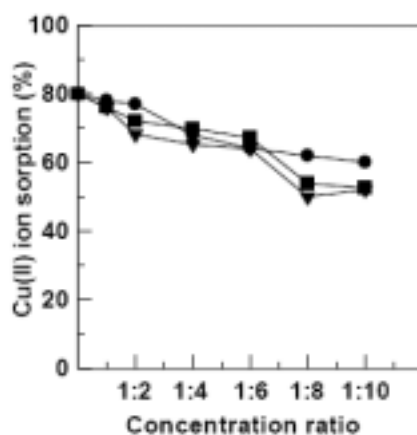


Fig. 4. Effect of diverse metal ion on Cu(II) ion sorption. Particle size of expanded perlite = 150 μ m, solution of pH = 6, symbol as in Fig. 1

Desorption study: Desorption studies help evaluate the mechanism of adsorption and recover metal ions investigated and the adsorbent recycling. The per cent desorption of Cr(III), Cr(VI), Cu(II), Cd(II) and Zn(II) from the spent of perlite adsorbent loaded with 10 mg/L of each metal ions increases from 5, 7, 9, 10 and 15 % at pH 7 to 83, 87, 93, 95 and 99 % at pH 1 for Zn(II), Cu(II), Cd(II) and Cr(III) ions, respectively, as it can be seen in Fig. 5. The desorption studies indicates that ion exchange seems to be important in the adsorption process of metal ions by expanded perlite.

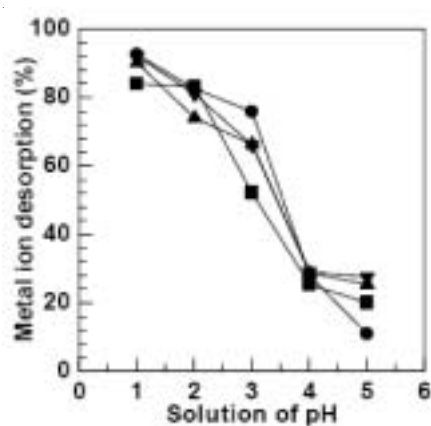


Fig. 5. Effect of solution of pH on desorption on metal ions. Symbol as in Fig. 1

Removal of metals ion from wastewater: In order to verify the capability of the expanded perlite to removal of metal ions in wastewater sample, the present geosorbent was applied to removal metal ions such as chromium, zinc, copper and cadmium present in laboratory wastewater. The sample was filtered and adjusted to pH *ca.* 6 by adding of appropriate volume of buffer solution. The volume sample used is 250 mL and the results obtained are shown in Table-1. The percentages of metal ions removal by the present perlite sorbent were shown a good agreement compared with the commercial activated carbon.

TABLE-1
REMOVAL OF METAL IONS FROM THE LABORATORY WASTEWATER

Metal ion	Concentration found (mg/L)	Metal ion removal (%)*	
		Perlite	Activated carbon
Chromium	3.7	82.5	84.3
Copper	4.5	79.0	80.0
Zinc	4.1	80.3	81.0
Cadmium	3.9	78.6	76.0

In conclusion, the present method could be used to remove toxic heavy metals present in wastewater significantly.

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