ACCUMULATION OF COPPER, CADMIUM AND ZINC BY MOSS IMMOBILIZED ON SILICA GEL

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ABSTRACT

Moss was successfully immobilized on silica substrate and used in adsorption procedure that removed copper, cadmium and zinc from waste water. Several parameters that can affect metals uptake such as particle size, pH and metal ion concentration were described. At the optimal conditions, the copper, cadmium and zinc ions removal from aqueous solutions are 85, 87 and 92 %, respectively. After the adsorption of metal ions, the analyte retained in the moss-silica gel resin could be recovered almost completely by eluting with dilute hydrochloric acid. The method was applied to removal of copper, cadmium and zinc present in the laboratory waste water.

INTRODUCTION

Since the number of health problem associated with environmental contamination continuous to rise, the removal of toxic pollutants such as phenol, ammonia and toxic metals from sewage and industrial waste water has received great attention.

Although carbon adsorption or synthetic ion-exchanger resin are effective for treatment of waste water, they are often unsuitable for the mass removal of toxic pollutant because their cost are rather expensive. This has led to the investigation of alternative technologies, which consider low cost beside their abilities as adsorption material. Therefore, development of low-cost sorbents for this purpose are needed.

The use of biological materials or industrial by product such as apple waste[1], tea leaf[2], coconut husk[3], chitosan[4] and rice husk[5-7] has been investigated to removal heavy metals from waste water. The biosorbent materials has been treated with phosphorus oxychloride[1] or coating with dyes[3,5]. Moreover the use of algae for the sorption and preconcentration of metals has been reported elsewhere[8-10].

Metals uptake by biological materials are believed to occur through sorption process involving the functional groups associated with proteins, polysaccharides, lignin and other biopolimers found in the cell or cell walls[11]. Unlike the conventional ion-exchanger resin, biosorbent materials can contain numerous functionality's including amino, carboxylate, hydroxide, imidazole, sulfate and sulphydryl groups. These polyfunctional biosorbent often exhibit unique metals adsorption abilities. Other advantages of this kind of sorbing is that the can be regenerated or reused.

Recently we have found that moss[12] has potential as biosorbent for removal of toxic pollutant from waste water. Unfortunately, the small diameter of the cells and their lack of rigidity severely restrict the fluent flow and render the column inoperable when gravity feed is employed. Immobilization of moss on or in a support matrix which is more rigid and or is of a larger diameter circumvents this problem. Ramelow and Harris[13] have entrapped alga cells in an ethyl acrylate-ethylene glycol dimethacrylate copolymer. Jeffer et al.[14] have

ISSN : 0853-8018

immobilized peat moss, algae, yeast, and bacteria in polysulfone beads.

We have reasoned that silica would be a good substrate for immobilization because it is relatively inert, is non-compressible, and is available in a variety of sizes. Additionally , the siloxyl groups provide potentials sites for chemical modification for moss attachment. The purpose of this research is to immobilize moss on silica gel, which could be enables the moss to be used as a resin for removal of copper, cadmium and zinc from waste water.

MATERIAL AND METHODS

Chemicals and apparatus

All reagents employed in this work were of analytical reagent grade or better, and obtained from E.Merck (Darmstadt, Germany), unless otherwise noted. Aqueous standard solutions of metal chlorides, namely Cu(II), Cd(II) and Zn(II) were prepared from the stock solution (containing 1,000 mg/L of each metal) and obtained from Wako Pure Chemicals Co. (Osaka, Japan). Column experiment were conducted in glass tube (150 x 10 mm id). Glass wool was inserted at the top to prevent the substrate from floating. All metal ions concentration were analyzed by using Anal. Tech. model Ana-Lab atomic absorption spectrophotometer.

Treatment of moss

Moss were washed with an excess of pure water, dried at room temperature for a day. Then ground and screened to within the particle range of 150 – 500 µm. To remove the trace amounts of metal ions indigenous to moss, 10 g of moss particle is rinsed with 25 mL of 1% hydrochloric acid, and then washed with 50 mL of pure water. After the washing solution is discarded, the moss particle was dried at room temperature for 1 day before used.

Immobilization procedure

Approximately 10 g of the treated moss particle is mixed with 20 g of silica gel. All materials were dried at 105 °C for 20 min prior to weighing. The mixture was wetted with a minimal amount of water and thoroughly mixed. The resulting paste was heated in an oven and 105 °C for 20 min to drive off the water. The wetting and drying step was repeated to maximize the contact between the moss and silica surface, thereby improving the immobilization efficiency. The silica-moss briquette was removed from the oven allowed to cool and gently broken apart using a spatula to regain the original particles.

Procedure for column adsorption studies

3 g of treated moss-silica gel resin was inserted into the column made of glass tube. Water was then slowly added to wet the packing. The copper, cadmium and zinc metals solution having a known concentration of metal ion was passed through the column. The initial and final concentration of metal ion is determined.

The procedure for removal of metal ions from waste water is as follows : 1 L of waste water sample is flowing into the column experiment. The flow rate of sample inserted to the column and the flow rate of the eluate were controlled to be the same. The initial concentration of metal ions present in waste water and the final concentration after the column was determined as described above.

After the adsorption was completed, the adsorbed metal ions were eluted with diluted.

RESULTS AND DISCUSSION

Effect of the particle size on metal ion adsorption

The adsorption capacity of moss-silica gel resin strongly depends on the surface activity, viz., specific surface area available for solute-surface interaction, which is accessible to the solutes. Consequently, it is expected that the adsorption capacity increases with increasing surface area of the moss-silica gel resin. This means that sorption materials having a larger surface area, in other words, smaller particles, could adsorb more metal ions.

Figure 1 shows the percentage of metal ions uptake versus the particle size of moss immobilized silica gel. When the particle size of the resin was changed from 150 to 500 µm, the increase in particle size decreases the percentage of metal ions sorption by the resin from 85% to nearly 40% for all metal ions investigated. Therefore, 150 µm was selected as the particle size of the husk for the following experiments.

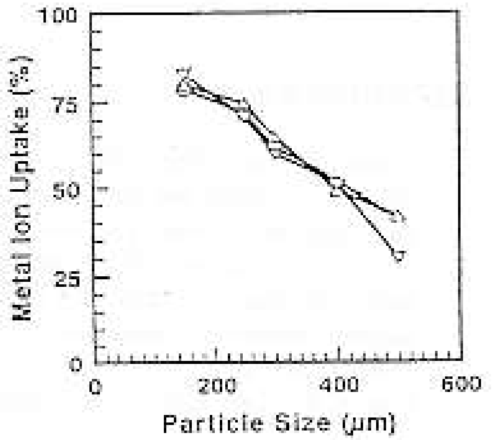

Figure 1. Effect of particle size of the moss-silica gel resin on metal ion adsorption. △ = Cu(II) ; ▽ = Cd(II) and O = Zn(II)

Effect of pH on metal ion adsorption

It is well-known that adsorption of heavy metal ions onto solid substrates much depends on pH values of the solution. Figure 2 shows the effect of pH on copper and cadmium and zinc adsorption onto the moss-silica gel.

As can be seen in Figure 2, the moss-silica gel resin showed favorable sorption properties in the pH range of 4.5 to 6.5. The acidity of the solution influenced both the stability of aqueous metal ions and surface binding of the resin. At low pH values (smaller than 4) the surface of the sorbent is surrounded by the hydronium ions (H_3O^+), which would prevent the metal ions, e.g., copper(II), cadmium(II) and zinc(II), from reaching the binding sites of the sorbent owing to the repulsive forces. The uptake increased with increasing pH up to the point (around pH 6.5) where the metal ions investigated precipitated. In the optimum range from 4.5 to 6.5 maximum uptake of copper(II), cadmium(II) and zinc (II) ions by the moss-silica gelresin were 75, 70, 79 and 80%, respectively. For this reason pH 5.5 was selected as the optimum.

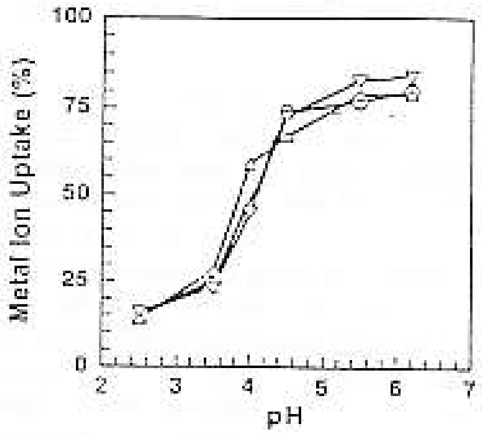

Figure 2. Effect of pH on the metal ions adsorption. △ = Cu(II); ▽ = Cd(II) and O = Zn(II).

Metal ion elution

Dilute hydrochloric acid and nitric acid could elute the metal ions retained on the column. The adsorbed copper(II), cadmium(II) and zinc(II) ions eluted with 0.1 M HCl or 0.1 M HNO_3. Fractions of the effluent were collected and analyzed by FAA. These elution tests were performed in duplicate on new columns of the resin. The results suggest that HCl have a greater eluting efficiency than HNO_3. Quantitative recovery of the metal ions of copper(II), cadmium(II) and zinc(II) eluted by using 0.1 M HCl are 93, 95, 94 and 98%, respectively. On the other hand, the recoveries obtained by using 0.1M HNO_3 were 75, 79, 81 and 85%, respectively.

Removal of metal ions from wastewater

In order to verify the capability of the moss-silica gel resin for removal metal ions in wastewater sample, the present method was applied to remove copper, cadmium and zinc ions present in laboratory wastewater. The sample was filtered and the pH was adjusted to approximately 5.5 by adding appropriate volume of sodium hydroxide solution. The volume of sample used is 1L. The results obtained are shown in Table 1.

Table 1. Removal of toxic metals from the laboratory wastewater.

Metal ion	Concentration (mg L^{-1})		Metal uptake (%)
	Original	Effluent	
Cu(II)	1,90	0.86	55
Cd(II)	2.40	1.20	50
Zn(II)	1.60	0.64	60

As can be seen in the table, the percentage of copper, cadmium and zinc ion removal from real wastewater sample were 55, 50 and 60%, respectively. These removal efficiencies seem to be less than those obtained by using the standard single metal ions. The reason may be due to the possibility of mutual competition of the metal ions for the adsorption sites. This is because the amount of ions adsorbed would depend on the ionic size, the stability of the metal ion-resin bonding, nature of metal ion-resin interaction and the distribution of the reactive groups on the resin.

In conclusion, the moss-silica gel resin could be used as a potential biosorbent for the removal of toxic metals from wastewater. However, the possibility of metal ion competition for adsorption sites needs to be assessed.

Acknowledgements

The author wishes to thank Indonesia Toray Science Foundation (ITSF) for the research grant offers (ITSF research grant 1997) which make this research feasible.

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