Recovery of Metals from Acid Mine Drainage Using Organic Polymer

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Abstract

Metal recovery efficiency of chitosan was investigated in order to prepare “mixed” gelatin hydrogels including some organic solids with a high metal adsorption capacity. At pH 5, 0.1 g of chitosan recovered approximately 90 % of Cu from 50 mL of the simulated solution. Cu recovery using chitosan was affected by pH. At relatively higher pH (>3.0), over 90 % of Cu recovery was maintained. In contrast, lower Zn was recovered in comparison with Cu. Mn recovery was hardly detected within the pH range of 2-5. From these results, it was considered that “mixed” gelatin hydrogel blended with chitosan had a potential for the high-peformance adsorbent for Cu recovery.

Keywords: acid mine drainage, adsorption, natural organic polymer

Introduction

Acid mine drainage (AMD) is a serious environmental pollution issue in the mining industry. Some materials including accumulated mining waste, flotation tailings and unmined minerals, etc. often cause the AMD. The generated AMD can have an extremely acidic pH and contain various metal ions (Fe, Cu, Pb, Zn, etc.). Besides, the AMD generation continues even if mining operation is closed. Thus, such AMD pollution issue is also very serious for Japan where almost all mines have already been closed. In order to prevent such ecological threat due to AMD flowing out of the mine area, the AMD should be treated by removal of the contained hazardous metals. A neutralization process is generally applied to the AMD treatment. It is a very effective treatment process because the hazardous metals can be removed from the AMD as hydroxides while a strong acidic pH is adjusted by alkaline chemicals. This neutralization method contributes to reduction of the environmental impact due to the AMD. But, generated metal sludge is sent to repository sites without any reutilization of the metals in many AMD treatment sites. Because the AMD often contains some valuable metals, to use the AMD as a source of metals is desirable for some countries which is poor in metal resources.

Adsorption is one of the effective techniques for recovery of metal ions from water. Recovery and separation of metals by adsorption can achieve both purification of the AMD and metal recovery. Some research topics related to metal removal by adsorption have been reported (Patila et al. 2016). Especially, we are focusing attention on metal recovery using natural organic polymers such as proteins or sugars. And we have investigated a novel adsorbent prepared from using gelatin, a fibrous protein, for recovery of cationic metal ions from AMD (Bessho et al. 2017). In previous study, it was confirmed that alkaline-extracted gelatin hydrogel could had a potential for recovery of some metals from aqueous solutions. But, the Cu recovery efficiency was not sufficient. Generally, increase in the number of adsorption sites will lead to the improvement of adsorption capacity of the gelatin hydrogels. There are some approaches to development of the gelatin hydrogel having an excellent adsorption capacity of Cu. These approaches includes 1) addition of polar groups to gelatin by chemical modification, 2) preparation of "hybrid" gels with gelatin and other organic compounds and 3) preparation of "mixed" gelatin hydrogels including some organic solids. Considering the simplicity of the hydrogel adsorbent, preparation of the "mixed" gelatin hydrogel is much suitable. Besides, such a "mixed" hydrogel can prevent solid dispersion in liquids.

Thus, chitosan were selected as a natural organic compound to include in gelatin hydrogels. Chitosan is a nitrogenous polysaccharide composed mainly of poly (β-1-4)-2-amino-2-deoxy-d-glucopyranose, and a suitable natural organic polymer as an adsorbent for metal ions due to the presences of the amino and hydroxyl groups (Chatterjee et al. 2005). Chitosan is usually produced through the deacetylation of chitin, a long-chain polymer of N-acetylglucosamine, which composes the carapace or shell of a shrimp or a crab. Possibly, chitosan adsorbents can be produced from food waste. In this study, Cu, Zn and Mn aqueous solutions were prepared as a model solution for AMD. And then, we investigated the basic adsorption behavior of these metal ions to chitosan.

Methods

Materials

As an adsorbent material for metal recovery, chitosan with medium molecular weight was purchased from Sigma-Aldrich Japan Co., Japan. This chitosan sample had a shape of powder and/or chips, and then was used without any purification.

In this study, three kinds of simulated metal solutions were used. Two millimolar of copper, zinc and manganese were prepared from copper sulfate pentahydrate ($CuSO_4.5H_2O$), zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) and manganese sulfate pentahydrate ($MnSO_4.5H_2O$), respectively. These sulfates were purchased from Wako Pure Chemical Industries, Ltd., Japan. Solution pH was, as needed, adjusted to given pH by H_2SO_4 solutions (Wako Pure Chemical Industries). For metal recovery test, 2 mM of simulated Cu solutions at various pHs were mainly used. The simulated Zn and Mn solutions were used to estimate the effect of metal species on recovery of metals using chitosan.

Metal recovery test using chitosan samples

Adsorption tests for a metal recovery using chitosan were mainly performed at room temperature, using the following procedure. After prescribed volumes (10-200 mL) of each simulated solution containing 2 mM of the metal at different pHs was poured into a glass beaker, 0.1 g of chitosan was introduced into the simulated metal solution. The simulated solutions with the chitosan samples were stirred with a magnetic bar for the predetermined time.

Quantitative analysis of metals in solutions

For a quantitative analysis, simulated metal solutions were filtrated through a 0.45 μm mesh membrane filter after the recovery tests. Copper, zinc and manganese concentrations in the filtered solutions were measured by inductively-coupled plasma optical emission spectrometry (ICP-OES, SPS 5510, Seiko Instruments Inc., Japan). Based on results of the ICP analysis, the amount or rate of metal recovery were calculated.

Results

Recovery capacity of Cu using chitosan samples

Figure 1 shows change in the Cu concentration after adding 0.1 g of chitosan to 10 mL of simulated solution at pH 5. This result revealed the Cu concentration drastically decreased just after addition of chitosan. It took about one hour to recover almost all copper from the solution. To estimate the efficiency of Cu recovery by chitosan, the Cu recovery tests were conducted by changing the volume of the simulated solutions. Figure 2 shows the effect of solution volume on recovery of Cu at pH 5. Closed circles and recltangles represent Cu concentration in the simulated solutions and Cu recovery rate, respectively. Initial Cu concentration corresponds to approx. 130 mg/L. In case of 50 mL of the solution volume, over 90 % of Cu could be recovered from the solution. The Cu concentration finally decreased to approx.

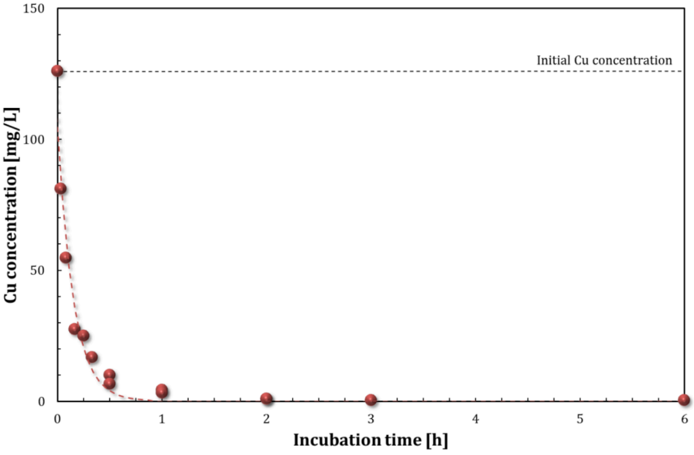

Figure 1 *Time course of the Cu concentration after adding 0.1 g of chitosan to 10 mL of simulated solution.*

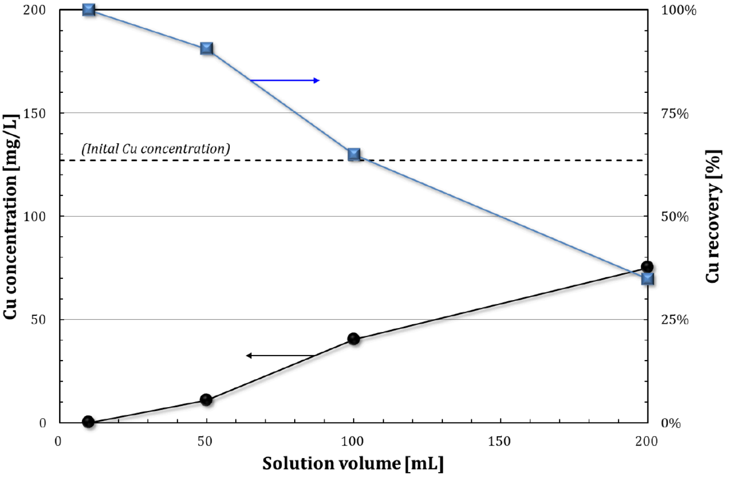

Figure 2 *Effect of solution volume on recovery of Cu using 0.1 g of chitosan sample at pH 5.*

10 mg/L. But, the Cu recovery rate generally decreased with increase in the solution volume. In accordance with that, the final Cu concentration increased. Figure 3 shows relationship between solution volume and Cu adsorption capacity at pH 5. This figure implied total mass of Cu recovery from the solution increased while the Cu recovery rate decreased. Finally, Cu adsorption capacity reached approx. 1.2 mmol/g-chitosan.

Effect of pH on Cu recovery using chitosan samples

The effect of pH on Cu recovery using chitosan was investigated. At a pH of 2.0-5.0, 0.1 g of chitosan was added to 50 mL of the simulated Cu solutions, and then they were stirred for 24 h. Figure 4 shows chitosan samples after 24 h incubation in the simulated Cu solutions. In case of pH 2.0, the change in state of chitosan sample was not detected. In contrast, the color of the chitosan sample was changed into blue at over pH 3.0. It was considered that the change to blue reflected Cu recovery by adsorption into the chitosan.

Table 1 shows the result of Cu recovery test at various pH values. When the initial pH was 2.0, Cu recovey from the simulated solutions was not detected. This may imply that chitosan dissolved in the solution with lower pH. To the contrary, approx. 90 % of Cu could be recovered from the solutions at

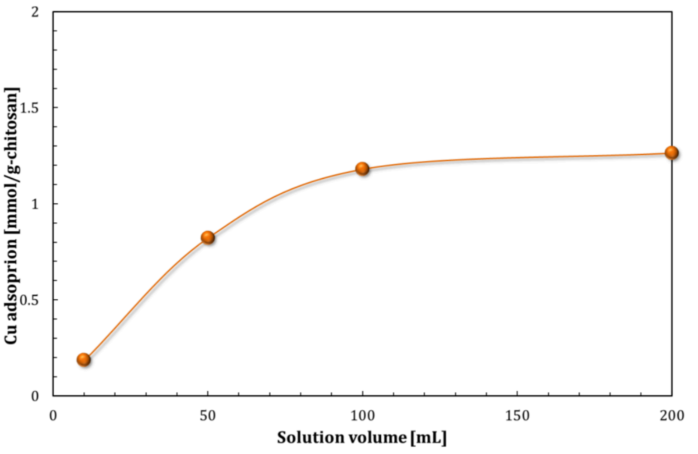

Figure 3 *Relationship between solution volume and Cu adsorption capacity at pH 5. To the simulated Cu solutions, 0.1 g of chitosan was added.*

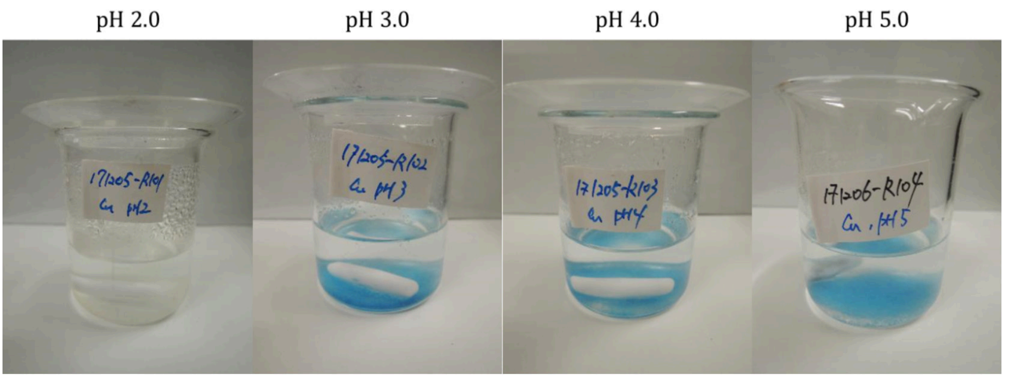

Figure 4 *Change in chitosan samples after 24 h incubation in 2 mM of simulated Cu solutions at various pHs.*

Table 1 *Result of Cu recovery test using chitosan.*

pH		Cu recovery	
(before)	(after)	[mg]	[wt%]
2.0	2.4	0.0	0%
3.0	5.0	5.0	90.8%
4.0	5.2	5.0	91.1%
5.0	5.4	4.8	87.9%

pH 3.0-5.0. At the same time, the solution pH also increased to around 5. Chitosan has lots of amino (-NH_2) and hydroxyl (-OH) groups. It is considered that metal can be adsorbed into chitosan due to formation of chelate compounds with cationic metal ions generally. It was implied that Cu recovery using chitosan was mainly induced by formation of chelate compounds.

Comparison of Cu recovery using chitosan with Zn and Mn

To estimate the effect of metal species on recovery using chitosan, Zn and Mn recovery tests were carried out. At a pH of 2.0-5.0, 0.1 g of chitosan was added to 50 mL of the simulated Zn or Mn solutions, and then they were stirred for 24 h. Figure 5 shows recovery of Zn and Mn by chitosan at pH 5. For comparison, the result of Cu recovery was also presented in Figure 5. As mentioned above, around 90 % of Cu could be recovered from the solutions at over pH 3. At pH 2.0, Zn and Mn were not recovered same as Cu. Dissolution of a part of chitosan into the

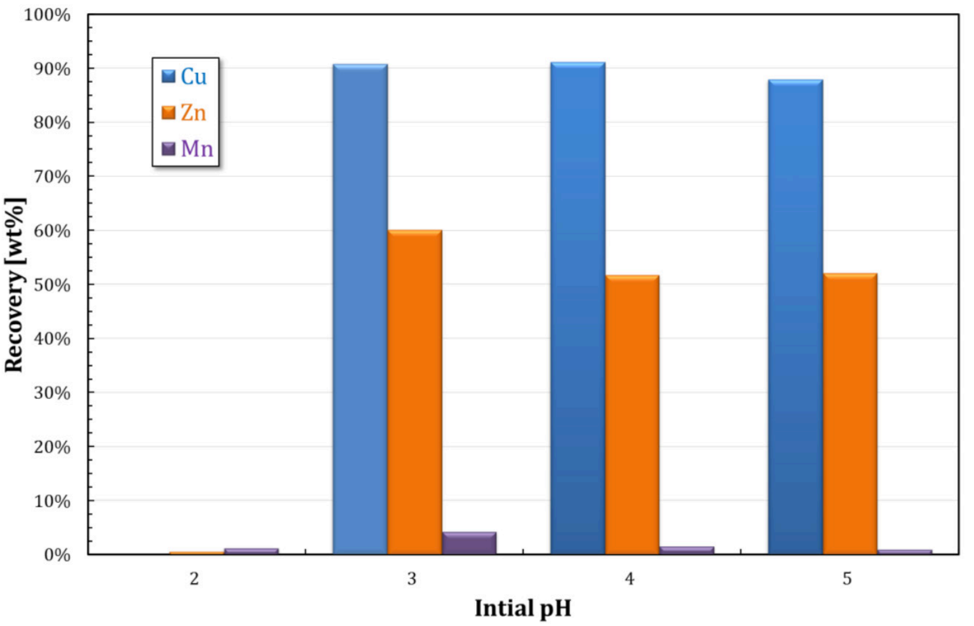

Figure 5 *Effect of pH on recovery of various metals using the chitosan samples.*

solutions caused no Zn and Mn recovery. At over pH 3.0, it was also confirmed that all the pHs of Zn and Mn solutions increased to around 6. In case of Zn, some amount of Zn was recovered at over pH 3.0. But, the recovery rate of Zn was between 50 and 60 %, less than that of Cu. The recovery test using the simulated Mn solutions revealed that Mn recovery was hardly detected in the pH range of 2.0-5.0. These results suggest that metal recovery using chitosan may be affected by some properties of metal ions such as ionic radius, ionization tendency and so on.

Consequently, chitosan powder had a possibility for a high performance of Cu recovery from wastewater. From these results, it was also possible that chitosan could selectively recover Cu from solutions containing Cu and Mn ions within the pH range of 3-5. Thus, "mixed" gelatin hydrogel blended with chitosan can be expected to be used as the high-peformance adsorbent for Cu recovery.

Conclusions

In order to develop gelatin hydrogels having a high-performance adsorption capacity for metal recovery from AMD, preparation of "mixed" gelatin hydrogels blended with other natural organic compound was suggested. Thus, metal recovery efficiency of chitosan was investigated using 2 mM of simulated metal solutions.

When 0.1 g of chitosan was added to 10 mL of simulated Cu solution at pH 5, the Cu concentration drastically decreased just after addition of chitosan. Finally, almost all copper could be recovered from the solution after one hour. Additionally, the Cu recovery tests were conducted by changing the volume of the simulated solutions. In case of up to 50 mL of the solutions, a small amount (0.1 g) of chitosan could recover 90 % of Cu. And then, the Cu recovery rate generally decreased with increase in the solution volume. The Cu adsorption capacity reached approx. 1.2 mmol/g-chitosan.

When the effect of pH on Cu recovery using chitosan was investigated, approx. 90 % of Cu could be recovered from the solutions at pH 3.0-5.0. However, Cu recovery was not detected at pH 2.0. Thus, it was considered that adjustment of solution pH allowed to recover Cu from acidic wastewater. Chitosan mainly has lots of amino and hydroxyl groups. It was implied that Cu recovery using chitosan was mainly induced by formation of chelate compounds.

To estimate the effect of metal species on recovery using chitosan, the behavior of Zn and Mn recovery was investigated. This experiment revealed that much higher Cu recovery rate was provided in comparison with Zn and Mn. Because chitosan especially had a high-performance of Cu recovery, it was considered that "mixed" gelatin hydrogel blended with chitosan had a potential for the high-peformance adsorbent for Cu recovery.

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