

Removal of Dissolved Metals from Acid Wastewater Using Organic Polymer Hydrogels

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Abstract The possibility of using different type of cross-linked gelatin hydrogels for recovery and removal of metals from acidic wastewater by adsorption was investigated. Acid extraction (Type A) and alkaline extraction (Type B) gelatin hydrogels were cross-linked by glutaraldehyde. This gave sufficient cross-linking to both types of gelatin hydrogels. Copper recovery test revealed that the cross-linked Type B gelatin hydrogels could recover more Cu than the Type A gelatin ones and that Cu recovery by Type B gelatin was dependent on pH. Recovery was mainly affected by carboxyl groups on the side chains of gelatin molecules in hydrogels.

Key words acid mine drainage, adsorption, hydrogel, gelatin

Introduction

Acid mine drainage (AMD) is a serious environmental pollution issue in the mining industry. AMD is caused by the oxidation of sulfides such as pyrite, chalcopyrite, galena or sphalerite by surface or ground water (Gissinger et al. 1998; Zhang et al. 1998). It can have an extremely acidic pH and contain various metal ions (Fe, Cu, Pb, Zn, etc.). The ecological threat posed by AMD continues after mining ceases, since AMD can also be formed when rain water passes through tailings or mine wastes in repository sites. In Japan, there are numerous closed mines, such as the former Matsuo mine. Generally, neutralizing agents such as CaCO₃ have been added to AMD for pH adjustment and precipitation of metal ions as hydroxides in order to prevent degradation of the surrounding environment. However, precipitation of metal hydroxides disturbs efficient recycling of the potentially valuable metal ions contained in the AMD. Thus, to use AMD as a resource, the separation of metals as well as their removal from AMD is required. A way to purify AMD that would lead to recycling of major or minor metal elements is desirable.

Adsorption is an effective technique for recovery of metal ions from water. Recovery and separation of metals by adsorption can achieve both purification of the AMD and metal recovery. This study aims to develop a novel adsorbent for recovery of cationic metal ions from AMD, using natural organic polymers. In this study, organic polymer hydrogels for adsorbents were prepared with gelatin. First, cross-linking of the gelatin hydrogels was investigated because they dissolve in warm water and decompose in acidic water. We also investigated the basic adsorption behavior of metal ions to the cross-linked gelatin hydrogels. Copper was used as a model substance, for it is a common AMD metal.

Methods

Materials

As an adsorbent material for metal recovery, gelatins isolated from a porcine skin by an acid process (Type A) and a bovine skin by an alkaline process (Type B), were purchased from Sigma-Aldrich Japan Co., Japan. Type A and Type B gelatins had an isoelectric point (IEP) of 8-9 and 4-5, respectively.

Preparation and cross-linking of gelatin hydrogels

The gelatins were dissolved in distilled water at 50 °C. Prescribed volumes of 25% glutaraldehyde solution (Wako Pure Chemical Industries, Ltd., Japan) were added as a cross-linker to 50 mL of gelatin solutions. Immediately, they were introduced to 8 cm square plastic dishes. They were eventually transformed into hydrogels by storage at room temperature. The cross-linked gelatin hydrogels were 5 mm thick. The cross-linked gelatin hydrogels were then immersed in distilled water, and totally swelled for 72 h at room temperature. The distilled water for swelling was exchanged every 24 h.

Specific water content of cross-linked gelatin hydrogels

The extent of cross-linking was estimated via the specific water content. The wet weight (W_w) of the cross-linked gelatin hydrogels was measured after swelling and the dry weight (W_d) after freeze-drying. The specific water content was calculated according to the following equation:

$$\text{Specific water content} = (W_w - W_d) / W_d$$

Adsorption test of metal into cross-linked gelatin hydrogels

Recovery tests for a metal using gelatin hydrogels were performed in an aqueous solution containing 2 mM of Cu at different pHs. The copper solutions were prepared from copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; Wako Pure Chemical Industries, Ltd., Japan), and the solutions were adjusted to various pH values by H_2SO_4 solutions (Wako Pure Chemical Industries). For the adsorption test, a cross-linked hydrogel sheet (2 cm-square shape) was cut out, and incubated in 10 mL of aqueous copper solution at room temperature for 24 h.

Quantitative analysis of Cu in solutions

After the recovery tests, the cross-linked gelatin hydrogel sheets were removed from the solutions. Copper concentrations in these solutions were measured by inductively-coupled plasma optical emission spectrometry (ICP-OES, SPS 5510, Seiko Instruments Inc., Japan). And then, recovery rate of copper from the solution was calculated.

Results and discussion

Glutaraldehyde-induced-cross-linking of gelatin hydrogels

Figure 1 shows the gelation time of Type A and Type B gelatin hydrogels with or without the cross-linker (glutaraldehyde solution) at room temperature. Without cross-linker, 25 mg/

mL of Type A and Type B gelatin solutions had about 33 and 25 min of gelation time, respectively. These gelation times decreased with an increase in gelatin concentration. When glutaraldehyde was added to the gelatin solutions, glutaraldehyde-induced-cross-linking of gelatin molecules (Figure 2) reduced gelation time to both kinds of gelatin solutions. In the case of 50 mg/mL of Type A gelatin solution, the gelation time was reduced to 6 min after addition of 0.5 mL of the glutaraldehyde solution, while the gelatin without cross-linking had 17 min of gelation time. With the Type B gelatin, the gelation time was reduced to 4 min. In addition, over 1 mL of glutaraldehyde gave immediate gel formation. It is well known that glutaraldehyde can be used to cross-link amino-groups in gelatin (Tabata et al. 1998). These results indicate that cross-linking reaction by glutaraldehyde affected hydrogel formation.

The volume of gelatin hydrogels cross-linked by glutaraldehyde was not changed, but the hydrogels became smaller, after incubation in distilled water, compared with non-crosslinked ones. Generally, hydrogels can include water through weak hydrogen-bonds (Muta et al. 2001). In this case, it was implied that the cross-linked gelatin hydrogels could not expand themselves and thus increase cross-linking points.

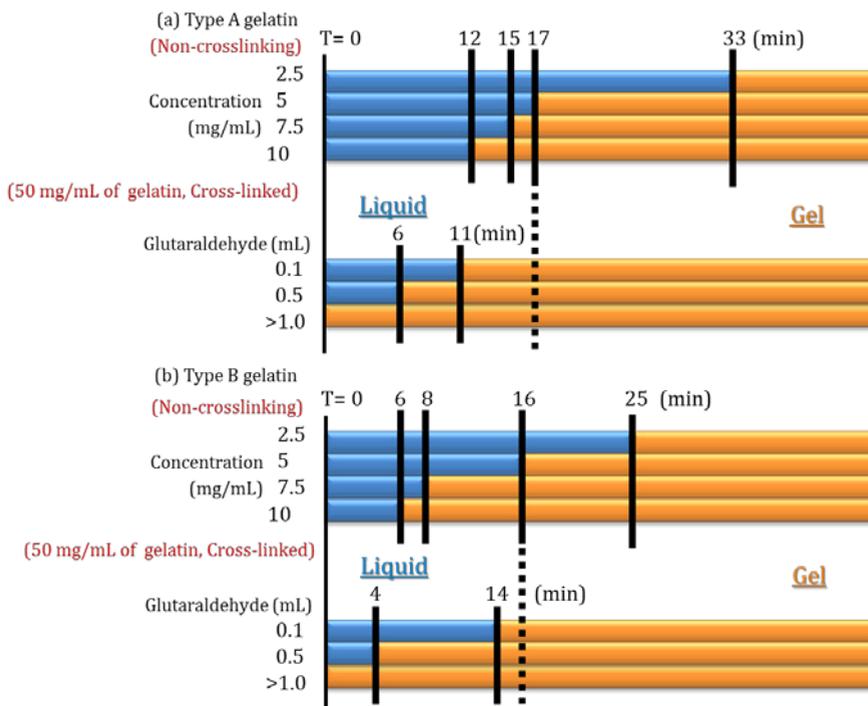


Figure 1 Gelation time of Type A (a) and Type B (b) gelatin hydrogels with or without cross-linking at room temperature. Gelatin hydrogels with 5 mm thick were prepared in 8 cm square plastic dishes. Glutaraldehyde solutions were added to 50 mL of gelatin solutions

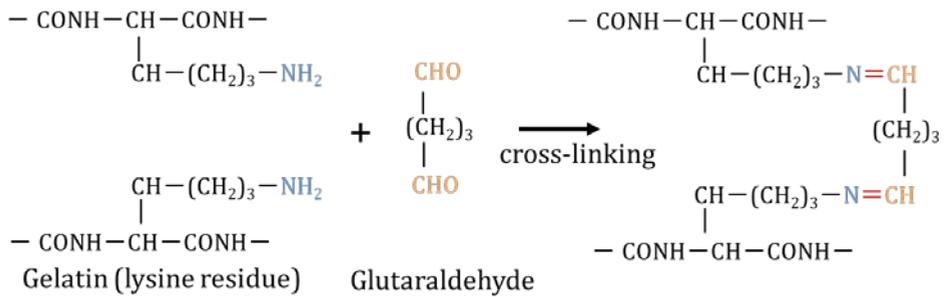


Figure 2 Schematic illustration of cross-linking reaction between glutaraldehyde and gelatin.

Figure 3 shows the specific water content of cross-linked hydrogels prepared from 100 mg/mL of gelatin solutions. The apparent specific water content of 100 mg/mL of non-crosslinked gelatin hydrogels before immersion corresponded to approx. 9. However, the specific water content of cross-linked gelatin hydrogels was higher than that.

Cu Recovery by cross-linked Type A and Type B gelatin hydrogels

The Cu recovery test was performed using 2 cm square gelatin hydrogel sheets cross-linked by 0.5 mL of glutaraldehyde solution. First, the relationship between initial gelatin concentration and Cu recovery rate was evaluated. Figure 4 shows that effect of initial gelatin concentration on Cu recovery at pH 5. The pH of the Cu solutions was not changed after the adsorption tests and no metal precipitation was observed. Consequently, the cross-linked Type B hydrogel had a higher Cu recovery rate than Type A. The recovery rate increased almost proportionally with the increase in initial gelatin concentration.

Then, cross-linked hydrogel sheets were prepared from 100 mg/mL of gelatin aqueous solutions to investigate the effect of pH on Cu recovery from aqueous solutions. The rate of Cu recovery by Type A and Type B gelatin hydrogel sheets were plotted against liquid pH (Figure 5). Again, the pH of the Cu solutions was not changed after the adsorption tests. With Type A gelatin, Cu recovery rate was almost constant, irrespective of pH. With Type B gelatin, recovery was almost the same as Type A gelatin for a pH of 1 to 2, but increased to around 45% at pH >3.

These differences between Type A and Type B gelatin was affected by the method of gelatin polypeptide production. Gelatin is the denatured fraction of collagen extracted from animal skin or bone. Bovine and porcine polypeptide is extracted by acidic solution (Type A gelatin) or by alkaline solution (Type B gelatin) for gelatin production. Generally, the gelatin derived from mammals such as bovine and porcine consists of various amino acids, and includes glutamine (Glu) and asparagine (Asp), which have an amide group (-COONH₂) as a side chain. The amino acid composition of mammalian gelatin is not affected by animal species. Extraction in alkaline solution yields Type B gelatin with a high density of carboxyl groups (-COOH), due to hydrolysis of amide groups of collagen. In contrast, amide groups of Type

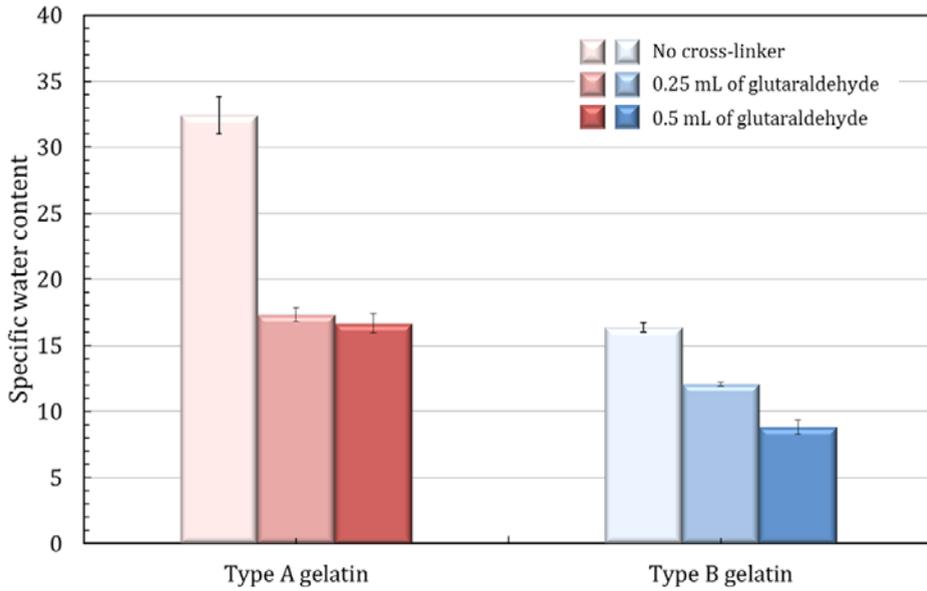


Figure 3 Effect of addition of cross-linker on specific water content of Type A (a) and Type B (b) gelatin hydrogels. Glutaraldehyde solutions as a cross-linker were added to 50 mL of gelatin solutions

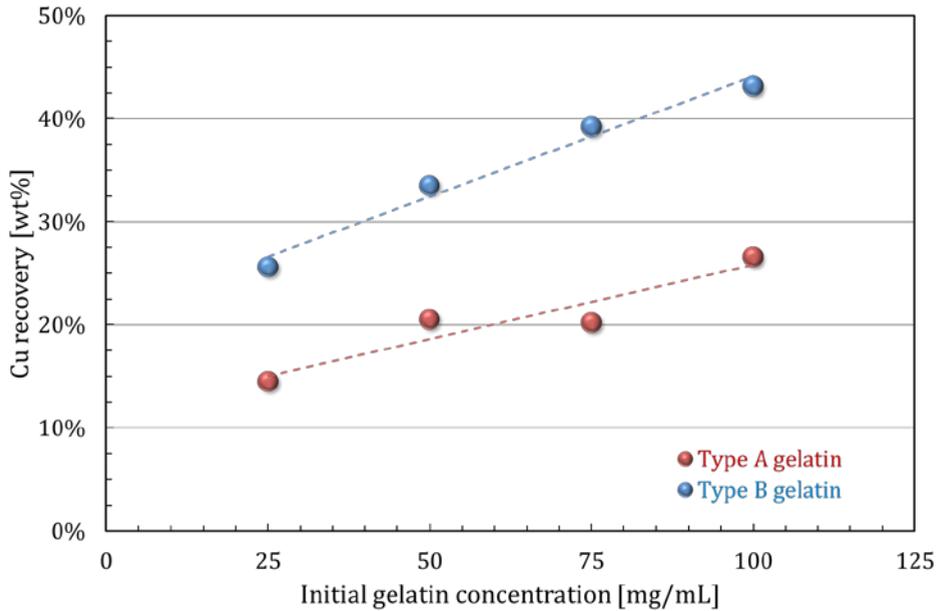


Figure 4 Effect of initial gelatin concentration on recovery of Cu at pH 5. The initial concentration of Cu was 2 mM. Cross-linked hydrogel sheets were incubated in 10 mL of Cu solution at room temperature for 24 h.

A gelatin are hardly transformed into carboxyl groups by extraction in an acidic solution (Tabata et al. 1998). As a result, Type B gelatin has an IEP of 4–5, different from Type A gelatin and collagen (approx. 8–9).

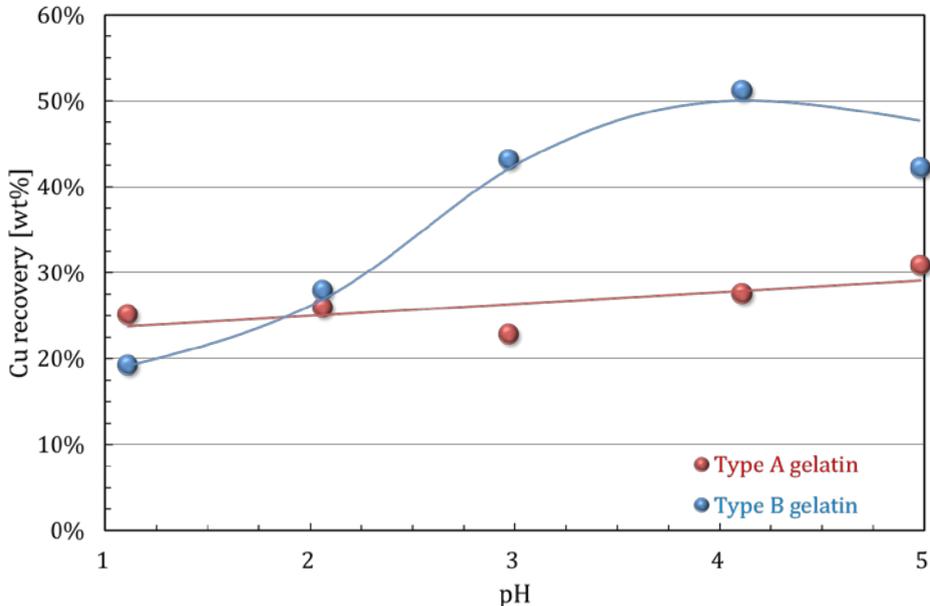


Figure 5 Effect of pH on Cu recovery using cross-linked gelatin hydrogels. Cross-linked hydrogel sheets were prepared from 100 mg/mL of gelatin aqueous solutions

This carboxyl group often plays an important role on adsorption of metal ions (Gotoh et al. 2004). But, at lower pHs, it appears that carboxyl groups did not adsorb Cu ion because the recovery rate for Type B gelatin was almost same as that for Type A, which rarely had carboxyl groups as side chains. This may imply that liberation of a proton from the carboxyl group is required for adsorption of metals to gelatin. In the case of Type B gelatin, it appears that the increased Cu recovery was mainly due to electrostatic adsorption of Cu^{2+} to the carboxyl group without a proton.

For Type A gelatin, Cu recovery was also detected (Figures 3 and 4). Gelatin includes not only Glu and Asp but also other amino acids with polar groups, such as proline, arginine, and lysine. Thus, recovery of Cu by Type A gelatin hydrogels seems to be related to adsorption to these amino acids. However, taking the Cu recovery test results into consideration, it is suggested that Cu recovery was related to a factor other than adsorption. That is, the metal recovery mainly consisted of “adsorption to gelatin molecules” and “absorption into hydrogels”. Cross-linked hydrogels initially have a plenty of water without any metal. Thus, Cu^{2+} moved from the solution into the hydrogel due to diffusion when the hydrogel sheet was introduced in the solution containing Cu^{2+} . The volume of water Type A gelatin hydro-

gels contain supports that almost all of the recovery was caused by absorption of Cu into them. It is possible that the Type B gelatin hydrogels also recovered Cu by absorption. But, at higher pH, adsorption surely contributed to Cu recovery. Therefore, it appears that Type B gelatin is a more suitable adsorbent material to recover cationic metal ions.

Conclusions

In order to develop a novel adsorbent for recovery of cationic metal ions from AMD, organic polymer hydrogels were prepared with two kinds of gelatin. Cross-linking of the gelatin hydrogels was evaluated and then we investigated basic adsorption behavior of metal ions to cross-linked gelatin hydrogels using copper solutions.

Glutaraldehyde was used for cross-linking of Type A and Type B gelatin hydrogels. It gave sufficient cross-linking to both types of gelatin hydrogels, and the gelation time at room temperature was remarkably reduced. The relative decrease in specific water content of the Type A and Type B hydrogels with the addition of glutaraldehyde supported the promotion of the cross-linking reaction.

The cross-linked Type B gelatin hydrogels recovered more Cu than the Type A gelatin. Recovery by Type B gelatin hydrogels was dependent on pH. Metal recovery by gelatin hydrogels mainly consisted of adsorption to gelatin molecules and absorption into hydrogels. Adsorption was rarely detected with Type A gelatin. In contrast, Cu recovery using Type B gelatin hydrogels was mainly affected by carboxyl groups on side chains of gelatin molecules in hydrogels at higher pH.

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