Continuous Removal of Copper from Wastewater by the Process Consisting of Ferric/Limestone Coagulation, Polymer Flocculation, and Lamellar Sedimentation

Chang Duk Kang*, Sang Jun Sim†, and Woo Sik Kim*

Department of Chemical Engineering, Sungkyunkwan University, Suwon, Kyunggi 440-746, Korea
*Department of Chemical Engineering, Kyung Hee University, Yongin, Kyunggi 449-701, Korea

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Abstract: Removal of copper from wastewater by ferric/limestone coagulation and polymer flocculation followed by lamellar sedimentation was studied at laboratory scale. From jar test experiments, the optimum dosages of inorganic coagulant and polymer flocculant were Fe(III) 50 mg/L and 0.1% SA 407 solution 0.5−1.0 mL/L, respectively. A novel process was developed for continuous copper removal, in which a limestone aeration bed, a rapid-mixing tank, a slow-mixing tank, and a sedimentation tank with lamellae were applied systematically. In the limestone aeration bed alkalinization and coprecipitation of copper ion with Fe(III) were performed cocurrently. Flocculation of the ferric hydroxide/copper aggregates was performed efficiently with a minute quantity of the polymer flocculant in the mixing tank. The flocs were settled down in the sedimentation tank with lamellae and were separated from treatment water. The pH was maintained around 7.6 during the whole process and the performance results of the process showed copper removal efficiency over 99%. Copper removal efficiency was dependent on hydraulic retention time (HRT) and especially the HRT in the limestone aeration bed was a limiting factor.

Keywords: Copper wastewater, limestone, ferric chloride, coagulation, sedimentation

Introduction

The presence of heavy metals in the environment can be detrimental to a variety of living species. The most important feature that distinguishes heavy metals from other toxic pollutants is their non-biodegradability and that even have a tendency to accumulate in living material. Therefore, the elimination of heavy metals from wastewater is an important subject for public health [1]. In recent year, the awareness of environmental dangers posed by the discharge of copper wastewater increases according as the amount of effluent containing copper from the electronics industries increases in Korea. Particularly, copper is highly toxic as it is carcinogens and mutagens in nature [2], and the Korean Ministry of Environment specifies an upper limit of 1.0 mg/L in drinking water and 3.0 mg/L in effluent [3].

Many methods have been developed for the removal of heavy metals such as chemical precipitation, ion exchange, membrane separation and adsorption [4-6]. Among these methods, the most common is chemical precipitation. Chemical precipitation is based on the fact that many of the metal ions form relatively insoluble hydroxides and consists of hydroxide precipitation of the metals at an alkaline pH, followed by removal of the resulting solids by simple sedimentation and sometimes filtration. This method presents several limitations, such as incomplete precipitation, chemical instability of the precipitates and the formation of large sludge volumes, which are difficult to filtrate [7-10].

In this study, we propose a novel copper removal process including coagulation with ferric chloride, alkalinization with limestone granules, flocculation with polymer having polyacrylamide group, and sedimentation. The coagulation was performed in the limestone aeration bed. The aeration in the limestone bed prevented the deposition of precipitates on limestone granules,
allowed longer and higher alkalinization performance. The flocculation of ferric hydroxide/copper aggregates was performed in the rapid-mixing tank and the slow-mixing tank, subsequently. The sedimentation of the flocs and separation of the treatment water were performed in the sedimentation tank with lamellae.

### Experimental

Raw water of copper, cadmium, and lead was prepared by dissolving copper chloride (CuCl₂, Kanto, Japan), cadmium chloride (CdCl₂, Junsei, Japan), and lead chloride (PbCl₂, Junsei, Japan) in deionized water, respectively. Ferric coagulant was prepared in a solution of 3000 mg/L by dissolving ferric chloride (FeCl₃, Aldrich, USA) in deionized water and was used varying Fe(III) concentration. 0.1% SA 407 solution (1000 mg/L of SA 407) was prepared for polymer flocculant by dissolving SA 407 powder (Songwon, Korea) in deionized water, which was anionic or nonionic polymer with polyacrylamide group. The general properties including a molecular formula of the polymer are shown in Table 1. Raw limestone was obtained from Dae-Gog mining company at Danyang, Chungbuk, Korea. The raw limestone was crushed, screened and graded by 7~10 mesh size sieve.

Jar test experiments were conducted to investigate effects of coagulant and flocculant on copper removal at room temperature (about 15°C). Fe(II) solution was added to 10 mg/L of copper solution varying Fe(II) concentration from 0 to 100 mg/L. After mixing at 200 rpm for 20 min, this solution (1.7 L) was supplied to the limestone aeration bed and aerated with 50 L/min of upflow air for 40 min. The limestone aeration bed was packed with 1200 g of limestone granules having 7~10 mesh size. The working volume of the limestone bed was 1.7 L. The limed water from the limestone aeration bed flowed to a rapid-mixing tank that the polymer flocculant was added continuously and then stirred at 150 rpm. After rapid mixing, the wastewater flowed to a slow-mixing tank and stirred slowly at 40 rpm. The flocculated water was settled in a sedimentation tank with lamellae. The treatment water from the sedimentation tank was collected and analyzed for residual concentration of copper and iron. Figure 1 shows a schematic diagram of the copper removal process. Continuous process experiments were carried out varying dosage of 0.1% SA 407 solution to investigate effect of flocculant dosage on copper removal. To investigate effect of hydraulic retention time (HRT) in each unit on copper removal, continuous process experiments were conducted varying flow rate of raw water and working volume of each unit. The continuous process was operated at room temperature (about 15°C).

Residual metal concentration of all samples throughout this research was analyzed by a Z-8200 Atomic absorption spectrophotometer (Hitachi, Japan). The pH in the samples was measured by an M 250 pH meter (Corning, USA).

### Table 1. General properties of polymer flocculant (SA 407)

<table>
<thead>
<tr>
<th>Properties</th>
<th>White granular powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical form</td>
<td></td>
</tr>
<tr>
<td>Formula</td>
<td>[ \text{CH}_2 - \text{CH} - \text{COONa} ] _m _n</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>_m _n = 5 : 95</td>
</tr>
<tr>
<td>Ionic characteristic</td>
<td>Anionic or nonionic</td>
</tr>
<tr>
<td>Apparent specific gravity (g/cm³)</td>
<td>0.65</td>
</tr>
<tr>
<td>Viscosity of solution at 25°C (cps)</td>
<td>350</td>
</tr>
</tbody>
</table>
Results and Discussion

Coagulation of Copper using Fe(III)/Limestone, followed by Flocculation using Polymer (0.1% SA 407 solution) in Jar Tester

Ferric hydroxides (Fe(OH)₃) are formed by the hydrolysis of ferric ions and have a significant capacity to remove heavy metals from solution (co-precipitation). That is, other heavy metals such as cadmium, copper, or lead are included in the amorphous ferric hydroxide precipitates and are removed. More removal of heavy metals is achieved than is predicted by the solubility of metal hydroxides [9-13]. Limestone has calcium carbonate as a main component, which provides an alternative means of neutralizing acid water. Its main advantage over lime is its lower price and the production of smaller sludge volume [14].

In order to investigate effects of Fe(III) coagulant and polymer flocculant on copper removal, jar test experiments were conducted varying dosage of 0.1% SA 407 solution in the oxidized water from the limestone aeration bed at various Fe(III) concentration (Figure 2). When the polymer was added as a primary coagulant without Fe (III) addition, residual copper concentration of treatment water was very high (> 8.0 mg/L) regardless of dosage of the polymer [15]. In case of only Fe(III) coagulation without polymer addition, the copper concentration of treatment water was over 1.0 mg/L due to small size of non-settlement flocs. When the polymer was added as a flocculant after Fe(III) coagulation, the copper was removed over 98% with 0.33 mL/L of polymer. Further more increase in the flocculant dosage did not improve and even decrease the removal efficiency. The latter might be due to the so-called overdosing phenomenon.

One of the most likely actions of this anionic and nonionic polymer was that it bridged the ferric hydroxide flocs and formed large size of flocs more and more, which led to enhanced settling capability [16,17]. When 10 and 25 mg/L of Fe(III) were added to raw water, the copper concentration of treatment water was higher than the cases of 50 and 100 mg/L of Fe(III) addition. There was no significant difference in copper removal yield between 50 mg/L and 100 mg/L Fe(III) coagulation. Thus, Fe(III) 50 mg/L was chosen for next phase of experiments considering its cost.

Removal efficiency of copper was investigated varying copper concentration of raw water from 5 to 100 mg/L. Figure 3 shows the copper removal efficiency with respect to polymer flocculant dosage. For all cases of copper contaminated water, copper removal efficiency was over 99% with 0.67 mL/L of polymer flocculant. The copper removal efficiency was not improved for more dosages of the polymer. As the copper concentration of raw water increased, the pH increase by aeration in the limestone bed was limited as shown in Figure 4. The residual copper concentration of the treatment water increased with increment of copper in the raw water.

In order to investigate removal efficiency for other metals as well as copper, jar test experiments were conducted with raw water containing 10 mg/L of copper, cadmium, and lead. As presented in Figure 5, all of metals contained in the raw water showed high removal efficiency with 0.67 mL/L of polymer flocculant. The removal efficiency of copper, cadmium and lead was over 99, 98, and 99%, respectively. The metal removal efficiency was not improved for more dosages of the polymer.
Figure 3. Effect of polymer flocculant dosage on copper removal in various concentration of copper contaminated water (Coagulant: Fe(III) 50 mg/L, Polymer flocculant: 0.1% SA 407 solution).

Figure 4. The pH profiles of raw water during aeration in the limestone bed under various initial copper concentration (Coagulant: Fe(III) 50 mg/L).

Removal of Copper by Process consisting of Ferric/Limestone Coagulation, Polymer Flocculation, and Lamellar Sedimentation

A copper removal process was developed on the basis of the optimum jar test result considered pH increase by limestone, ferric coagulant cost, and dosage of polymer flocculant. The process consisted of a limestone aeration bed, a rapid-mixing tank, a slow-mixing tank, and a sedimentation tank with lamellae (Figure 1).

10 mg/L of copper solution containing 50 mg/L of ferric ion was supplied at the rate of 50 mL/min to the bottom of the limestone aeration bed packed with 1200 g of limestone granules with 7 ~ 10 mesh size. The upflow aeration was fed at the rate of 50 L/min to mix the limestone granule and raw water. The upflow velocity and the hydraulic retention time of the raw water in the limestone bed were 0.009 cm/sec and 40 min, respectively. The pH increase of the raw water by limestone was maintained around 7.6 for 10-hour operation as shown in Figure 6. The pH level was maintained during the whole process operation since the deposits on the
surface of the limestone were removed consecutively by aeration [18]. It is important to maintain the surface of the limestone granule fresh to keep the pH to 7.6. In this experiment, the aeration bubble effectively removed the iron/copper complex deposit on the surface of limestone during the operation. The flocculation of oxidized water from the limestone aeration bed was performed with 1.0 mL/L of SA 407 solution in the rapid-mixing tank and the slow-mixing tank subsequently. The hydraulic retention time in the rapid-mixing tank and the slow-mixing tank was 2 and 40 min, respectively. The flocculated water was settled down for 60 min and the separation of the flocs and treatment water was performed in the sedimentation tank with lamellae. The lamellae were employed to improve the separation efficiency of treatment and precipitates [19]. Both copper and ferric ions were removed over 99% as shown in Figure 6. The progress of iron concentrations was similar to that of copper, which supports the copper removal by coprecipitation with ferric ions and flocculation of the coprecipitates.

Effect of Polymer Flocculant Dosage and Hydraulic Retention Time (HRT) in Each Unit on Copper Removal in Continuous Process

Continuous process experiments were carried out varying dosage of polymer flocculant (0.1% SA 407 solution) from 0.5 to 2.0 mL/L. The results are shown in Figure 7. When the input rate of raw water was 42.5 mL/min, the copper concentration of treatment water was below 0.08 mg/L in all cases of polymer addition. The copper concentration of treatment water was constant on variation of polymer dosage. When the inflow rate of raw water was 85.0 mL/min (a half of hydraulic retention time), the copper concentration of treatment water was below 0.26 mg/L, higher than the former case to some degree. There was not significant difference in copper removal yield on variation of polymer dosage like the former case. From these results, we found that removal efficiency of copper was dependent on hydraulic retention time (HRT) rather than polymer flocculant dosage in continuous process.

The copper concentration of treatment water according to variation of HRT in each unit was compared in Figure 8. When the HRT in entire process was reduced to half, the copper concentration of treatment water increased from 0.08 to 0.26 mg/L. The increment of the copper concentration by reduction of the HRT in the limestone aeration bed occupied a major portion in copper concentration increment. In the rapid-mixing tank and slow-mixing tank, the copper concentration of treatment water was not affected on variation of the HRT. When the HRT in the sedimentation tank was reduced to half, the copper concentration of treatment water increased a little from 0.08 to 0.13 mg/L. From these results, it was presumed that the HRT in the limestone aeration bed is the most dominant to effect of the HRT on copper removal in continuous process.

Conclusions

Treatment of artificial copper wastewater was conducted by the novel process consisting of a limestone aeration bed, a rapid-mixing tank, a slow-mixing tank,
and a sedimentation tank with lamellae. The removal yield of copper was over 99%. The HRT in the limestone aeration bed was the limiting factor to determine copper removal efficiency and the pH in the limestone aeration bed was maintained around 7.6 during whole process operation.

Cheap and durable limestone was used as a liming agent instead of chemicals such as sodium hydroxide. The polymer addition and lamellae employment in sedimentation tank caused to improve separation efficiency of treatment water and precipitates, and membrane unit was not induced in this process. We expect that this process can supply another alternative for the treatment of heavy metal wastewater from the viewpoint of economical treatment and simple operation without membrane.

References