Metal recovery from electroplating wastewater using acidophilic iron oxidizing bacteria: Pilot-scale feasibility test

SEPARATIONS

Metal Recovery from Electroplating Wastewater Using Acidophilic Iron Oxidizing Bacteria: Pilot-Scale Feasibility Test

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Wastewater from electroplating plants contains several valuable metallic ions such as iron, nickel, and zinc. In general, neutralization followed by sedimentation has been used for the treatment of electroplating wastewater because of low treatment cost and high stability of treated water quality. However, this method results in the production of large amounts of heavy metal sludge that may cause secondary pollution and additional cost. In addition, the recovery of valuable metallic contents from the wastewater sludge has not been technically feasible. It would be highly desirable economically as well as environmentally if a metal recovery process from the wastewater is developed. In the present work, we developed a biological process for metal recovery from electroplating wastewater. Wastewater from electroplating plants contains iron in the form of ferrous ion together with other metal ions. To add economic value to the chemical sludge, iron should be separated from other metals such as nickel and zinc in the wastewater. The iron could be separated from the mixture of metal ions in wastewater by using biological oxidation of ferrous ion into ferric ion followed by stepwise chemical precipitation with hydroxide ion since ferric ion begins to precipitate around pH 4 while ferrous ion precipitates around pH 7 similarly to the other metal ions (nickel and zinc). To improve the biological oxidation, an immobilized bioreactor using polyurethane foam as support media was developed. The bioreactor system showed a very good performance and worked stably over a long period of time.

Introduction

Wastewater from electroplating plants contains valuable metallic ions such as iron, nickel, and zinc. Due to economic concerns, as well as greater awareness of the ecological impacts of heavy metals released into the environment, a number of studies on metal removal and/or recovery from wastewater have been launched.[1,2] The removal of heavy metals from electroplating wastewater has been performed by physicochemical processes before discharging the effluents into water-body systems. Physicochemical processes in use for heavy-metal removal from wastewater include precipitation, coagulation, reduction, ion exchange, and membrane processes (such as ultrafiltration, electrodialysis, and reverse osmosis). Among them, neutralization followed by sedimentation has been generally used in electroplating wastewater treatment because of low treatment cost and high stability of treated water quality. However, this method results in the production of large amounts of

chemical sludge that may cause secondary pollution and additional operational cost.[3] Moreover, it is difficult to recover valuable metals from the sludge. Adsorption on ion-exchange resin or activated carbon can be used as alternative methods for the removal and recovery of heavy metals from electroplating wastewater.[4,5] However, high costs have limited their use in real electroplating wastewater treatment, and it is impossible to separate each metal from the sludge. Therefore, development of specific metal recovery process from the wastewater would be of economical and environmental interest.
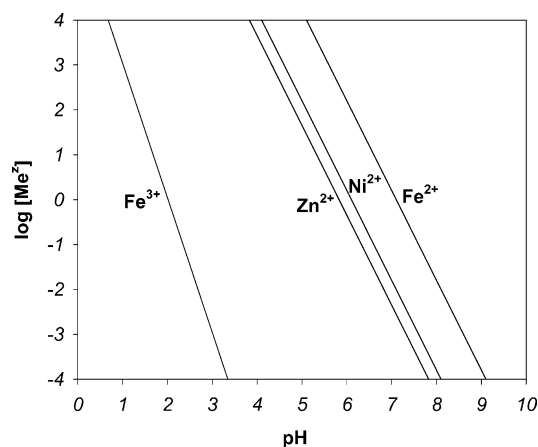
For adding economic value to the chemical sludge, iron should be separated from other metals such as nickel and zinc in the wastewater. Wastewater from electroplating lines contains iron in the form of ferrous ion together with only zinc or nickel, depending on the electroplating process. Ferric ion begins to precipitate around pH 4, while ferrous ion begins to precipitate around pH 7 similarly to zinc and nickel ions (Figure 1). Therefore, it is possible to separate iron from a mixture of metal ions in wastewater using the oxidation of ferrous ion into ferric ion followed by stepwise chemical precipitation with hydroxide ion. In this process, the key reaction is the oxidation of ferrous ion into ferric ion. Various methods can be used for the

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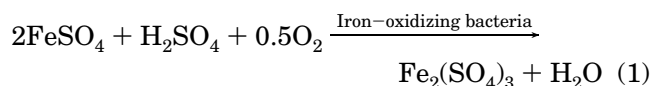
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Figure 1. Solubility of metal hydroxides at equilibrium state. Solubility product constants (K_{sp}) of each metal hydroxides were as follows: $Fe(OH)_3$, 1.1×10^{-36}; $Fe(OH)_2$, 1.6×10^{-14}; $Ni(OH)_2$, 1.6×10^{-16}; $Zn(OH)_2$, 4.5×10^{-17}. [6]

Table 1. Various Methods Capable of Oxidizing Ferrous Ion into Ferric Ion

oxidation method	performance	comments
electrochemical (electrolysis)	99% oxidized in 40 min	high cost and ceramic diaphragm choking
chemical (using H_2O_2)	99% oxidized in 60 min	low initial cost but high running cost
biological (iron-oxidizing bacteria)	>99% oxidized in 30–120 min	low running cost

oxidation of ferrous ion into ferric ion (Table 1). Among them, the biological oxidation of ferrous ion using iron-oxidizing bacteria may be the most efficient and environmentally friendly.[7]

Biological oxidation of ferrous ion is a well-researched area in the bioleaching and treatment of acid mine drainage.[7,8] A variety of iron-oxidizing bacteria have been isolated from acidic mine drainage or places where an ore body is naturally exposed to water and the atmosphere. Most of them have been characterized as *Acidithiobacillus ferrooxidans* and *Leptospirillum ferroxidans*. Ferrous ion is oxidized according to the following reaction:

$$2FeSO_4 + H_2SO_4 + 0.5O_2 \xrightarrow{\text{Iron-oxidizing bacteria}} Fe_2(SO_4)_3 + H_2O \quad (1)$$

The iron-oxidizing bacteria are (i) chemolithotrophic—energy for growth and maintenance, etc., is derived from the oxidation of ferrous ion; (ii) autotrophic—CO_2 is the cellular carbon source requiring N and P as nutrients for cellular growth and synthesis along with trace mineral nutrients of K^+, Na^+, Mg^{2+} and Ca^{2+}; (iii) aerobic—strictly; (iv) mesophilic—a temperature between 20 and 40 °C promotes growth and iron oxidation with an optimal temperature near 33 °C and with the growth and oxidation rate decreasing rapidly above the optimal temperature; (v) acidophilic—growth occurs at a pH between 1.0 and 4.5 with an optimum between 2.0 and 2.3.[7,8] These microbial characteristics of iron-oxidizing bacteria make them survivable in the electroplating wastewater without any supply of additional nutrients or pH control of the biological oxidation process.

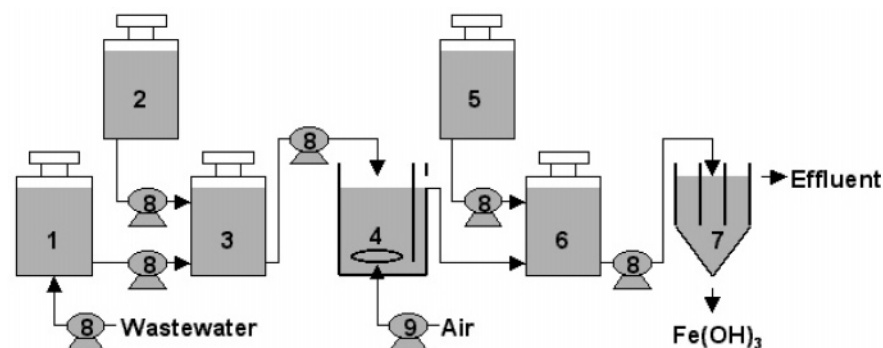In this study, we incorporated a biological oxidation process with a chemical precipitation process for metal recovery and sludge volume reduction in the treatment of wastewater from an electroplating line. For efficient performance, iron-oxidizing bacteria were immobilized in a packed-bed reactor using polyurethane foam as support media. Feasibility to various electroplating wastewaters was examined. A pilot plant for ferrous ion oxidation was operated for three months with real wastewater. The optimum conditions for ferrous ion oxidation and iron separation were investigated.

Materials and Methods

Microorganisms, Medium, and Growth Conditions. The culture used in this study was screened from the activated sludge in a domestic wastewater treatment plant (Pohang, Korea) and is a complex mixture of autotrophic bacterial strains capable of oxidizing ferrous ion into ferric ion, largely consisting of *A. ferrooxidans* and *L. ferrooxidans* species. These iron-oxidizing bacteria were grown in the $FeSO_4$-based 9K medium containing the following (g/L): $FeSO_4 \cdot 7H_2O$, 5.0; $(NH_4)_2SO_4$, 3.0; K_2HPO_4, 0.5; $MgSO_4 \cdot 7H_2O$, 0.5; KCl, 0.1; and $Ca(NO_3)_2$, 0.01.[9] The medium was adjusted to pH 2.0 with concentrated H_2SO_4. High-density culture of the iron-oxidizing bacteria was carried out under forced aeration in a 3-L continuous stirred tank reactor (CSTR) with cell recycle at room temperature (25 ± 3 °C). The resulting bacteria were inoculated in an immobilized bioreactor as discussed in the following section.

Feasibility Test. For the feasibility test, a 1-L immobilized bioreactor was employed. The main part of the bioreactor consists of a glass column with a diameter of 5 cm and a height of 51 cm. The bottom part incorporated inlets for the influent and air, and the top part incorporated outlets for the effluent and air. Polyurethane foam cubes (12-mm length) were used as support media. An inoculum (100% v/v) obtained from the CSTR was immobilized in the polyurethane foam. The immobilization was carried out in a batch operation of the bioreactor for 1 day. Then, the bioreactor was continuously operated with the 9K medium containing 200 mg/L of ferrous ion until a steady state was attained. The liquid flow rate was increased stepwise from 0.3 to 1.5 L/h until the reactor system maintained its steady state performance of ferrous ion oxidation. Air flow rate was 2 L/min. The bioreactor was operated at room temperature. Samples were taken from the effluent of the bioreactor and analyzed for the pH and ferrous ion and ferric ion concentrations.

Pilot Plant Test. A 100-L immobilized bioreactor was employed for pilot plant tests with a real electroplating wastewater. Figure 2 shows the schematic diagram of the pilot plant operated for 3 months. The plant consisted of five facility groups: (1) wastewater storage facility, (2) pH 2 control facility using the waste acid from the plant, (3) biological oxidation facility of ferrous ion, (4) pH 4 control facility using sodium hydroxide, and (5) settling facility of ferric hydroxide. Automatic operation of the pilot plant was achieved using commercial software (AUTOBASE version 8.00, HANSOL Tech). Air flow rate was 50 L/min. In contrast to the 1-L immobilized bioreactor system, the liquid flow of the pilot plant system was down-flow corresponding to countercurrent of air flow. During the operation of the pilot plant, the temperature in the bioreactor was 10–20 °C. After a two-month period of adaptation of iron-oxidizing bacteria to a real electroplating waste-
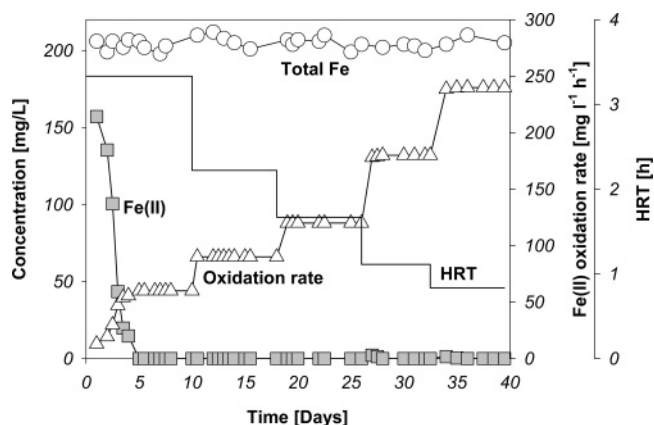
Figure 2. Schematic diagram of the pilot plant for iron separation using iron-oxidizing bacteria: 1, wastewater storage tank; 2, waste acid (2−3% H_2SO_4) storage tank; 3, pH 2 control tank; 4, immobilized bioreactor; 5, alkali (10 M NaOH) storage tank; 6, pH 4 control tank; 7, settler; 8, wastewater pump; 9, air blower.

water in a 50-L CSTR, the inoculum was immobilized into the bioreactor through batch operation with an additional supply of ferrous ion (i.e., energy source) for 10 days. Then, the pilot plant was continuously operated as the following operating strategy: (i) Run 1, 2 h of hydraulic retention time (HRT) without pH 2 control; (ii) Run 2, 1 h of HRT without pH 2 control; and (iii) Run 3, 1 h of HRT with pH 2 control using the waste acid. The waste acid was a 2−3% sulfuric acid solution discharged from the pickling step of an electroplating line, the alkali was a 10 M sodium hydroxide solution. For a shock test using waste acid, the waste acid of 10 L was added into the wastewater of about 200 L. The precipitation experiments of ferric and zinc ions by hydroxide ion were examined with the effluent of the bioreactor at various pH solutions.

Analytical Methods. A colorimetric method was used to measure the ferrous ion and total iron concentrations in the effluent.[10] The red-orange complex, formed from 1,10-phenanthroline and ferrous ion in acidic solution, was spectrophotometrically analyzed at 510 nm (Spectronico Genesystm 5, Spectronic Ins). The yellow complex, formed from 5-sulfosalicylic acid and total iron in basic solution, was spectrophotometrically analyzed at 425 nm. The ferric ion concentration was then calculated from the difference between the total iron and ferrous ion concentrations. The concentration of Zn(II) was determined by using an atomic absorption spectrophotometer (SpectrAA 800, Varian) at 213.9 nm. An X-ray diffractometer (Rigaku D/Max-2400, Rigaku) was used to analyze the chemical composition of the obtained ferric hydroxide precipitate.

Results and Discussion

Stabilization of the Immobilized Bioreactor. The 1-L immobilized bioreactor using polyurethane foam as support media was operated for 40 days (Figure 3). Initially, the concentration of ferrous ion in the effluent of the bioreactor rapidly decreased and then completely oxidized into ferric ion in 5 days. Then, the liquid flow rate was increased stepwise until the bioreactor system maintained its performance of ferrous ion oxidation. The time to achieve steady state conditions varied depending on the liquid flow rate, but normally the steady states were reached within 1 day. The oxidized ferric ion at the effluent around pH 2 flowed from the bioreactor without precipitating with other ions. As mentioned before, ferric ion is precipitated above pH 4.[6] The oxygen content in the bioreactor was sufficient for ferrous ion oxidation (above 2 mg/L). As the liquid flow rate

Figure 3. Ferrous ion oxidation in the 1-L immobilized bioreactor. The influent was 9K medium containing 200 mg/L of Fe(II) (the oxidation rate was based on working volume of the bioreactor).

increased, the oxidation rate of ferrous ion increased from 60 to 240 mg/L·h. Though hydraulic retention time (HRT) was decreased, the bioreactor showed very good performance in ferrous ion oxidation for 35 days.

Generally, it has been known that the maximum specific growth rate of *A. ferrooxidans* is 0.06−0.25 h^{-1}.[8] Thus, the dilution rate above 1 h^{-1} may result in the wash out of iron-oxidizing bacteria within the suspended culture system such as CSTR.[11] To deal with this problem, an immobilized bioreactor system was employed for ferrous ion oxidation above the dilution rate of 6 h^{-1}.[12,13] The fastest ferrous ion oxidation rate of 34 g/L·h was obtained from the immobilized bioreactor using polyurethane foam as support media.[13] Therefore, it could be concluded that the immobilized bioreactor using polyurethane foam as support media is the most promising process for biological ferrous ion oxidation process.

Feasibility Test. There are two types of electroplating wastewaters discharged from steel plating facilities, depending on whether the electroplating line uses sulfuric acid or hydrochloric acid to pickle the surface of steel before electroplating with zinc or nickel. Wastewater from a zinc electroplating line was examined in this study. Most of the wastewater was generated from rinsing steel after the acid treatment and electroplating steps (about 2000 m^3/day). Table 2 shows the composition of chloride- or sulfate-based electroplating wastewater. Chloride-based wastewater contained more iron and zinc ions than sulfate-based wastewater. Particularly, it is meaningful to note that most of the iron was in the form of ferrous ion. Chloride-based wastewater

Table 2. Composition of Chloride- or Sulfate-Based Electroplating Wastewater

	total Fe (mg/L)	Fe²⁺ (mg/L)	Zn²⁺ (mg/L)	Cl⁻ (mg/L)	SO₄²⁻ (mg/L)	pH
chloride-based wastewater	15−21	15−20	300−450	3000−5000	150−200	1.4−2.1
sulfate-based wastewater	10−16	9−15	150−350	<1	500−800	2.6−3.2

contained above 3000 mg/L of chloride ion, whereas sulfate-based wastewater contained below 1 mg/L of chloride ion. The concentration of sulfate ion in sulfate-based wastewater was four times higher than that in chloride-based wastewater. Sulfate ion in chloride-based wastewater might be due to plating solution, i.e., a concentrated zinc sulfate solution. Meanwhile, other cationic and anionic ions existed below 10 mg/L.

A synthetic sulfate-based wastewater containing only 200 mg/L ferrous ion and 500 mg/L sulfate ion was fed into the immobilized bioreactor (Figure 4). Though the wastewater did not contain mineral nutrients such as ammonium, phosphate, or other trace metal ions, the iron-oxidizing bacteria could completely oxidize ferrous ion into ferric ion.
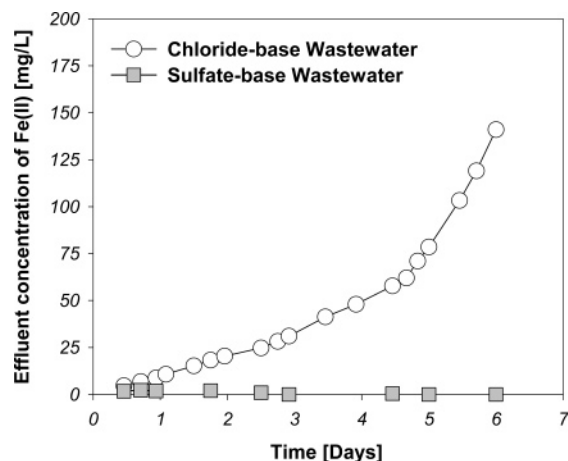
Meanwhile, a synthetic chloride-based wastewater containing 200 mg/L ferrous ion and 3000 mg/L chloride ion was also fed into the bioreactor. In contrast to the sulfate-based wastewater, the chloride-based wastewater seriously inhibited the ferrous ion oxidation activity of the iron-oxidizing bacteria (Figure 4). The switch of the influent to the sulfate-based wastewater stabilized the bioreactor within 3 days, but adding significant amounts of sulfate ion into the chloride-based wastewater did not improve the ferrous ion oxidation in the bioreactor. Besides chloride ion, nitrate ion above 500 mg/L recognizably inhibited the ferrous ion oxidation by iron-oxidizing bacteria (data not shown). However, since the real electroplating wastewater contained nitrate ion below 10 mg/L, the inhibition by nitrate ion was not an obstacle to the application of the bioreactor system. No more inhibition by any other ions was observed under the experimental conditions which were similar to those of the real electroplating wastewater.

It has been well-known that sulfate ion should be supplied to iron-oxidizing bacteria for successful ferrous ion oxidation, while the existence of chloride ion strongly inhibits the ferrous ion oxidation.[14−18] The reasons are as follows: (i) *A. ferrooxidans* needs an oxyanion-stabilized hexa-aquated complex of ferrous ion
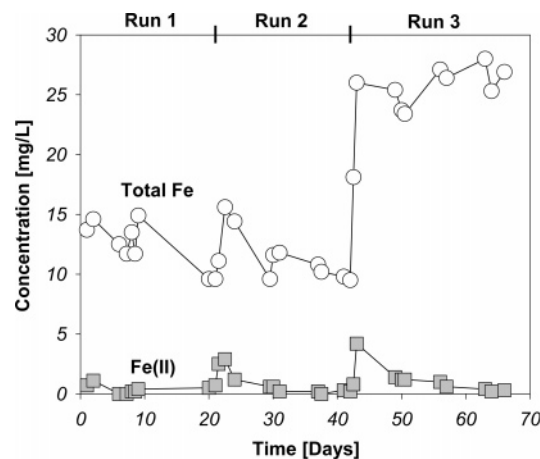
as substrate for iron oxidation; (ii) sulfate ion facilitates the electron transfer from the three-iron−sulfur cluster to the copper of rusticyanin; (iii) chloride ion destabilizes the required substrate complex by replacing sulfate ion in the outer sphere; and (iv) chloride ion is an inhibitor of cell-free iron-cytochrome *c* reductase relating with ferrous ion oxidation. Although a novel iron-oxidizing bacterium requiring NaCl for growth was isolated from seawater recently,[19] it may not be easy to apply it to the proposed process, for recovery of valuable metals using iron-oxidizing bacteria, in a chloride-based electroplating wastewater. Thus, a pilot plant test was conducted only with a real sulfate-based electroplating wastewater.

Pilot Plant Test. A 100-L immobilized bioreactor system was applied to a real sulfate-based electroplating wastewater containing about 15 mg/L of iron ion and about 300 mg/L of zinc ion (Table 2). After immobilization of iron-oxidizing bacteria on the support media, the pilot plant was continuously operated for 70 days (Figure 5). The operational condition of the pilot plant was changed twice: (i) Run 1, HRT = 2 h, without pH control; (ii) Run 2, HRT = 1 h, without pH control; and (iii) Run 3, HRT = 1 h, with pH control using waste acid (pH = 2).
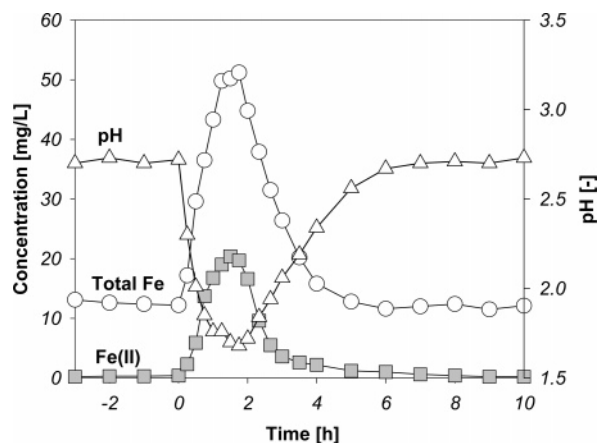
As shown in Figure 5, the bioreactor reached steady state in 5 days, and showed above 98% ferrous ion oxidation efficiency (Run 1). However, at least 10 days were required to reach a steady state after decreasing HRT from 2 h to 1 h. For Run 2, ferrous ion oxidation efficiency was also above 98% at steady state. During Runs 1 and 2, total iron concentration in the influent of the bioreactor was in the range of 8−16 mg/L, the influent pH was varied from 2.6 to 3.2. Run 3 was operated for making the bioreactor conditions more suitable to ferrous ion oxidation by iron-oxidizing bacteria. The optimum pH for ferrous ion oxidation and growth of iron-oxidizing bacteria was known to be around 2.[7,8] Since the waste acid contained about 1200 mg/L of ferrous ion, the influent of the bioreactor

Figure 4. Ferrous ion oxidation in the 1-L immobilized bioreactor. A chloride- or sulfate-based wastewater was synthesized with pure water, contained 200 mg/L of ferrous ion. The solution pH of wastewater was 2.0, HRT was 1.67 h⁻¹.

Figure 5. Ferrous ion oxidation in the 100-L immobilized bioreactor. A real zinc-electroplating wastewater was supplied into the bioreactor with or without pH 2 control using waste acid. During the operation of the bioreactor, the pH of the wastewater was in the pH range 2.6−3.2.
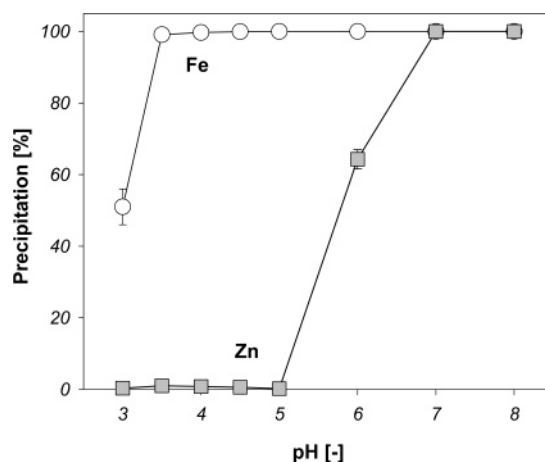
Figure 6. Dynamics of total Fe, Fe(II), and pH in the effluent of the bioreactor. Waste acid was abruptly added into the influent of the bioreactor at 0 h.

Figure 7. Precipitation of iron and zinc ions by hydroxide ion at various pHs. The effluent of the bioreactor contained 14 mg/L of ferric ion and 327 mg/L of zinc ion.

contained ferrous ion in the range of 22−28 mg/L during Run 3. As shown in Figure 5, the bioreactor required 15 days to be stabilized for Run 3, and the corresponding ferrous ion oxidation efficiency was above 98%.

To evaluate the pilot-scale bioreactor system, a shock test using waste acid was conducted. Abrupt supply of waste acid into the wastewater induced the increase in ferrous ion concentration and the decrease in pH value. As can be seen in Figure 6, the bioreactor did not show stable and efficient performance in ferrous ion oxidation, though iron-oxidizing bacteria could survive under these conditions (below 60 mg/L of ferrous ion at pH 1.7−2.8). Thus, the abrupt fluctuation of ferrous ion concentration and pH in the influent should be avoided for a stable operation of the pilot plant. It is meaningful to note that the amount of uniform wastewater was continuously generated from the electroplating line except during some repair periods.

Though there was no inhibition by chloride ion during the pilot plant test, the oxidation rate of ferrous ion was much lower than that in the feasibility test. The possible reasons are as follows: (i) the low temperature (usually 10−15 °C) during the bioreactor operation might reduce the bacterial activity, (ii) zinc ion might inhibit ferrous ion oxidation by iron-oxidizing bacteria, though zinc ion concentration was below 350 mg/L (Table 2). If the concentration ratio of inhibitor versus substrate is enough high, low inhibitor concentration can inhibit the reaction related with a competitive or noncompetitive inhibition.[20] In this study, zinc ion concentration was higher than ferrous ion at least 20 times (Table 2).

After biological oxidation of ferrous ion, chemical precipitation followed by a sedimentation processes was applied to separate the oxidized ferric ion from the effluent of the bioreactor. Figure 7 shows the precipitation of ferric and zinc ions by hydroxide ion at various pHs. Half of the ferric ion existing in the effluent was precipitated at pH 3.0 and complete precipitation occurred above pH 3.5. While zinc ion was not precipitated below pH 5, complete precipitation occurred above pH 7. Therefore, for the complete separation of iron from zinc, pH 4 was determined as the optimum pH for the iron precipitation/sedimentation process. During the operation of the pilot plant, the effluent of the bioreactor was efficiently adjusted to pH 4−5 in the pH control tank. The final effluent from the settler contained no iron ion through the bioreactor operations.

Furthermore, the ferric hydroxide precipitates obtained from the settler contained hardly any zinc ion (below 0.1%).

Conclusions

A biological process for recovery of valuable metals from an electroplating wastewater was developed as an alternative to the conventional process of neutralization followed by sedimentation. To improve the biological oxidation rate, an immobilized bioreactor using polyurethane foam as support media was applied and showed very stable and efficient performance in ferrous ion oxidation. The developed process was applied to a real sulfate-based electroplating wastewater. During the three-month period of operation, the pilot-scale bioreactor showed stable oxidation efficiency (98%) of ferrous ion. Optimal pH was determined as 4.0 for complete separation of the oxidized ferric ion from the solution containing other ions.

The biological ferrous ion oxidation coupled with stepwise chemical precipitation process showed possibility of selective recovery of valuable metals such as iron, zinc, or nickel from the electroplating wastewater. Although this process may be not cheaper than the conventional process, due to the initial investment cost and operating cost, not only metal recovery but also sludge volume reduction in the wastewater treatment is, beyond doubt, very meaningful from an environmental aspect. Furthermore, the reuse of recovered metals may reduce the operating cost of this process to some degree.

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