

## Process Development for the Removal of Copper from Wastewater using Ferric/Limestone Treatment

Chang Duk Kang\*, Sang Jun Sim<sup>†</sup>, Young Sang Cho\*\* 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

\*\*Clean Technology Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

(Received 9 May 2002 • accepted 8 November 2002)

**Abstract**—The removal of copper from wastewater by ferric/limestone coagulation followed by screen filtration was carried out at a laboratory scale. The optimum coagulant ( $\text{FeCl}_3$ ) dose and working pH were 50 mg/l of Fe(III) and pH 7.5, respectively, through jar tests. For the efficient removal of copper from wastewater, we developed a novel process including the co-precipitation of copper with  $\text{FeCl}_3$ , alkalization in a limestone aeration bed, and separation of precipitates in a sedimentation tank coupled with internal stainless steel screen filter. The performance results showed that removal of copper from the solution was over 99.5%. The pH was effectively maintained over 7.5 in limestone bed during the whole process. Ferric hydroxide/copper aggregates were removed over 99% by stainless steel screen filter of 1,450 mesh. Periodic air backwashing alleviated fouling of the filter surface.

Key words: Copper, Limestone, Ferric Chloride, Coagulation, Filtration

### INTRODUCTION

Heavy metals are ubiquitous in nature, and as civilizations have become more sophisticated, there has been an increasing potential for metallic poisoning—particularly in industry. The remaining heavy metals are foreign to the body and most are toxic [Homburger et al., 1983]. In recent years, the environmental awareness of dangers posed by the discharge of copper wastewater has increased as the amount of effluent containing copper from the electronics industries has increased in Korea. In particular, copper is highly toxic as it is carcinogenic and mutagenic in nature [Gupta and Ali, 2000], and the Korean Ministry of Environment specifies an upper limit of 1.0 mg  $l^{-1}$  in drinking water and 3.0 mg  $l^{-1}$  in effluent [The Korean Ministry of Environment, 1996].

Copper cation can be removed from wastewater by several processes such as chemical precipitation, adsorption, solvent extraction, membrane separation, electrolytic treatment or ion exchange [Blanchard et al., 1984; Gloaguen and Morvan, 1997; Jeon et al., 2001; Kim et al., 1998; Lee et al., 1998; Reed and Nonavinakere, 1992]. Among these methods, chemical precipitation is the most common.

The treatment of copper wastewater by chemical precipitation 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 [Lee et al., 1998; Agelidis et al., 1988; Higgins and Sater, 1984; Rao and Sitharamayya, 1996; Rubio and Tessele, 1997].

In this paper we propose a novel copper removal process includ-

ing coagulation, alkalization with limestone granules, and precipitation coupled with filtration using stainless steel screen filter. The aeration in the limestone bed prevented the deposition of precipitates on limestone granules, allowing longer and higher alkalization performance. Filtration and sedimentation was performed simultaneously in the sedimentation tank coupled with submerged stainless steel screen filter.

### EXPERIMENTAL

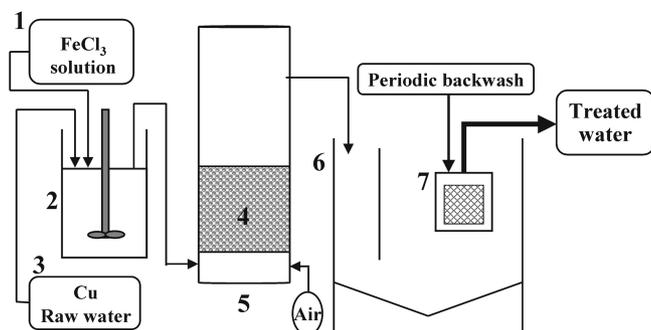
Raw water containing 10 mg  $l^{-1}$  of copper was prepared by dilution of 1,000 mg  $l^{-1}$  of copper stock solution that was made by dissolving 97% copper chloride ( $\text{CuCl}_2$ , Kanto, Japan) in deionized water. Ferric chloride, as a coagulant, was prepared in a solution of 3,000 mg  $l^{-1}$  by dissolving 97% ferric chloride ( $\text{FeCl}_3$ , Aldrich, USA) in deionized water, which was used varying the Fe(III) concentration. Raw limestone was obtained from Dae-Gog mining company at Danyang, Korea. Raw limestone was crushed, screened, and graded by 7-10 mesh size sieve. Stainless steel screen filter cartridges were made of stainless steel mesh having 1,000, 1,450, and 2,000 mesh pore sizes, respectively.

Jar test experiments were conducted to investigate effects of coagulant dosage and pH on copper removal at room temperature (about 15 °C). The jar test experiments were performed by using a series of six glass jars. Raw water containing 10 mg  $l^{-1}$  of copper was placed in each jar and various dosages of ferric coagulant (25, 50, and 100 mg  $l^{-1}$  of Fe(III)) were added. After the addition of the Fe(III), the copper solution was mixed sufficiently. The pH of the solution was adjusted to the desired level (pH 5.0-12.0) with 1 N sodium hydroxide (NaOH). The solution was quickly stirred at 150 rpm for 1 minute and then slowly stirred at 70 rpm for another 20 minutes. The precipitates were allowed to settle for 30 minutes and supernatant was analyzed for the residual copper and iron concentration.

In a continuous process, the ferric coagulant was added to 10 mg

<sup>†</sup>To whom correspondence should be addressed.

E-mail: simsj@yurim.skku.ac.kr



**Fig. 1. Schematic diagram of copper removal process using coagulation with  $\text{FeCl}_3$  and filtration by stainless steel screen filter.**

1. Storage tank of the coagulant ( $3,000 \text{ mg l}^{-1}$  of  $\text{FeCl}_3$  solution), 2. Mixing tank of copper wastewater and coagulant, 3. Storage tank of the copper raw water, 4. Limestone granules (7-10 mesh size, 1,200 g), 5. Limestone aeration bed, 6. Sedimentation tank, 7. Stainless steel screen filter.

$\text{l}^{-1}$  of copper solution. After sufficient mixing, this solution was supplied to the bottom of a limestone aeration bed at the rate of  $50 \text{ ml min}^{-1}$  cocurrently with upflow aeration using  $50 \text{ l min}^{-1}$  of air. The limestone bed was packed with 1,200 g of limestone granules having 7-10 mesh size. The working volume of the limestone bed was  $1.7 \text{ l}$  (Fig. 1). The limed water eluted from the limestone aeration bed was settled in a sedimentation tank coupled with a stainless steel screen filter cartridge, and non-sediments were filtered through the screen filter. Continuous process experiments were conducted varying the screen mesh size from 1,000 to 2,000 mesh to investigate the effect of the screen mesh size on filtration performances of the resulting precipitates including copper. When the vacuum pressure generated inside the filter by fouling on the screen during the filtration increased up to 10 cm Hg, backwash operation was automatically performed with  $10 \text{ l min}^{-1}$  of air to prevent damage of the screen. The continuous process was operated at room temperature (about  $15^\circ\text{C}$ ).

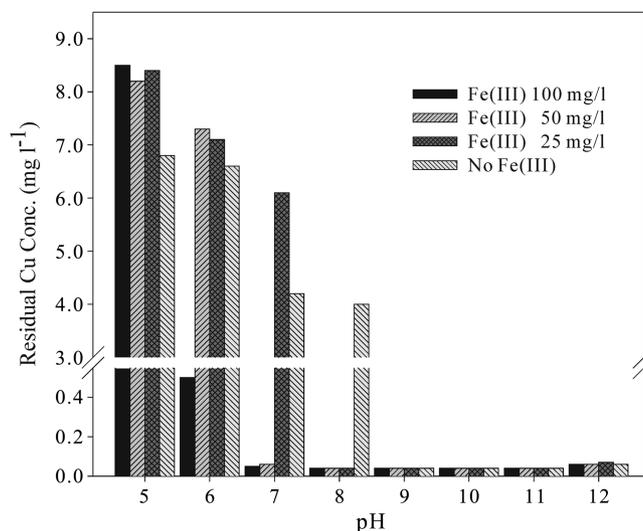
Concentration of the copper and iron in all samples throughout this research was analyzed by a Z-8200 Atomic absorption spectrophotometer (Hitachi, Japan). The pH in the samples was measured by an M 250 pH meter (Coming, USA). The size of the ferric hydroxide flocs formed through the limestone aeration bed was measured by a LS 230 Particle size analyzer (Coulter Corp., USA).

## RESULTS AND DISCUSSION

### 1. Coagulation of Copper using Ferric Ion in Jar Tester

Ferric hydroxides [ $\text{Fe}(\text{OH})_3$ ] 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 [Rao and Sitharamayya, 1996; Rubio and Tessele, 1997; Al-Malack et al., 1999; Jiang and Graham, 1998; Martinez and McBride, 1998].

Coagulation of copper using ferric ions was investigated through the jar tests prior to continuous process experiments. The jar tests were carried out by varying pH conditions under various  $\text{Fe}(\text{III})$  doses



**Fig. 2. Residual copper concentration of treatment water in jar test experiments: (Raw water:  $\text{Cu}(\text{II}) 10 \text{ mg l}^{-1}$ , pH adjustment with 1 N NaOH).**

(Fig. 2). When  $100 \text{ mg l}^{-1}$  of  $\text{Fe}(\text{III})$  was added to the raw water containing  $10 \text{ mg l}^{-1}$  of copper, the formation of amorphous ferric hydroxide flocs and clear settling took place over pH 7.0. The concentration in the treatment water of both copper and ferric ions used as a coagulant decreased nearly to zero ( $<0.05 \text{ mg l}^{-1}$ ). During the formation of ferric hydroxide precipitates, copper was included in the formed flocs and it co-precipitated with the flocs when  $100 \text{ mg l}^{-1}$  of  $\text{Fe}(\text{III})$  was added and pH was adjusted to over 7.0. When  $50 \text{ mg l}^{-1}$  of  $\text{Fe}(\text{III})$  was added to the raw water, amorphous ferric hydroxide flocs were formed and were settled clearly between pH 7.0 and 8.0. Also, copper and ferric ions were removed more than 99.5%. On the other hand in the case of  $25 \text{ mg l}^{-1}$  of  $\text{Fe}(\text{III})$  addition, the same removal yield of copper was achieved at higher pH than the cases of higher  $\text{Fe}(\text{III})$  dosage. When the copper was removed by chemical precipitation using only pH adjustment without coagulant addition, the copper concentration of the treatment water was nearly zero ( $<0.04 \text{ mg l}^{-1}$ ) at pH greater than 9.0. From these results, it appeared that the most important factor in copper precipitation with ferric chloride was the pH of the wastewater. A similar discussion was also handled by the Terashima group [Terashima et al., 1986].

In cases of 25 and  $50 \text{ mg l}^{-1}$  of  $\text{Fe}(\text{III})$  addition, supernatants of the treatment water were tinged with light red when the pH was adjusted to over 11.0. Roques [Roques, 1996] suggested that some ferric hydroxide [ $\text{Fe}(\text{OH})_3$ ] flocs can be re-ionized to  $\text{Fe}(\text{OH})_6^{3-}$  under high concentration of  $\text{OH}^-$ . It was also supported by our results that there was a slight increase of iron concentration of treatment water under higher pH than 10.0 (Table 1).

### 2. Coagulation of Copper with Ferric Ion in Limestone Aeration Bed

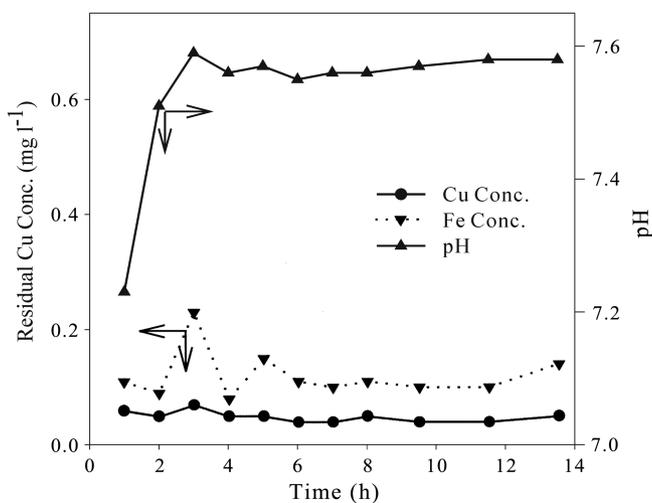
A copper removal process (Fig. 1) consisting of a limestone aeration bed and a sedimentation tank coupled with a stainless steel screen filter cartridge was developed for continuous copper removal from wastewater. The process was designed on the basis of the optimum jar test result considering both pH increase by limestone and

**Table 1. Residual concentration of iron added as a coagulant in treatment water in jar test experiments: (Raw water: Cu(II) 10 mg l<sup>-1</sup>, pH adjustment with 1 N NaOH)**

pH	Residual Fe concentration (mg l <sup>-1</sup> )		
	Fe(III) 100 mg l <sup>-1</sup> addition	Fe(III) 50 mg l <sup>-1</sup> addition	Fe(III) 25 mg l <sup>-1</sup> addition
5.0	86.70	35.20	18.30
6.0	3.70	12.40	11.10
7.0	0.14	0.17	6.20
8.0	0.09	0.09	3.45
9.0	0.10	0.11	0.12
10.0	0.12	0.10	0.13
11.0	0.14	0.27	0.32
12.0	0.37	0.67	0.87

its coagulant cost, which was pH 7.5 under Fe(III) 50 mg l<sup>-1</sup>, respectively. 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 [Plessis and Maree, 1994].

10 mg l<sup>-1</sup> of copper contaminated water containing 50 mg l<sup>-1</sup> of ferric ion was supplied at the rate of 50 ml min<sup>-1</sup> to the bottom of the limestone aeration bed packed with 1,200 g of limestone granules with 7-10 mesh size. 50 l min<sup>-1</sup> of upflow aeration was fed 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 0.011 cm sec<sup>-1</sup> and 35 minutes, respectively. The pH increase of the raw water by limestone was maintained over 7.5 for 14-hour operation (Fig. 3). Since the surface of the limestone was not contaminated during the initial operation, pH level increased gradually to 7.5. However, there is no further increment of pH due to the deposit of the ferric hydroxide/copper aggregates on the surface of



**Fig. 3. Profiles of residual metal concentration and pH in effluent from the limestone aeration bed, filtered with filter paper having 5 μm of pore size: (Raw water: Cu(II) 10 mg l<sup>-1</sup>, Coagulant: Fe(III) 50 mg l<sup>-1</sup>, Aeration for 35 min of HRT in the limestone aeration bed packed with 1,200 g of 7-10 mesh size limestone).**

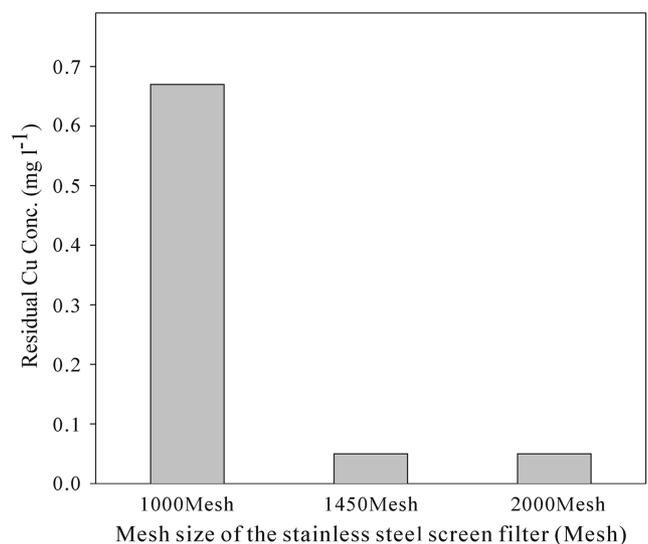
the limestone. The pH level was maintained during the whole process operation since the deposits on the surface of the limestone were removed consecutively by aeration [Sim et al., 2001]. It is important to maintain the surface of the limestone granule fresh to keep the pH over 7.5. In this experiment the aeration bubble effectively removed the iron/copper complex deposit on the surface of limestone during the operation. Both copper and iron concentrations were removed over 99.5%. The progress of iron concentrations was similar to that of copper, which supports the copper removal by co-precipitation with ferric ions.

### 3. Separation of Ferric Hydroxide/Copper Aggregates from Oxidized Wastewater using Stainless Steel Screen Filter

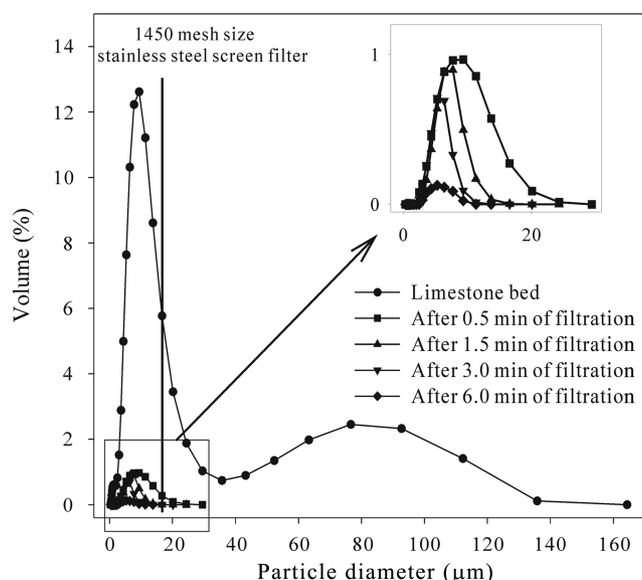
The separation unit of the flocs from oxidized wastewater was engaged by sedimentation tank which embodied a stainless steel screen filter cartridge inside (Fig. 1). The settlement of copper/iron precipitates from the limestone aeration bed and filtration of the non-sediments were performed simultaneously in one unit. The operating mode is dead-end in which filtrated water is permeated by pumping. The flux of the stainless steel screen filter was 306 l m<sup>-2</sup> hr<sup>-1</sup>.

Continuous process experiments were carried out varying the screen mesh size from 1,000 to 2,000 mesh (Fig. 4). In the cases of the screen filter of 1,450 and 2,000 mesh size, residual copper concentration of the filtrated water was below 0.05 mg l<sup>-1</sup>. When the 1,000 mesh screen filter was used, the residual copper concentration of the treatment water was over 0.65 mg l<sup>-1</sup> which is higher than that of former two screen filters. The 1,450 mesh screen filter was found to be the best considering its price.

Fig. 5 shows the particle size distribution of flocs before and after the filtration by 1,450 mesh stainless steel screen filter. Some flocs stuck to the membrane surface as the filtration progressed, resulting in decrease of the membrane pore size. The number and size of flocs in the treatment water eluted through the membrane de-



**Fig. 4. Effect of mesh size of the stainless steel screen filter on the separation of amorphous ferric-hydroxides flocs including copper and treatment water: (Raw water: Cu(II) 10 mg l<sup>-1</sup>, Coagulant: Fe(III) 50 mg l<sup>-1</sup>, Flux of the screen filter: 306 l m<sup>-2</sup> hr<sup>-1</sup>, Pore size of each mesh: 1,000 mesh - 28 μm; 1,450 mesh - 16-18 μm; 2,000 mesh - 10-12 μm, Results after 8-hr operation).**

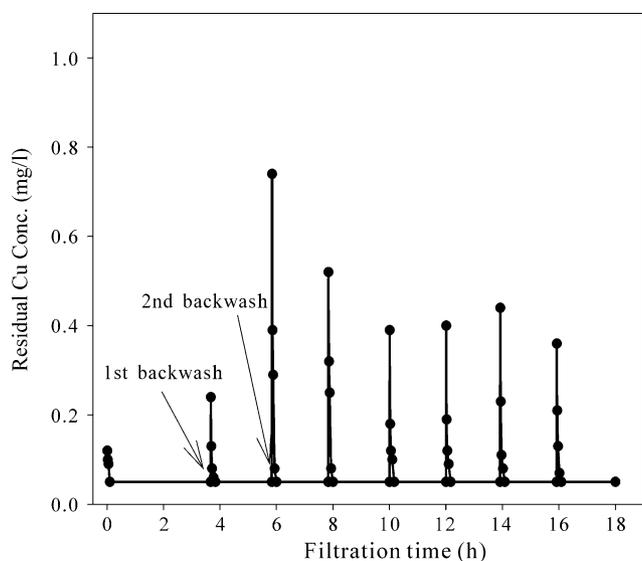


**Fig. 5.** Particle size distribution of flocs as measured by an LS 230 PSA: (Raw water: Cu(II) 10 mg l<sup>-1</sup>, Coagulant: Fe(III) 50 mg l<sup>-1</sup>, Aeration for 35 min of HRT in the limestone aeration bed packed with 1,200 g of 7-10 mesh size limestone).

creased gradually with progress of the filtration and the small size flocs including fine particles were filtered together after all.

When the vacuum pressure inside the screen filter reached 10 cm Hg, periodic backwash was performed by 10 l min<sup>-1</sup> air to remove the deposits on the filter surface.

Fig. 6 shows the change of residual copper concentration during the cycle of filtration by the 1,450 mesh stainless steel screen filter. The copper concentration of the treatment water rose dramatically for a few minutes after backwashing of the screen filter. After back-



**Fig. 6.** Profile of residual copper concentration in the treatment water filtered with the 1,450 mesh size of stainless steel screen filter: (Raw water: Cu(II) 10 mg l<sup>-1</sup>, Coagulant: Fe(III) 50 mg l<sup>-1</sup>, Flux of the screen filter: 306 l m<sup>-2</sup> hr<sup>-1</sup>, Backwash with 10 l min<sup>-1</sup> of air for 1 min).

washing, most of the deposits on the screen were removed. Precipitates in the sedimentation tank were floating from the bottom of the sedimentation tank due to the reverse flow from the filter. This might lead to high concentration of copper in the sedimentation tank and the periodic peaks of copper concentration profiles. However the average copper concentration of the treatment water in storage tank remained stable under 0.06 mg/l.

In this study, over 99.5% copper from the synthetic wastewater was removed by ferric/limestone process in which coagulation, precipitation, and filtration were applied subsequently.

This process is simple to design and easy to install even in a small area. We expect that this process can suggest another alternative for the treatment of heavy metal wastewater because cheap and durable limestone was used as a liming agent instead of chemicals such as sodium hydroxide. In addition, the stainless steel screen is not only inexpensive but also easier to operate than conventional polymer membrane from the view point of constant flux and low pressure drop ( $\Delta P$ ) of the membrane.

## ACKNOWLEDGMENTS

This work was partially supported by the Ministry of Science and Technology (MOST), Korea.

## REFERENCES

- Agelidis, T., Fytianos, K., Vasilikiotis, G. and Jannakoudakis, D., "Lead Removal from Wastewater by Cementation Utilizing a Fixed Bed of Iron Spheres," *Environ. Pollut.*, **50**, 243 (1988).
- Al-Malack, M. H., Abuzaid, N. S. and Elmubarak, A. H., "Coagulation of Polymeric Wastewater Discharged by a Chemical Factory," *Wat. Res.*, **33**, 521 (1999).
- Blanchard, G., Maunaye, M. and Martin, G., "Removal of Heavy from Waters by Means of Natural Zeolites," *Wat. Res.*, **18**, 1501 (1984).
- Gloaguen, V. and Morvan, H., "Removal of Heavy Metal Ions from Aqueous Solution by Modified Barks," *J. Environ. Sci. Health*, **A32**, 901 (1997).
- Gupta, V. K. and Ali, I., "Utilisation of Bagasse Fly Ash (a Sugar Industry Waste) for the Removal of Copper and Zinc from Wastewater," *Separation and Purification Technology*, **18**, 131 (2000).
- Higgins, T. E. and Sater, V. E., "Combined Removal of Cr, Cd, and Ni from Wastes," *Environmental Progress*, **3**, 12 (1984).
- Homburger, F., Hayes, J. A. and Pelikan, E. W., "A Guide to General Toxicology," KARGER, New York (1983).
- Jeon, C., Park, J. Y. and Yoo, Y. J., "Removal of Heavy Metals in Plating Wastewater using Carboxylated Alginic Acid," *Korean J. Chem. Eng.*, **18**, 955 (2001).
- Jiang, J. Q. and Graham, N. J. D., "Observations of the Comparative Hydrolysis Precipitation Behaviour of Polyferric Sulphate and Ferric Sulphate," *Wat. Res.*, **32**, 930 (1998).
- Kim, S. J., Jeung, S. Y. and Moon, H., "Removal and Recovery of Heavy Metal Ions in fixed and Semi-fluidized Beds," *Korean J. Chem. Eng.*, **15**, 637 (1998).
- Lee, S. H., Jung, C. H., Chung, H., Lee, M. Y. and Yang, J. W., "Removal of Heavy Metals from Aqueous Solution by Apple Residues," *Process Biochemistry*, **33**, 205 (1998).
- Martinez, C. E. and McBride, M. B., "Solubility of Cd<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, and

- Zn<sup>2+</sup> in Aged Coprecipitates with Amorphous Iron Hydroxides," *Environ. Sci. Technol.*, **32**, 743 (1998).
- Plessis, P. and Maree, J. P., "Neutralisation of Acid Water in the Chemical Industry with Limestone," *Wat. Sci. Tech.*, **29**, 93 (1994).
- Rao, P. R. and Sitharamayya, S., "Comparative Study of Different Techniques in the Removal of Heavy Metal Ions from Wastewaters," Proceedings of the Asia-Pacific Biochemical Engineering Conference, Dec. 1996, Massey University, New Zealand, 768 (1996).
- Reed, B. E. and Nonavinakere, S. K., "Metal Adsorption by Activated Carbon," *Separation Science and Technology*, **27**, 1985 (1992).
- Roques, H., "Chemical Water Treatment," VCH Publishers, Inc., New York (1996).
- Rubio, J. and Tessele, F., "Removal of Heavy Metal Ions by Adsorptive Particulate Flotation," *Minerals Engineering*, **7**, 671 (1997).
- Sim, S. J., Kang, C. D., Lee, J. W. and Kim, W. S., "Treatment of Highly Polluted Groundwater by Novel Iron Removal Process," *J. Environ. Sci. Health*, **A36**, 25 (2001).
- Terashima, Y., Ozaki, H. and Sekine, M., "Removal of Dissolved Heavy Metals by Chemical Coagulation, Magnetic Seeding and High Gradient Magnetic Filtration," *Wat. Res.*, **20**, 537 (1986).
- The Korean Ministry of Environment, "Regulatory Limits for Drinking Water and Wastewater," *J. Environmental Hi-technology*, **4**, 148 (1996).