

Precipitation Chelation of Cyanide Complexes in Electroplating Industry Wastewater

Naim, R.^{1,2*}, Kisay, L.¹, Park, J.¹, Qaisar, M.², Zulfiqar, A. B.², Noshin, M.² and Jamil, K.²

¹Department of Environmental Engineering and Biotechnology, Myongji University, Yongin, 449-728, Korea

²Department of Environmental Sciences, COMSATS Institute of Information Technology Abbottabad, Pakistan

Received 17 Aug. 2009;

Revised 10 March 2010;

Accepted 25 March 2010

ABSTRACT: Electroplating industry wastewater (EIW) characterized by high chemical oxygen demand (COD) is a big source of water and air contamination with heavy metals. The formation of cyanide complex with heavy metals is responsible for its elevated COD. The concentration of heavy metals in EIW can be removed by the use of different precipitating agents (sulfide and hydroxide). But the major bottleneck in the removal of these metals is the presence of cyanide in EIW resulting in chelation with all the metals that are soluble in water. The present work focused on, the treatment of EIW containing Cr, Ni, Zn and CN and the optimization of dosage concentration which was reliable for the dissociation of cyanide complex for maximal removal efficiency. We used hydroxide, sulfide and carbonate precipitation from different precipitating agents (NaOH, Ca(OH)₂, CaCO₃, Na₂S5H₂O, NaHS and NaHSO₃). Sulfide precipitation was a viable option for the treatment of EIW as compared to hydroxide and carbonate precipitation. Moreover, COD reduction capacity of sulfide precipitation was higher than others. It was also found that Ni and Cr made a complex with cyanide that halted the removal efficiency while there was no evidence for Zn complexation; otherwise fragile complexation was evidenced.

Key words: Chelation precipitation, Cyanide complexes, Electroplating industry wastewater

INTRODUCTION

Discharges from electroplating industries are one of the major concerns of the present world. The establishment of electroplating industries is prohibited due to their heavy metals and other toxic chemical emissions (Aziz *et al.*, 2008). The effluent discharged from these industries can contaminate the water resulting in toxic effect to our health and ecosystem due to their potential of bioaccumulation (Yassi *et al.*, 2001). The effluent waste water from the electroplating industries contain chromium, cyanide, nickel, copper, zinc and lead (Aziz and Adlan, 2008; XU and Ti-Xu, 2008; Jeon *et al.*, 2001). In electroplating industry wastewater (EIW), cyanide has a great affinity for heavy metals forming complexes with almost all the metals that are responsible for increase in COD of EIW. As cyanide causes breathing problems, neurotoxic effects, nerve damage even death (Dash *et al.*, 2008). However, metal-cyanide complexes themselves are much less toxic than free cy-

nide. So, some preventive measures should be adopted to get rid of its toxic and hazardous effects. Heavy metals can be removed from EIW by the process of precipitation and ion exchange resins (Mikhopadhyay and Sundquist., 2007; Jeon *et al.*, 2001). But the major problem is again the removal or breakage of metal-cyanide complex as a function of solution pH (Dash and Balomajumder., 2008) agitation time, settling time and precipitant dosage also (Feng *et al.*, 2000). The metal-cyanide complex can breakdown under alkaline pH.

The specific objective of the present study was to test the suitability of precipitation chelation for heavy metals recovery from EIW using sulfide, hydroxide and carbonate as precipitants.

MATERIAL & METHODS

EIW was collected from an electroplating industry named as "Myung-Sung 344-7 Wonchun-

*Corresponding author E-mail: naimkanwar@yahoo.com

dong, Younngtong-gu, Suwon, 443-823, Korea” The range of heavy metal concentration was similar to the previous reports/studies of waste water. Based on previous studies, it was found that most of the electroplating industries have the metal concentration in the range of 100-200 mg/L in their effluent water (Jeon *et al.*, 2001; Anon., 1980).

All the chemicals used for the study were of analytical grade. The stock solutions were made in distilled water and their pH was adjusted by adding 0.1M H₂SO₄ or 0.1M NaOH. As most of the electroplating industries possess Cr, Ni, Zn and cyanide, we prepared the stock solution of Cr, Ni, Zn and cyanide by using the chemicals (98% pure) Cr₂O₆, NiNO₃·6H₂O ZnSO₄·7H₂O, NaCN respectively. The composition of target EIW solution was Cr 200 mg/L, Ni 200 mg/L, Zn 100 mg/L and cyanide as 150 mg/L. All the experiments were conducted at an ambient temperature of 25°C. A cylindrical batch reactor was used with a working volume of 1L. Various doses of precipitants were used according to the requirements. The chemicals were thoroughly mixed for 15 minutes by using a magnetic stirrer with 200-300 rpm. After the process of precipitation the solution was passed through a filter with a pore size of 0.45 micrometer for heavy metal determination.

After the precipitation experiment, solution was analyzed by “Atomic Absorption Spectrophotometer” for the detection of heavy metals concentration. The COD was measured according to standard methods (APHA, 2005).

RESULTS & DISCUSSION

Initially, the mixing time of the EIW with precipitant was optimized that was 10-15 minutes for each experiment. In hydroxide precipitation, we used two precipitating agents like NaOH and lime in the presence and absence of cyanide in order to compare their removal efficiency and the optimum dosage required for the maximum removal of heavy metals. Moreover, the effect of cyanide was also the point of concern. As cyanide has detrimental effects on removal efficiency, by its complexation with metals that are soluble in nature. When we conducted the experiment using NaOH (in the absence of cyanide), it was found that 400mg/L dosage of NaOH was high enough to give about 99% removal of Ni and Zn while Cr shows a removal of 66%. The pH at this dosage was 10-11.5. It was also observed that chromium showed amphoteric behavior, as its removal decreased with increasing doses of soda ash. While, in the presence of cyanide Zn, Ni and Cr removed up to 99%, 86% and 36% respectively at the dosage of 500 mg/L of NaOH. It was observed that the Ni removal retarded when NaOH dosage was added, even though the removal reached 44% with a NaOH

dosage of 700mg/L. While the removal of Cr increased from 13 to 36% at the same dosage (Fig 1a & b). It implied that, the cyanide did not make a complex with Zn or this complex broke at this dosage while Ni formed a complex with cyanide that could breakdown at low dosage or slightly alkaline pH and this complex got its strength with an increasing concentration of NaOH resulting in decreased removal efficiency. In case of Cr, the existence of this cyanide complex was observed but it breaks down at increased dosage. So, we have to use some other means to remove remaining Cr in the presence of cyanide that can be “ion exchanged” for further polishing of EIW.

The use of lime has advantage over caustic soda due to its lower cost and its production of higher settled sludge with high dewatering capacity (Beasley and Glass., 1998; Aziz and Smith., 1992). So, we were interested to have a look at lime precipitation and to optimize its various parameters as like caustic precipitation in the absence and presence of cyanide. When we used lime, it showed 99% removal of Cr, Ni and Zn with an optimum dosage of 600mg/L and the pH at this dosage was in the range of 9-10. Here again we observed that Cr showed amphoteric phenomenon regarding its removal, as it showed 76%, 55% and 100% removal with a dose of 200, 400 and 600mg/L, respectively. So, we concluded that the Cr removal was pH dependent, as lime dosage was responsible for the change in solution pH. In the presence of cyanide, lime addition caused removal of Ni and Zn very successfully (99-100%) at dose of 600 mg/L. But in case of Cr the removal efficiency was quite low i.e. 71% only while Ni again comes into solution if we increase the dosage up to 800mg/L (Fig 2a & b).

If we compare both of the precipitating agents, it can be concluded that lime precipitation is more effective than that of caustic precipitation, as it gives higher removal efficiency of Zn, Ni, and Cr as well, but the dosage required is more (600mg/L) than other (i.e. 200mg/L). Secondly, it was seen that Cr and Ni make a complex with CN that is pH sensitive phenomenon while Zn does not make any complex; additionally, lime removes Ni even in the presence of cyanide. But its amphoteric ability also appears in lime precipitation. In hydroxide precipitation process, the COD reduced in the range of 800-900 to 400-450 mg/L by the use of lime and caustic.

Various researchers have reported that lime stone is also a potential candidate for the removal of heavy metals from most of the industrial waste water (Aziz *et al.*, 2008). In our experiment we used CaCO₃ for the treatment of our target waste water, CaCO₃ resulted in a maximum removal efficiency of 46%, 15% and 16% for Cr, Ni and Zn respectively even though in the

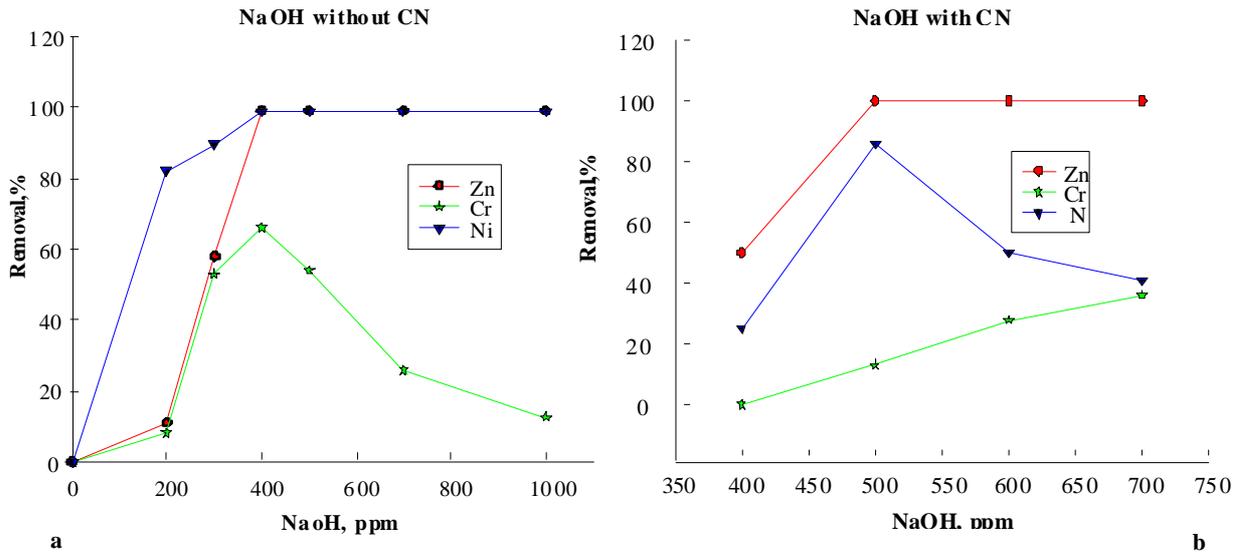


Fig. 1. Hydroxide precipitation with NaOH

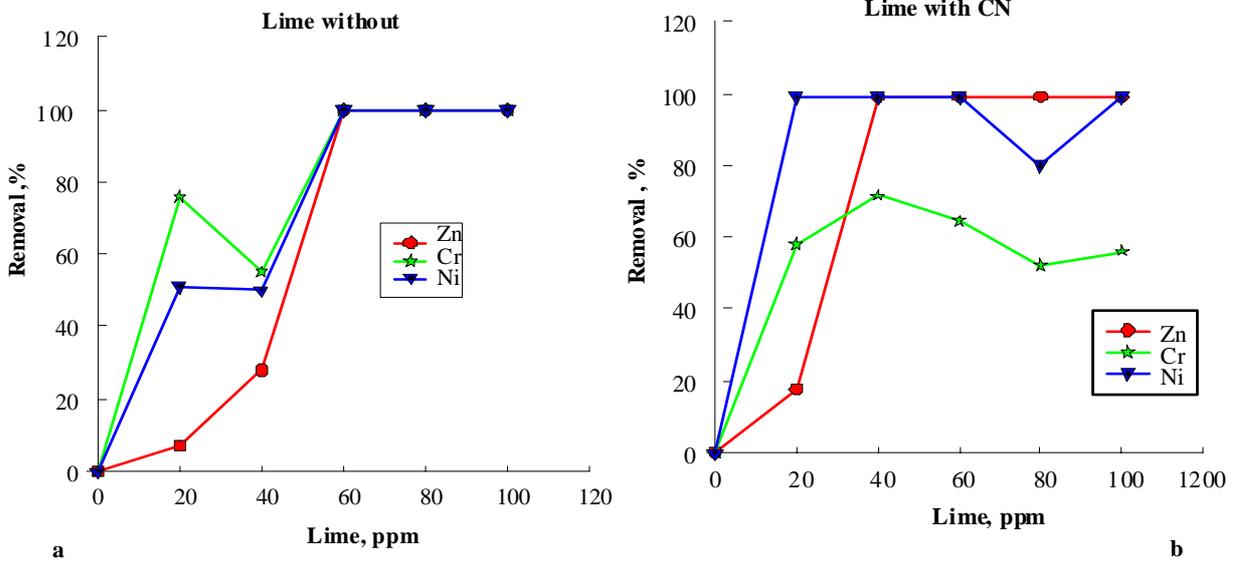


Fig. 2. Hydroxide precipitation with $\text{Ca}(\text{OH})_2$

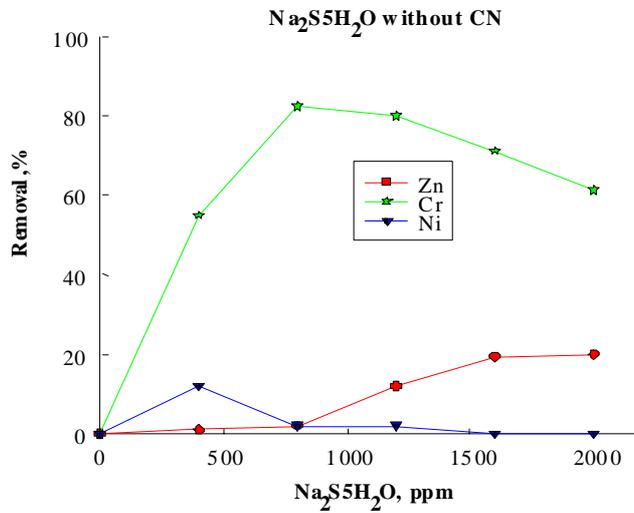


Fig. 3. Carbonate precipitation with CaCO_3

absence of cyanide (Fig. 3). Moreover, the dosage required is quite high as compared to caustic and lime precipitation resulting, increase in pH of effluent waste and sludge volume also. So, we concluded that lime stone was not a better choice for the treatment of EIW possessing heavy metals like Ni, Zn and Cr. We used different sulfide precipitating agents showing the following results. Fig. 4 shows that in the absence of cyanide Cr can be removed up to 82% while Zn and Ni up to 20 and 12% only. The pH of the solution after this treatment was in the range of 5-6. In the presence of cyanide this chemical showed very effective and interesting results that it removed all the Cr and Ni at the dosage of 800mg/L while Zn was completely removed at 1200mg/L concentration. An important finding in this treatment may be that sulfide precipitation i.e. $\text{Na}_2\text{S}5\text{H}_2\text{O}$ may be more beneficial than hydroxide or limestone precipitation. As in the presence of this precipitating agent the chelation of CN^- with other chemicals dissociates completely and makes insoluble compounds. But the limiting factor to use this kind of technique is that, the dosage required in this experiment is high enough that will cause high sludge volume. The pH value of this effluent was 5-6.

NaHS was used as a precipitating agent by the addition of sulphuric acid to keep the pH value less than 3. In the absence of cyanide a complete removal of all the metals including Cr was obtained with a dosage of about 800 mg/L. While in the presence of cyanide there was the complete removal of Zn and Cr but Ni could be removed up to 94% and Ni again released into the solution with increase in dosage (Fig 5a&b). Here we can see that sulfide precipitation is quite sat-

isfactory technique for the breakage of cyanide-metal complexes. The pH of the solution after this treatment was about 4.

The removal of heavy metals by the use of NaHSO_3 was done with the addition of lime, as it is a precipitating agent and it maintains the pH of the medium in alkaline range. In the absence of cyanide there was complete removal of all the metals at an optimum dose of 800 mg/L. When the cyanide was present in the solution, the removal efficiency of this agent halted. It removed Ni up to 99% at a dosage of about 400-500mg/L, but at this concentration there was only 70-80% removal of Cr and Zn. Cr and Zn removed at a dosage of 800mg/L, additionally Ni comes into the solution with increased dose of NaHSO_3 due to the reason that it may form complex with cyanide that is soluble in water (at which Zn and Cr is removed) (Fig 6a&b). So, it is not possible to remove all the metals at a single dosage. In sulfide precipitation COD of the waste water was reduced up to the level of 310 mg/L. Sulfide precipitation is also capable to remove metals from waste water (Bhattacharyya *et al.*, 1981; Larson *et al.*, 1976). Sulfide precipitation generates high level of sludge solids, but the problem with this kind of precipitation results in the emission of sulfide gases which are toxic to health as well as produce bad smell.

In our experiment, we used hydroxide and sulfide precipitation to remove heavy metals; it was found that, the presence of cyanide in the solution was a major bottleneck towards the removal of heavy metals (Ni, Cr, and Zn). Among these heavy metals, only nickel formed a chelate with cyanide i.e. $[\text{Ni}(\text{CN})_4]^{2-}$, while other metals precipitated easily in the form of their

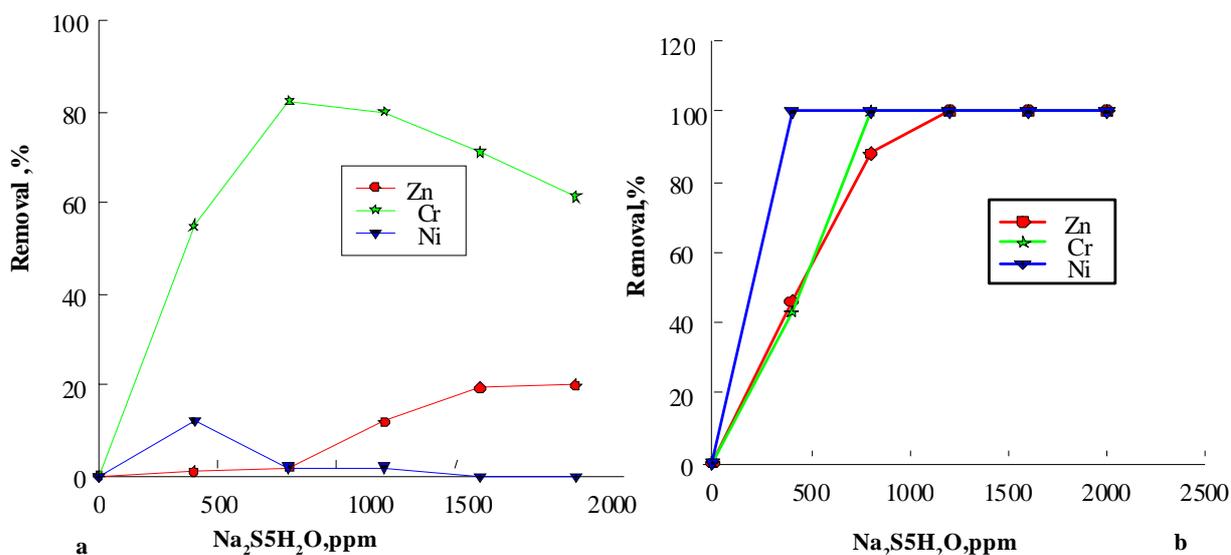


Fig. 4. Sulfide precipitation using $\text{Na}_2\text{S}5\text{H}_2\text{O}$ (a) In the absence of cyanide (b) In the presence of cyanide

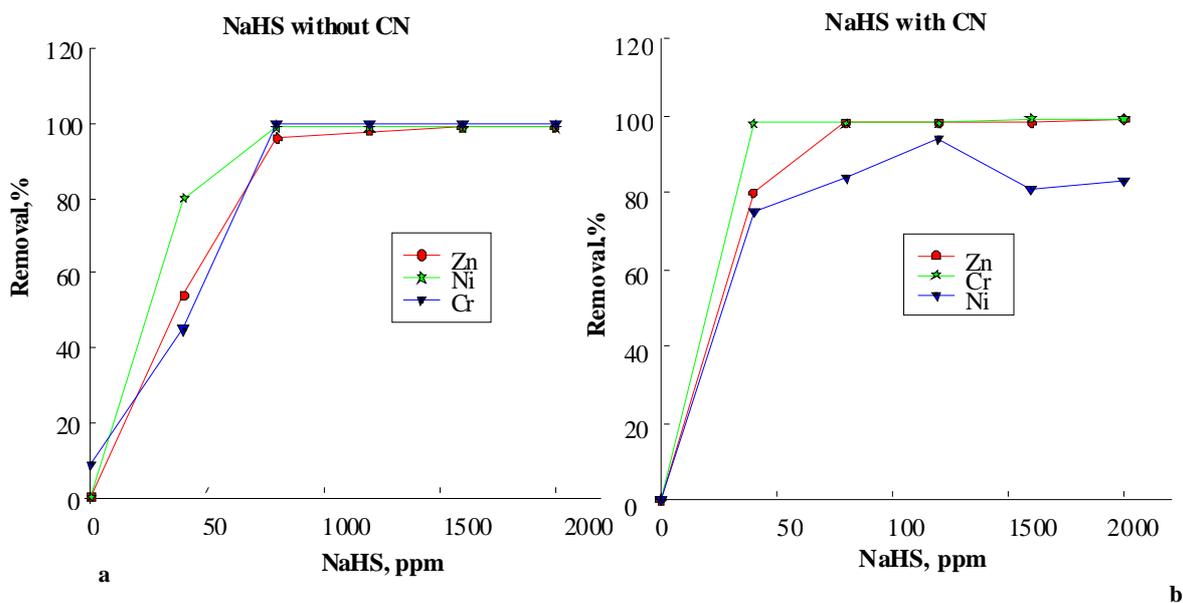


Fig. 5. Sulfide precipitation with NaHS

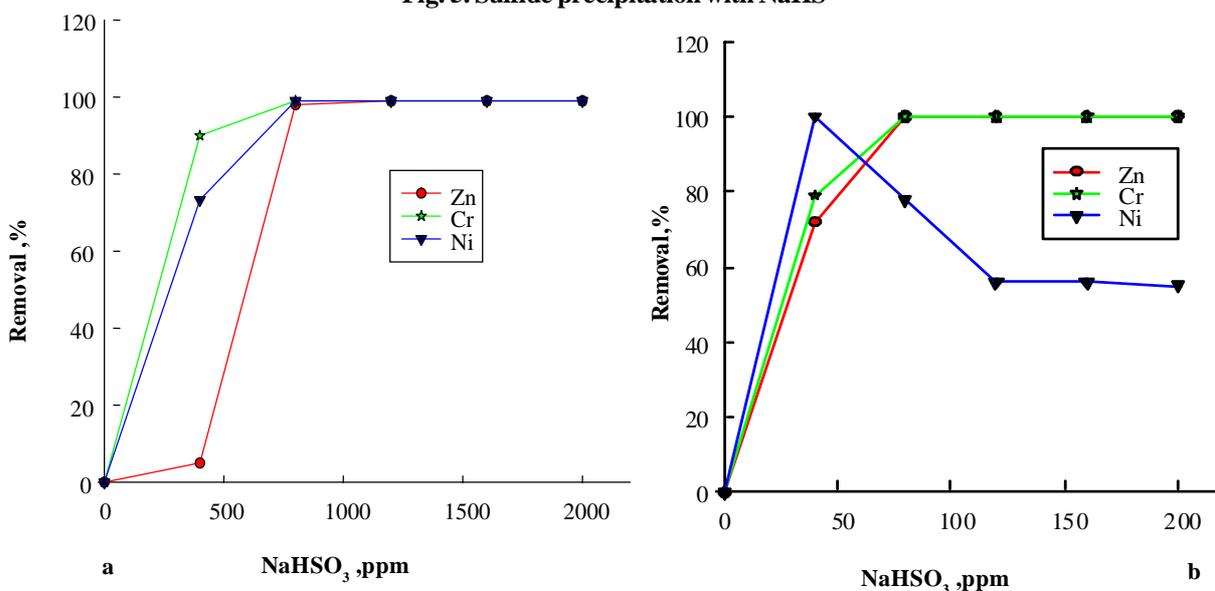


Fig. 6. Sulfide precipitation with NaHSO₃

hydroxides or sulfides at certain pH value. Two most common alkalis, caustic soda and lime were used for the formation of insoluble hydroxides. Lime has advantage over caustic soda of lower per unit cost for neutralizing capacity; further the settled sludge from the lime treatment was higher in solids content and much easy to dewater (Beasley *et al.*, 1998). By the use of sulfide precipitation, a high level of metal insolubility was achieved (Cheremisionoff, 1995) but it generated large volume of sludge as compared to hydroxides. In our experiment, we optimized the conditions (dosage mg/L, pH, mixing time) for different precipitating agent (hydroxide, carbonate and sulfide) like NaOH, Ca(OH)₂, Na₂S, NaHS and NaHSO₃. Calcium carbonate is also an alternative and potential candi-

date for metal removal with low price and smaller sludge volume but comparatively low removal efficiency (Feng *et al.*, 2000; Anon., 1980). We compared the removal efficiency of each agent in the presence and absence of cyanide with an optimal dosage value. It was found, that hydroxide precipitation was more convenient than sulfide precipitation, regarding its removal efficiency and the effect of metal-cyanide complex as well.

CONCLUSION

The EIW can be treated very efficiently by the use of hydroxide and sulfide precipitation. In the absence of cyanide there is no hurdle for the treatment, but in the presence of cyanide there is the formation of metal chelate that is soluble in water. Ni and Cr are the metals

that form a soluble complex with cyanide but in case of Zn there was no evidence or effect of cyanide in metal removal. If we compare the removal efficiency of lime and caustic in the presence of cyanide, lime seems to be effective and more efficient agent, as it removes Zn and Ni but Cr is removed only up to 66%. In our experiment, it was seen that Ni showed an amphoteric behavior with the precipitant dosage whether it was hydroxide, carbonate or sulfide. Sulfide precipitation proved to be a good choice for the treatment of electroplating waste water containing Cr, Ni, Zn and cyanide as compared to carbonate and hydroxide precipitation. The order of efficiency of various precipitants was Sulfide > Hydroxide > Carbonate. In case of sulfide precipitation we could see that there was no inhibitory effect of cyanide towards the removal of metals while in hydroxide this phenomenon was very common. Sulfide precipitation requires more dosage than others resulting in high sludge volume but it is viable option in the process of waste water treatment due to its high removal capacity and low capital cost. The COD reduction capacity of sulfide was also higher than other precipitations.

ACKNOWLEDGEMENTS

The authors would like to thank Higher Education Commission of Pakistan (HEC) and Myongji University, South Korea, for providing financial support for this research.

REFERENCES

- APHA, (1992). American Public Health Association. Standard methods for the Examination of Water and Wastewater. 18th Ed., WPCF, 1-18.
- Yassi, A., Kjellstrom, T., Kok, T. D. and Guidotti, T. L. (2001). Basic environmental health, Industrial pollution and chemical safety (pp. 335). Oxford University Press.
- Anon, 1980. Control and treatment technology for the metal finishing industry: sulphide precipitation, No. EPA 625/8-80-003. EPA Technology Transfer Report.
- Beasley, D. M. G. and Glass, W. I. (1998). Cyanide poisoning; Pathophysiology and treatment recommendations. *Occup. Med. (Lond)*, **48**, 427-31.
- Mikhopadhyay, B., Sundquist, J. and Schmitz, R. J. (2007). Removal of Cr(VI) from Cr-contaminated groundwater through electrochemical addition of Fe(II). *Journal of Environmental Management*, **82**, 6-76.
- Bhattacharyya, D., Sun, G., Sund, H. and Schwitzgebel, K. (1981). Precipitation of heavy metals with sodium sulfide: bench-scale and full-scale experimental results. *AIChE Symposium series*, **77**, 31-38.
- Feng, D., Aldrich, C. and Tan, H. (2000). Treatment of acid mine water by use of heavy metal precipitation and ion exchange. *Minerals Engineering*, **13**, 623-642.
- Jeon, C., Park, J. Y. and Yoo, J. (2001). Removal of heavy metal in electroplating waste water using Carboxylated Alginic Acid. *Korean Journal Chemical Engineering*, **18**, 955-960.
- Aziz, H. A., Adlan, M. N. and Ariffin, K. S. (2008). Heavy metals (Cd, Pb, Ni, Cu, and Cr(III)) removal from water in Malaysia: Post treatment by high quality limestone. *Biosource Technology*, **99**, 1578-1583.
- Aziz, H. A. and Smith, P. G. (1992). The influence of pH and coarse media on manganese precipitation from water. *Water Research*, **26**, 853-855.
- Joseph, D. E. (1995). *Industrial wastewater treatment 1st ed* (pp. 51). CRC Press Inc New York.
- Osathapan, K., Boonpitak, T. and Laopirojana, T. (2008). Removal of cyanide and Zn-cyanide complex by ion-exchange process. *Water Air Soil Pollution*, **194**, 179-183.
- Awan, M. A. (2004). Reduction of chemical oxygen demand from tannery wastewater by oxidation. *Electronic Journal of Environmental Agricultural and Food Chemistry*, **3**, 625-628.
- Cheremisionoff, P. N. (1995). *Handbook of heavy metal removal. Heavy metals/Cyanide removal* (pp. 421-423). CRC Press Inc New York.
- Dash, R. R., Balomajumder, C. and Kumar, A. (2009). Removal of cyanide from water and wastewater using granular activated carbon. *Chemical Engineering Journal*, **146**, 408-13.
- Dash, R. R., Balomajumdar, C. and Kumar, A. (2008). Treatment of metal cyanide bearing wastewater by simultaneous adsorption and biodegradation (SAB), *Journal of Hazardous Material*, **152**, 387-396.
- Larson, H. P. and Ross L. W. (1976). Two-stage process chemically treats mine drainage to remove dissolved metals (pp. 349). *Operating Handbook of Mineral Processing*.
- Xu, Y. and Xu, T. (2008). Heavy metal complexes wastewater treatment with chelation precipitation (pp. 2789-2793). *Bioinformatics and Biomedical Engineering. ICBBE 2008. The 2nd International Conference*.
- Yassi, A., Kjellstrom, T., Kok, T. D. and Guidotti, T. L. (2001). Basic environmental health, Industrial pollution and chemical safety (pp. 335). Oxford University Press.