

**THE EFFECT OF EDTA AND CYANIDE ON
THE REMOVAL OF HEAVY METALS
BY PRECIPITATION PROCESS**

By

M. R. Lasheen, A. Ashmawy and H. Sayed

ABSTRACT

Industrial wastewater generated in electroplating and metal finishing industries typically contains toxic heavy metals. Depending on their origin this wastewaters may also contains chelating agents such as EDTA and cyanide.

This paper addresses the effect of strong chelating agent, EDTA and cyanide on the removal of copper, cadmium, hexavalent chromium and zinc using hydroxides, carbonate and sulfide treatment. The over all efficiency of the different precipitation techniques for single and multi - metals removal increased in the following order :

sulfide > combined (hydroxide and carbonate) > hydroxide > carbonate

The presence of cyanide and EDTA highly inhibited metals removal. The inhibition depends on metals types and metal - ligand molar ratio.

Pretreatment of wastewater before metals precipitation should involve segregation or destruction of EDTA and Cyanide, chromium reduction, and or neutralization.

INTRODUCTION

Water pollution by heavy metals resulting from anthropogenic impact is causing serious ecological problems in many parts of the world. This situation is

The Effect of EDTA and Cyanide on the Removal

aggravated by the lack of natural elimination processes for metals. As a result metals shift from one form within the aquatic environment to another, including the biota, often with detrimental effects where sufficient accumulation of the metals in biota occurs through food chain transfer, there is also an increasing toxicological risk for man (1).

Industrial effluent controls are now required to protect the large financial investment in the infrastructure and ensure maximum potential reuse of the effluent and sludge. Many heavy metals effluents require chemical treatment because they are highly toxic to biological processes.

According to the Egyptian environmental legislation, law 93 / 1962 which is modified under Ministerial Decree 9 / 89 controls the discharge of toxic and hazardous substances to the sewerage network. Law 48 of 1982 regulates discharge of wastewaters into Nile water and its waterways from pollution.

A number of specialized processes have been developed for the removal of metals from waste discharges. These unit operations include chemical precipitation coagulation / flocculation, ion exchange / solvent extraction, concentration, complexation, electrochemical operations, biological operations, adsorption, evaporation, filtration and membrane processes (2 - 5).

In industry however chemical precipitation is by far the most widely used process to remove heavy metals, nearly 75% of the electroplating facilities employ precipitation treatment (using either hydroxide, carbonate, or sulfide treatment or some combination of these treatments) to treat their wastewaters (6).

The main objectives of this study were to examine the removal of cadmium, chromium (VI), copper and zinc single and multi - metals by using chemical precipitation (hydroxide, carbonate, sulfide or their combination) and to evaluate the effect of EDTA and cyanide on metals removal.

MATERIALS AND METHODS

The laboratory - scale experimental studies were conducted using synthetic wastewater prepared using double distilled water and 10 mg / L for each of Cd (II), Cr (VI), Cu (II) and Zn (II) individually or in combinations.

The jar test procedure was carried out to evaluate the removal levels of metals using calcium oxide, sodium carbonate, ferrous sulfide, sodium sulfide and their combinations.

Hexavalent chromium was reduced firstly at pH 2 - 3 using 1.56 time the theoretical stiochiometric requirement of ferrous sulfate.

To evaluate the effect of EDTA and cyanide they were added to metal prior to the jar test to assure enough equilibrium time for complexation at different molar ratios.

Samples were digested by concentrated nitric acid and metals were measured using a Perkin - Elmer Atomic Absorption Spectrophotometer (7).

RESULTS AND DISCUSSION

Four basic techniques were used to remove heavy metals from solution. These techniques include formation of metal hydroxides metal carbonates, metal sulfides or combination of them.

1- Hydroxide Precipitation :

The results presented in Figure (1) showed that lime effectively precipitates metals. Cadmium and zinc removal reached 95 % at pH 10.5. However, copper removal was 95 % at pH 9.0. Multi metals removal increased by increasing CaO dose. The highest multi - metals removals were > 99 % at pH 10.5 (Figure 2). It is worth mentioning that Cr (III) removal rate was > 99 % at pH 6.4.

Grosse (8) reported that because the optimum pH for hydroxide

precipitation is different for each metal ion, treatment of mixed metal aqueous wastes may require some adjustment. However, this adjustment must stay within the limits of regulation. Typically hydroxide precipitation is optimum at pH values between 9.5 and 12.

2- Carbonate Precipitation :

From Figure (1) it can be observed that cadmium and copper removal were 94 % and 91 % at pH 9.5. Carbonate removal system was not effective for zinc removal as that of the hydroxide. Maximum removal was only 87 % at pH 10.5. Multi / metals removal reached > 99 % at pH 9.5. Similar to the hydroxide system, Cr (III) removal was > 99 % at pH 6.6 (Figure 2).

Similar results were achieved by Cliffored et al., (3) and Patterson, et al. (9), they reported that carbonate precipitation of heavy metals has been shown to be an effective treatment alternative to hydroxide precipitation.

3- Combined Precipitation (hydroxide and carbonate combination) :

Lime was added first to raise the pH to around 7 then various concentrations of carbonates were added to raise the pH.

The results of this study showed that the combined precipitation system using carbonate and hydroxide combination increased single metal removal rates for Cd, Cu and Zn to 93 %, 97 % and 91 %, respectively (Figure 1). Multi - metals removal were \geq 98 % at pH 9.0 (Figure 2).

4- Hexavalent Chromium Reduction and Precipitation :

Since hexavalent chromium is typically present as an anion, its direct precipitation is not usually practical. Instead, the anionic species is reduced to trivalent chromic ion and then precipitated as chromic hydroxide by lime.

A comparison between two systems of chromium reduction is shown in Figure (3). Hexavalent chromium was completely reduced to trivalent chromium using $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ or FeS . The optimum dose of Ferrous sulfate capable of reducing hexavalent chromium to trivalent chromium was 1.56 times the stoichiometric amount at pH 2 - 3. Removal rates for single and multi - metals were > 99 % with an effective source of alkalinity at pH 6.5 (Figure 4 and 5).

Siegel and Clifford (10) found that ferrous ion reacts with Cr (VI) rapidly at pH levels below pH 3.0 and acid must be added for adjustment. In order to obtain a complete reaction, an excess dosage of 2.5 time the theoretical addition of ferrous sulfate must be made. Each 1 mg / L Cr needed 16.03 mg / L $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$. Typically the chemical dosage needed for Cr (VI) reduction is two times the stoichiometric requirement (12 and 13).

5- Sulfide Precipitation :

The two processes employed to precipitate metals as sulfide are soluble sulfide precipitation and insoluble sulfide precipitation using sodium sulfide and ferrous sulfide, respectively.

Ferrous sulfide treatment system was used to supplement hydroxide precipitation system for chromium reduction and increased single and multi metal removal to ≥ 97 % at pH 8.0. Ferrous sulfide can be used at pH 7.0 as reducing and polishing system to precipitate dissolved multi - metals of Cd, Cr (VI), Cu and Zn from wastewater after the insoluble multi - metals hydroxide has been precipitated, and the removal rate was 99 % (Figure 5 and 6).

When sodium sulfide treatment system, with an effective source of alkalinity was used, the removal rate of Cd, Cu and Zn was 91%, 95% and 92% at pH 8.0. Sodium sulfide was very effective for multi - metals (Cd, Cu and Zn) removal. The recorded removal rates were ≥ 97 at pH 8.0 (Figure 5 and 6).

Similarly, Resta et al (14) evaluated the effectiveness and feasibility of soluble sulfide precipitation for the removal of heavy metals (Cd, Cr, Cu, Pb, Ni and Zn), they found that the removal rate ranged from 81.7% to 98% and the maximum residual rate concentration was 0.41 mg / L.

The over all efficiency of the different precipitation techniques for single and multi - metals removal increased in the following order :

sulfide > combined (hydroxide and carbonate) > hydroxide > carbonate.

6- Effect of EDTA and Cyanide :

The results (Figure 5) showed that the presence of EDTA reduced substantially the removal of Cd, Cu, and Zn. There was no significant removal specially at 1 : 5 Metal - EDTA molar ratio which indicated the formation of soluble metals - EDTA complexes for all metals investigated.

U. S. EPA (15) suggested that when chelating compounds enter the waste stream, they inhibit the precipitation of metals so that additional treatment chemicals must be used, and these treatment chemicals may end up in the sludge and contribute to the volume of hazardous wastes.

Bhattacharyya, et al., (16) reported that the presence of chelating agents highly influences the extent of sulfide precipitation mainly because of the competition between the formation of metal sulfide and metal chelates.

Cyanide affected the removal efficiency of single metal (Cd, Cu and Zn). At (1 : 1) Metals - CN molar ratio, the removal rates were reduced to 60 %, 66 %, and 0.0 %, respectively (Figure 7). The efficiency decreased in the following order : $Cu \geq Cd > Zn$.

Davis (17) and Nordqvist (18) suggested that for the removal of copper, cadmium and zinc cyanide destruction step should be placed upstream from the

metal treatment step and it is the most logical approach for minimizing cyanide interference. Chlorination may be needed to break down the complex organic metallic compounds prior to chemical precipitation (6).

On the other hand in our study, ferrous sulfide was able to precipitate copper as copper sulfide even in the presence of (1 : 10) Cu - EDTA molar ratio, the removal rate was 90 % at pH 9.0.

Similarly, U. S. EPA (15) reported that in the presence of chelating agent, hydroxide precipitation is not possible at high pH, while sulfide precipitation of copper is possible.

CONCLUSION

Excellent metal removal were achieved using metal sulfide precipitation. Considerably lower residual metal concentration could be achieved as compared to metal hydroxide precipitation. The presence of EDTA and cyanide severely inhibited removal of heavy metals.

The overall efficiency of the different precipitation technique for single and multi - metals removal increased in the following order :

sulfide > combined (hydroxide and carbonate) > hydroxide > carbonate.

Finally in Egypt, despite a strongly worded law requiring treatment of all industrial wastes entering (discharged) into Nile, its canal, drains and groundwater (law 48 / 1982), the great majority of industries have not yet installed wastewater treatment facilities. Indeed, there is very little information available on the concentrations and loads of pollutants discharged from individual facilities.

REFERENCES

- 1- Water Quality Assessment ed. by D. Chabman Published by Chabman and Hall London U. K. 1992.
- 2- Patterson, T. W., (1988) "Metal Treatment and Recovery" pp 333 - 345, In : Metal Speciation Theory, Analysis and Application. Kramer, J. R. and Allen, H. E. Eds. Lewis Publishers, INC. Chelsea, MI.
- 3- Clifford, D.; Subramanian, S. and Sorg, T. J., (1986) "Removing Dissolved Inorganic Contaminants from Water" Environ. Sci. Technol. 20 (11) : 1072 - 1080.
- 4- Patterson, J. W. and Minear, R. A. (1975) "Physical - Chemical Methods of Heavy Metals Removal". pp 261 - 276. "In Heavy Metals in the Aquatic Environment". P. A. Krenkel, ed., Pergamon Press, Oxford, England.
- 5- Brooks, Cyde, S., (1991) "Metals Recovery from Industrial Waste" Lewis Pub., INC., Chelsea, MI. U. S. A.
- 6- Patters, R. W. and Ku, Y., (1985) "Batch, Precipitation Studies for Heavy Metal Removal by Sulfide Precipitation". AICHE Sympos. Series Separation of Heavy Metals and Other Contaminants 81 (243) : 9 - 27.
- 7- APHA - AWWA - WPCF, (1989) "Standard Methods for the Examination of Water and Wastewater". Edition Washington, D. C., American Public Health Association 17th edition.
- 8- Grosse, D. W., (1987) "Metal Bearing Hazardous Waste Streams". In : Treatment Technologies for Hazardous Wastes. England, H. M. and Mafrika, L. f. eds., APCA reprint Series - Rs - 13, U. S. A.
- 9- Patterson, J. W.; Allen, H. E. and Scala, J. J., (1977) "Carbonate Precipitation for Heavy Metals Pollutants". J. Water Pollut. Control Fed., 49 (12) : 2397 - 2410.

- 10- Siegel, S. and Clifford, D. A., (1988) "Removal of Chromium from Ion Exchange Regenerate Solution". PB 88 - 158 084 / AS NTIS, Springfield, Va.
- 11- Eckenfelder, W. W., Jr., (1989) "Industrial Water Pollution Control". Micraw - Hill Book Co. London.
- 12- U. S. Environmental Protection Agency, (1980) "Summary Report : Control and Treatment Technology for the Metal Finishing Industry, Sulfide Precipitation". EPA - 625 / 8 - 80 - 003.
- 13- Kunz, R. G.; Hess, I. G.; Yen, A. F. and Arseneaux, A. A, (1980) "Kinetic Model for Chromate Reduction in Cooling Tower Blowdown". JWPCF, 52, 2327 - 2339.
- 14- Resta, J. J.; Daly, M. and Pressman, M., (1984) "Soluble - Sulfide Precipitation Treatment of Metal Finishing Wastewater". Proc. 16th Mid-Atlantic Indust. Waste Conf., Vol. 16 pp 265 - 278.
- 15- Environmental Protection Agency, (1992) "The Metal Finishing Industry". Guides to Pollution Prevention EPA / 625 / R - 92 / 011.
- 16- Bhattacharyya, D.; Jumawan, A.; Sun, C. and Schwitzebel, K., (1981) "Precipitation of Sulfide : Bench - Scale and Full - Scale Experimental Results". AICHE Symposium Series, 77 (209), pp 31 - 42.
- 17- Davis, J. A., (1977) "Adsorption of Trace Metals and Complexing Ligands at the Oxide / Water Interface". Ph. D. thesis, Stanford Univ. Stanford Calif., U. S. A.
- 18- Nordqvist, K. R.; Benjamin, M. M. and Ferguson, J. F., (1988) "Effects of Cyanide and Polyphosphates on Adsorption of Metals from Simulated and Real Mixed - Metal Plating Wastes". Wat. Res. 22, pp 837 - 846.

تأثير المركبات العضوية المخلبية والسيانيد

على إزالة المعادن الثقيلة بطرق

الترسيب المختلفة

تعتبر الصناعات المعدنية من المصادر الرئيسية للملوثات الغير عضوية وخاصة المعادن الثقيلة. ولذلك أهتمت الدراسة بتقييم كفاءة المرسبات المختلفة وكذلك تأثير تواجد كلاً من EDTA والسيانيد على كفاءة المعالجة وقد أوضحت النتائج أن كفاءة المعالجة للمعادن منفردة كانت أم مجتمعة تزداد كما يلي :

الكبريتيدات > خليط من الهيدروكسيد والكريونات > الهيدروكسيد > الكريونات

وكان لكلاً من EDTA والسيانيد تأثيره السلبي على كفاءة المعالجة يعتمد على نوع المعدن ونسبة التركيز الجزيئي بين كل من EDTA والسيانيد والمعدن. وبزيادة تركيز السيانيد قلت كفاءة الإزالة للمعادن منفردة كالتالي :

الخاصين > الكادميوم \geq النحاس

وكذلك بزيادة تركيزات EDTA قلت كفاءة الإزالة للمعادن منفردة كالتالي :

النحاس > الخاصين > الكادميوم

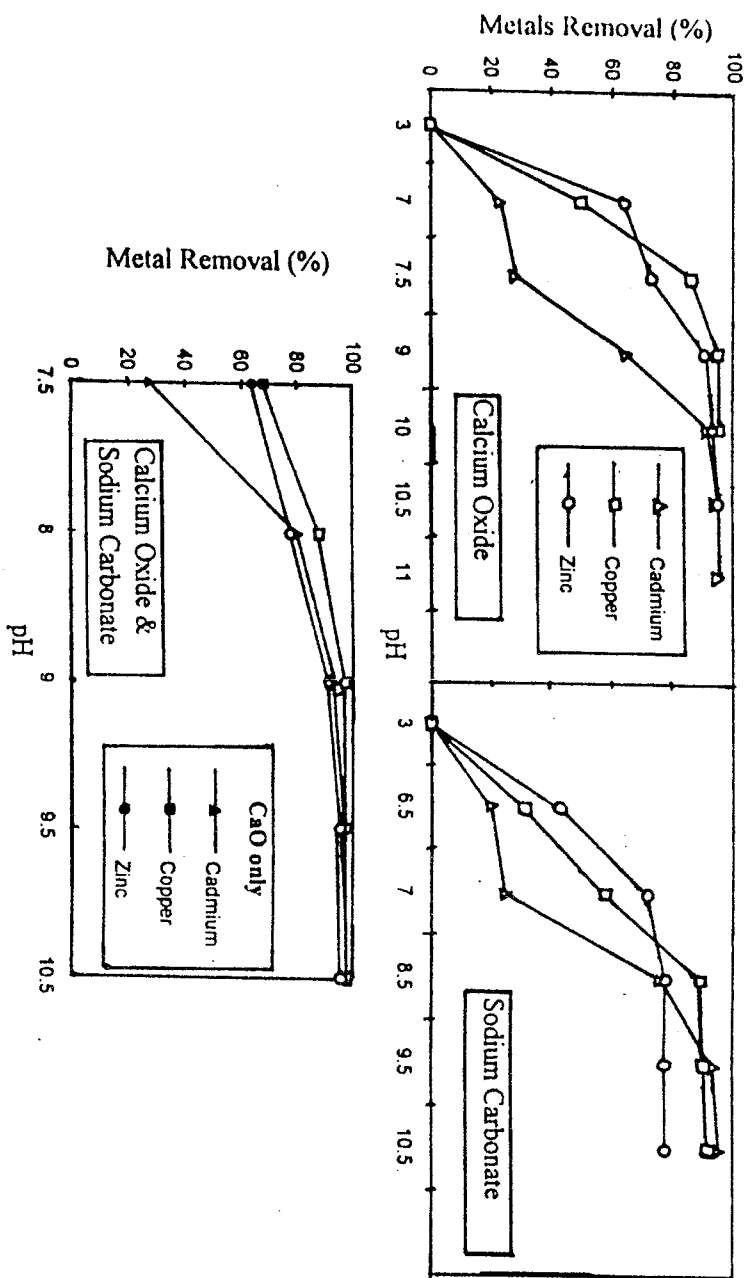


Fig. (1) Single Metal Removal by Calcium Oxide, Sodium Carbonate and Combination of Calcium Oxide & Sodium Carbonate.

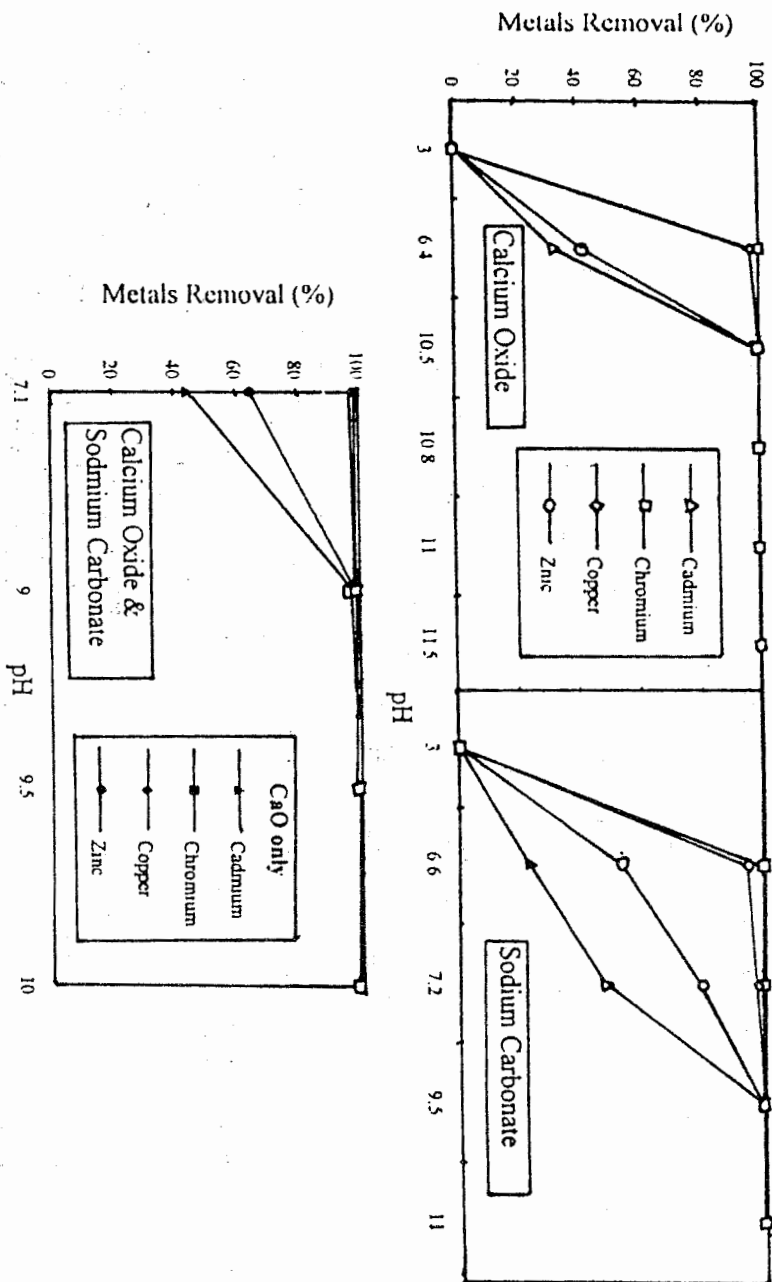


Fig. (2) Multi Metals Removal by Calcium Oxide, Sodium Carbonate and Combination of Calcium Oxide & Sodium Carbonate .

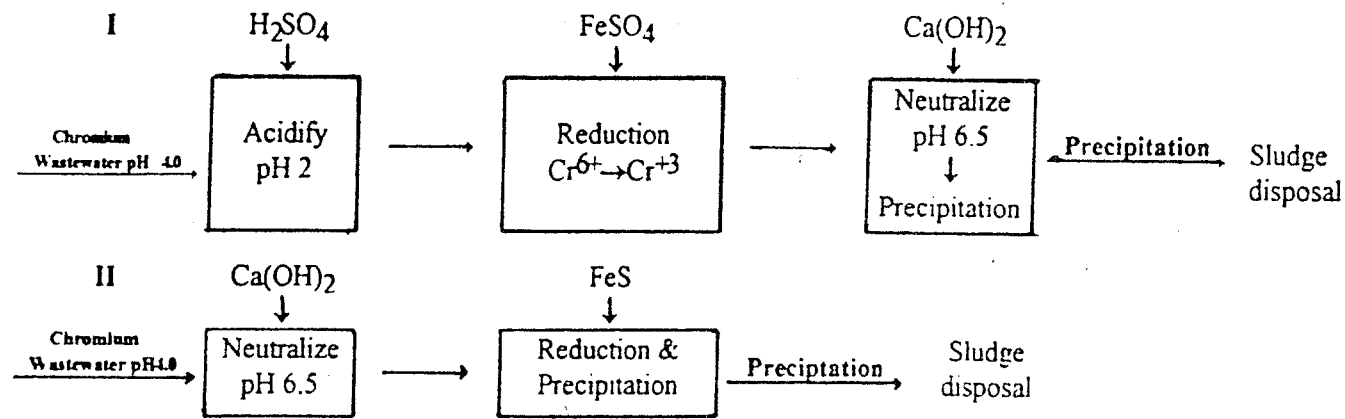
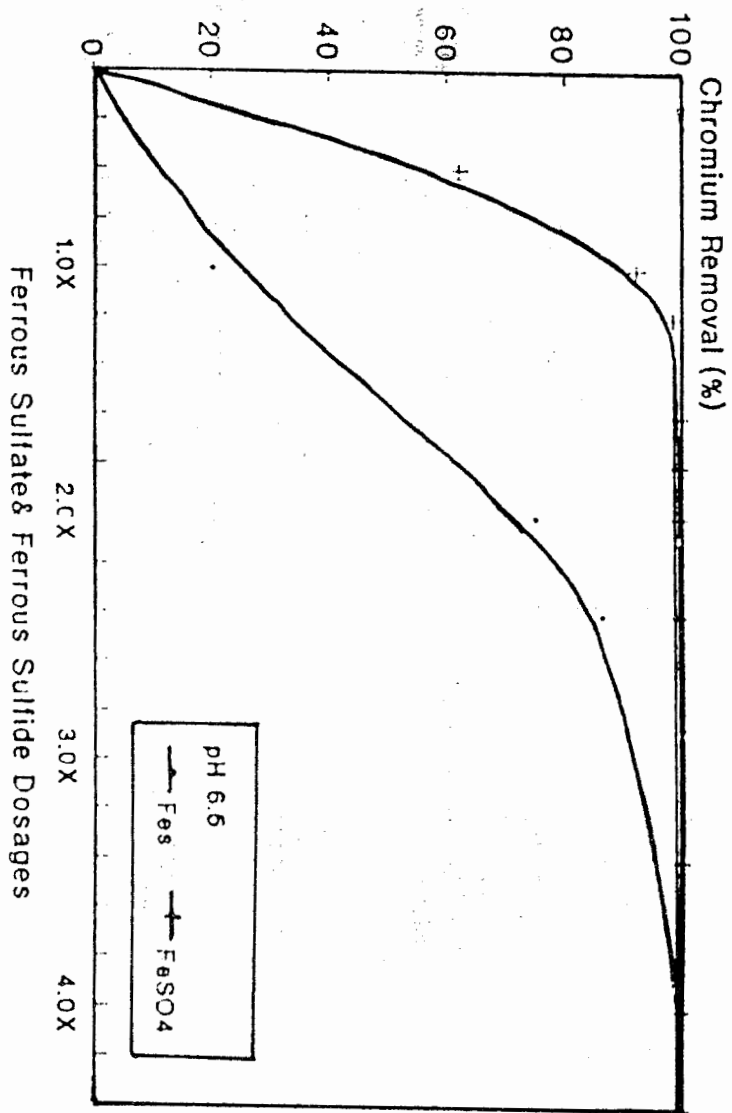


Fig. (3) Comparison of Chromium Reduction Treatment Sequences (I) Chemical and (II) Insoluble Sulfide



Ferrous Sulfate & Ferrous Sulfide Dosages
Fig.(4) Effect of Ferrous Sulfate and
Ferrous Sulfide on Chromium Reduction.
X-Stoichiometric equivalent

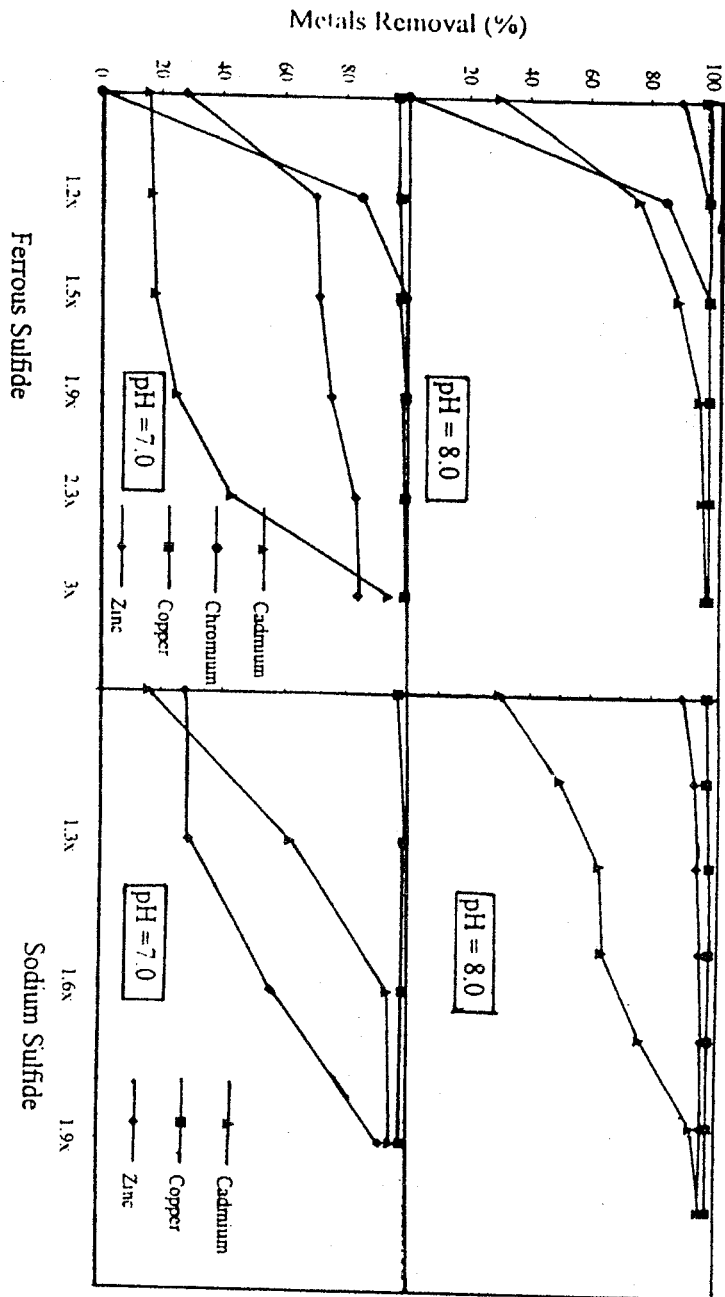


Fig. (5) Multi Metals Removal by Sulfides.
X = Stoichiometric equivalent.

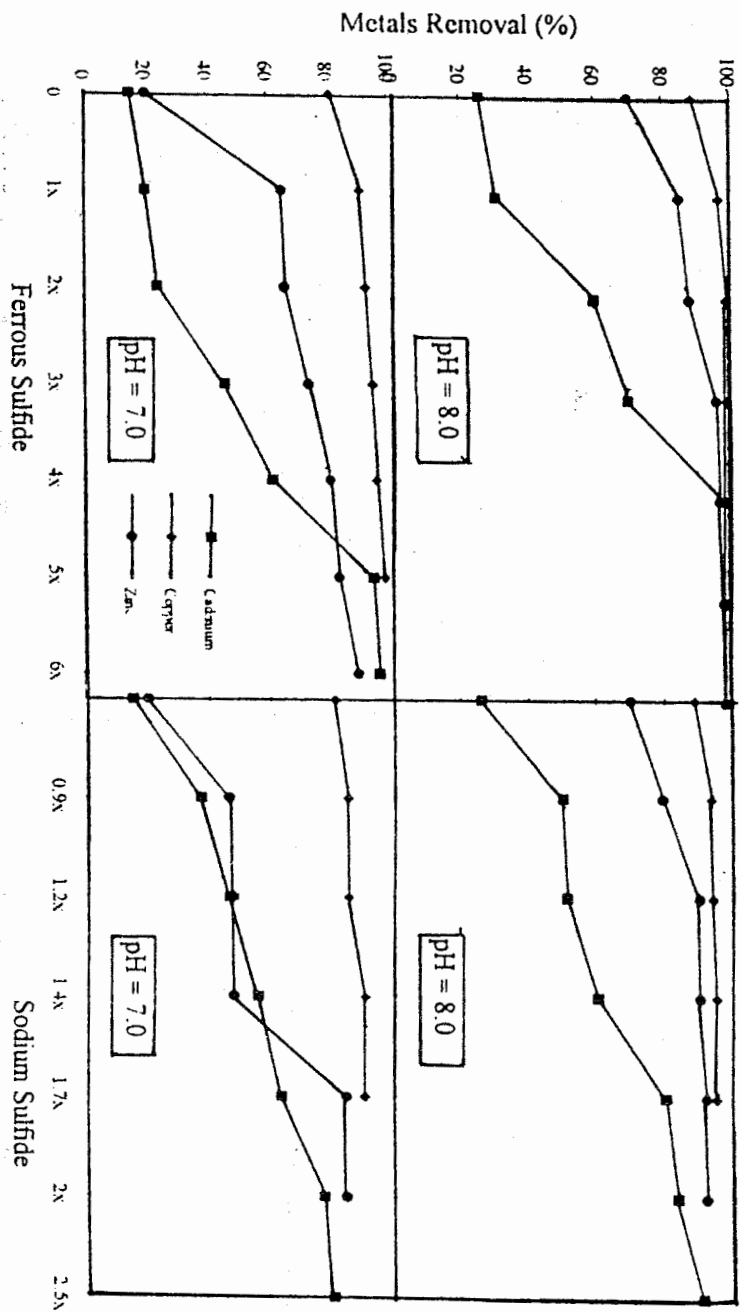


Fig. (6) Single Metal Removal by Sulfides.
X = Stoichiometric equivalent.

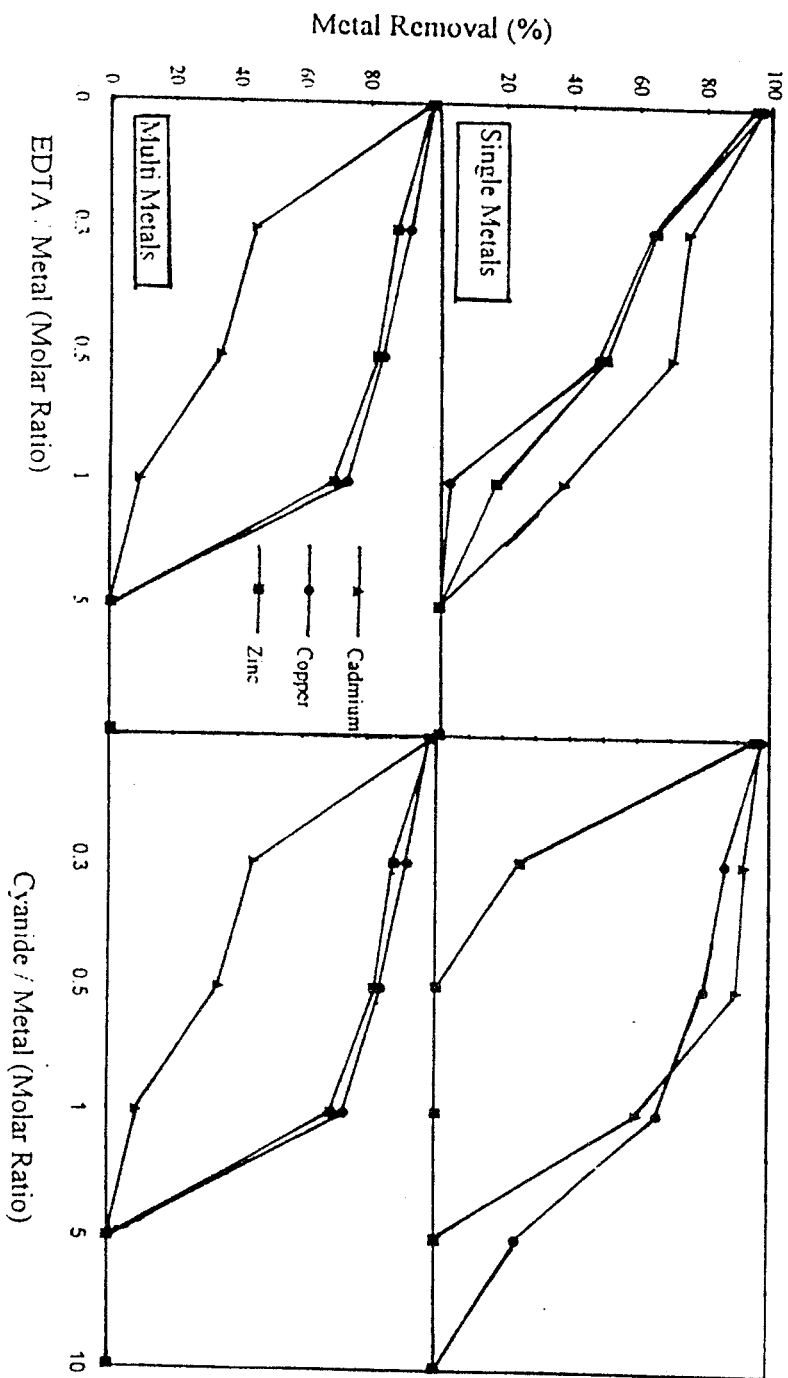


Fig.(7) Effect of EDTA and Cyanide on Metals Removal