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Technical Note

Electroplating wastewater treatment through chemical precipitation and electrodialysis

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ABSTRACT

In the present work, treatment of an electroplating wastewater in a high chromium concentration has been studied through chemical precipitation (CP) and electrodialysis (ED). It has been found that chemical precipitation or electrodialysis alone could not produce a qualified water to be recycled to electroplating lines as rinsing water. Accordingly, a novel process, combined chemical precipitation and electrodialysis (CP-ED), has been tested on the wastewater. The experimental results have shown that the CP-ED process greatly eliminated chromium from the wastewater, about 95% Cr (VI) removal, leaving the cleaned water assaying 0.18mg/l Cr(VI). Also, the CP-ED process effectively removed other ions such as Na^+ and Cl^- that were involved into the wastewater because of adding precipitants in the CP step. Compared with CP treatment, CP-ED process allowed a large saving at reagent cost and operation cost, and less environmental concerns.

Keywords: Electroplating wastewater; Chemical precipitation; Electrodialysis

1. INTRODUCTION

In electroplating industry, as it is known, only 30 to 40% of used metals are actually plated on articles, while the others are collected by water in the form of ions (Zhao *et al.*, 1999). Accordingly, the wastewater from electroplating lines always contains a high concentration of heavy metal ions such as Cr(VI), Cu^{2+}, Zn^{2+} and Ni^{2+}, etc. The ions are non-biodegradable, and some of them are toxic and of carcinogenic effect, leading to a great environmental concern on the wastewater.

Currently, in China there are about 15,000 electroplating shops, employed about 500,000 workers and produced the values of about 1.5 billion US dollars annually (Fan *et al.*, 2001). However, the electroplating industry also produces a large amount of electroplating wastewater, accounted about $4\times10^9 m^3$/year. If such a large amount of the wastewater were discharged into rivers and lakes without any treatment, a big environmental disaster would have been caused, which would be detrimental to not only human beings, but also animals and plants.

The most common process to treat the wastewater is chemical precipitation (CP), in which heavy metal ions first form sulfides or hydroxides or other salts by adding specific reagents, and then precipitate from the wastewater. After that, the precipitates are separated from water through sedimentation or filtration, leaving the effluent in a very low concentration of heavy metal ions (Aldrich, 1987). The quality of the effluent depends on the solubility of metal salts or precipitates in aqueous solutions. Obviously, the CP process is a simple and effective treatment for electroplating wastewater. However, the water from CP treatment still contains a high concentration of other kinds of ions such as Fe^{3+}, Na^+, Cl^-, S^{2-} and SO_4^{2-} because of the addition of precipitants. To recycle the water to the electroplating lines before deionization would be a detrimental to the quality of electroplating products in adhesion, brightness, uniformity, smoothness, pitting, spotting, staining, and clarity of deposit (Zhao and Duncan, 1998; Hirsch, 1999). Therefore, the water treated by CP process is usually discharged into rivers or lakes although electroplating lines need a large amount of water for plating and rinsing.

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Also, it is very hard to treat the sludge from the CP process. A direct disposal of the sludge at landfill sites may cause a serious pollution of soil and underground water through a gradual ionic leaching process (Gan, 2000).

From the viewpoint of environmental concerns, the best wastewater treatment process should completely recycle treated water to producing lines. In the case of electroplating wastewater treatment, it might be realized by chemical precipitation followed by other process such as biological treatment, reverse osmosis, ion exchange, adsorption, and electrodialysis (Bakkaloglu *et al.*, 1998; Ahn *et al.*, 1999; Ribeiro *et al.*, 2000). Compared with other processes, electrodialysis (ED) process is characterized by high efficiency, high reliability and low capital and operation costs. Accordingly, in this work, ED process was tested to combine with CP process to treat electroplating wastewater.

The objective of this work is to study the feasibility and efficiency of electrodialysis following chemical precipitation to treat electroplating wastewater in order to establish a close water circuit (or effluent-free) for electroplating industry.

2. EXPERIMENTAL

2.1. Materials

The electroplating wastewater used in this work was collected from the Datong (DT) electroplating factory in Shanxi province of China. The concentrations of elements and ions in the wastewater are given in Table 1. For electrodialysis tests, four wastewater samples, namely C1, C2, C3 and C4 were used, three of which were prepared with reagent potassium chromate ($K_2Cr_2O_7$) and water and the other was prepared by diluting the DT electroplating wastewater with the tap water. Table 2 gives the conductivity, Cr(VI) concentration and the preparation of the four samples.

Table 1
Concentration of elements and ions of the DT electroplating wastewater (mg/l)

SO_4^{2-}	PO_4^{3-}	Cl^-	F^-	Cr	Na	Mg	Ca
57.4	11.1	15.7	0.9	19.03	7.087	11.338	28.555

Table 2
Conductivity, Cr(VI) concentration and preparation of the samples used for electrodialysis tests

Sample	Conductivity (μs/cm)	Cr(VI) concentration (mg/l)	Preparation
C1	28.6	2.54	Chromium solution prepared with distilled water
C2	200	0.81	Chromium solution prepared with the tap water
C3	364	7.62	Chromium solution prepared with the tap water
C4	381	22.81	DT wastewater diluted with the tap water

Potassium chromate from Beijing Chemical Reagent Ltd. with analyzed purity was used for preparing chromium solutions. Sodium sulfide (Na_2S) and ferrous chloride ($FeCl_2$) used for the reduction of Cr(VI) to Cr(III) and sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) used for pH adjustment were also from Beijing Chemical Reagent Ltd with analyzed purity.

2.2. Chemical precipitation

The flowsheet of the CP process in this work is illustrated in Fig. 1. Chromium solutions or the wastewater were first treated with Na_2S and $FeCl_2$ to chemically reduce the hexavalent chromium (Cr(VI)) to Cr(III). Then, they were adjusted pH 8 to 10 by using NaOH or H_2SO_4 to precipitate Fe^{3+} and Cr(III) in the form of hydroxides. After sedimentation terminated, the solution was sent for conductivity determination.

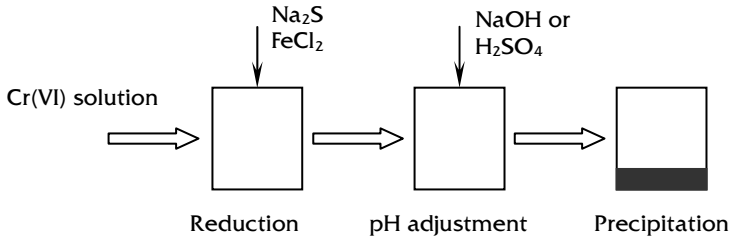

Figure 1. Flowsheet of the chemical precipitation tests

2.3. Electrodialysis treatment

An electrodialysis equipment made in our laboratory was used for ED tests in this work, which was schematically represented in Fig. 2. It consists of two dilute compartments, two concentrate compartments and two electrode compartments, each of them in 24cm length and 14cm width. The cationic exchange membrane (CEM) and anionic exchange membrane (AEM) with an effective area of 150cm^2 were obtained from Shanghai Chemical Plant. The distance between the membranes was 0.1cm. The flow rates of diluted and concentrated water were controlled at 5L/h and 2L/h, respectively, and the temperature was kept at 30±3°C through whole the tests.

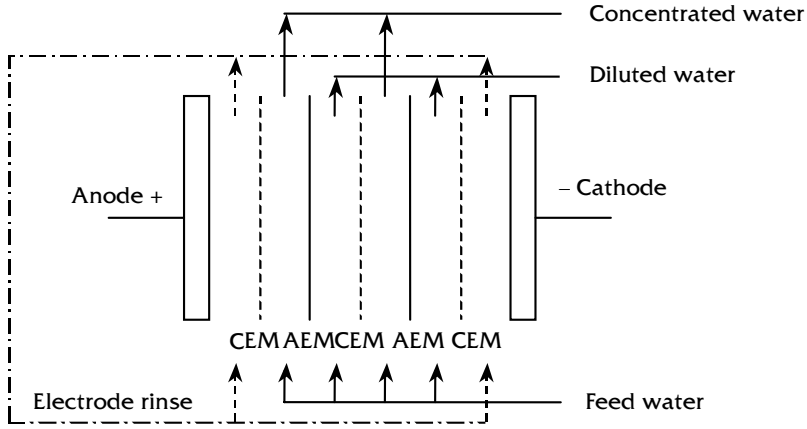

Figure 2. Schematic representation of the electrodialysis cell

2.4. Combined chemical precipitation and electrodialysis (CP-ED) process

The flowsheet of combined chemical precipitation and electrodialysis process applied to electroplating wastewater treatment in this work is shown in Fig. 3. The DT wastewater first past through the CP process in which sodium sulfide, ferrous chloride and sodium hydroxide were used to precipitate the metallic ions. After sedimentation, the sludge (precipitate) was separated from solution. Next, the solution went through two-step rougher and one-step scavenger ED treatment. From this procedure, one diluted water and one concentrated water were produced. In the test, feed water, CP treated water, diluted water, and concentrated water were sampled for the determination of conductivity, element and ion concentration.

2.5. Determination of conductivity, element and ion concentration

The conductivity of tested solutions was determined by using a Conductivity/TDS meters made by Hanna Instruments Pte Ltd. An inductively coupled plasma (ICP) made by Jarrell-Ash Division was used to determine the concentrations of elements (Cr, Na, Mn, Zn, Ca, Mg, Cu, Cd, S and P) in solutions. The concentrations of ions (SO_4^{2-}, Cl^- and PO_4^{3-}) in solutions were determined by using an Ion Chromatography meter made by Dionex Co.

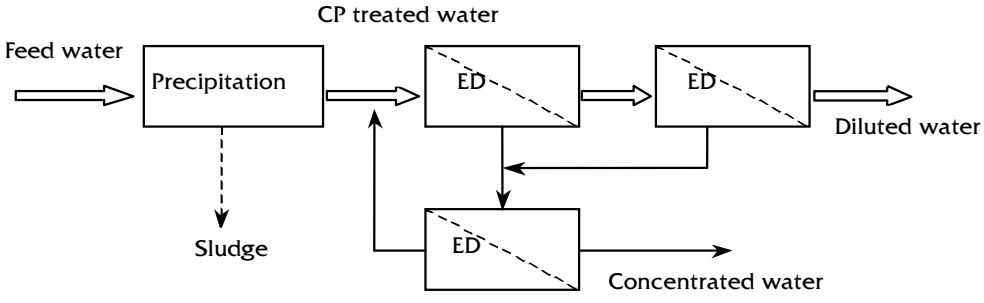

Figure 3. Flowsheet of the combined chemical precipitation and electrodialysis process

3. RESULTS AND DISCUSSIONS

3.1. Chemical precipitation treatment

Fig. 4 illustrates the conductivity of chromium ($K_2Cr_2O_7$) solution as a function of Cr(VI) concentration before and after chemical precipitation. As it can be seen, the conductivity of the solution greatly increased due to the CP treatment, indicating a big increase on the concentration of ions in the solution. This increase might be attributed to the involvement of Na^+, SO_4^{2-} and Cl^- because of the addition of precipitants. Obviously, the CP treatment could not produce a water in a low ion concentration, although Cr(VI) can be removed effectively. Such a high salinity strongly prevents the water from being reused in electroplating lines. Also, it can be noted from this graph that without the CP treatment, the conductivity linearly increased with Cr(VI) concentration. With CP treatment, the conductivity increase as increasing Cr(VI) concentration was much more marked in the low concentration range (<50mg/l) than in the high range.

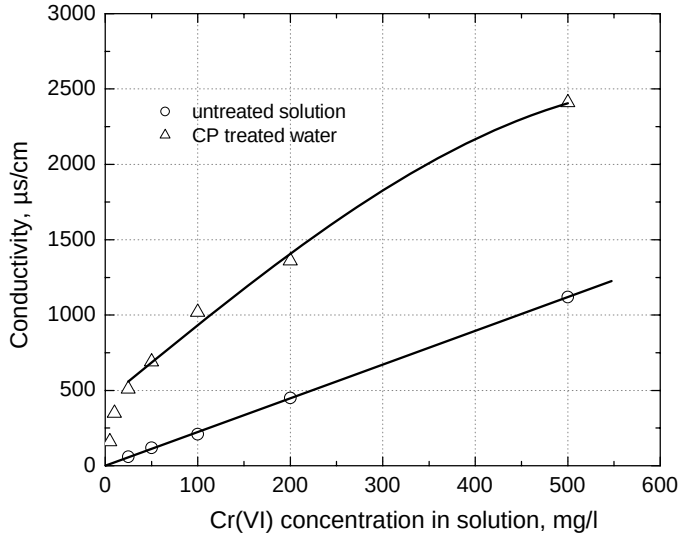

Figure 4. Conductivity of chromium solutions as a function of Cr(VI) concentration before and after the chemical precipitation treatment

3.2. Electrodialysis treatment

Electrodialysis was also tested on the treatment of Cr(VI) solutions and wastewater. The results of Cr(VI) removal are given in Table 3. As it can be noted from this table, the ED process achieved a good Cr(VI) removal and desalination from the solutions (C1, C2 and C3) and wastewater (C4), about 89% to 99% and 86% to 98%, respectively, indicating that electrodialysis is an effective process to remove Cr^{6+} and other ions from wastewater. In the case of the samples C1, C2 and C3, the diluted water assayed much less than 0.5mg/l Cr(VI), the national discharge standard of China. However, the diluted water from the treatment of sample C4 contained about 1mg/l Cr(VI), which can not be legally discharged into rivers and lakes in China. This might be resulted from the high Cr(VI) concentration in the sample C4. Accordingly, a pretreatment is necessary to combine with electrodialysis process, in order to remove heavy metals and other ions completely from the electroplating wastewater.

Table 3
Results of Cr(VI) removal for Cr(VI) solutions and the DT wastewater by electrodialysis treatment

		C1	C2	C3	C4
Feed water	Cr(VI) concentration (mg/l)	2.54	0.81	7.62	18.33
	Conductivity (μs/cm)	28.6	200	364	380
Diluted water	Cr(VI) concentration (mg/l)	0.041	0.091	0.057	1.004
	Conductivity (μs/cm)	4.0	11.9	6.5	13.0
Concentrated water	Cr(VI) concentration (mg/l)	3.19	3.07	147.64	147.24
	Conductivity (μs/cm)	194	1030	914	768
	Removal of Cr(VI) (%)	98.4	88.8	99.3	94.5
	Desalination (%)	86.0	94.0	98.2	96.6

3.3. Combined chemical precipitation and electrodialysis

Combined chemical precipitation and electrodialysis process was tested on the DT electroplating wastewater. The feed water, CP treated water, diluted water and concentrated water from ED treatment were sampled and then were assayed. The results are given in Table 4. It is shown that high metallic and ionic removals have been achieved, ranging from 93.8% to 100%. The diluted water from the ED process assayed very low heavy metals, far from the national discharge standard of China. The concentrations of the other metals and ions were also very low, leading to a conductivity of 31μs/cm. Such a treated water is qualified to be recycled to electroplating lines for rinsing water, allowing a large saving on water consumption in electroplating industry. Clearly, combined chemical precipitation and electrodialysis is an effective and potential process for electroplating wastewater treatment in order to establish a close water circuit for electroplating industry. In addition, it can be seen that there were still high concentrations of ions and metals in the CP treated water. Although the Cr concentration reduced from 19.03mg/l to 3.62mg/l after the CP treatment, the concentrations of Cl^- and Na^+ increased significantly from 15.7 to 111mg/l and 7.1 to 44.4mg/l, respectively, resulting in a large increase on conductivity. This increase has to be due to the addition of Na_2S, $FeCl_2$ and NaOH as precipitants. Also, it can be observed that the CP treatment is effective to eliminate heavy metals, but not for Ca^{2+} and Mg^{2+}. Obviously, this CP treated water can not be recycled to electroplating lines without any further purification.

Table 4
Results of combined chemical precipitation and electrodialysis treated the DT electroplating wastewater

	SO_4^{2-}	PO_4^{3-}	Cl^-	Cr	Na	Mg	Ca
Feed water	57.4	11.1	15.7	19.03	7.09	11.34	28.56
CP treated water	43.5	13.3	111	3.62	44.41	9.72	21.10
Concentrated water	47.0	8.9	429	1.85	151.4	12.20	15.69
Diluted water	2.6	0.0	4.2	0.18	2.25	0.60	1.03
Removal, %	94.0	100	96.2	95.0	94.9	93.8	95.1

4. CONCLUSIONS

- The experimental results from this work have shown that combined chemical precipitation and electrodialysis is an effective process to treat electroplating wastewater in a high chromium concentration. This process considerably eliminated not only Cr(VI) from the wastewater, but also other ions such as Na^+, Cl^-, Ca^{2+} and Mg^{2+}, so that the treated water from the process can be recycled to electroplating lines for rinsing water, allowing a large saving on water consumption and a less environmental concern.
- The CP treated water contained a higher ion concentration than feed water, which might be due to the significant increase of Na^+ and Cl^- because of the addition of precipitants.
- Electrodialysis treatment alone could not effectively treat an electroplating wastewater in a high Cr(VI) concentration.

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