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Elimination of Cr(VI) from Electroplating Wastewater by Electrodialysis Following Chemical Precipitation

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ABSTRACT

In this work, the elimination of Cr(VI) from an electroplating wastewater in China was studied by chemical precipitation (CP), electrodialysis (ED), and their combination. The experimental results show that CP was effective as a rougher treatment for removing Cr(VI) from a high Cr(VI) wastewater, but not for a deep Cr(VI) elimination. ED alone failed to achieve a deep Cr(VI) elimination from a high Cr(VI) wastewater, although it was very effective for a medium Cr(VI) wastewater. The mechanism might be attributed to the sedimentation of chromatic ions

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as polychromates in the pores of ED membranes because of high Cr(VI) concentration in wastewater, which may block the pores and thus stop the transportation of the ions through the pores. It was found that the combined chemical precipitation and electrodialysis (CP + ED) process is an effective and economic process to treat high Cr(VI) electroplating wastewater. This process allows treated water to be completely recycled to electroplating lines, fewer environmental concerns, and lower reagent and operation costs.

Key Words: Electrodialysis; Chemical precipitation; Chromium ions; Electroplating wastewater.

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INTRODUCTION

Wastewater from electroplating processes usually contains a high concentration of heavy metal ions such as Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr(VI), etc. If it was discharged into a natural water body without any treatment, there would have been an environmental disaster, because these inorganic micropollutants are nonbiodegradable, highly toxic, and of carcinogenic effect.[1] In China, there are about 15,000 electroplating plants or workshops, producing a large quantity of electroplating wastewater, about $4 \times 10^9\ m^3$ annually.[2] Therefore, there is a great significance for developing an effective and economic process to remove the ions from electroplating wastewater before it can be discharged into rivers and lakes.

Chemical precipitation (CP) is a commonly used process to treat electroplating wastewater, in which heavy metal ions first precipitate in the form of hydroxides or sulfides, and then are removed from the water by means of solid–liquid separation.[3,4] It has been found that this process is effective for removing the heavy metallic ions such as Cu^{2+}, Zn^{2+}, Ni^{2+}, and Cr^{3+} from wastewater, but not Cr(VI) because it does not precipitate in any form. Usually, Cr(VI) is reduced to Cr^{3+} before CP is applied.[4,5]

Treated water from the CP cannot be recycled to electroplating lines before deionization, because it contains high concentrations of various ions (Fe^{3+}, Na^+, Cl^-, S^{2-}, and SO_4^{2-}), which are very detrimental to the quality of electroplating products in adhesion, brightness, uniformity, smoothness, pitting, spotting, staining, and clarity of deposit.[6,7] Usually the treated water is discharged into rivers or lakes, although electroplating lines need a large amount of water for plating and rinsing. From the viewpoint of environmental concerns, treated water should be recycled to the producing lines, which not only allows saving water, but also lowers water pollution.

In addition, in order to eliminate Cr(VI) and the other heavy metal ions from the wastewater deeply, a large number of coagulants and reductants

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have to be added, generating a large amount of sludge and leading to a high reagent cost. As is known, direct disposal of the sludge at landfill sites may cause serious pollution of soil and underground water through a gradual ionic leaching process.[8] Therefore, it is significant to combine CP with another process to treat electroplating wastewater, in order to reduce the sludge production and reagent cost. There are several processes for the elimination of the ions from wastewater at a low concentration, for instance, biological treatment, reverse osmosis, ED, adsorption, and ion exchange. ED is a membrane separation process based on the selective migration of aqueous ions through ion-exchange membranes under electrical driving forces. It has been commercially used for desalination, wastewater treatment, ultra-pure water production, electrolytes and nonelectrolytes separation, etc.[9,10] It features high efficiency, high reliability, and low capital and operation costs.

In this work, an attempt has been made to eliminate Cr(VI) from an electroplating wastewater by using a combined chemical precipitation and electrodialysis (CP + ED) process, in order to establish a close water circuit (or no wastewater discharge) for electroplating industry use with a lower operation cost and less environmental concern. The objective is to study the feasibility and efficiency of the process, as well as ED and CP alone to treat a high Cr(VI) electroplating wastewater. In addition, the effects of several parameters, namely Cr(VI) concentration, conductivity, and flow rate of feed wastewater, on the effectiveness of ED treatment were investigated; and the mechanism by which the effectiveness of ED sharply declined when it is applied to a high Cr(VI) wastewater was presented.

EXPERIMENTAL

Materials

The electroplating wastewater used in this work was collected from the Datong (DT) electroplating plant in Shanxi province of China. The concentrations of elements and ions in the wastewater are given in Table 1. Obviously, there was a very high chromium ion concentration in this wastewater.

Cr(VI) solutions were prepared by using reagent potassium chromate ($K_2Cr_2O_7$) with distilled water in a given Cr(VI) concentration for some tests.

Table 1. The chemical analysis of the DT electroplating wastewater.

Ions	Cr(VI)	Zn^{2+}	Cu^{2+}	Cd^{2+}	pH
Concentration (mg/L)	19.0	2.45	10.0	0.06	6

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The sodium sulfide (Na_2S) and ferrous chloride ($FeCl_2$) used for the reduction of Cr(VI) to Cr(VI), sodium hydroxide (NaOH) used for pH adjustment, sodium chloride for conductivity adjustment, and potassium chromate for preparing Cr(VI) solutions were from Beijing Chemical Reagent Ltd. with analyzed purity.

Chemical Precipitation

The CP was performed by using Na_2S and $FeCl_2$ (the ratio of 1 : 10 by weight) to reduce Cr(VI) in the electroplating wastewater to Cr^{3+} first. Then, NaOH solution was added into the wastewater to precipitate Cr^{3+}, Cu^{2+}, Zn^{2+}, and Fe^{3+} in the form of hydroxides. The pH was kept at 9.0 throughout the tests. After that, the precipitates coagulated because of the existence of Fe^{3+}, followed by sedimentation to separate the coagulates from the water. With this procedure, a CP-treated water and a sludge (the coagulates) were produced. In combined CP + ED process, the CP-treated water was sent to the ED step as feed wastewater.

ED Treatment

ED equipment made in our laboratory was used for ED tests in this work; it is schematically represented in Fig. 1. It consists of two dilute

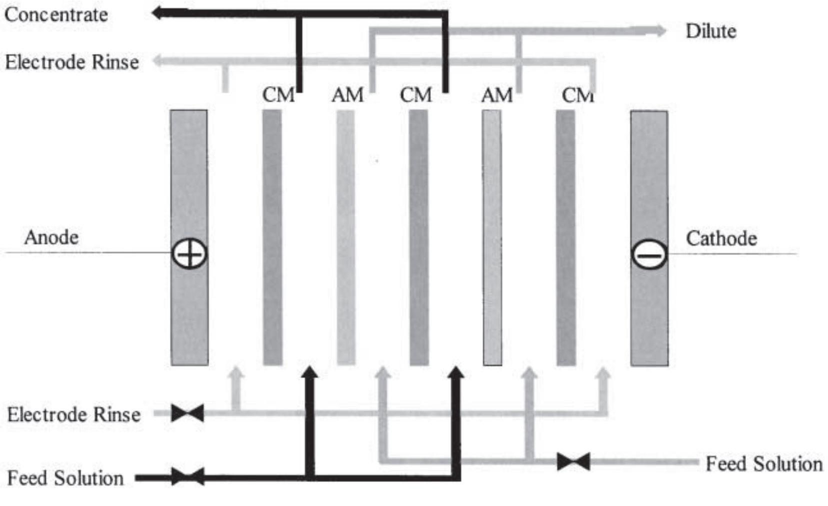

Figure 1. Schematic representation of the electrodialysis cell used in this work.

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compartments, two concentrate compartments, and two electrode compartments, each of them 24 cm in length and 14 cm in width. Three cationic exchange membranes (CM) and two anionic exchange membranes (AM) with an effective area of 150 cm^2 were used, which were obtained from Shanghai Chemical Ltd. The distance between the membranes was 0.1 cm. A DH1702-1 power supply (Beijing Electrical Ltd.) was used to provide a constant DC current. Wastewater was fed into the ED system, producing a dilute water and a concentrate water. The flow rates of the diluted water and concentrated water were controlled at 5 and 2 L/hr, respectively, unless it is especially noted. The temperature was kept at $30 \pm 3°C$ throughout the tests.

Conductivity Measurement

The conductivity of tested solutions was determined by using a TDS conductivity meter (Hanna Instruments Pte. Ltd.).

Determination of Concentration of Elements and Ions

The concentration of Cr(VI) in solutions or wastewater was analyzed by using a UV-2102 spectrophotometer (Unico Shanghai Instrument, China). Zn^{2+}, Cu^{2+}, and Ni^{2+} concentrations were determined by using an AA320 atomic absorption spectrophotometer (Shanghai Analytical Instrument Overall Factory, China). Concentrations of elements (Cr, Na, Zn, Ca, Mg, Cu, S, and P) were analyzed by using an inductively coupled plasma (Jarrell-Ash Division, AtomComp Series 1100). The concentrations of SO_4^{2-}, Cl^-, and PO_4^{3-} were determined by using an ion chromatography (4500i, DioneX Co. USA). Distribution of elements in membranes was analyzed by using a scanning electron microscope (SEM) and attached energy despersive x-ray spectroscopy (EDX) (Cambridge Instruments, USA).

RESULTS AND DISCUSSION

Chemical Precipitation

Table 2 gives the experimental results of Cr(VI) removal and sludge production in the CP-sedimentation of the DT electroplating wastewater with various amount of reductants ($FeCl_2$ and Na_2S). As it can be seen, as the addition of the reductant increased, the Cr(VI) removal increased. This increase was very marked in the low reductant addition range, but became

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Table 2. Effect of reductants ($FeCl_2 : Na_2S = 10 : 1$) addition on Cr concentration in treated water, Cr(VI) removal, and sludge production.

Reductant addition (mg/L)	Cr concentration in treated water (mg/L)	Sludge production (mg/L)	Cr(VI) removal (%)
0	19.0	0	0
55	6.16	51	67.6
110	1.54	117	91.9
165	0.71	163	96.3
220	0.47	231	97.5
275	0.23	283	98.8
330	0.14	370	99.3
385	0.10	431	99.5

milder and milder after 110 mg/L addition. For instance, the increase of Cr(VI) removal from 67.6% to 91.9% only consumed 55 mg/L reductants, while the increase from 91.9% to 99.3% needed the addition of 220 mg/L reductants. At 330 mg/L reductant addition, the CP-treated water contained 0.14 mg/L Cr, compared with 1.54 mg/L Cr at 110 mg/L addition and 19 mg/L Cr in the feed wastewater. This result indicates that the CP-sedimentation is very effective as a rougher treatment for removing Cr(VI) from wastewater, but not for the deep elimination of Cr(VI).

Also, it can be noted in Table 2 that the sludge production increased linearly with the reductant addition. At 99.3% Cr(VI) removal, 370 mg/L sludge was produced from the CP treatment, compared with 117 mg/L sludge at 91.9% Cr(VI) removal. Clearly, from the viewpoint of reagent cost and sludge production, it is better to remove the majority of Cr(VI) from wastewater with CP in a small amount of reductants and coagulants, followed by another process to eliminate the rest of Cr(VI) deeply and effectively.

ED Treatment

Figure 2 illustrates the Cr(VI) removal and desalination as a function of Cr(VI) concentration in feed water in the ED treatment of the DT electroplating wastewater. The Cr(VI) concentration in feed water was adjusted by diluting the wastewater with distilled water, while other ions were also diluted. As can be seen from Fig. 2, the Cr(VI) removal and desalination increased with the increase of the Cr(VI) concentration until reaching the maximums, and then sharply declined. It is clear that the ED treatment for Cr(VI) removal and desalination was only effective in the medium Cr(VI) concentration

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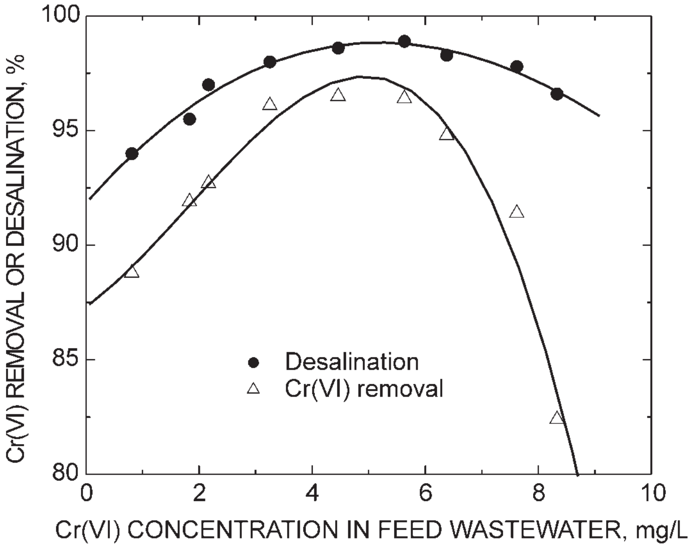

Figure 2. Cr(VI) removal and desalination as a function of Cr(VI) concentration in feed wastewater in the ED treatment of the DT electroplating wastewater.

range. It is very difficult to realize the complete penetration of the ions in feed wastewater through membranes, so there is always a low concentration of ions in ED-treated water, which might be attributed to the low Cr(VI) removal and desalination in the low Cr(VI) concentration range. However, the decline of the Cr(VI) removal and desalination in the high Cr(VI) concentration range might be due to the blocking up of the membranes that stops ion penetration. Obviously, ED treatment cannot be solely used to eliminate Cr(VI) from a high Cr(VI) wastewater.

Figure 3 shows the relationship between the Cr(VI) concentration in feed wastewater and in dilute water in the ED treatment of the DT electroplating wastewater. As noted, Cr(VI) concentrations in the dilute water increased with increasing Cr(VI) concentration in feed wastewater. This increase was much sharper in the high Cr(VI) concentration range than the low one. Since there is a maximum discharge level for chromium, for instance, 0.5 mg/L in China, wastewater fed to ED treatment must not contain a high Cr(VI) concentration, say 5 mg/L according to Fig. 3. In the case of electroplating wastewater, the Cr(VI) concentration changes from one electroplating plant to another, and is usually over 5 mg/L. Therefore, a combination of ED with another process, instead of itself alone, has to be used for the deep elimination of Cr(VI) from electroplating wastewater.

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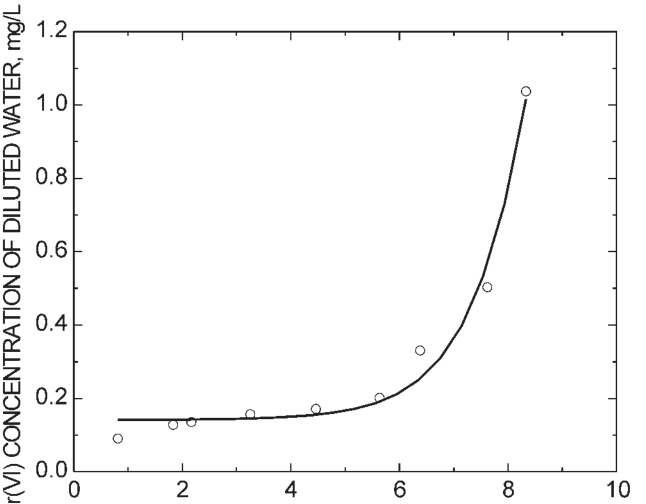

Figure 3. Effect of Cr(VI) concentration in feed wastewater on that in dilute water in the ED treatment of the DT electroplating wastewater.

In addition, the effects of two important factors, namely conductivity and flow rate of feed wastewater, on the ED treatment of the DT electroplating wastewater were studied in this work. Figure 4 shows the Cr(VI) removal and desalination as a function of feed wastewater conductivity. The conductivity of feed wastewater was adjusted by adding a proper amount of sodium chloride, while Cr(VI) concentration in the wastewater was fixed. It can be seen that the desalination sharply increased with increasing feed wastewater conductivity until it reached a plateau at about 50 μS/cm, while the Cr(VI) removal decreased and then flattened out. These results suggest that in the ED treatment, the effect of feed-water conductivity is very marked in the low conductivity range, but very mild in the high range. Since electroplating wastewater usually has a high conductivity, over 100 μS/cm, feed-water conductivity may not strongly influence the ED treatment of the wastewater.

The effect of flow rate of feed wastewater on the Cr(VI) removal and desalination in the ED treatment of the DT electroplating wastewater is illustrated in Fig. 5. The Cr(VI) removal and desalination declined with the increase of the flow rate. This decline was much stronger in the high flow rate range than in the low range. As feed flow rate closely correlates with the capacity of wastewater treatment, it is necessary to optimize the flow rate in ED treatment in order to achieve a good balance of the capacity and desalination.

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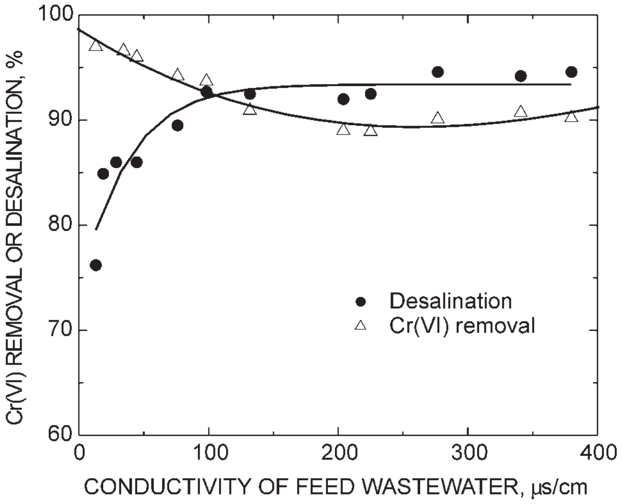

Figure 4. Cr(VI) removal and desalination from the ED treatment of the DT electroplating wastewater as a function of conductivity of feed wastewater.

Combined CP + ED

Combined CP + ED process was tested on the DT electroplating wastewater for the elimination of Cr(VI) and other ions. The flowsheet is schematically represented in Fig. 6. In the CP step, 10 mg/L Na_2S and 100 mg/L $FeCl_2$ were added to reduce Cr(VI) to Cr^{3+}; in the ED, a 10 V direct electrical field was applied to system. The feed wastewater, CP-treated water, dilute water, and concentrate water from the ED step were sampled and chemically analyzed. The results are given in Table 3. It is shown that high removals of the elements and ions have been achieved. The ions and elements concentrations in the diluted water were very low, having the conductivity of 31 μS/cm. Such a cleaned water is qualified to be recycled to electroplating lines as rinsing water, allowing a large saving on water consumption in the electroplating industry. It is clear that this process is an effective means to treat an electroplating wastewater with high Cr(VI) concentration and for establishing a close water circuit in the electroplating industry.

In addition, it can be seen from the data that the CP-treated water had much higher ion concentrations than the feed wastewater. The CP-treated water had determined 720 μS/cm conductivity, compared with 464 μS/cm for the feed wastewater. After the CP, Cr concentration reduced from 19.03 to 3.62 mg/L, while the concentrations of Cl^- and Na^+ increased significantly from 15.7 and 7.09 mg/L to 111 and 44.41 mg/L, respectively, which resulted

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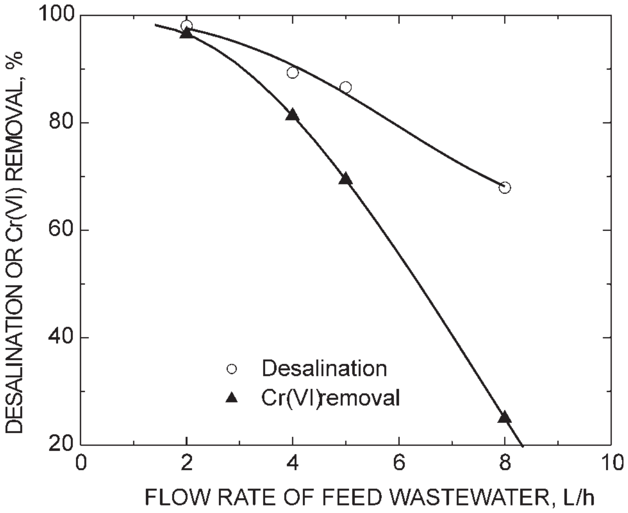

Figure 5. Cr(VI) removal and desalination from the ED treatment of the DT electroplating wastewater as a function of flow rate of feed.

from the addition of Na_2S, $FeCl_2$, and NaOH. Also, it can be observed that the CP effectively eliminated the heavy metallic ions, but not Ca^{2+}, Mg^{2+}, etc. Obviously, the CP-treated water cannot be recycled to electroplating lines before any further purification is applied, because the high concentration of ions (Na^+, Cl^-, Ca^{2+}, and Mg^{2+}) is very detrimental to the quality of electroplating products.

From the results mentioned, it is clear that combined CP + ED process is superior to the CP process alone for eliminating Cr(VI) and other metallic ions from electroplating wastewater, in the following aspects: (1) the water treated by the CP + ED process could be completely recycled to electroplating lines,

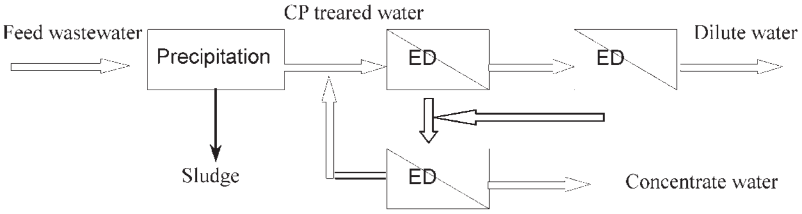

Figure 6. Flowsheet of the combined CP + ED process for electroplating wastewater treatment.

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Table 3. Results of combined CP + ED process to treat the DT electroplating wastewater.

	Cond. (µS/cm)	Concentration of ions or elements (mg/L)										
		SO_4^{2-}	PO_4^{3-}	Cl^-	F^-	Cr	Na	Mn	Zn	Mg	Cu	Ca
Feed wastewater	464	57.4	11.1	15.7	0.9	19.03	7.09	0.02	2.45	11.34	10.04	28.6
CP-treated water	720	43.5	13.3	111	0.0	3.62	44.4	0	0.07	9.72	0.1	21.1
Concentrate water	1656	47.0	8.9	429	2.6	1.85	151	0.04	0.2	12.2	0.2	15.7
Dilute water	31.2	2.6	0	4.2	0	0.18	2.25	0	0	0.6	0	1.03
Removal in ED step (%)	95.7	94.0	100	96.2	100	95.0	94.9		100	93.8	100	95.1
Removal in CP + ED (%)	93.3	95.5	100	73.3	100	99.0	68.3	100	100	94.7	100	96.4

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leading to a large saving on water consumption in the electroplating industry and a low pollution to natural water body; (2) the CP + ED process greatly reduced the addition of reductants (from 330 to 110 mg/L), allowing a large saving on reagent cost; and (3) the CP + ED process produced much less sludge (117 mg/L) than the CP process (370 mg/L), leaving a much smaller pollution.

Mechanism of Cr(VI) Elimination by ED

The hydrolysis of chromium ion can be expressed as follows:[11,12]

$$CrO_4^{2-} + H^+ \longleftrightarrow HCrO_4^- \quad (1)$$

$$2HCrO_4^- \longleftrightarrow Cr_2O_7^{2-} + H_2O \quad (2)$$

$$Cr_2O_7^{2-} + H^+ \longleftrightarrow HCr_2O_7^- \quad (3)$$

$$HCrO_4^- + Cr_2O_7^{2-} + H^+ \longleftrightarrow Cr_3O_{10}^{2-} + H_2O \quad (4)$$

$$HCr_2O_7^- + CrO_4^{2-} + H^+ \longleftrightarrow Cr_3O_{10}^{2-} + H_2O \quad (5)$$

$$HCrO_4^- + Cr_3O_{10}^{2-} + H^+ \longleftrightarrow Cr_4O_{13}^{2-} + H_2O \quad (6)$$

$$2HCr_2O_7^- \longleftrightarrow Cr_4O_{13}^{2-} + H_2O \quad (7)$$

From the reactions, it is clear that chromium species in aqueous solutions exists in the form of chromate (CrO_4^{2-}) and polychromate ($Cr_nO_{3n+1}^{2-}$). The fraction of these chromium species in aqueous solutions depends on pH and chromium ion concentration. In a low chromium ion concentration, the chromium species mainly appear in the form of CrO_4^{2-}. In a high chromium ion concentration, polymerization happens to the ion of CrO_4^{2-}, forming $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$, etc. The fraction of the ions depends on total Cr(VI) concentration. The higher the Cr(VI) concentration, the larger the fraction of highly polymerized chromium ions (or larger n) is. For example, $HCrO_4^-$ starts to convert to $Cr_2O_7^{2-}$ in an acidic aqueous solution if Cr(VI) concentration in the solution is about $1.26–1.74 \times 10^{-5}$ mol/m^3.[13]

Figure 7 schematically represents the structure of chromium species CrO_4^{2-}, $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$, and $Cr_4O_{13}^{2-}$. The former ion is illustrated in details, and the latter three ions (polychromate) are made in a simple schematic diagram. From the graph, it can be seen that the highly polymerized chromate ions have a large size. The stronger the polymerization, the larger the polychromate ion. It is noted that the volume occupied by $Cr_4O_{13}^{2-}$ would be much larger than the sum of the four single CrO_4^{2-} because of the arrangement of the atoms.

Ion-exchange membranes, as shown in Fig. 8, are made of macromolecular materials or a skeleton, with ionizable groups or functional groups. Pore

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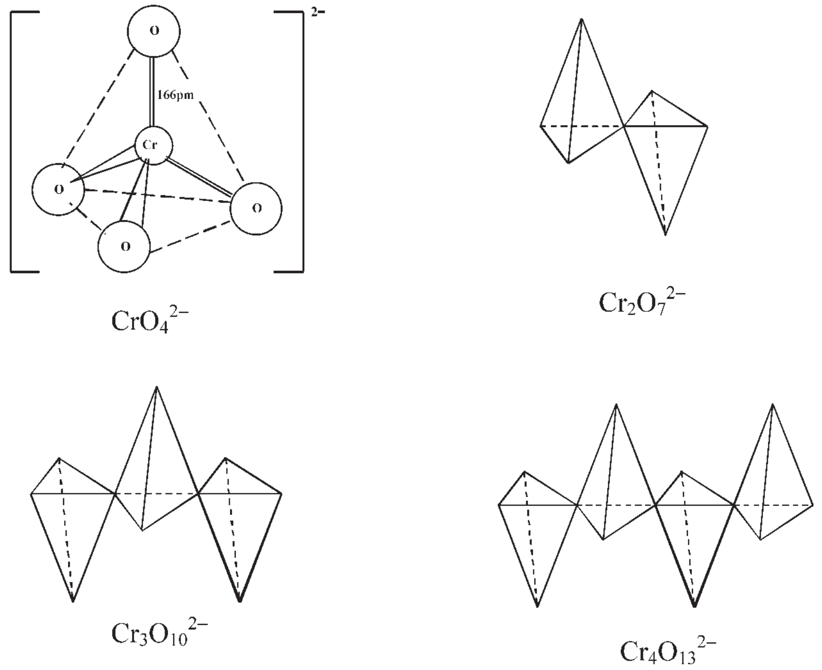

Figure 7. Schematic representation of the structure of chromate ion and polychromate ions.

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size varies from 1 to 10 nm. Based on the nature of functional groups attached to the matrix, the membranes are categorized into CM and AM. Commonly used functional groups are sulfonic ($-SO_3^-$) in CM and alkyl ammoniums ($-NR_3^+$, $-NHR_2^+$, $-NH_2R^+$) in AM. Once membranes are impregnated with an aqueous solution, the ions are electrically neutralized by mobile ions in opposite sign, which are called counter-ions or compensator ions. Counter-ions are cations in CM, and anions in AM. Under an electric field, cations can pass through CM, but anions cannot; and anions can pass through AM, but cations cannot.

Assuming that the transportation of chromate ions in aqueous solutions through an ED membrane would vary with Cr(VI) concentration, Fig. 8 illustrates the situation of this transportation in low and high Cr(VI) solutions. In the case of a low Cr(VI) concentration, as shown in Fig. 8(a), the chromium species are CrO_4^{2-}. This kind of chromate ion penetrates through the pores of membranes easily, leaving a high ion Cr(VI) removal by ED. This explains the experimental results as shown in Figs. 2 and 3 in the low Cr(VI) concentration range.

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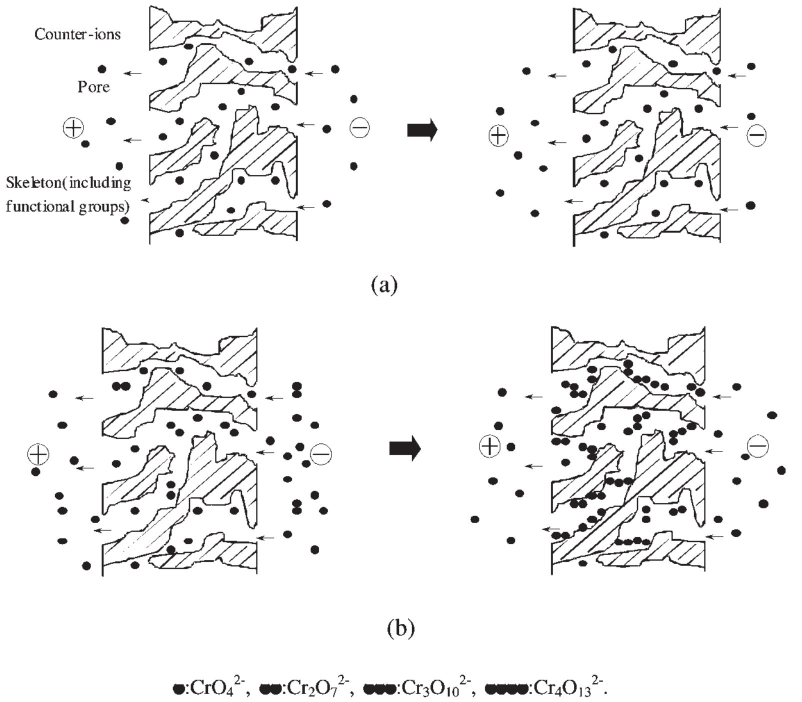

Figure 8. A model of Cr(VI) ions passing through a membrane at low or high Cr(VI) solutions.

In the case of a high Cr(VI) concentration as shown in Fig. 8(b), there are chromate and polychromate ions in the solution. Under an electrical field, the chromate and polychromate ions pass through the pores of the membrane. Obviously, Cr(VI) concentration inside the pores is much higher than in the bulk solution, because of the small volume of the pores and the slow movement of polychromate ions. According to Eqs. 1–7, the chromium ions inside the pores would strongly polymerize, leaving a large amount of polychromate ion ($Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$, etc.) in the pores. The higher the Cr(VI) concentration is in wastewater, the more and larger the polychromate ions are. Polychromate ions are hard to move through the pores because of the in large size, settling down in the pores. The larger the polychromate ion, the stronger the sedimentation is. The accumulation of this sedimentation would block the pores, preventing Cr(VI) ions from further penetration through the membranes. This might be the mechanism by which the effectiveness of ED treatment for Cr(VI) removal declined sharply in the high Cr(VI) solution, as shown in Figs. 2 and 3.

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Table 4. Percentage of Cr^{6+} to total ions in an anion membrane before and after being used in Cr^{6+} solutions.

Unused	Used in a 4.46 mg/L Cr(VI) solution	Used in a 8.33 mg/L Cr(VI) solution
0	1.702	6.976

In order to prove the assumption as shown in Fig. 8, Cr(VI) remaining in an anionic membrane before and after being used for ED treatment was analyzed by using SEM and EDX. In the membrane, there are large amounts of ions, and Cl^- and S^{2-} ions are the overwhelming majority. The analysis only reported the percentage of Cr(VI) in total ions in the membrane. Table 4 gives the analysis results. The latter two membrane samples were obtained by being first used in 4.46 and 8.33 mg/L Cr(VI) solutions, respectively, and then being used in a 4.46 mg/L Cr(VI) solution for 1 hr. This preparation may dispel the effect of ion concentration on the ion remaining in membrane pores due to ion exchange. It can be seen from Table 4 that there was no chromium ion in the unused membrane. In the membrane used in 4.46 mg/L Cr(VI) solution, about 1.7% chromium was found. However, there was about 7% chromium in the membrane used in 8.33 mg/L Cr(VI) solution. The chromium remaining in the pores increased about four fold. This increase might be attributed to the much stronger sedimentation of chromate ions in the pores due to the formation of large polychromate ions, as shown in Fig. 8(b).

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CONCLUSION

1. The combined CP + ED treatment was found to be very effective to treat high Cr(VI) electroplating wastewater. This process allows the treated water to be completely recycled to the electroplating lines, fewer environmental concerns, and lower reagent and operation costs.
2. The effectiveness of ED treatment to eliminate Cr(VI) from an electroplating wastewater declined sharply in a high Cr(VI) concentration range, although it was very high in a low concentration range. This decline might be attributed to slow movement and sedimentation of chromatic ions in the pores of the membranes in the form of polychromate due to the high Cr(VI) concentration in wastewater, which may block the pores and then stop ion transportation through the membranes.

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3. In the ED treatment of electroplating wastewater, the Cr(VI) removal and desalination were not strongly influenced by the conductivity of the wastewater in the high conductivity range.

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REFERENCES

1. Zhao, M.; Duncan, J.R.; Van Hille, R.P. Removal and recovery of zinc from solution and electroplating effluent using azolla filiculoides. Water Res. **1999**, *33* (6), 1516.
2. Fan, H.; Zuo, D.; Hu, T. Analysis of investigation in requirement of technology harmless to environment in electroplating industry. Plating Finishing **2001**, *23* (5), 16 (in Chinese).
3. Aldrich, J.R. Ferrous and Sulfide Treatment of Electroplating Wastewater. US Patent 4,705,639, 1987.
4. Sedlak, D.L.; Chan, P.G. Reduction of hexavalent chromium by ferrous iron. Geochim. Cosmochim. Ac. **1997**, *61* (11), 2185.
5. Zhang, H.; Rechmond, J.B. Light-induced of aqueous chromium(III) in the presence of iron(III). Environ. Sci. Technol. **1999**, *33* (3), 588.
6. Hirsch, S. Deionization for electroplating. Metal Finishing **1999**, *97* (2), 149.
7. Zhao, M.; Duncan, J.R. Removal and recovery of nickel from aqueous solution and electroplating rinse effluent using Azolla filiculiodes. Process Biochem. **1998**, *33* (3), 249.
8. Gan, Q. A case study of microwave processing of metal hydroxide sediment sludge from printed circuit board manufacturing wash water. Waste Manage. **2000**, *20*, 695.
9. Valerdi-Perez, R.; Ibñez-Mengual, J.A. Current-voltage curves for an electrodialysis reversal pilot plant: determination of limiting currents. Desalination **2001**, *141* (1), 23.
10. Shaposhnik, V.A.; Kesore, K. An early history of electrodialysis with permselective membranes. J. Membr. Sci. **1997**, *136* (1), 37.
11. Vallejo, M.E. Electrotransport of Cr(VI) through an anion exchange membrane. Sep. Purif. Technol. **2000**, *21* (1), 63.

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12. Sata, T. Electrodialytic transport properties of anion-exchange membranes prepared from poly(vinyl alcohol), poly(*N*-ethyl 4-vinylpyridinium salt) and β-cyclodextrin. J. Membr. Sci. **2001**, *181* (1), 170.
13. Weber, T.J. Wastewater treatment. Metal Finishing **1999**, *97* (1), 801.

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