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Removal of copper ions from electroplating rinse water using electrodeionization*

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Abstract: An improved configuration of the membrane stack was adopted in the electrodeionization (EDI) cell to prevent precipitation of bivalent metal hydroxide during the running. The operational parameters that influenced the removal of copper ions from the dilute solution were optimized. The result showed that a moderate decrease in the inlet pH value and a moderate increase in the applied voltage could achieve a better removal effect. The steady process of electroplating wastewater treatment could be achieved with a removal efficiency of more than 99.5% and an enrichment factor of 5~14. The concentration of copper in purified water was less than 0.23 mg/L. This demonstrated the applicability of recovering heavy metal ions and purified water from electroplating effluent for industrial reuse.

Key words: Electrodeionization (EDI), Electroplating wastewater, Heavy metal, Precipitation
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INTRODUCTION

Electroplating rinse water is one of the major contributors to heavy metal pollution in surface waters. Treatment and removal of heavy metals have received considerable attention because of their toxicity and association with various health problems (Jüttner *et al*., 2000; Janssen and Koene, 2002). Copper, well verified in mammals for its role in carcinogenicity, is being widely used in electroplating industries. As only 30%~40% of all metals used in the electroplating process are effectively utilized, the waste effluents are responsible for the supply of heavy metal pollutants to the environment. Therefore, importance should be attached to how to effectively remove metal ions in electroplating wastewater. With this aim in mind, various physicochemical treatment methods have been employed.

Ion exchange has been widely applied for the removal of heavy metal ions from electroplating effluent because it is effective and easy to operate. However, ion exchange resins must be regenerated by additive chemical reagents (acid and alkali) when they are saturated and this causes serious secondary pollution. As an alternative technique, electrodialysis is not economical for treating dilute solution because of its high electrical resistance and the development of concentration polarization phenomena (Korngold *et al*., 1998).

Electrodeionization (EDI) is a hybrid system combining ion exchange with electrodialysis which is obtained by introducing ion exchange resins into electrodialysis chambers. The combination allows the treatment of very dilute solution (Souilah *et al*., 2004), and ion exchange resins inside are continuously regenerated electrochemically by hydrogen and hydroxide ions produced by water electrolysis occurring in the two external electrode compartments (Monzie

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et al., 2005). Therefore, EDI has been commercially used for the production of deionized water in industries such as microelectronics, power generation and pharmaceuticals.

However, application of the EDI process in the field of wastewater treatment is still at the research stage, and previous EDI stack configurations (Grebenyuk *et al.*, 1998; Koene and Janssen, 2001; Spoor *et al.*, 2002a; 2002b; 2002c; 2002d; Dzyazko and Belyakov, 2004) cannot avoid the precipitation of bivalent metal hydroxide as a result of metal ion reacting with hydroxide ion present in the EDI stack. Consequently, the application of EDI in wastewater treatment has been greatly limited by this drawback.

An improved configuration of the EDI membrane stack that avoids nickel hydroxide precipitation has been previously reported (Chen and Wu, 2005). To further examine the effectiveness of the configuration and optimize operational parameters for testing applicability, we focused on recovering copper ions from electroplating rinse water as well as from purified water for reuse in an EDI operation in the electroplating industry.

MATERIALS AND METHODS

Ion exchange resins and ion exchange membranes

The D001 strongly acid styrene-divinylbenzene cation exchange resin (CER) and D201 strongly alkali styrene-divinylbenzene anion exchange resin (AER) (Hangzhou Resin Co., China), as well as the polyethylene heterogeneous cation exchange membrane (CEM) and polyethylene heterogeneous anion exchange membrane (AEM) (Lin'an Water Treatment Equipment Co., China) were used. Characteristics of the resins and membranes are listed in Table l.

Prior to use, the membranes were immersed in deionized water for 3 d and the resins were pretreated with the following procedures to remove any contamination:

(1) Immersion of CER and AER respectively in two resin volumes of deionized water for 24 h.

(2) Immersion of CER in two resin volumes of 1.0 mol/L NaOH solution and AER in two resin volumes of 1.0 mol/L HCl solution for 8 h, respectively, and rinsing in deionized water until the effluents were pH neutral.

(3) Immersion of CER in two resin volumes of 1.0 mol/L HCl solution and AER in two resin volumes of 1.0 mol/L NaOH solution for 8 h, respectively, and rinsing in deionized water until the effluents were pH neutral.

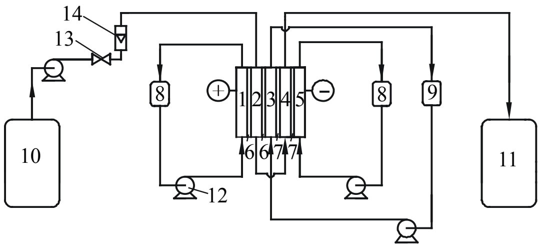
Experimental set-up

Fig.1 shows that the experimental set-up consisted of five separate compartments: anode compartment, CER-loaded compartment, concentrate compartment, AER-loaded compartment and cathode compartment. The compartments were separated from one another by four membranes, and the effective area of each membrane was 38.8 cm^2. The CER-loaded compartment was separated from the anode compartment and the concentrate compartment by two CEMs, and the AER-loaded compartment was separated from the concentrate compartment and the cathode compartment by two AEMs. The two outer electrode compartments had dimensions of 19.4 cm×2.0 cm×1.4 cm and each contained a Ti substrate RuO$_2$ (Ti/RuO$_2$) net electrode with effective area of 38.8 cm^2. The CER-loaded compartment, the concentrate compartment and the AER-loaded compartment had the same dimensions of 19.4 cm×2.0 cm×0.7 cm. One-thousand ml deionized water was circulated through the concentrate compartment and 500 ml of electrode solutions through the anode and cathode compartments, respectively, by using three AP 1200 pumps. Wastewater was fed in turn through the CER-loaded compartment and the AER-loaded compartment. A regulated direct current (DC) power

Table 1 Characteristics of the ion exchange resins and ion exchange membranes

		Water content (wt%)	Exchange capacity	Density (g/ml)	Electrical resistance (Ω·cm^2)	Particle size (mm)	Permselectivity (%)
Resin	CER	45~55	≥1.75 (mmol/ml)	1.25~1.28		0.3~1.2	
	AER	50~60	≥1.15 (mmol/ml)	1.06~1.10		0.3~1.2	
Membrane	CEM	40~55	≥2.0 (meq/g)		≤15		≥92
	AEM	30~45	≥1.8 (meq/g)		≤15		≥90

Note: CER: cation exchange resin; AER: anion exchange resin; CEM: cation exchange membrane; AEM: anion exchange membrane



1: Anode compartment; 2: CER-loaded compartment; 3: Concentrate compartment; 4: AER-loaded compartment; 5: Cathode compartment; 6: CEM; 7: AEM; 8: Electrode solution reservoir; 9: Concentrated solution reservoir; 10: Wastewater reservoir; 11: Purified water reservoir; 12: Pump; 13: Valve; 14: Flowmeter

Fig.1 Schematic diagram of the experimental set-up for wastewater treatment

supply (WYL1701, China) was used to provide a steady voltage.

Water purification

The CER-loaded compartment was filled with 30 ml pretreated CER, and in addition the AER-loaded compartment was packed with 30 ml pretreated AER. The 0.05 g/L Na_2SO_4 solution was circulated through the anode and cathode compartments, respectively. The applied voltage was set at the desired values (20, 30 and 40 V, respectively). Copper-containing simulated electroplating wastewater of 50 mg/L Cu^{2+} was continuously treated with a flow rate of 3 L/h. At interval of 1 h, the Cu^{2+} concentrations of both the concentrated solution and the purified water were determined, and the pH value of the concentrated solution was measured.

Copper ions were determined by the atomic absorption spectrophotometry method. The pH value was measured with a Mettler Toledo 320-S pH meter.

RESULTS AND DISCUSSION

Effect of inlet pH value on copper enrichment and water purification

The solubility product constant (K_{sp}) of $Cu(OH)_2$ at 18~25 °C is 2.2×10^{-20}. Concentration of Cu^{2+} in the target water was 50 mg/L. When the pH value of the target water was higher than 5.72, precipitation of $Cu(OH)_2$ would form. Therefore the target water was adjusted with 1.0 mol/L H_2SO_4 solution at pH 5.23, pH 4.28 and pH 3.22, respectively. Enrichment of copper ions with respect to the running time at a constant cell voltage of 30 V for different inlet pH values is shown in Fig.2a. From Fig.2a it can be seen that the enrichment effect was in the order: pH 4.28>pH 3.22>pH 5.23. A relatively high or low: pH value caused water dissociation, and resin electro-regeneration and corresponding removal of copper ions were restrained. This was manifested by Cu^{2+} concentration in the purified water after 8 h, i.e., 0.06 mg/L for inlet pH value of 4.28, 0.17 mg/L for pH 3.22 and 0.23 mg/L for pH 5.23.

Effect of applied voltage on copper enrichment and water purification

The amount of copper transported into the concentrate compartment with relative to time, with the same inlet pH value of 4.28 at different applied voltages, is illustrated in Fig.2b. Fig.2b shows that the Cu^{2+} concentration in the concentrated solution obviously increased as the cell voltage rose from 20 V to 30 V or 40 V. When the applied voltage was respectively 20, 30 and 40 V, the corresponding Cu^{2+} concentration in the purified water after 8 h was 0.19, 0.06 and 0.02 mg/L, respectively. High applied voltage was beneficial to copper ions enrichment and removal. However, the higher potential made

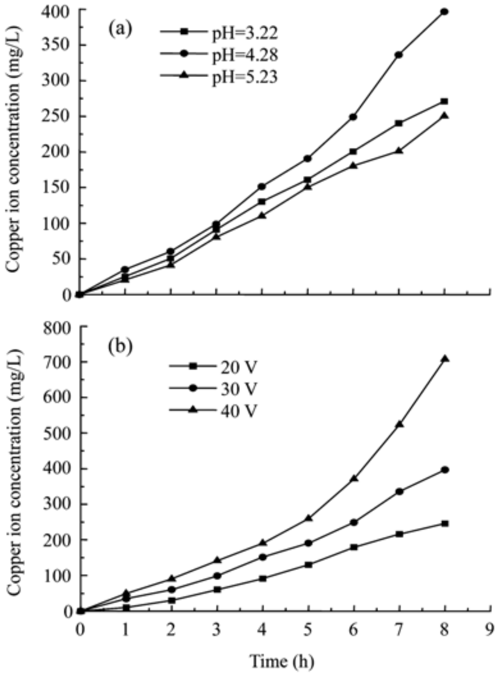


Fig.2 Copper ion concentration of the concentrated solution at (a) different inlet pH value and (b) different applied voltages

excessive H^+ and OH^- generated from the electrode reactions also migrate to the concentrate compartment, and this caused a decrease in current efficiency. Therefore, an appropriate applied voltage should be chosen for a better enrichment effect, better removal effect and lower energy consumption.

Metal hydroxide precipitation

According to the solubility product principle, if the ion product (Q_c) of two kinds of ions, for instance, A^+ and B^-, is greater than K_{sp} of the compound AB, the precipitation of AB will form, or else no precipitation of AB forms. K_{sp} of $Cu(OH)_2$ at 18~25 °C is 2.2×10^{-20}. Q_c of Cu^{2+} and OH^- is equal to $[Cu^{2+}]\cdot[OH^-]^2$.

Figs.3a and 3b represent the pH value of the concentrated solution with relative to time for the same experiments represented in Figs.2a and 2b, respectively. By combining Figs.2a and 2b with Figs.3a and 3b, we calculated and obtained $-\lg Q_c$ of Cu^{2+} and OH^-, as listed in Table 2. From the table it can be seen that $-\lg Q_c$ was consistently greater than $-\lg K_{sp}$ of $Cu(OH)_2$, i.e., Q_c was far less than K_{sp}, and there was no precipitation of $Cu(OH)_2$ that formed during the whole process of water purification.

In the EDI cell, when DC is applied, the following reactions Eq.(1) and Eq.(2) may occur in the anode and cathode compartments, respectively:

$$2H_2O-4e\rightarrow O_2+4H^+, \quad (1)$$

$$2H_2O+2e\rightarrow H_2+2OH^-. \quad (2)$$

H^+ produced from the anode reaction in the anode compartment transferred through the CEM under the external electric field to exchange with Cu^{2+} adsorbed in the CER. The CER was regenerated and the desorbed Cu^{2+} and part of H^+ migrated through the other CEM into the concentrate compartment. Similarly, OH^- generated from the cathode reaction migrated through the AEM into the AER-loaded compartment to replace SO_4^{2-} adsorbed in the AER. The AER was regenerated and then the desorbed SO_4^{2-} and part of OH^- transferred through the other AEM into the concentrate compartment, too. It was well known that the migration rate of H^+ was the greatest among those of Cu^{2+}, SO_4^{2-}, Na^+, H^+ and OH^-, therefore H^+ migrated to the concentrate compartment earlier than OH^-. Under the same conditions, the number of H^+ transferred to the concentrate compartment was larger than that of OH^-, and this acidic environment was very favorable for avoiding $Cu(OH)_2$ precipitation in the concentrate compartment.

Furthermore, Cu^{2+} and OH^- would not coexist in CER or AER. Consequently, hydroxide precipitation would not occur.

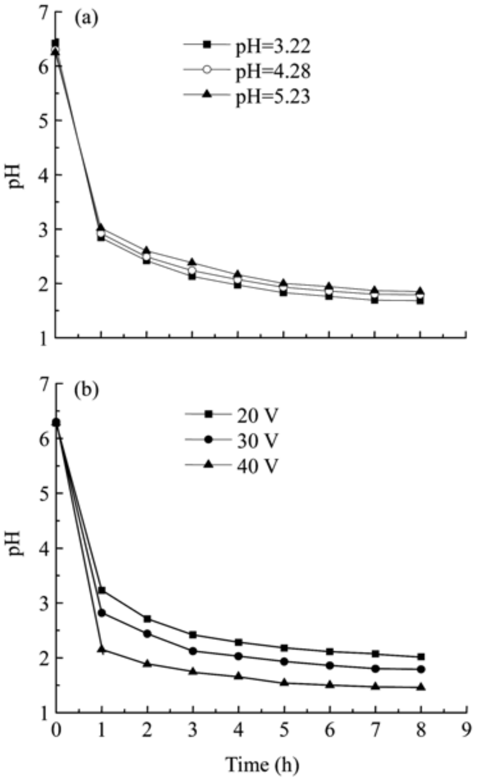


Fig.3 pH value of the concentrated solution with relative to time at (a) different inlet pH values and (b) different applied voltages

Table 2 $-\lg Q_c$ of Cu^{2+} and OH^- during water purification

Time (h)	At different inlet pH value			At different applied voltage (V)		
	3.22	4.28	5.23	20	30	40
1	25.72	25.62	25.46	25.34	25.62	26.81
2	26.26	26.14	25.99	26.49	26.14	27.09
3	26.58	26.57	26.14	26.18	26.57	27.17
4	26.75	26.56	26.44	26.28	26.56	27.20
5	26.94	26.66	26.63	26.33	26.66	27.31
6	26.98	26.69	26.67	26.33	26.69	27.23
7	27.04	26.68	26.76	26.33	26.68	27.14
8	27.01	26.62	26.70	26.37	26.62	27.03

Note: $-\lg K_{sp}$ of $Cu(OH)_2$ is equal to 19.66

Water treatment

The EDI performance was evaluated in terms of removal efficiency (*re*) (Marder *et al*., 2004) and enrichment factor (*ef*), defined respectively by Eq.(3) and Eq.(4):

$$re=\frac{C_\mathrm{i}-C_\mathrm{f}}{C_\mathrm{i}}\times 100\%, \tag{3}$$

$$ef=\frac{C_\mathrm{c}}{C_\mathrm{i}}, \tag{4}$$

where C_i and C_f are the initial and final concentrations of the ion, respectively; C_c is the concentrated concentration of the ion.

As shown in Figs.2a and 2b, Cu^{2+} could be concentrated as high as 245~707 mg/L, and the corresponding enrichment factor was about 5~14.

According to Fig.2, the final concentration of Cu^{2+}, removal efficiency of Cu^{2+} was 99.54%~99.96%.

CONCLUSION

The inlet pH value and applied voltage had a remarkable influence on copper enrichment and water purification. A moderate decrease in the inlet pH value and a moderate increase in the applied voltage could achieve a better removal effect.

During the EDI process, the concentrated solutions were always acid enough to prevent precipitation of metal hydroxide which was common in other EDI processes, and this suggested that the improved EDI configuration could feasibly realize continuous and long-term wastewater purification.

Treatment of copper-containing simulated electroplating wastewater by using the improved EDI configuration showed that the wastewater was purified and could be drained or recycled for reuse in the electroplating industry.

References

Chen, X., Wu, Z., 2005. A new configuration of membrane stack for retrieval of nickel absorbed in resins. *Journal of Zhejiang University SCIENCE*, **6B**(6):543-545. [doi:10.1631/jzus.2005.B0543]

Dzyazko, Y.S., Belyakov, V.N., 2004. Purification of a diluted nickel solution containing nickel by a process combining ion exchange and electrodialysis. *Desalination*, **162**(1-3):179-189. [doi:10.1016/S0011-9164(04)00041-4]

Grebenyuk, V.D., Chebotareva, R.D., Linkov, N.A., Linkov, V.M., 1998. Electromembrane extraction of Zn from Na-containing solutions using hybrid electrodialysis-ion exchange method. *Desalination*, **115**(3):255-263. [doi:10.1016/S0011-9164(98)00044-7]

Janssen, L.J.J., Koene, L., 2002. The role of electrochemistry and electrochemical technology in environmental protection. *Chemical Engineering Journal*, **85**(2-3):137-146. [doi:10.1016/S1385-8947(01)00218-2]

Jüttner, K., Galla, U., Schmieder, H., 2000. Electrochemical approaches to environmental problems in the process industry. *Electrochimica Acta*, **45**(15-16):2575-2594. [doi:10.1016/S0013-4686(00)00339-X]

Koene, L., Janssen, L.J.J., 2001. Removal of nickel from industrial process liquids. *Electrochimica Acta*, **47**(5):695-703. [doi:10.1016/S0013-4686(01)00750-2]

Korngold, E., Aronov, L., Kedem, O., 1998. Novel ion-exchange spacer for improving electrodialysis I. Reacted spacer. *Journal of Membrane Science*, **138**(2):165-170. [doi:10.1016/S0376-7388(97)00216-0]

Marder, L., Bernardes, A.M., Ferreira, J.Z., 2004. Cadmium electroplating wastewater treatment using a laboratory-scale electrodialysis system. *Separation and Purification Technology*, **37**(3):247-255. [doi:10.1016/j.seppur.2003.10.011]

Monzie, I., Muhr, L., Lapicque, F., Grévillot, G., 2005. Mass transfer investigations in electrodeionization processes using the microcolumn technique. *Chemical Engineering Science*, **60**(5):1389-1399. [doi:10.1016/j.ces.2004.10.010]

Souilah, O., Akretche, D.E., Amara, M., 2004. Water reuse of an industrial effluent by means of electrodeionization. *Desalination*, **167**(1-3):49-54. [doi:10.1016/j.desal.2004.06.112]

Spoor, P.B., Grabovska, L., Koene, L., Janssen, L.J.J., ter Veen, W.R., 2002a. Pilot scale deionisation of a galvanic nickel solution using a hybrid ion-exchange/electrodialysis system. *Chemical Engineering Journal*, **89**(1-3):193-202. [doi:10.1016/S1385-8947(02)00009-8]

Spoor, P.B., Koene, L., Janssen, L.J.J., 2002b. Potential and concentration gradients in a hybrid ion-exchange/electrodialysis cell. *Journal of Applied Electrochemistry*, **32**(4):369-377. [doi:10.1023/A:1016321129861]

Spoor, P.B., Koene, L., ter Veen, W.R., Janssen, L.J.J., 2002c. Electrodeionisation 3: The removal of nickel ions from dilute solutions. *Journal of Applied Electrochemistry*, **32**(1):1-10. [doi:10.1023/A:1014217831398]

Spoor, P.B., Koene, L., ter Veen, W.R., Janssen, L.J.J., 2002d. Continuous deionization of a dilute nickel solution. *Chemical Engineering Journal*, **85**(2-3):127-135. [doi:10.1016/S1385-8947(01)00216-9]