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A new configuration of membrane stack for retrieval of nickel absorbed in resins^{*}

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Abstract: A new configuration integrated ion exchange effect with both electro-migration and electrochemical reaction in a single cell was developed to effectively retrieve metal ions from simulated wastewater using ion exchange resins without additive chemicals. By simply assembling cation exchange resins and anion exchange resins separated by homogeneous membranes, we found that the system will always be acidic in the concentrate compartment so that ion exchange resins could be in-situ regenerated without hydroxide precipitation. Such a realizable design will be really suitable for wastewater purification.

Key words: Nickel, Ion exchange resin, Electro-migration, Electrochemical

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INTRODUCTION

To meet the needs of wastewater recovery and reuse, ion exchange was commonly used especially for the purification of electroplating rinse water containing nickel and other heavy metal ions (Koivula *et al.*, 2000). Although ion exchange resins have many advantages over chemical precipitation, some drawbacks of the method are inevitable. When the ion exchange resins are saturated with metal ions, additive chemical reagents (acid and alkali) are needed to regenerate the resins and this produces large amounts of wastewater, which would again pollute the environment. So how to regenerate the resins without producing environmental pollution is of significant importance for the more general use of ion exchange resins. In order to solve the secondary pollution problem, electrodeionization (EDI) has been developed to conserve the advantages of the ion exchange

technology.

The main distinction of the EDI process from the conventional ion exchange technology (EX) is that ion exchangers in EDI are in-situ electrochemically regenerated in contrast to the periodic chemical regeneration in the latter. EDI is a process combining the merits of ion exchange and electrodialysis. Fedorenko (2004)'s comparison between EDI and EX showed that the EDI method is more effective than the traditional EX process from the technological and the economic standpoints. For these reasons, it has been commercially used for production of deionized water in microelectronics, power generation and pharmaceuticals industries, although the application of this process for wastewater treatment is still being in the research stage (Widiasa *et al.*, 2004; Dzyazko and Belyakov, 2004). The difficulty of the method is that hydroxide precipitation occurring at the resins interface or anion exchange membranes cannot be avoided.

In this Letter we report a method adopting a new configuration of the membrane stack in the EDI cell for the successful retrieval of nickel absorbed in resins.

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EXPERIMENTS AND METHODS

Fig.1 shows that the apparatus has five separate compartments: anode compartment, CERs-loaded (cation-exchange resins loaded) compartment, concentrate compartment, AERs-loaded (anion-exchange resins loaded) compartment and cathode compartment, respectively. The compartments were separated from one another by four membranes. The outer two compartments were electrode compartments, with volumetric capacity of approximately 300 cm^3 each width of 2 cm. Both anode and cathode with effective areas of 136.5 cm^2 were ruthenium net coated with ruthenium oxide. The CERs-loaded compartment was separated from the anode compartment and the concentrate compartment by two polyethylene heterogeneous cation exchange membranes (CEM) with effective area of 136.5 cm^2 . The AERs-loaded compartment was separated from the concentrate compartment and the cathode compartment by two polyethylene heterogeneous anion exchange membranes (AEM) with effective area equal to that of the CEM.

Ion exchange resins were prepared in Spoor *et al.*(2001)'s. Two-hundred ml of ion exchange resins saturated with 0.1 mol/L NiSO_4 for 3 d, and then rinsed with deionized water. A regulated DC power supply (WYL1701, China) was used to provide a steady voltage.

Fig.1 Schematic diagram of experimental setup

1: Anode; 2: Cathode; 3: Anode compartment; 4: Cathode compartment; 5: Concentrate compartment; 6: AEM; 7: CEM; 8: AER; 9: CER; 10: Reservoir; 11: Pump

Anode compartment, concentrate compartment and cathode compartment of the cell were close-cycled, respectively. Five-hundred cm^3 of de-

ionized water was circulated between the outer reservoir and each compartment with the use of an AP1200 pump.

RESULTS AND DISCUSSION

Table 1 lists the pH of anode compartment, concentrate compartment and cathode compartment measured after 3 h. It was found that both anode compartment and concentrate compartment were always acidic, while the cathode compartment was alkaline. This implied that no nickel hydroxide precipitation deposited in the resins or at the surface of the AEM.

Table 1 pH value in anode, concentrate and cathode compartments

Applied voltages (V)	pH		
	Anode compartment	Concentrate compartment	Cathode compartment
10	2.38	3.35	11.96
30	2.07	2.55	12.15

During this process, a large amount of H^+ produced from the electrochemical reactions in the anode and transferred through CEM under the external electric field to exchange with the nickel ions initially absorbed in the CERs. And then the desorbed Ni^{2+} ions and a part of H^+ transferred through the other CEM into the concentrate compartment. In the cathode compartment, a large amount of OH^- generated in the cathode from the electrode reaction migrated through the AEM into the AERs-loaded compartment to exchange with SO_4^{2-} absorbed in the AERs. The desorbed SO_4^{2-} and a part of OH^- migrated through the other AEM into the concentrate compartment. It was not difficult to understand that the migration rate of H^+ was the highest among all ions. Therefore, H^+ must migrate to the concentrate compartment earlier than the other ions. Under the same conditions, the number of H^+ ions transferring to the concentrate compartment was larger than that of the OH^- ions. Table 1 shows that pH was 2.07 in the anode compartment and 12.15 in the cathode compartment, which elucidated that the number of H^+ ions migrating to the concentrate compartment was larger than that of OH^- ions and was very favorable for avoiding

the nickel hydroxide precipitation in the concentrate compartment.

Furthermore, nickel ions and hydroxyl ions would not coexist in the cation exchange resins or in the anion exchange resins so hydroxide precipitations would not occur.

The electrolyte of the solution will significantly affect ions migration. Fig.2 shows that an addition of a small amount of Na_2SO_4 solution could enormously accelerate the outward migration of Ni^{2+} ions from the CERs-loaded compartment and SO_4^{2-} from the AERs-loaded compartment to the concentrate compartment because the number of H^+ ions produced in deionized water is rather small. The Na_2SO_4 electrolyte introduced into the electrode compartment is a "starting reagent" instead of "regenerating reagent". The Ni^{2+} ion concentration in the concentrate compartment was 1450 mg/L after 3 h, that is, the Ni^{2+} ion's mole number was 0.0124. It was obvious that the amount of Ni^{2+} ions transferred to the concentrate compartment was larger than that of Na^+ ions initially added with the mole number of 0.00352. So we can conclude that with the experiment going on, the Ni^{2+} ions would be continuously regenerated by the H^+ ions from the electrode reaction. After 3 h, the regenerating current increased to a reasonable value for maintaining continuous regeneration.

Fig.2 Concentration of nickel ions in concentrate compartment

Operational conditions: applied voltages, 30 V

The effect of applied voltages on the Ni^{2+} migration (Fig.3) shows that the migration rate increased obviously when the cell voltages rose from 10 V to 30 V. Under the condition of 10 V potential, there were nearly no ions transferred to the concentrate com-

partment. However, a large amount of ions appeared in the concentrate compartment when the potential was increased to 20 V or 30 V. It can be illustrated that ion migration rate will be enhanced with the applied voltages increasing.

Fig.3 The effect of applied voltages on the Ni^{2+} migration
Operational conditions: 0.5 g/L Na_2SO_4

CONCLUSION

Applying the new membrane stack configuration for the removal of nickel and sulfate ions absorbed in the resins showed that the method can feasibly realize nickel removal and in-situ regeneration of the resins simultaneously without the problem of the hydroxide precipitation. The methodology developed here will lead to comprehensive application of this promising process for wastewater purification.

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