Removal of Cr(VI) from wastewater by simplified electrodeionization

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ABSTRACT

A newly simplified electrodeionization (SEDI) system was proposed and tested for the removal of Cr(VI) from synthetic wastewater. By comparing with the conventional electrodeionization, our SEDI has no anion exchange membranes. It only used a pair of cation exchange membranes to separate the resin from the electrodes. The experimental results indicated that the exhausted resin could be effectively regenerated at high current density. The average concentration of Cr(VI) in the regeneration solution was 724 mg/L. 44% of the resin was regenerated, and the power consumption was only 8.4 kWh/mol Cr(VI). The regenerated resin exhibited a good performance for Cr(VI) removal. After treatment, the Cr(VI) concentration decreased from the initial 50 mg/L to less than 0.5 mg/L. The regeneration solution was further concentrated by electrodialysis (ED) to 17.5 g chromic acid/L and only consumed about 1.1 kWh/mol Cr(VI). The method we developed has the potential to be used in engineering.

Keywords: Electrodeionization; Wastewater; Cr(VI); Resin; Electrical regeneration

1. Introduction

Wastewater from electroplating, tanning, metal finishing, pulp producing, ore and petroleum refining processes usually contain hexavalent chromium, Cr(VI) [1], which is known to be carcinogenic, mutagenic and teratogenic to biological systems [2]. The concentration of Cr(VI) in these wastewaters is usually kept at a low level of tens to hundreds of mg/L. Although several methods for removing this metal from wastewater have been developed, it is still difficult to meet environmental standards after most conventional treatments [3,4]. For example, the upper limit of Cr(VI) in China's comprehensive wastewater discharge standard is 0.5 mg/L, but many treatments are not able to reduce the concentration to this level [5,6]. Meanwhile, Cr(VI) is a kind of recyclable resource due to its high economic value. Therefore, it is very necessary for the industry to simultaneously remove and recover Cr(VI) from wastewater.

Currently, the main methods for treating wastewater containing Cr(VI) include reverse osmosis, nanofiltration, electrodialysis (ED), electrodeposition, ion exchange, adsorption and electrodeionization (EDI) [7–15]. Among the available treatment methods, ion exchange is an attractive method for treating wastewater containing low concentrations of Cr(VI). This process can reduce Cr(VI) to a very low level to meet any stringent environmental standards and the effluent can be reused [15,16]. However, the conventional ion exchange method not only consumes a large number of chemicals for regeneration but also introduces a large amount of undesired impurities. To recover pure chromic acid, some extra units must be added to increase the complexity of the operation.

In recent years, more and more attention has been paid to EDI, which combines ED with ion exchange. It has

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been widely used for the production of pure water in the industry [17]. This technique was also reported for the removal of cationic heavy metal ions, such as Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} from wastewater [18–21]. In addition, some studies have shown that the use of EDI can effectively remove and recover Cr(VI) from wastewater [22–25]. Although EDI offers various advantages of ion exchange and ED while overcoming the problems of these separate processes, this technique has not been widely used in wastewater treatment yet. One of the most important reasons is undoubtedly the complexity of its structure. EDI is, in principle, equivalent to the ED with ion-exchange resins in dilute chambers. To improve its efficiency in industrial applications, a large number of anion and cation exchange membranes have to be packed to form many dilute chambers and concentrated chambers. The use of numerous membranes makes EDI very complex in structure. This will lead to a significant increase in costs and great inconvenience in maintenance, thus limiting its wide industrial application in wastewater treatment. In this work, a new simplified electrodeionization (SEDI) system operated in batch was proposed and tested for the removal of Cr(VI) from synthetic wastewater. Unlike conventional EDI, this new system had no anion exchange membranes. It only used a pair of cation exchange membranes to separate the resin from the electrodes.

The main purpose of this study was to investigate the effect of resin regeneration from Cr(VI) to test the performance of recycled resin for wastewater containing low concentrations of Cr(VI) and explore the feasibility of using ED to further concentrate the dilute chromic acid solution obtained during the regeneration process.

2. Material and methods

2.1. Resin regeneration principle of SEDI

The principle of regenerating the exhausted resin for the new SEDI system is illustrated in Fig. 1. During the regeneration process, the resin chamber is supplied with direct current (DC) electricity, and deionized water (DI water) continuously passes through the resin chamber. The ionization of H_2O is significantly enhanced by the influence of DC electricity at high current density. The produced OH^- ions can be effectively exchanged with the $HCrO_4^-$ ions in the resin so that the exhausted resin can be gradually regenerated. Meanwhile, the $HCrO_4^-$ ions accumulate in the aqueous phase and come out directly from the resin chamber as a dilute chromium acid solution. The main reactions during the regeneration process are shown below:

Ionization of H_2O:

$$H_2O \rightarrow H^+ + OH^- \tag{1}$$

Regeneration of resin:

$$R - HCrO_4 + OH^- \rightarrow R - OH + HCrO_4^- \tag{2}$$
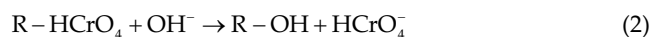
Formation of chromium acid:
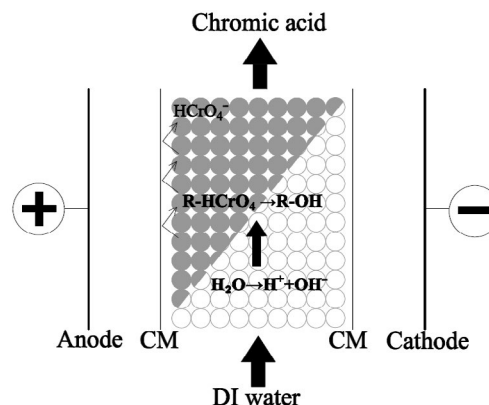
$$HCrO_4^- + H^+ \rightarrow H_2CrO_4 \tag{3}$$

Fig. 1. Principle of using the strong electrical field for resin regeneration.

It should be noted that the new system is quite different from conventional EDI. Traditional EDI usually requires a large amount of cation exchange membranes (CM) and anion exchange membranes (AM). However, the new system has only two CMs, so the structure is much simpler. In addition, the conventional EDI involves the step of migrating $HCrO_4^-$ ions across AM, but the new system does not require such a step. The Cr(VI) species are directly carried out from the resin chamber of the new system through the aqueous flow. It provides more potential to optimize our system.

2.2. Experimental set-up

The experimental set-up is schematically shown in Fig. 2. The SEDI system consisted of three separate chambers: an anode chamber (200 mm × 20 mm × 15 mm), a cathode chamber (200 mm × 20 mm × 15 mm), and a resin chamber (200 mm × 20 mm × 12 mm). The anion exchange resin was packed in the resin chamber. The electrode chambers and the resin chamber were separated by two cation exchange membranes (CM, Nafion®117, DuPont Co.,
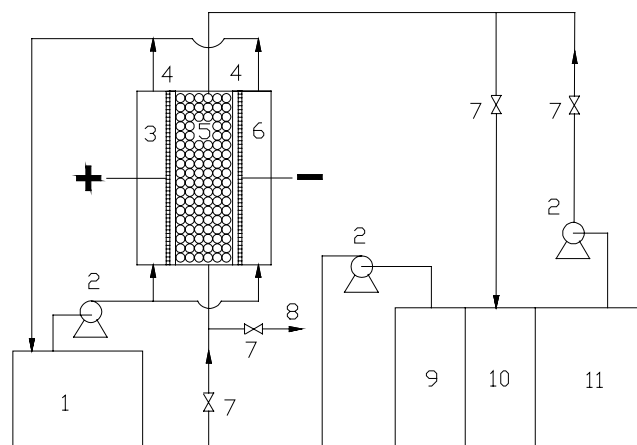

Fig. 2. Experimental setup ((1) electrode solution reservoir, (2) pump, (3) anode chamber, (4) cation exchange membrane, (5) resin chamber, (6) cathode chamber, (7) valve, (8) effluent, (9) DI water reservoir, (10) regeneration solution reservoir, and (11) wastewater reservoir).

USA). Both membranes had an effective area of 40 cm^2 (200 mm × 20 mm). The net spacing between two CM was 12 mm. Ti/Ru$_2$O$_3$-SnO$_2$-Sb$_2$O$_5$ and titanium meshes were used as the anode and the cathode, respectively. The Ti/Ru$_2$O$_3$-SnO$_2$-Sb$_2$O$_5$ anode was fabricated using RuCl$_3$·H$_2$O, SnCl$_4$·5H$_2$O, and SbCl$_3$ as precursors. The detailed preparation procedures can be found elsewhere [26]. Both electrodes had the same effective area as the membranes. They were fixed 10 mm away from the membranes by inserting gaskets and meshes. Wastewater was delivered downward through the resin chamber by using a diaphragm-type metering pump (JM-10.72/0.42, AILIPU, China). After the resin was exhausted, DI water was delivered upward through the resin chamber at a given current density for the resin regeneration by using another diaphragm-type metering pump (JM-10.72/0.42, AILIPU, China). A DC power supply (QJ1503S, Qiujing, China) was used to maintain a constant current. To increase the conductivity, a 1% H$_2$SO$_4$ solution was used as the anolyte and catholyte, which was recycled by the third diaphragm-type metering pump (JM-10.72/0.42, AILIPU, China).

2.3. Resin treatment

All the anion exchange resins were obtained from Zhengguang Co. (Hangzhou, China). Prior to the study, each type of resin was immersed in 10% H$_2$SO$_4$ for 6 h first, then washed with DI water, fully regenerated with 5% NaOH, and finally washed with DI water again. After treatment, 48 mL of resin, which had been completely converted to R-OH form, was charged in the resin chamber.

2.4. Wastewater preparation

Wastewater with a Cr(VI) concentration of 50 mg/L was synthesized by dissolving an appropriate amount of chromium trioxide (CrO$_3$) in DI water.

2.5. Analysis

Cr(VI) concentrations were analyzed with a spectrophotometer (DR/2500, Hach, USA) according to the standard methods [27]. The detectable limit was 0.01 mg/L.

3. Results and discussion

3.1. Resins selection

The performance of the SEDI system is highly dependent on the properties of the ion exchange resins. Therefore, the selection of resins was carried out first. In this work, four common anion exchange resins, including the macro-porous strong-base resin, the gel strong-base resin, the macro-porous weak-base resin, and the gel weak-base resin, were examined. Their properties are given in Table 1. All experiments were conducted under the same conditions for 1 h, and the results are shown in Table 2. It was found that the gel weak-base resin with the acrylic matrix (321) had poor conductivity. The voltage jumped over 150 V in 20 min, exceeding the range of the DC power supply used. Meanwhile, the temperature of the resin was higher than 50°C, exceeding the maximum allowable operating temperature of 312. This type of resin was not suitable for this work. Although the voltages for regeneration of the macro-porous strong-base resin (D201) and the gel strong-base resin (201 × 4) were low, their efficacy for resin regeneration and Cr(VI) recovery were poor. The macro-porous weak-base (D301) resin was found to be the best one, which demonstrated the good efficacy for Cr(VI) removal and recovery, and relatively low power consumption required. Therefore, all the subsequent work was carried out using this type of resin.

For comparison, the performance of the new D301 resin was first investigated for the removal of Cr(VI), and the result is shown in Fig. 3. As a result, it was found that the Cr(VI) concentration in the effluent was less than 0.5 mg/L in the first 38 h, indicating that the resin for removing Cr(VI) was

Table 1
Main properties of the anion exchange resins studied (obtained from manufacturer)

Resin	D201	201 × 4	D301	312
Type	Strong-base	Strong-base	Weak-base	Weak-base
Matrix	Styrene	Styrene	Styrene	Acrylic
Porosity	Macro-porous	Gel	Macro-porous	Gel
Functional group	–N(CH$_3$)$_3$OH	–N(CH$_3$)$_3$OH	–N(CH$_3$)$_2$	–N(CH$_3$)$_2$
Total exchange capacity, eq/L	≥1.20	≥1.10	≥1.45	≥1.60
Maximum operating temperature, °C	80	80	100	40

Table 2
Performances of regeneration packed with different resins (DI water temperature = 10°C, hydraulic retention time (HRT) = 1.9 min, current density = 375 A/m^2, regeneration time = 1 h)

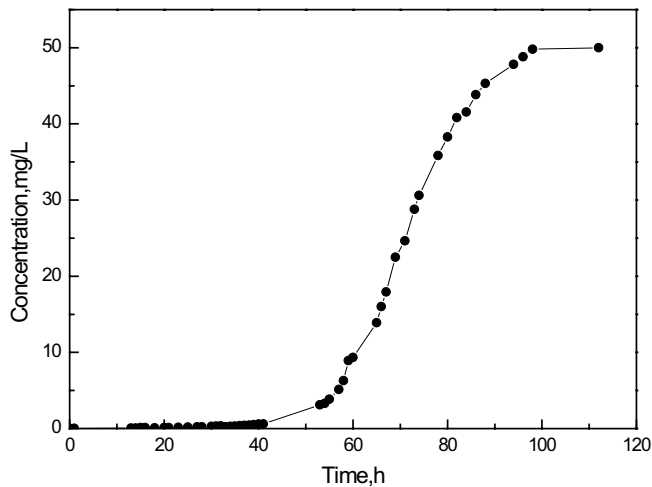| Resin	D201	201 × 4	D301	312
Cr(VI) regenerated, mg/L	366.86	271.26	556.3	–
Voltage, V	62–81	60–68	85–92	>150
Power consumption, kWh/mol Cr(VI)	9.37	12.29	8.24	–

Fig. 3. Breakthrough curve for the new ion exchange resin (flowrate = 1.2 L/h and influent Cr(VI) = 50 mg/L).
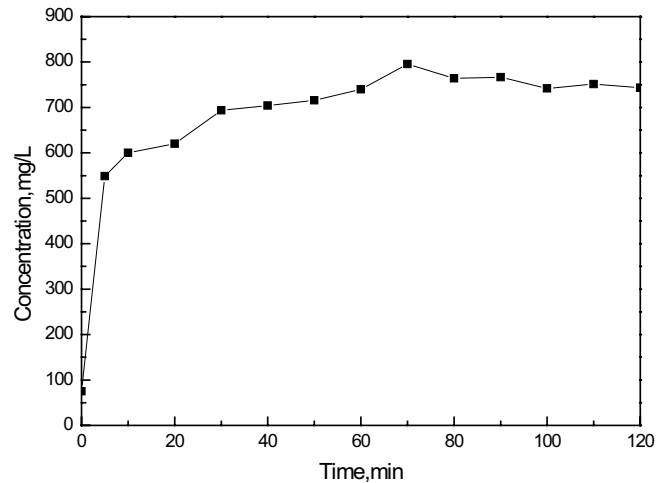

Fig. 4. Variation of Cr(VI) concentration in regeneration solution with time (DI water temperature = 10°C, HRT = 2.4 min, current density = 375 A/m², and regeneration time = 2 h).

highly efficient. The Cr(VI) concentration increased sharply after that, and reached the same level as that in the influent after 98 h, revealing the complete exhaustion of the resin. The total exchange capacity of the new D301 resin was calculated to be 1.59 mol Cr(VI)/L wet resin according to the breakthrough curve, which was in good agreement with the value provided by the resin manufacturer, as shown in Table 1.

3.2. Efficacy in resin regeneration

Fig. 4 displays the variation of Cr(VI) in the regeneration solution. The result was obtained under the conditions of a DI water temperature of 10°C, a hydraulic retention time (HRT) of 2.4 min and a current density of 375 A/m². It was found that the Cr(VI) concentration increased sharply in the initial 5 min, indicating that the exhausted resin could be regenerated effectively. The Cr(VI) concentration then increased slowly and reached the maximum value of 795 mg/L after 70 min. As the regeneration continued, the Cr(VI) concentration tended to decrease gradually but remained above 740 mg/L. The Cr(VI) concentration variation can be partially explained by the dynamic balance mentioned previously as Eq. (2). The average concentration of Cr(VI) in the regeneration solution was 724 mg/L, and the total amount of Cr(VI) regenerated within 2 h was 1.74 g. It should be noted that the Cr(VI) species in the regeneration solution only came from resin, which was saturated with Cr(VI) before the DC electricity was supplied. Based on the total resin capacity and the mass balance calculation of Cr(VI) accumulated in the regeneration solution, about 44% of the resin was regenerated.

It should be noted that the regeneration efficiency of the resin is largely determined by the current density and regeneration time. As the current density and regeneration time increase, the regeneration efficiency will increase accordingly. The regeneration efficiency is also related to the height of the resin layer. As mentioned before, DI water passed through the resin chamber in the upward direction during the regeneration process. Therefore, regeneration starts from the bottom and then moves up gradually. The top resin had a much lower regeneration percentage than the other resin layers. The regeneration efficiency could increase when the height of the resin increased.

3.3. Voltage and power consumption

Fig. 5 shows the voltage between the anode and the cathode as a function of regeneration time. A small fluctuation in voltage was observed for each experimental run. This may be due to the accumulation and release of the oxygen and hydrogen gas bubbles generated in the electrode chambers [22]. Despite the small fluctuation, the overall trend was that the voltage first decreased and then gradually increased. This was mainly attributed to the change of the solution concentration. The concentration may affect the structure of resin at the molecular level, and resins with different structures can have different response upon current. It should be noted that the resistivity of R-OH is much higher than R-HCrO$_4^-$ [22]. In the beginning, the Cr(VI) concentration in the liquid phase increased sharply, and the rate of the increase of R-HCrO$_4^-$ in the resin was much higher than R-OH, so the voltage decreased. As the regeneration proceeded, the resin resistance increased due to the resin conversion from R-HCrO$_4^-$ to R-OH. Although the solution resistance decreased due to an increase in the concentration of Cr(VI) in the liquid phase, the effect of the former was greater than the latter. Therefore, the voltage increased gradually until the end of the experiment. The average voltage was about 94 V.

The power consumption could be calculated according to Eq. (4):

$$E = \frac{MI\bar{U}t}{\bar{C}V} \tag{4}$$

where E is the power consumption, kWh/mol Cr(VI); M is the molar weight, g/mol; I is the current, A; $\bar{U}$ is the average voltage between the anode and the cathode, V; t is the
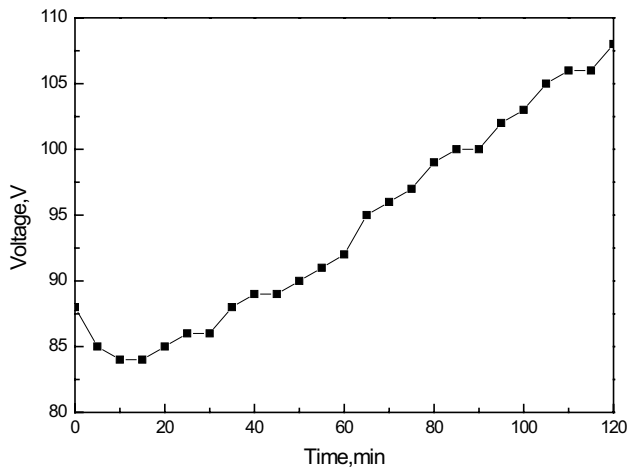
Fig. 5. Variation of voltage between the electrodes with time (current density = 375 A/m²).

Fig. 6. Work curve for the ion exchange resin regenerated compared to the new ion exchange resin (flowrate = 1.2 L/h and influent Cr(VI) = 50 mg/L).

regeneration time, h; $\bar{C}$ is the average Cr(VI) concentration in the regeneration solution, mg/L; and V is the volume of the resin chamber, L. Using Eq. (4), E was calculated to be about 8.4 kWh/mol Cr(VI). This value is a little higher than the ones reported in previous studies [23,28], and it indicates our simplification decreases energy efficiency. Some optimizations should be done in the future to improve the energy efficiency of our simplified method.

3.4. Performance of the resin regenerated for Cr(VI) removal

The performance of the regenerated resin for Cr(VI) removal was investigated under the same conditions as before, and the result is shown in Fig. 6. As expected, the resin still exhibited good performance for Cr(VI) removal. The Cr(VI) concentration in the effluent was below 0.5 mg/L within the initial 17 h and then increased gradually. This result indicated that the resin regenerated had an effective working period of about 44% of the new resin, which is consistent with the percentage of the regenerated resin.

3.5. Regeneration solution concentrating

It has been demonstrated that the new ion-exchange system can be used for purifying wastewater containing a low concentration of Cr(VI) effectively. However, the concentration of the regeneration solution is not high enough for reuse, and thus further concentrating is necessary.
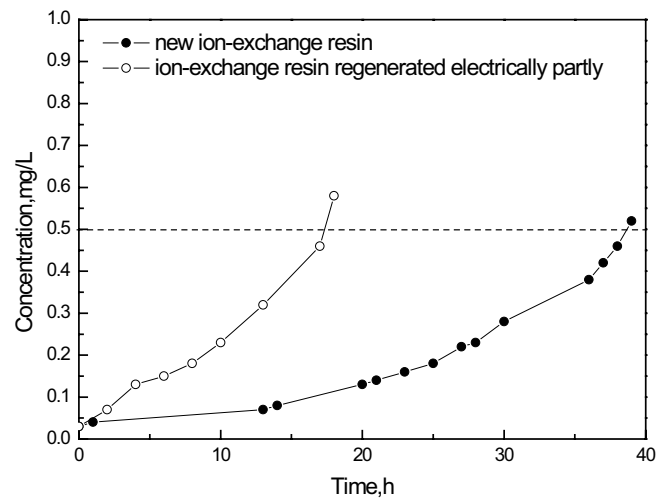
In this work, ED was selected to concentrate on the regeneration solution due to its good efficacy in recovering Cr(VI) [29]. The results are given in Table 3. High concentration efficiencies were obtained. At a current of 0.8 A and a voltage of 24.4 V, the chromic acid concentration in the concentrated effluent reached 17.5 g/L, with a power consumption of about 1.1 kWh/mol Cr(VI) only. The Cr(VI) concentration in the dilute effluent of ED was still over 10 mg/L. However, this effluent was only about one-fifth of the original wastewater in terms of the flow rate and could be purified together with the original wastewater using the SEDI system.

4. Conclusions

In this study, we developed a novel SEDI system to remove Cr(VI) from wastewater. The experimental results show that this SEDI system packed with a pair of CM has high efficiency in removing Cr(VI) from the wastewater. Four different types of resins were studied, and it was found that macro-porous weak-base (D301) resin had the best effect on removing Cr(VI). The average concentration of Cr(VI) in the regeneration solution was 723.5 mg/L, and about 44% of the resin was regenerated, with a power consumption of about 8.4 kWh/mol Cr(VI). The resin after regeneration exhibited a good Cr(VI) removal performance. After treatment, the Cr(VI) concentration decreased from the initial 50 mg/L to

Table 3
Concentrating efficiencies of ED with different currents

Current, A	Voltage, V	H_2CrO_4 in concentrated effluent, g/L	Cr(VI) in dilute effluent, mg/L	Power consumption, kWh/mol Cr(VI)
0.5	16.8	7.1	95.2	0.53
0.6	18.6	10.9	78.0	0.69
0.7	20.6	14.6	53.5	0.86
0.8	24.4	17.5	11.6	1.09

less than 0.5 mg/L. The regeneration solution could be concentrated further to a level of 17.5 g chromic acid/L by ED, with a power consumption of about 1.1 kWh/mol Cr(VI) only. In general, our proposed method is expected to be able to feasibly treat electroplating wastewater in engineering, as well as provides a new direction for the removal and recovery of different types of metal resources.

Acknowledgment

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