Analysis of Trace Ions in Chromium-Containing Wastewater on the Performance of RED Stack and Cr(VI) Reduction Rate

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Abstract. Salt gradient energy (SGE) is a kind of chemical potential difference energy existing between electrolyte solutions with different concentrations, which can be converted into high-grade mechanical energy or electrical energy by certain technical means. Reverse electrodialysis (RED) can convert this kind of energy into electric energy, and it has become the main technology of salt difference energy recovery because of its direct conversion and simple equipment. Chromium (Cr(VI)) in sewage discharged from human production and living activities will threaten human health through enrichment. Therefore, reducing Cr(VI) wastewater with high toxicity to Cr(III) with low toxicity and then discharging it is the main technical means adopted in sewage treatment at present, but the current reduction technology has some problems such as high cost and high energy consumption. Recovering salt differential energy and reducing chromium-containing wastewater with RED can reduce Cr(VI) in wastewater and convert salt differential energy into electric energy. The effects of common ions (Cu^{2+}, Zn^{2+} and Fe^{3+}) in chromium-containing wastewater on the performance of the stack and the reduction of Cr(VI) were studied. These ions were added to the cathode solution of Cr(VI) by the method of controlled variables, and their effects on the output performance of RED stack and the reduction rate of Cr(VI) were analyzed. The results show that adding different concentrations of Cu^{2+}, Zn^{2+} and Fe^{3+} to the cathode solution can significantly promote the reduction rate of Cr(VI) by more than 20%, especially adding Cu^{2+} to the cathode solution of Cr(VI). Further study on the concentration of trace ions and the flow rate of electrolyte shows that there is an optimal concentration for each ion to promote the reduction of Cr(VI), and the reduction rate of Cr(VI) is higher at low flow rate of cathode solution. Additionally, adding trace ions can effectively reduce the internal resistance of the RED stack, but does not significantly enhance the performance of the RED stack.

Keywords: Key words: salt difference energy; Reverse electrodialysis; sewage disposal

1   Introduction

Salinity gradient energy (SGE) refers to the energy generated by the chemical potential difference between seawater and fresh water or salt solutions with different concentrations. It is a kind of marine energy stored in the form of chemical energy and widely exists at the junction of rivers and seas.[1, 2]. Reverse electrodialysis(RED) is an effective technical means to recover salt differential energy and directly convert it into electric energy[2, 3]. At present, chromium compounds are widely used in metal electroplating, paint, pigment, leather processing, textile dyeing, printing ink and wood preservation.[4]A large amount of chromium-containing wastewater is discharged, which is mutagenic and carcinogenic to human body.[5]. At present, the technology for treating hexavalent chromium requires high-yield input or secondary pollution by-products[6,7]. Therefore, the reduction of Cr(VI) with RED technology in this paper can not only achieve the reduction of Cr(VI) but also achieve higher stack performance output. Aiming at the possible influence of trace metal ions in chromium-containing wastewater on the output performance of RED stack and Cr(VI) reduction, the real Cr(VI) wastewater was simulated as cathode solution, in which trace metal ions with different concentrations were added respectively. The effects of different parameters of electrode solution on Cr(VI) reduction and stack performance were tested on the RED experimental platform.

2   Experiment

In order to verify the feasibility of reducing Cr(VI) to Cr(III) and generating electricity by using RED technology, this experiment built a RED experimental platform for related research. The experimental process is shown in Figure 1.
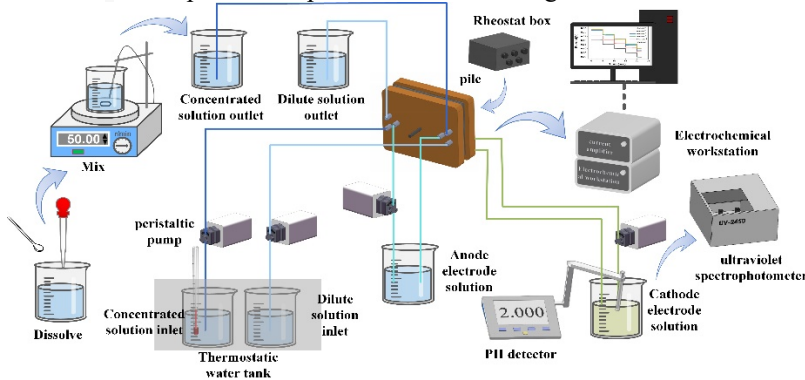
Fig. 1. experimental principle system diagram

RED stack is the core device for reducing Cr(VI). Electrochemical workstation and current amplifier are connected in series to detect the performance of RED stack, such as measuring short-circuit voltage and power density. The pH detector is used to measure the pH value of the electrode solution; The variable resistance box is used to adjust

the external resistance; The peristaltic pump for feeding solution and electrode liquid is used to provide flow power and control flow rate; The constant temperature water tank ensures that the feed solution is maintained at a constant temperature; Ultraviolet spectrophotometer is used to detect the concentration of Cr(VI). Ultra-pure water purifier, electronic balance, magnetic stirrer and beaker are used for the configuration of electrode washing liquid.

3   Result and Discussion

3.1   Influence of Trace Ion Concentration in Short Circuit State

Figures 2 and 3 show that under the conditions that the temperature is 25°C, the pH value is 2, the flow rate is 40 mL/min, and the concentration of the concentrated solution and the diluted solution of the working solution are maintained at 3 mol/L and 0.03mol/L, respectively, three ions of Fe^{3+}, Cu^{2+} and Zn^{2+} are added to the cathode solution of Cr(VI) at 5 ppm, 20 ppm, 35 ppm and 50 ppm respectively.
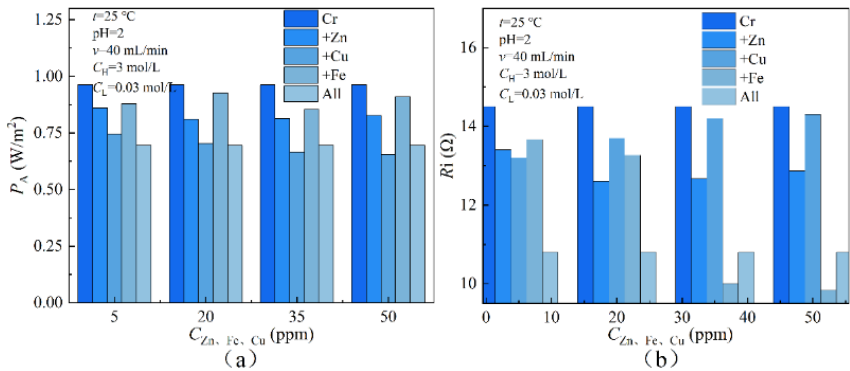
As can be seen from Figure 2(a), the reduction rate of Cr(VI) in the cathode solution containing Fe^{3+}, Cu^{2+} and Zn^{2+} and all ions is higher than that in the pure chromium cathode solution. Therefore, adding different concentrations of Fe^{3+}, Cu^{2+} and Zn^{2+} to the cathode solution can improve the reduction rate of Cr(VI). The reduction rate of Cr(VI) in pure chromium solution is 46.17%. When the addition amounts of Fe^{3+}, Cu^{2+} and Zn^{2+} are 5 ppm respectively, the reduction rate of Cr(VI) is the highest when Cu^{2+} is added, which is 23.13% higher than that in pure chromium cathode solution. The reduction rate of Cr(VI) in chromium solution with Fe^{3+} at 20 ppm is 26.18% higher than that in pure chromium cathode solution, which is the best. When adding Zn^{2+} at 35 ppm, the reduction rate of Cr(VI) increased the most, which was 26.6% higher than that of pure chromium cathode solution. The reduction rate of Cr(VI) with Cu^{2+} at 50 ppm is 30.07% higher than that of pure chromium cathode solution. When all ions exist simultaneously, the reduction rate of Cr(VI) is 16.19% higher. This shows that different ion concentrations have significant effects on the reduction of Cr(VI).

As can be seen in Figure 2(b), the addition of Fe^{3+}, Cu^{2+} and Zn^{2+} has little effect on the OCV of RED stack, and the basic output voltage is about 4.4 V.Among them, when adding 5 ppm, 35 ppm and 50 ppm to Cr(VI) cathode solution, the OCV of electrode solution containing Zn^{2+} is the highest, which is 4.71 V, 4.3 V and 4.27 V respectively.

As can be seen from Figure 3(a), the output power density of the RED stack is 0.96 W/m^2 when only chromium is reduced, while the output power of the RED stack decreases when Fe^{3+}, Cu^{2+} and Zn^{2+} are added to the cathode solution to reduce Cr(VI) respectively, but the output power density of the stack remains the best when reducing Cr(VI) cathode solution containing Fe^{3+}. As can be seen in Figure 4.3(b), when adding Fe^{3+}, Cu^{2+} and Zn^{2+} to the catholyte to reduce Cr(VI) respectively, the internal resistance of the RED stack decreased, and the internal resistance of the catholyte containing Fe^{3+} was basically lower.
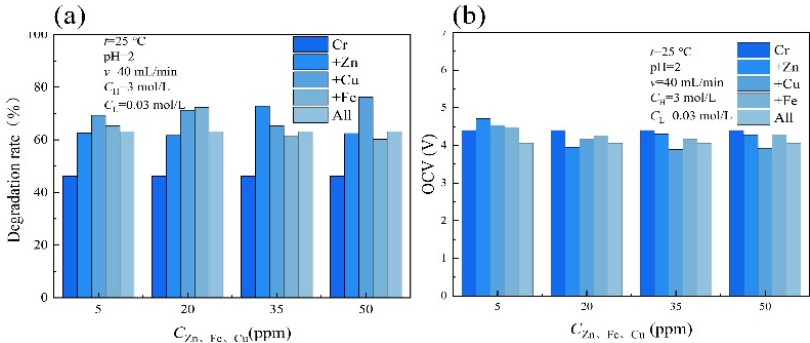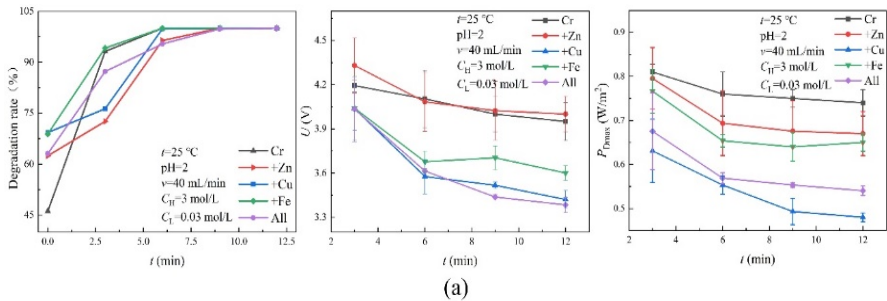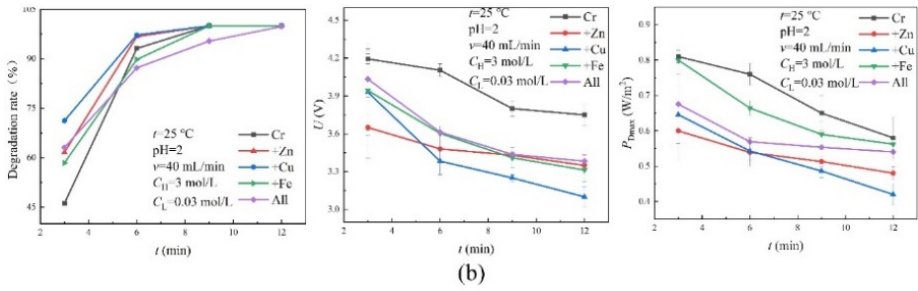
Fig. 2. effect of different trace ion concentrations on that output voltage and Cr(VI) reduction efficiency of the stack unde short-circuit condition.

Fig. 3. Influence of different trace ion concentrations on the output power density and internal resistance of the stack under short circuit condition.

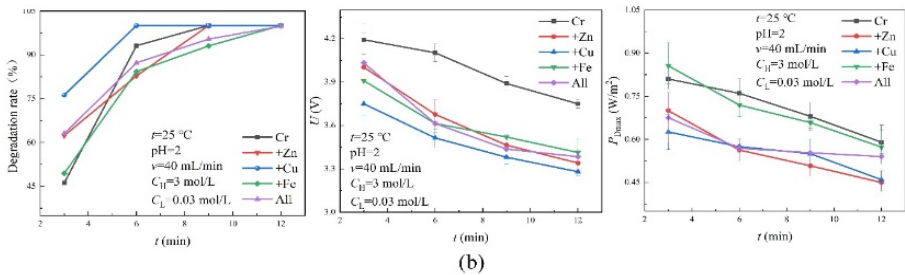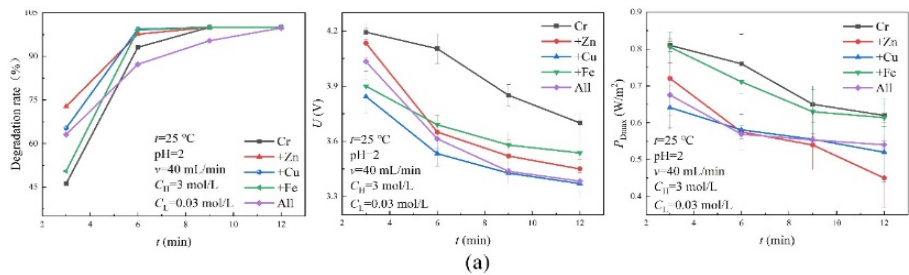## 3.2   Influence of Trace Ion Concentration in Channel State

Fig. 4. Effect of trace ion concentration of 5 ppm and 20 ppm on stack performance and Cr(VI) reduction in channel state.

Figs. 4 and 5 show the output performance and Cr(VI) reduction law of the RED stack when 5 ppm, 20 ppm, 35 ppm and 50 ppm of Fe^{3+}, Cu^{2+} and Zn^{2+} ions and all ions are added to the cathode solution respectively in the channel state. It can be seen from the figure that the increase of metal ion concentration promotes the reduction rate of Cr(VI). Firstly, the addition of Zn^{2+} in the range of 20 ppm to 35 ppm can promote the reduction rate of Cr(VI). Cu^{2+} can continuously promote the reduction rate of Cr(VI) when the amount of Cu^{2+} is 20 ppm-50 ppm. The addition of Fe^{3+} can basically promote the reduction of Cr(VI) at 5 ppm-50 ppm, and it can greatly promote the reduction of Cr(VI) at 35 ppm. Although trace ions with different concentrations have different effects on the reduction rate of Cr(VI), they are basically completed within 12 min

As can be seen from Figure 4 and Figure 5, Cr(VI) solution added with trace ions basically does not promote the output voltage and power density of the stack, but reduces the output voltage and power density of the RED stack. Fig. 4(a) shows that when Fe^{3+}, Cu^{2+} and Zn^{2+} are added at 5 ppm respectively, the output voltage and power density of the RED stack after the reduction of the Cr(VI) solution containing Zn^{2+} are the maximum values of 4 V and 0.67 W/m^2, which is 3.01% higher than that of the pure Cr(VI) solution, but the power density is 9.4% lower. In fig. 4(b), when Fe^{3+}, Cu^{2+} and Zn^{2+} are added at 20 ppm respectively, the influence of Cr(VI) solution containing trace ions on the output voltage of the RED stack is basically the same, while the output power of the RED stack is relatively high at 0.56 W/m^2 after the reduction of the Cr(VI) solution containing Fe^{3+}, but it is also lower than that of the pure Cr(VI) solution after the reduction.

Fig. 5. effect of trace ion concentration of 35 ppm and 50 ppm on stack performance and Cr(VI) reduction in channel state.

Fig. 5(a) shows that when Fe^{3+}, Cu^{2+} and Zn^{2+} are added at 35 ppm, the output voltage and power density of the RED stack are 3.54 V and 0.61 W/m² when the Cr(VI) solution containing Fe^{3+} is completely reduced, but the output voltage of the stack is 4.3% lower than that of the pure chromium solution, and the power density is almost the same as that of the pure chromium solution. Fig. 5(b) shows the variation law of output voltage and output power density of the RED stack when Fe^{3+}, Cu^{2+} and Zn^{2+} are added at 50 ppm. As can be seen from the figure, trace ions have little influence on the output voltage and power density of the stack.

4   Conclusion

This article utilizes a controlled variable method to study the impact of trace ions in wastewater on the output performance of RED stacks and the reduction rate of Cr(VI) by adding Zn^{2+}, Cu^{2+}, and Fe^{3+} ions into the Cr(VI) cathode solution and varying the ion concentrations. The conclusions are as follows:

Adding Zn^{2+}, Cu^{2+}, and Fe^{3+} ions to the Cr(VI) cathode solution can enhance the reduction of Cr(VI), and the enhancement effect is significant. The promotion of the Cr(VI) reduction rate is more than 20% higher compared to the pure chromium solution. Among these, Cu^{2+} shows the most significant effect in improving the Cr(VI) reduction rate. Compared to other metal ions, when Fe^{3+} is added, the RED stack exhibits the highest output voltage and maximum power density.

References

1. Roldan-Carvajal M, Vallejo-Castaño S, Álvarez-Silva O, et al. Salinity gradient power by reverse electrodialysis: A multidisciplinary assessment in the Colombian context[J]. Desalination, 2021, 503: 114933.
2. Boyu Liu, Li Shaohong, Wang Gang. Research progress of salt difference power generation technology [J]. Renewable Energy, 2010, 28(02): 141-144.
3. Olsson M, Wick G L, Isaacs J D. Salinity gradient power: Utilizing vapor pressure differences[J]. Science, 1979, 206(4417): 452-454.

4. Dhal B, Thatoi H, Das N, et al. Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: a review[J] . Journal of hazardous materials, 2013, 250: 272-2791. DOI: 10.1016/j.jhazmat.2013.01.048.
5. Qi Purong, Wang Guanghui. Research progress in photodegradation of azo dyes [J]. Dyes and Dyeing, 2007, 44(2): 1-4.
6. Cespon-Romero R, Yebra-Biurrun M, Bermejo-Barrera M. Preconcentration and speciation of chromium by the determination of total chromium and chromium (III) in natural waters by flame atomic absorption spectrometry with a chelating ion-exchange flow injection system[J]. Analytica Chimica Acta, 1996, 327(1): 37-45.
7. Kurniawan T A, Chan G Y, Lo W-h, et al. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals[J]. Science of the total environment, 2006, 366(2-3): 409-426.