

Article

Electrochemical Removal of Chromium (VI) from Wastewater

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Abstract: Removal of hexavalent chromium had attracted much more attention as it was a hazardous contaminant. Electrochemical reduction technology was applied to removal chromium (VI) from wastewater. The mechanism and parameters affect the reduction process were investigated. The results showed that the reduction efficiency was significantly affected by the concentration of H_2SO_4 , current density and reaction temperature. And the reduction efficiency was up to 86.45% at concentration of H_2SO_4 of 100g/L, reaction temperature of 70 °C, current density at 50 A/m², reaction time at 180 min and stirring rate of 500 rpm. The reduction process of chromium (VI) was followed pseudo-first-order equation, and the reduction rate could be expressed as $K_{obs} = k [H_2SO_4]^{1.4} [j]^{4.170/RT}$.

Keywords: Electrochemical; Chromium; Kinetic

1. Introduction

In recent years, heavy metal pollutions like Cr, Ni, Cd, Pb, Hg, Zn, Co and Cu that mainly discharge from industrial wastewaters have become a severe environmental issue[1-3]. Attribute to the toxicities, carcinogenicities, and natural-resource scarcity, it is urgent to remove and recovery the heavy metals from wastewaters[4]. Hexavalent chromium (Cr(VI)) is a high toxicity heavy metal contaminant that widely released by various industries such as tanning and leather industries, manufacturing industries, catalyst and pigments, fungicides, ceramics, crafts, glass, photography, electroplating industry and corrosion control application. The International Agency for Research on Cancer (IARC) had classified chromium (VI) in Group 1 (carcinogenic to humans) and it is of great urgency to removal chromium (VI) from wastewater before its discharge into the aquatic system.

Many methods have been demonstrated efficient for Cr(VI) removal, such as: ion exchange[5, 6], electrochemical treatment[7-9], chemical precipitation [10], coagulation [11], chemical reduction[12, 13], and adsorption[3, 14-17].Also some biological treatments [18, 19] (phytoremediation [20])are also applied to remove chromium (VI) in wastewater and groundwater. Lead sulfate as a precipitation is used to precipitate chromium (VI) and it can remove chromium (VI) from 0.2mol/L to 0.15 mmol/L[10], but lead sulfate is a second pollutant which is harmful for environment. In the same time, difficulties and challenges like high costs, large scale application and causing secondary pollution are still remained in current technologies. It is need to overcome these challenges and develop new effective techniques for removal of chromium (VI).

In recent study [8], an electro coagulation-like technology electro-reduction is applied to reduce hexavalent chromium to trivalent chromium. The results showed that the chromium (VI) was easily being reduced by Fe^{2+} and free electron, while the current intensity had little effect on the reduction process. In this paper, electrochemical technology was applied to reduce chromium (VI) in acidic medium. The mechanism and parameters including concentration of H_2SO_4 , reaction time, reaction temperature and current density affect the reaction were investigated; also the kinetic model was simulated.

2. Materials and Methods

2.1. Materials

All reagents are analytical grade including potassium dichromate ($K_2Cr_2O_7$), sulfate acid (H_2SO_4) and purchased from Kelong Co., Ltd, Chengdu, China. All solutions were prepared with deionized water with a resistivity greater than 18 MΩ/cm (HMC-WS10).

2.2. Experimental procedure

Reduction experiments were carried out in a 250 mL beaker fixed in a thermostatic water bath with a temperature precision of ± 0.1 °C. In the batch experiments, a volume of 100 mL solution contained 1.000 g/L chromium (VI) was prepared by dissolving a certain $K_2Cr_2O_7$ in distilled water, and the acidic medium was prepared by adding different volumes of H_2SO_4 , then the current supplied by a DC power was applied as the solution heated to a predetermined temperature. During the experiments, the samples were collected at different intervals (5 min), and analyzed for residual concentration of chromium (VI) in the solution[10]. The electrode used in the experiments was a plate-like dimensionally stable anode (Baoji Zhiming Special Metal Co., Ltd, China) with a surface area of 1 cm² (1 × 1 cm) (anode) and a same one with an identical area (cathode) were fixed at a distance of 2 cm[21].

The concentration of chromium (VI) in the solution was determined by inductive couple plasma-optical emission spectrometry (ICP-OES)[22]. And the reduction efficiency (η) was calculated as Equation (1):

$$\eta = \frac{C_1 \cdot V_1 - C_2 \cdot V_2}{C_1 \cdot V_1} \quad (1)$$

Where, C_1 and C_2 is the concentration of chromium in the solution before and after the experiment, g/L; V_1 and V_2 is the volume before and after the experiment, L.

2.3. Kinetics model

The reduction of chromium (VI) could be expressed by pseudo-first-order equation as described as Equation (2)[23-25].

$$v = \frac{dc}{dt} = -K_{obs} c \quad (2)$$

Integrate.

$$-lnc = K_{obs} t - lnc_0 \quad (3)$$

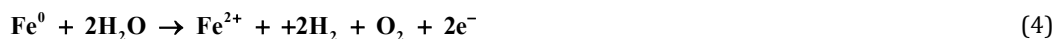
Where, v is the reduction rate of chromium (VI), c is the concentration of chromium (VI), c_0 is the initial concentration of chromium (VI), K_{obs} is the reaction constant.

3. Results and Discussion

3.1. Electro-reduction of Chromium (VI)

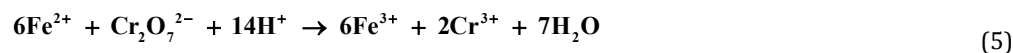
3.1.1. Reaction mechanism

The electro coagulation process of chromium (VI) [26-28] involved the following stages of reducing agent formation and subsequent reduction of chromium (VI) and chromium (III). The first step was the formation of Fe^{2+} , which was oxidized of steel electrode by a DC power.

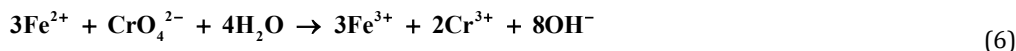


The second step was the reduction reaction between reducing agent and oxidant. In this process, it was the reaction between Fe^{2+} and chromium (VI). The reactions were described in Equation (5) to (6) by taking the pH of wastewater into account.

$0.5 < \text{pH} < 6.5$:



$\text{pH} > 6.5$:



While in this work, the reduction process was different from electro coagulation as the electrode used in this work was stable and not being corroded. The reducing agent in this work was only free electron (e^-) supplied by the DC power. The reaction was occurred between e^- and chromium (VI) followed Equations (7) to (10). And the Gibbs-free energy of the equations at different reaction temperatures was calculated and the results were showed in Figure 1. The negative of ΔG indicated that the reduction reaction was feasible in thermodynamics[29].

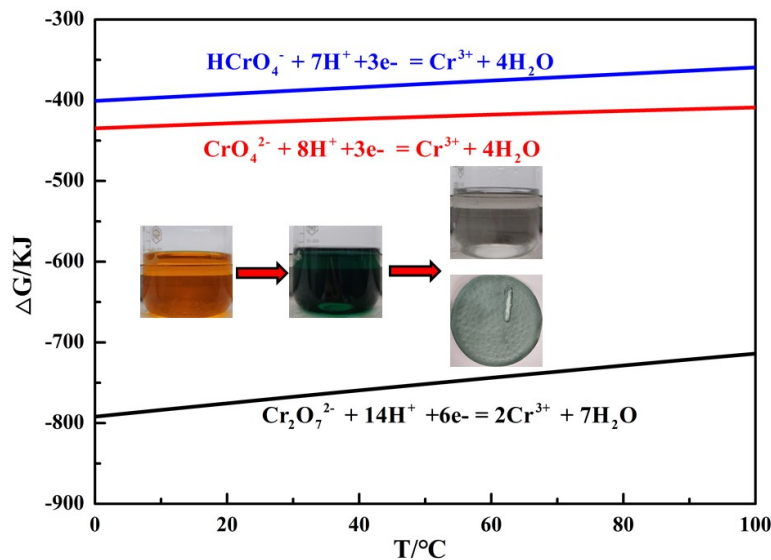
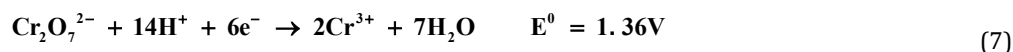


Figure 1. Relationship between ΔG and temperature of reduction of chromium (VI).

3.1.2. Effect of concentration of H_2SO_4

The effect of concentration of H_2SO_4 on the reduction efficiency was investigated while other conditions kept constant: initial concentration of Cr (VI) of 1.000 g/L, current density of 50 A/m², reaction temperature of 70 °C, and stirring rate at 500 rpm. The concentration of H_2SO_4 was set as 20g/L, 40g/L, 60g/L, 80g/L and 100g/L.

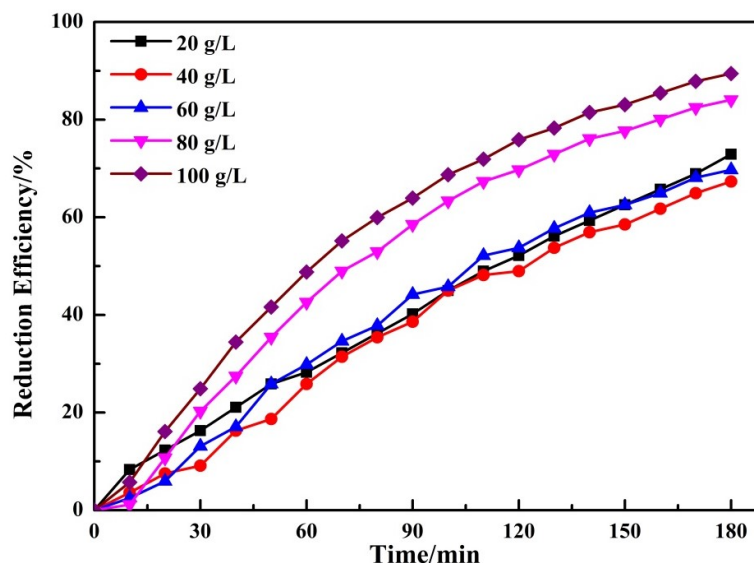


Figure 2. Effect of concentration of H_2SO_4 on reduction efficiency of chromium (VI).

The results showed in Figure 2 indicated that the reduction efficiency of chromium (VI) increased with the increasing of reaction time and acid concentration. The reduction of chromium (VI) in the process was acid-dependent and higher chromium (VI) reduction efficiency could be achieved at high acid concentration. The acceleration of Cr(VI) reduction in the system at the high acid concentration could be attributed to that the chromium (VI) species were more easily being reduced in acidic conditions than in neutral/ alkaline conditions according to Equation (7) and (10)[8]. And the molar fraction of the $\text{Cr}_2\text{O}_7^{2-}$ was drastically increased with increasing acid concentration according to Equation (9). Therefore, the concentration of 100 g/L was selected for further experiments.

3.1.3. Effect of reaction temperature

During the process, reaction temperature is an important parameter affected the reaction during the diffusion process [8, 10, 22, 30, 31]. The effect of reaction temperature on the reduction efficiency was conducted while other conditions kept constant: initial concentration of chromium (VI) of 1.000g/L, current density of 50 A/m^2 , concentration of H_2SO_4 of 100 g/L and stirring rate at 500 rpm. The results showed in Figure 3 indicated that the reduction of chromium (VI) could be easily achieved at higher reaction temperature ($\geq 50^\circ\text{C}$), which was partial consistent with recent study [8]. High temperature would decrease the diffusion resistance and favor the contact of free electron and chromium (VI) resulting in high reduction efficiency. Thus, reaction temperature of 70°C was chosen to be the optimal.

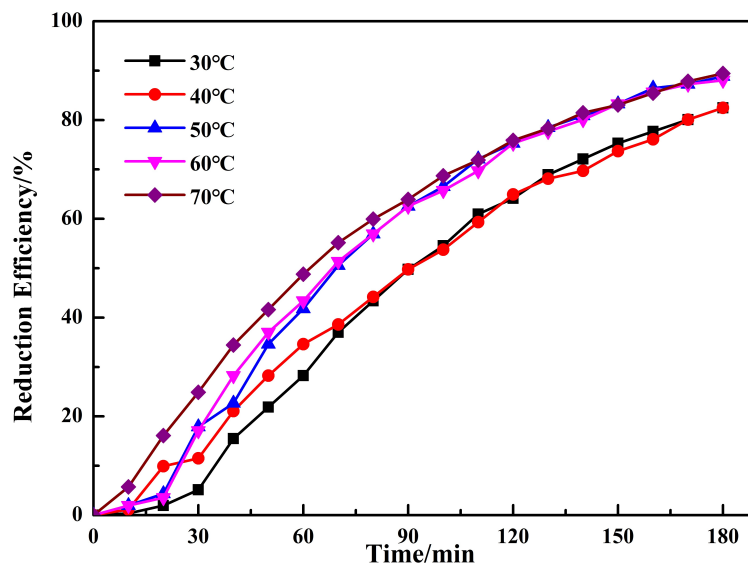


Figure 3. Effect of reaction temperature on reduction efficiency of chromium (VI).

3.1.4. Effect of current intensity

The free electron supplied by DC power was the main reducing agent which reduced chromium (VI) to chromium (III). The results showed in **Figure 4** summarized the effect of current density on the reduction efficiency as other conditions kept as: initial concentration of chromium(VI) of 1.000g/L, concentration of H_2SO_4 of 100 g/L, reaction temperature of 70 °C and stirring rate at 500 rpm. It could be seen that the reduction efficiency was increased with the increasing of current density, even though increased not too much. The reduction efficiency was up to 86.45% at current density of 50 A/m². In other words, higher current density could achieve high reduction efficiency.

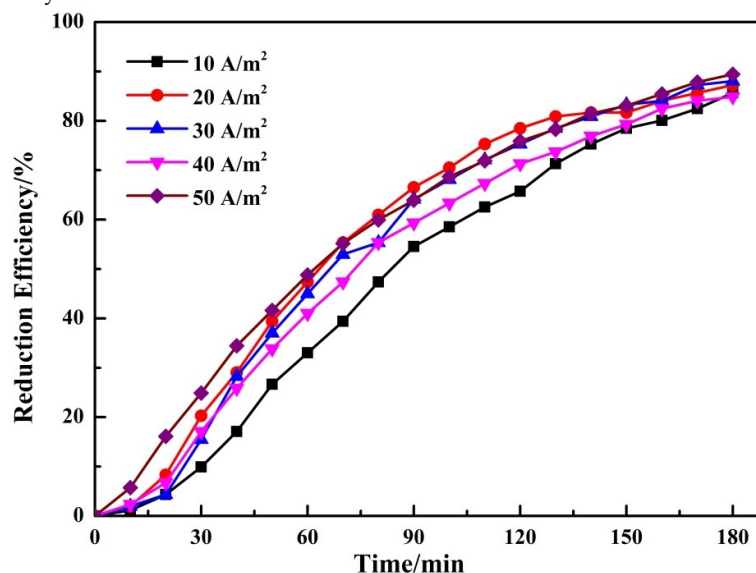


Figure 4. of current intensity on reduction efficiency of chromium (VI).

3.2. Kinetic model

The experimental data was fitted as Equation (3) and the results were displayed in **Figure 5a-Figure 5f** and **Table 1**. The results showed in **Figure 5.a-c** indicated that the reduction efficiency was fitted well following pseudo-first-order equation as the coefficient (R^2) was all closely to 1. The

results showed in **Figure 5a** indicated that the reduction rate (K_{obs}) was increased with the increasing of concentration of H_2SO_4 ($[H_2SO_4]$). **Figure 5d** displayed the relationship between K_{obs} and $[H_2SO_4]$ and the results showed that K_{obs} was changed linearly with $[H_2SO_4]$ and the relationship between them could be expressed as Equation (11). The effect of current density ($[j]$) had a little complicated, and the K_{obs} was showed multipower with $[j]$ followed Equation (12). The relationship between K_{obs} and reaction temperature (T) could be expressed with Arrhenius equation (Equation (13)) and the specific apparent activation energy could be calculated. The result showed in **Figure 5f** showed the simulated Arrhenius equation and the E_a was calculated as 4.74 KJ/mol, so the Arrhenius equation could be changed as Equation (14).

$$K_{obs} = 8.50E^{-5}[H_2SO_4] \quad (11)$$

$$K_{obs} = 3E^{-8}[j]^4 \quad (12)$$

$$\ln K_{obs} = \ln A - E_a/RT \quad (13)$$

$$K_{obs} = Ae^{-4170/RT} \quad (14)$$

Where E_a is the apparent activation energy, A is the pre-exponential factor, and R is the molar gas constant, K is the reduction rate constant at different reaction temperatures.

In summary, the chromium (VI) could be efficiently reduced by electricity, and the reduction process was significantly affected by the concentration of H_2SO_4 , current density and reaction temperature, the reduction rate could be express as Equation (15).

$$K_{obs} = \frac{dc}{dt} = \frac{d[Cr]}{dt} = k[H_2SO_4]^1[j]^4ge^{-4170/RT} \quad (15)$$

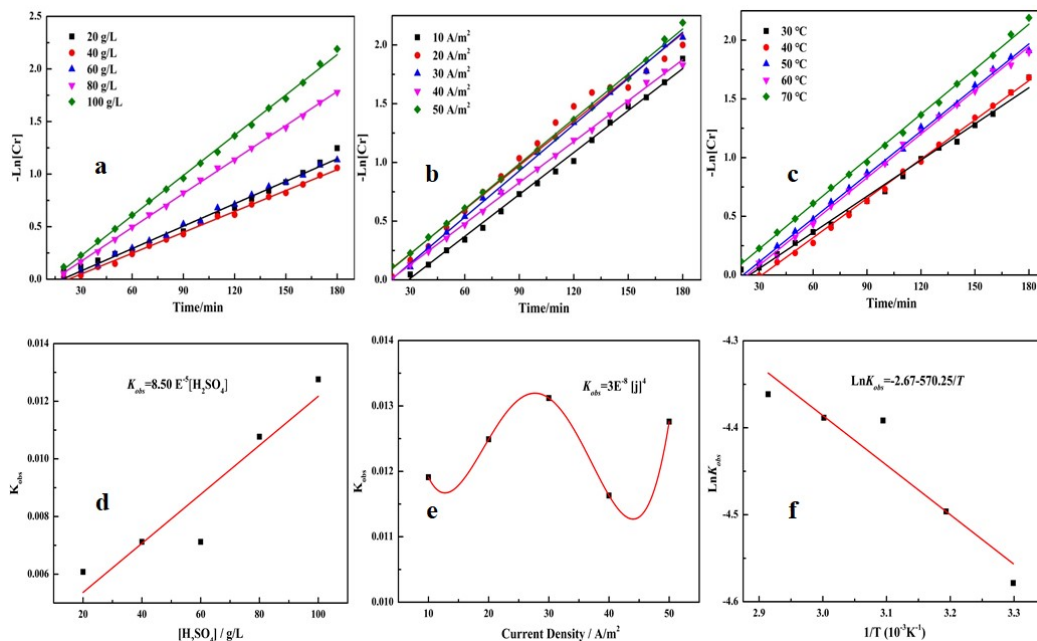


Figure 5. Pseudo-first-order models for reduction of chromium (VI).

Table 1. Constants and correlation coefficients of pseudo-first order for reduction of chromium (VI).

	K_{obs}	R^2
[H ₂ SO ₄]		
100 g/L	0.01276	0.9985
80 g/L	0.01077	0.9993
60 g/L	0.00712	0.9978
40 g/L	0.00712	0.9849
20 g/L	0.00608	0.9964
Current density		
50 A/m ²	0.01276	0.9985
40 A/m ²	0.01163	0.9987
30 A/m ²	0.01312	0.9975
20 A/m ²	0.01249	0.9836
10 A/m ²	0.01191	0.9946
Reaction temperature		
70 °C	0.01276	0.9985
60 °C	0.01242	0.9980
50 °C	0.01238	0.9983
40 °C	0.01115	0.9967
30 °C	0.01027	0.0017

5. Conclusions

The electrochemical reduction technology was succeeding in reducing chromium (VI) from wastewater. And the reduction efficiency was up to 86.45% at concentration of H₂SO₄ of 100g/L, reaction temperature of 70 °C, current density at 50 A/m², reaction time at 180 min and stirring rate of 500 rpm. The reduction process of chromium (VI) was followed pseudo-first-order equation, and the concentration of H₂SO₄, current density and reaction temperature had significant effect on the reduction process. The reduction rate could be expressed as $K_{obs} = k [H_2SO_4]^1 \cdot [j]^4 \cdot \exp^{-4170/RT}$.

Author Contributions: Conceptualization, Hao Peng; Methodology, Yumeng Leng; Validation, Hao Peng; Formal Analysis, Jing Guo; Investigation, Yumeng Leng; Resources, Hao Peng; Data Curation, Jing Guo; Writing-Original Draft Preparation, Hao Peng; Supervision, Hao Peng; Project Administration, Hao Peng; Funding Acquisition, Hao Peng.

Funding: This work was supported by the Science and Technology Project of Chongqing, China (cstc2018jcyjAX0018), and Talent Introduction Project of Yangtze Normal University (2017KYQD117).

Conflicts of Interest: The authors declare no conflict of interest.

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