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Article

Reduction Behavior of Chromium (VI) with Oxalic Acid in Aqueous Solution

Hao Peng *[1], Jing Guo, Binfang Yuan, Liping Lv, Huisheng Huang, Bing Li

College of Chemistry and Chemical Engineering, Yangtze Normal University, Chongqing 408100, China;

Email: cquguojing@126.com (J. Guo); 6781022@163.com (B. Yuan); lvliping@yznu.edu.cn (L. Lv); h.s.huang@hotmail.com (H. Huang); 1127753494@qq.com (B. Li)

* Correspondence: cqupenghao@126.com (H. Peng), Tel.: +86 15123031643 (H. Peng),

Abstract: The direct Cr (VI) reduction process by oxalic acid was conducted and the results showed that the Cr (VI) was efficiently reduced by oxalic acid at high reaction temperature and high dosage of oxalic acid. The reduced product, Cr (III), was easily generated stable complex compounds (Cr(HC2O4)3) with oxalate, which displayed a negative effect on the reduction process. The high reaction temperature and high acidic medium could destroy the stable structure of a complex compound to release oxalate, and facilitate the reduction of Cr (VI). Generally, the present study provided a versatile strategy for Cr (VI) reduction, exhibiting a bright application future for real wastewater treatment.

Keywords: Chromium; Reduction; Oxalic Acid

1. Introduction

Chromium (VI), placed in the fourth period of the periodic table [1-3], was a toxicity heavy metal ion and is classified in Group 1 (carcinogenic to humans) by the International Agency for Research on Cancer [4, 5]. It was harmful to the environment and human health and some treatments were needed.

Nowadays, many remediation techniques had been developed to remove chromium (VI) from wastewater. They were mainly divided into three kinds: physicochemical technology, electrochemical technology and advanced oxidation technology. Physicochemical technologies included membrane filtration, chemical precipitation, ion-exchange, and adsorption [6-8]. Electrocoagulation, electrochemical reduction, electrodialysis and electrode-ionization were belonged to electrochemical technology [9-11]. Photocatalysis and nanotechnology were advanced oxidation technology which was practical approaches in treating wastewaters [12, 13]. A recent study found that lead sulfate as precipitation was used to precipitate chromium (VI) and it could remove Cr (VI) from 0.2mol/L to 0.15 mmol/L [14], but lead sulfate was a second pollutant which was harmful for the environment. At the same time, difficulties and challenges like high costs, large scale applications and causing secondary pollution still remained in current technologies. It needed to overcome these challenges and develop new effective techniques for the removal of Cr (VI). Consequently, disposal of Cr (VI)-contaminated wastewaters was a serious environmental concern, and its reduction to Cr (III) attracted significant attention.

Oxalic acid, mainly from the decomposition of organic matter and plant root exudates, was one of the most widely natural existed organic acids [15]. It was extensively applied to reduce Cr (VI) because of its environmentally friendly nature and low cost [16, 17]. Mu found that in the direct Cr (VI) reduction process, the Cr (VI) concentration did not change obviously in the oxalic acid or Mn2+ aqueous solution. Interestingly, the addition of Mn2+ into the Cr (VI)/oxalic acid system, 99% Cr (VI) was reduced and they

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[1] Correspondence concerning this article should address to Hao Peng at cqupenghao@126.com

concluded that Mn2+ could promote Cr (VI) reduction with oxalic acid [18]. Many methods had been proposed to speed up the Cr(VI) reduction by oxalic acid, like catalyzed by TiO2, Al2O3 and FeOOH [19], but these oxalic acid-based methods were still not feasible for the practical application, especially in the case of groundwater remediation. The direct Cr (VI) reduction by oxalic acid was thermodynamically feasible [20], the reduction process and reaction mechanism were investigated in this paper.

2. Materials and Methods

2.1 Materials

Potassium dichromate (K2Cr2O7), sulfate acid (H2SO4), and oxalic acid (H2C2O4·2H2O) were purchased from Kelong Co., Ltd, Chengdu, China. All chemicals were used as received without further purified. All solutions were prepared with deionized water with a resistivity greater than 18 MΩ/cm (HMC-WS10).

2.2 Experimental procedure

All the 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 1000 mg/L Cr (VI) was prepared by dissolving analytical grade K2Cr2O7 in deionized water, then the oxalic acid was added into the solution 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 Cr (VI) in the solution [10, 11, 14].

The concentration of Cr (VI) in the solution was determined by inductive couple plasma-optical emission spectrometry (ICP-OES)[21]. And the reduction efficiency (η) was calculated as Equation (1):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (1)$$

Where, C0, is the initial concentration of Cr (VI) in the solution, mg/L; Ct, is the concentration of Cr (VI) in the solution at reaction time of t, mg/L.

3. Results and Discussion

It was known that $E^0(HCrO_4^-/Cr^{3+})$ =1.33 V and $E0(C_2O_4^{2-}/CO_2)$ =0.49 V, and therefore $H_2C_2O_4$ could be used as a reductant for Cr (VI) reduction. With a summarization of the potential-pH diagram of chromium and oxalic acid shown in **Figure 1a**, it was clear that the position of oxalic acid was always lower than Cr (VI), indicating that the electrode potential of oxalic acid was lower than oxalic acid. Therefore, oxalic acid could reduce Cr (VI) into Cr (III). The main reaction during the reduction process was between chromium and oxalic acid. The △G of main reactions were calculated at 298 K [21-23]. The results displayed in **Figure 1b** showed that the △G was negative, which indicated that the reduction of Cr (VI) with oxalic acid was feasible in thermodynamic.

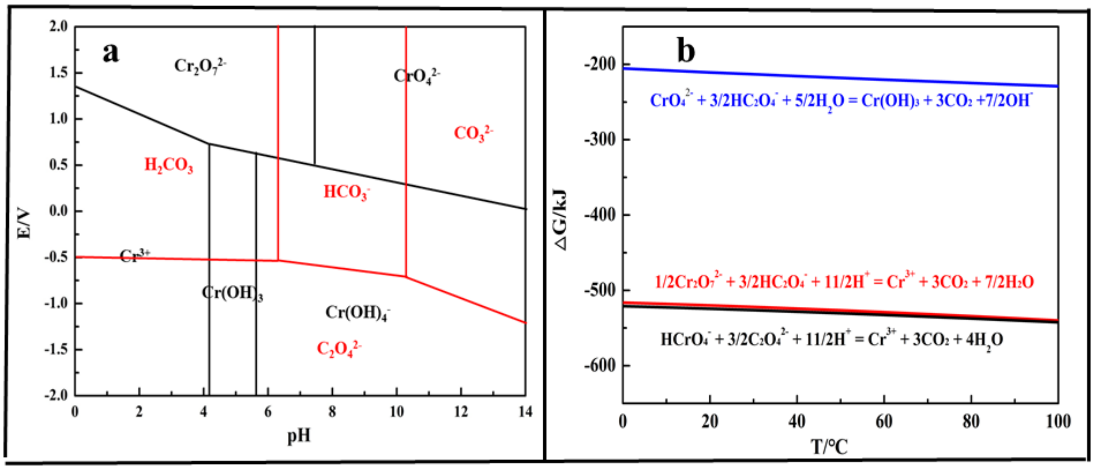

Figure 1 a) E-pH diagram of Cr (VI) and oxalic acid at 25 °C; b) Relationship between ΔG and temperature of reduction of Cr (VI)

3.1 Reaction mechanism

The existence of Cr (VI) in the reaction medium was measured by software Visual MINTEQ 3.0 and the result was showed in **Figure 3a**. During the Cr (VI) reduction process, the predominant Cr(VI) species was $HCrO_4^-$ and the reduction process was reacted following Equation (2) showed in **Figure 2**. The Cr (VI) was reduced to Cr^{3+} and $H_2C_2O_4$ was oxidized to CO_2. The reaction process could be divided into two parts: I) The formation of ester-like compounds between $HCrO_4^-$ and $H_2C_2O_4$ following Equation (3) showed in **Figure 2**. II) The electron migration between the inner of ester-like compounds following Equation (4) showed in **Figure 2** [18].

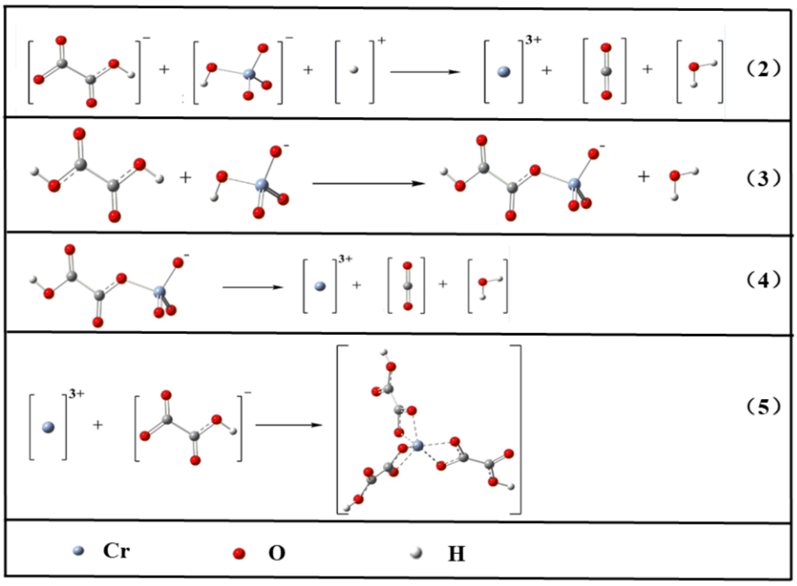

Figure 2 Reaction mechanism for reduction of Cr (VI) with oxalic acid

3.2 Reduction process

The dosage of oxalic acid played an important role during the reduction process as it was the main reaction reagent. A series of experiments were conducted to investigate the effect of the dosage of oxalic acid (n(O)/n(Cr)) on the reduction efficiency of Cr (VI) at reaction temperature of 70 °C with 500 rpm.

The results were shown in **Figure 3b** indicated that reduction efficiency was increased with the increase of dosage of oxalic acid. The reduction efficiency was increased from 24.3% to 99.9% as dosage of oxalic acid increased from n(O)/n(Cr)=1.5 to n(O)/n(Cr)=6.0. At the beginning of the reduction process, the reduction efficiency of Cr (VI) was high due to the high concentration of Cr (VI) and oxalic acid and fast reaction rate. Along with the reduction process, the increasing trend of reduction efficiency of Cr (VI) became smooth due to the formation of a soluble Cr (III)-organic products, which formed by Cr^{3+} and oxalate (**Equation (5)** showed in **Figure 2**)[18]. In order to improve the reduction efficiency of Cr (VI), the high dosage of oxalic acid should be added as there was no enough oxalate to reduce Cr (VI) at a lower dosage of oxalic acid. Thus, the n(O)/n(Cr)=6.0 was chosen as an optimal condition in further experiments.

The effect of reaction temperature on reduction efficiency of Cr (VI) was studied under the standard conditions: initial concentration of Cr (VI) of 1000 mg/L, n(O)/n(Cr) =6.0, and stirring rate of 500 rpm. It could be seen from **Figure 3c** that the reduction efficiency of Cr (VI) could up to 100% at all reaction temperatures with enough reaction time, and it was easily achieved at a higher reaction temperature in low reaction time, which was partially consistent with a recent study. Increasing the reaction temperature could increase the activity of atoms and molecules, enforced the reaction intensity, and promoted the reactions, and thus, was beneficial for the reduction of Cr (VI) [10, 11, 24]. Meanwhile, high reaction temperature could destroy the stable complex compound and release oxalate, which facilitated the reduction of Cr (VI), thus, the reduction efficiency of Cr (VI) was increased with the increase of reaction temperature. Therefore, the reaction temperature of 70 °C was chosen as an optimal condition for further experiments.

Figure 3d summarized the effect of stirring rate on the reduction efficiency of Cr (VI) at reaction temperature of 70 °C, n(O)/n(Cr)=6.0, and it showed that the reduction efficiency of Cr (VI) weas all the same as stirring rate ranged from 100 rpm to 500 rpm.

The acid condition favored the reduction of Cr (VI) to Cr (III) by oxalic acid according to **Equation (2)**. The Cr (VI) reduction by oxalic acid was investigated at concentration of H_2SO_4 ranged from 0 g/L to 300 g/L in this study. The results showed in **Figure 4** indicated that the addition of H_2SO_4 could facilitate Cr (VI) reduction process. It was widely accepted that pH-dependent Cr (VI) reduction was attributed to the speciation and redox potentials of Cr (VI) at different pH values. Theoretically, $HCrO_4^-$ was the predominant Cr(VI) species at $0.8 < pH < 6.8$, and CrO_4^{2-} was major species at $pH > 6.8$ (**Figure 3a**),while $HCrO_4^-$ was easier to be reduced into Cr(III) than CrO_4^{2-} as $HCrO_4^-$ was a much stronger oxidant ($E^0(HCrO_4^-/Cr^{3+}) = 1.35$ V, $E^0(CrO_4^{2-}/Cr^{3+}) = 0.56$ V). In high acidic medium, the complex compound was not stable and released oxalate, oxalate, which facilitated the reduction of Cr (VI), thus, the reduction efficiency of Cr (VI) was increased with the addition of H_2SO_4. Other way, the addition of H_2SO_4 could improve the reduction efficiency of Cr (VI), the dosage of H_2SO_4 had no obvious effect on the reduction efficiency at a high dosage of oxalic acid as the oxalate was enough.

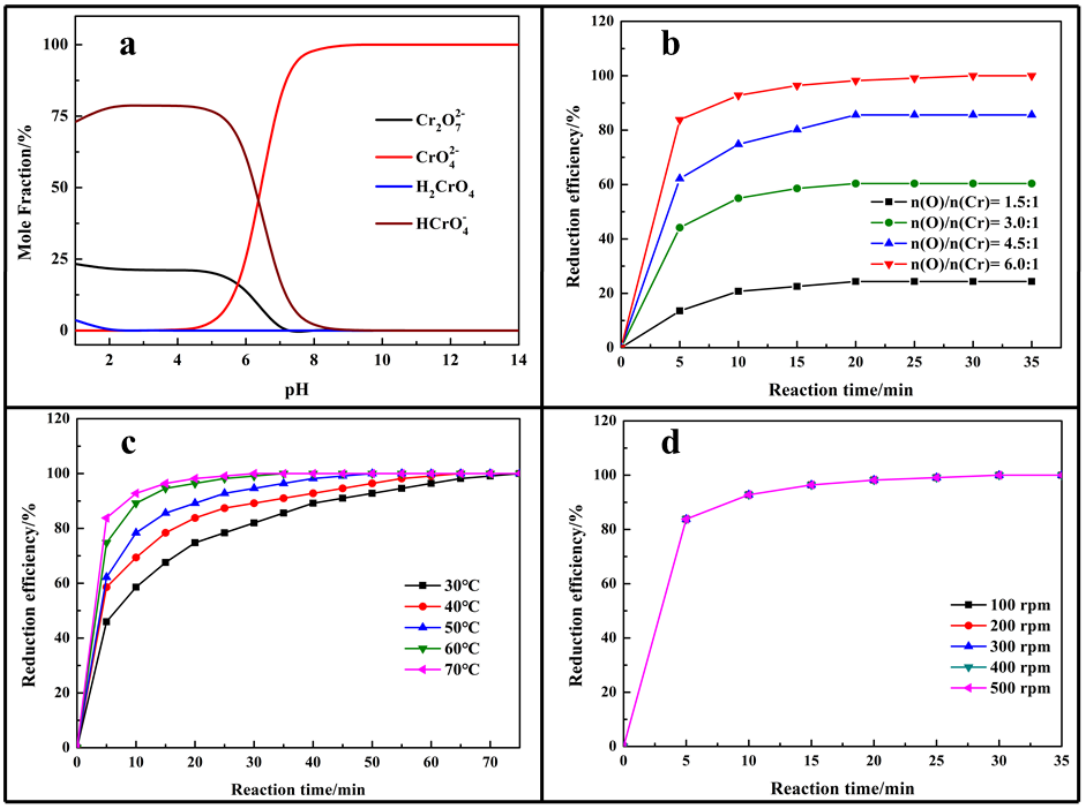

Figure 3 Effect of parameters on reduction efficiency of Cr (VI) a) mole fraction of Cr (VI) species at various pH; b) dosage of oxalic acid; c) reaction temperature; d) stirring rate

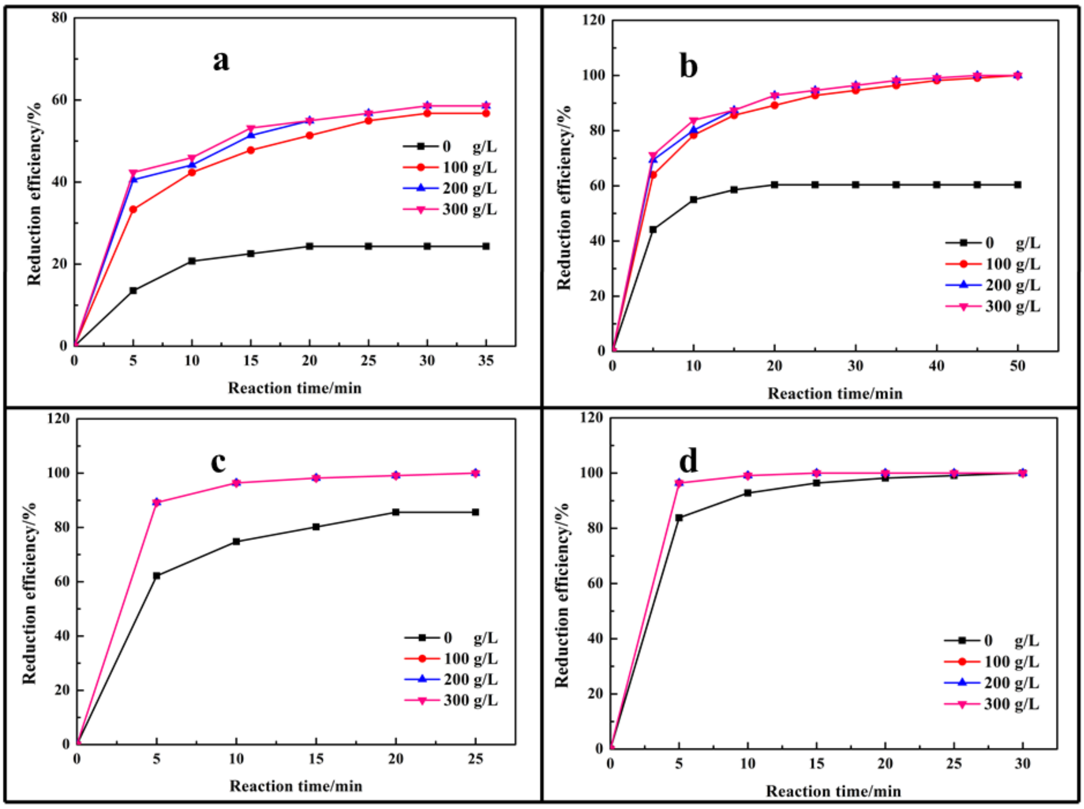

Figure 4 Effect of H_2SO_4 concentration on the reduction efficiency of Cr (VI) at various dosage of oxalic acid a) n(O)/n(Cr)= 1.5:1; b) n(O)/n(Cr)= 3.0:1; c) n(O)/n(Cr)= 4.5:1; d) n(O)/n(Cr)= 6.0:1

3.3 Kinetics analysis

The reduction of Cr (VI) could be expressed by pseudo-first-order equation as described as **Equation (6)** [25-27].

$$\upsilon = \frac{dC}{dt} = -K_{obs}C \tag{6}$$

Integrate.

$$-LnC=K_{obs}t-LnC_0 \tag{7}$$

Where v is the reduction rate of chromium (VI), C is the concentration of Cr (VI), C_0 is the initial concentration of Cr (VI), K_{obs} is the reaction constant.

The experimental data were fitted as **Equation (7)** and the results were displayed in **Figure 5a**. The results showed in **Figure 5a** indicated that the data was fitted well as the coefficient (R^2) all closely to 1, which indicated that the kinetic model was followed pseudo-first-order model equation. The relationship between K_{obs} and reaction temperature (T) could be expressed with the Arrhenius equation (**Equation (8)**) and the specific apparent activation energy could be calculated. The result showed in **Figure 5b** showed the simulated Arrhenius equation and the Ea was calculated as 22.49 KJ/mol, which was much larger than the apparent energy calculated for electrochemical reduction (4.74KJ/mol) [10]. It meant that the reduction process by oxalic acid was harder than electrochemical reduction, while the reduction efficiency (100%) was much more efficient (86.45%).

$$lnK_{obs}=lnA-Ea/RT \tag{8}$$

Where Ea 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.

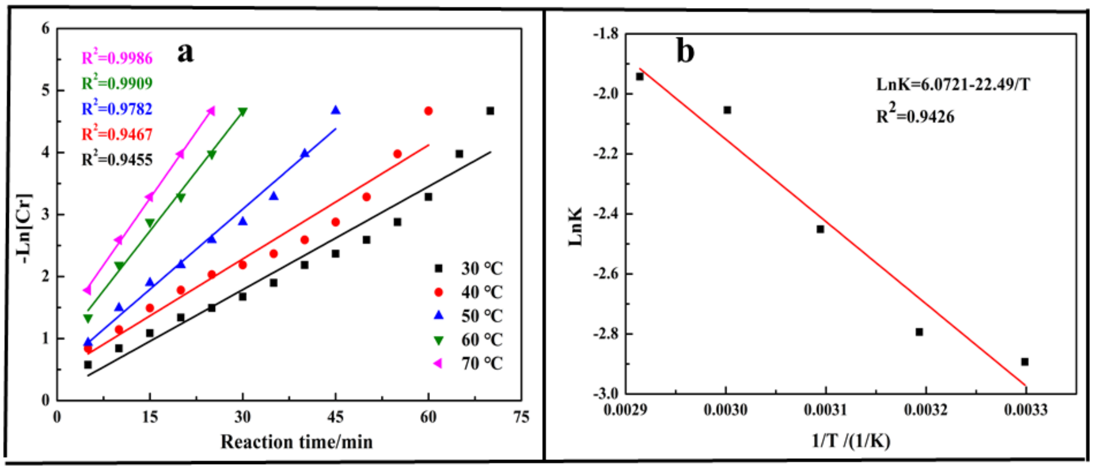

Figure 5 Kinetics plots: a) Plot of leaching kinetics of vanadium at various reaction temperatures; b) Natural logarithm of reaction rate constant versus reciprocal temperature

4. Conclusions

In this paper, the direct Cr (VI) reduction process by oxalic acid was conducted. The following conclusions could be obtained:

(1) The Cr (VI) was easily reduced by oxalic acid at high reaction temperature and a high dosage of oxalic acid in acidic medium. Nearly 99.9% of Cr (VI) was reduced at n(oxalic acid)/n(Cr)=6.0 and reaction temperature of 70 ℃. The dosage of acid concentration and stirring rate had no obvious effect on Cr (VI) reduction process.

(2) The reduced product, Cr (III), was easily generated stable complex compounds ($Cr(HC_2O_4)_3$) with oxalate, which displayed a negative effect on the reduction process. The high reaction temperature and high acidic medium could destroy the stable structure of a complex compound to release oxalate, and facilitate the reduction of Cr (VI).

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

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