Research Article

Direct advanced oxidation process for chromium(III) with sulfate free radicals

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Abstract

Sulfate radical had attracted much more attention due to its high efficiency for removal and hazard-free treatment of organic pollutant. In this paper, we investigated the oxidation process of chromium(III) (Cr(III)) with sodium persulfate ($Na_2S_2O_8$). The effect of parameters including dosage of sodium persulfate, acid concentration, reaction temperature and reaction time on the oxidation process were investigated. Results indicated that $SO_4^{·-}$ generated by heating $Na_2S_2O_8$ solution was an effective oxidant oxidizing Cr(III) to chromium(VI) [Cr(VI) under the optimize conditions: mass ratio of $Na_2S_2O_8$ to Cr of 13.2 g/g, reaction temperature of 90 °C, reaction time of 60 min]. The addition of catalyst could accelerate the oxidation process and decrease the reaction time. Other way, the direct advanced oxidation technology was successful applied in oxidizing industrial waste solution contained Cr(III) and could satisfy the requirements of the chemical enterprise.

Keywords Chromium · Direct advanced oxidation · Application

1 Introduction

Chromium is an important metal which is widely used in chemical manufacturing, electroplating, leather tanning, metal corrosion inhibition, and pigment productions [1–3]. Cr(III) and Cr(VI) are main chromium compounds, which are stable and shown different characteristics. Cr(VI) is mainly existed as dichromate ($Cr_2O_7^{2-}$) in acidic solution and chromate ($HCrO_4^-$, CrO_4^{2-}) in alkaline solution. As we all know, oxidative approach is a critical step for the disposal of large amount of Cr-contaminated solid wastes, radioactive tank wastes and refractory spinel mineral [4]. Many efforts have been done to intensify the oxidation process and improve the oxidation efficiency of Cr(III) for chromium resources utilization [5–8]. Conventionally, sodium roasting–water leaching technology, calcium roasting-acid leaching [4], and hydrometallurgical methods such as pressure oxidative leaching coupled with oxygen, ozone, permanganate, and ferrate have been developed [6, 9–12]. However, some problems were unstill unresolved, like high energy consumption, low overall resource utilization, as well as environmental pollution.

Sulfate radical had attracted much more attention due to its high efficiency for removal and hazard-free treatment of organic pollutant, and it can be generated by activating sulfate with UV, heat, or transition metal [13, 14]. In this paper, sodium persulfate ($Na_2S_2O_8$) acted as the oxidant with direct advanced oxidation process was applied to oxidize Cr(III) to Cr(VI). The effect of dosage of sodium persulfate, reaction temperature, reaction time and concentration of sulfuric acid on oxidation process were preferentially examined, also the oxidation mechanism.

2 Experimental

2.1 Materials

Chromium sulfate ($Cr_2(SO_4)_3$), sodium persulfate ($Na_2S_2O_8$), sulfuric acid (H_2SO_4) were analytical grade from Kelong Co., Ltd, Chengdu, China, and used as received without purification. Deionized water used in the experiments was produced by water purification system (HMC-WS10).

2.2 Apparatus and procedures

All experiments were performed in a glass beaker with a thermostatic mixing water bath pot.

A predetermined amount of chromium sulfate and deionized water was added into the beaker to produce homogeneous solution under constant stirring. The solution was heated to a predetermined temperature. Next, the sodium persulfate was added to the beaker [5, 15–17].
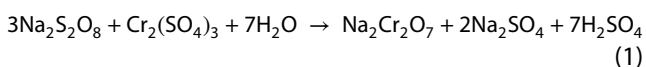
$$\Delta G_T^\theta = \Delta H_{298}^\theta - T\Delta S_{298}^\theta - T\left\{ \Delta a\left(\ln\frac{T}{298} + \frac{298}{T} - 1\right) + \Delta b \times 10^{-3}\left[\frac{1}{2T}(T - 298)^2\right] \right.$$
$$\left. + \frac{\Delta c \times 10^5}{2}\left(\frac{1}{298} - \frac{1}{T}\right)^2 + \Delta d \times 10^{-6}\left(\frac{T^2}{6} + \frac{298^3}{3T} - \frac{298^2}{2}\right) \right\} \tag{9}$$

After required reaction time, the concentration of Cr(III) and Cr(VI) was determined by inductive couple plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 6300DV).

3 Results and discussion

3.1 Technology principle

The main reaction during the oxidation process was between chromium sulfate and sodium persulfate reacted as Eq. (1) [18]. The ΔG_T^θ of Eq. (1) at different temperatures could be calculated with $\Delta_f H_{298}^\theta$, S_{298}^θ and C_p at 298 K, shown in Eqs. (2), (3) and (4) [18].

$$3Na_2S_2O_8 + Cr_2(SO_4)_3 + 7H_2O \rightarrow Na_2Cr_2O_7 + 2Na_2SO_4 + 7H_2SO_4 \tag{1}$$

$$\Delta G_T^\theta = \Delta H_T^\theta - T\Delta S_T^\theta \tag{2}$$

$$\Delta H_T^\theta = \Delta H_{298}^\theta + \int_{298}^T \Delta C_p dT \tag{3}$$

$$\Delta S_T^\theta = \Delta S_{298}^\theta + \int_{298}^T \frac{\Delta C_p}{T} dT \tag{4}$$

Equation (5) was obtained by merging Eqs. (2), (3) and (4).

$$\Delta G_T^\theta = \Delta H_{298}^\theta - T\Delta S_{298}^\theta + \int_{298}^T \Delta C_p dT - T\int_{298}^T \frac{\Delta C_p}{T} dT \tag{5}$$

The specific heat capacity, Cp, was calculated as Eq. (6).

$$C_p = a + b \times 10^{-3}T + c \times 10^5 T^{-2} + d \times 10^{-6}T^2 \tag{6}$$

And also △Cp was calculated as Eq. (7).

$$\Delta C_p = \Delta a + \Delta b \times 10^{-3}T + \Delta c \times 10^5 T^{-2} + \Delta d \times 10^{-6}T^2 \tag{7}$$
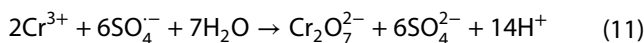
Then ΔG_T^θ was calculated like Eq. (8).

$$\Delta G_T^\theta = \Delta H_{298}^\theta - T\Delta S_{298}^\theta - T\int_{298}^T \frac{dT}{T^2}$$
$$\times \int_{298}^T \left(\Delta a + \Delta b \times 10^{-3}T + \Delta c \times 10^5 T^{-2} + \Delta d \times 10^{-6}T^2\right) dT \tag{8}$$

Integrate.

The $\Delta_f H_{298}^\theta$, $\Delta S_{T'}^\theta$, a, b, c and d in Eq. (9) could be obtained from the Ref. [18]. The calculating result was shown in Fig. 1.

The results shown in Fig. 1 indicated that the oxidation of Cr(III) with sodium persulfate was feasible in thermodynamics as the △G was negative [19].

During the oxidation process, $SO_4^{\cdot-}$ was generated by heat the sodium persulfate solution according to Eq. (10). And then the free Cr(III) was reacted with $SO_4^{\cdot-}$ and been oxidized to $Cr_2O_7^{2-}$ according to Eq. (11).

$$S_2O_8^{2-} \xrightarrow{\Delta} SO_4^{\cdot-} + SO_4^{\cdot-} \tag{10}$$

$$2Cr^{3+} + 6SO_4^{\cdot-} + 7H_2O \rightarrow Cr_2O_7^{2-} + 6SO_4^{2-} + 14H^+ \tag{11}$$

3.2 Effect of mass ratio of sodium persulfate to Cr

The effect of mass ratio of sodium persulfate to Cr (SPTCr) on the percentage of Cr(III) and Cr(VI) in reactant solution was preferentially examined under the following conditions: reaction temperature of 90 °C, reaction time of 60 min, and initial concentration of Cr(III) of 20 g/L. The experimental results were summarized in Fig. 2.

The results shown in Fig. 2 indicated that the mass ratio of sodium persulfate had significant effect on the oxidation process, which was consistent with the reaction shown in
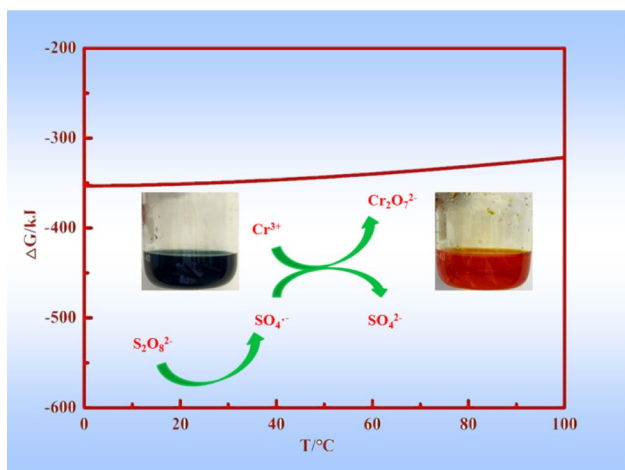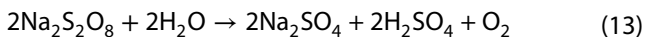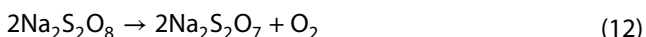
Fig. 1 Relationship between ΔG and temperature of oxidation of chromium(III)

Eq. (1). The percentage of Cr(VI) was increased with the addition of sodium persulfate. The SPTCr was 6.9 g/g in theory calculated based on Eq. (1) as Cr(III) was all oxidized to Cr(VI), while the real SPTCr was 13.2 g/g shown in Fig. 2. During the oxidation process, part of sodium persulfate was decomposed to sodium purosulfate and sodium sulfate according to Eqs. (12) and (13) [18], and the formation of H_2SO_4 had negative effect on the oxidation process. It should cost more sodium persulfate to oxidize Cr(III) to Cr(VI) in all.

$$2Na_2S_2O_8 \rightarrow 2Na_2S_2O_7 + O_2 \qquad (12)$$

$$2Na_2S_2O_8 + 2H_2O \rightarrow 2Na_2SO_4 + 2H_2SO_4 + O_2 \qquad (13)$$

3.3 Effect of reaction temperature

The reaction temperature was another important parameter that had significant influence on the oxidation process of chromium from both thermodynamic and kinetic consideration. Figure 3 summarized the effect of reaction temperature on the oxidation process under the constant conditions: SPTCr of 13.2 g/g, reaction time of 60 min, and initial concentration of Cr(III) of 20 g/L.

It could be concluded that reaction temperature was an important parameter during the oxidation process according to Eq. (10). The results shown in Fig. 3 indicated that the reaction temperature had significant effect on the oxidation process, which was consistent with the conclusion according to Eq. (10). When the reaction temperature was below 60 °C, the Eq. (10) could not react and there was no $SO_4^{\cdot-}$ generated, free Cr(III) was still stable in the solution. As the temperature increased, sodium persulfate was decomposed and generated $SO_4^{\cdot-}$ and the reaction reacted in the solution followed by Eqs. (10) and (11). The percentage of Cr(VI) in the solution was increased with the increase of reaction temperature. It was up to 100% when temperature was 90 °C or above. Therefore, high reaction temperature was an essential condition during the oxidation process.

3.4 Effect of reaction time

The effect of reaction time on the oxidation process was preferentially examined under the following conditions: SPTCr of 13.2 g/g, reaction temperature of 90 °C, and initial concentration of Cr(III) of 20 g/L. The experimental results were summarized in Fig. 4.
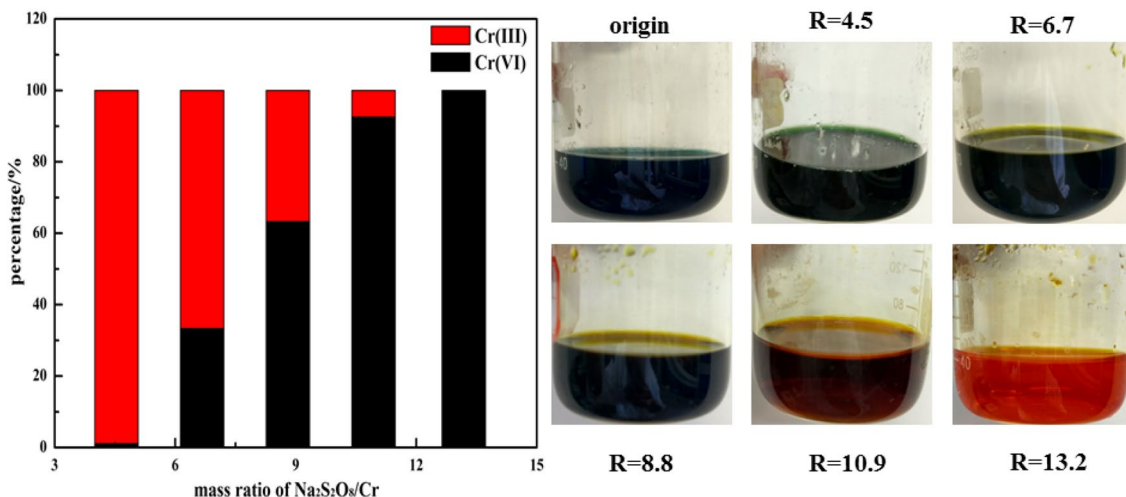

Fig. 2 Effect of mass ratio of $Na_2S_2O_8$ to Cr on the percentage of Cr(III) and Cr(VI) (R = mass ratio of $Na_2S_2O_8$ to Cr)
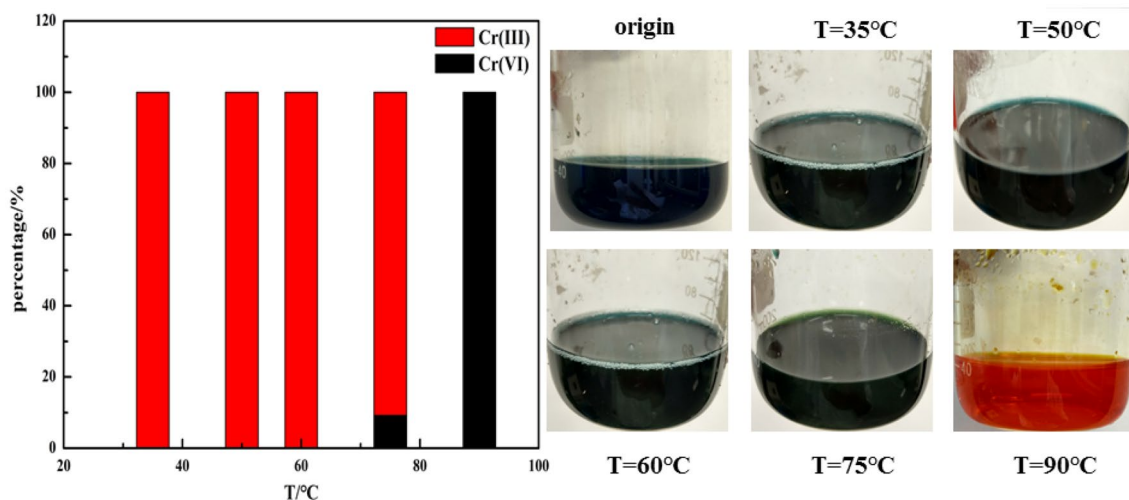
Fig. 3 The effect of reaction temperature on the percentage of Cr(III) and Cr(VI)
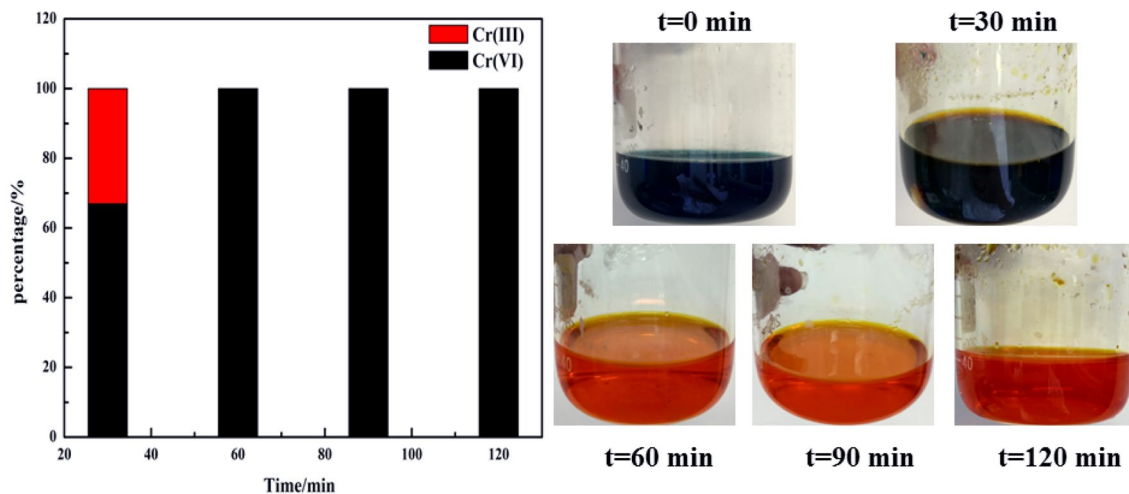

Fig. 4 The effect of reaction time on the percentage of Cr(III) and Cr(VI)

The results shown in Fig. 4 indicated that the oxidation of Cr(III) was very fast. About 68% Cr(III) was oxidized at 30 min and 100% Cr(III) was oxidized at 60 min. At the beginning of the reaction, the generation rate of $SO_4^{\cdot-}$ was slow and it was not enough to oxidize Cr(III) in all. With the increasing of reaction time, the $SO_4^{\cdot-}$ was much more to oxidize Cr(III). The oxidation process could be easily completed at a certain reaction time.

3.5 Effect of concentration of sulfuric acid

It was evidence that sulfuric acid in the solution was not beneficial for the oxidation of Cr(III) according to Eqs. (1),

(13) [18] and the results shown in Fig. 2. The effect of concentration of sulfuric acid on the oxidation process was examined under the following conditions: SPTCr of 13.2 g/g, reaction temperature of 90 °C, reaction time of 60 min, and initial concentration of Cr^{3+} of 20 g/L. The result was shown in Fig. 5.

The addition of sulfuric acid would increase the acidity of Cr(III) solution and increase the difficulty of oxidation of Cr(III) to Cr(VI) [19]. The results shown in Fig. 5 indicated that the percentage of Cr(VI) decreased with the increasing of concentration of sulfuric acid. In order to oxidize Cr(III) efficiently, the solution should be in low acidity condition or neutral condition.
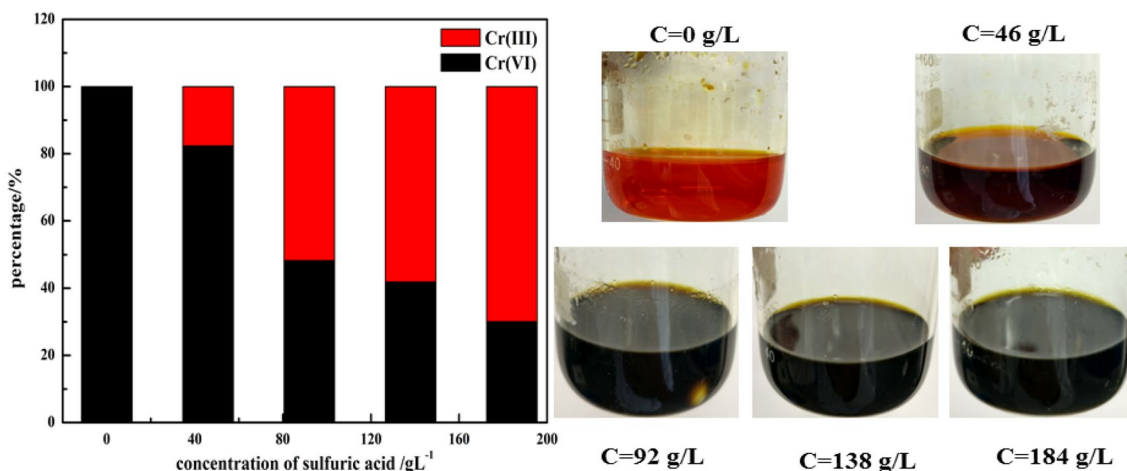
Fig. 5 The effect of concentration of sulfuric acid on the percentage of Cr(III) and Cr(VI)
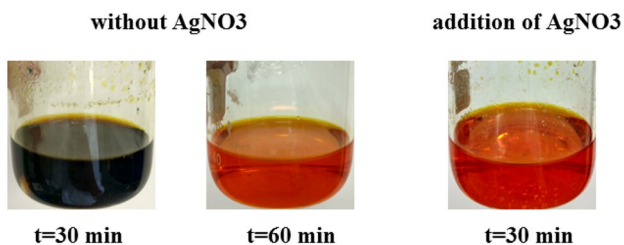

Fig. 6 The effect of catalyst ($AgNO_3$)

Table 1 The content of the industrial waste solution

Species	Original solution	Oxidation solution
Cr(III)	7.94 g/L	0.00 g/L
Cr(VI)	158.81 g/L	166.75 g/L

3.6 Effect of catalyst

It was well known that addition of catalyst was an efficient way to make the reaction easily and accelerate the reaction. $AgNO_3$ as catalyst was added during the oxidation process. The results shown in Fig. 6 indicated that addition of $AgNO_3$ could decrease the reaction time and had no side effect.

4 Engineering application

The optimize conditions were applied in oxidizing Cr(III) from the industrial waste solution containing Cr^{3+}, $Na_2Cr_2O_7$, and H_2SO_4, which collected from a chemical enterprise from Chongqing City, China. The content of the industrial waste solution before and after oxidation process were detailed in Table 1 (Only concentration of Cr was listed). The results indicated that Cr(III) could be oxidized to Cr(VI) in all. Then the industrial waste solution could be cycled in the industrial process. Compared to conventional process, the oxidation process was more economical and environmental-friendly.

5 Conclusions

In this paper, the direct advanced oxidation process of Cr(III) with sodium persulfate was investigated. The results were summarized as followed:

(1) SO_4^- generated by heating $Na_2S_2O_8$ solution was an effective oxidant oxidizing Cr(III) to chromium(VI) (Cr(VI)) under the optimal conditions: mass ratio of $Na_2S_2O_8$ to Cr of 13.2 g/g, reaction temperature of 90 °C, reaction time of 60 min. The addition of catalyst could accelerate the oxidation process and decrease the reaction time.

(2) The direct advanced oxidation technology was successful applied in oxidizing industrial waste solution containing Cr(III) and could satisfy the requirements of the chemical enterprise.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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