

Kinetics of oxidation-precipitation of cobalt() from solution by ozone

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Abstract: In order to precipitate cobalt() in cobalt chloride solution, a novel method using ozone as the precipitant for its strong oxidability was proposed. The results show that the precipitation reaction is diffusion-controlled. The main factors affecting the oxidation rate such as the stirring speed, solution temperature, ozone partial pressure, initial concentration and flow rate were investigated. The kinetics equation of each condition was established. The results indicate that the oxidation rate is independent of the initial concentration or solution temperature. The oxidation rate increases obviously with increasing the stirring speed. The linear relationship between ozone partial pressure or flow rate and oxidation rate is found.

Key words: ozone; diffusion control; cobalt chloride; oxidation; kinetics

1 Introduction

Ozone (O_3) is a triatomic molecule, consisting of three oxygen atoms. It is an allotrope of oxygen that is much less stable than the diatomic allotrope (O_2)[1]. Ozone, with a standard redox potential of 1.24 V in alkaline solutions, is one of the most powerful oxidizing agents, far stronger than O_2 , which has been extensively used in several fields including environmental protection[2–3], food preservation[4], pharmaceutical industry[5] and chemical industry[6], etc.

Now, the application of ozone in every field of people's life and the oxidation kinetics of organic compounds with ozone has been reported. HE et al[7] studied the degradation of fluorobenzene by using ozonation process, and investigated the influence on the reaction kinetics. JIA et al[8] investigated the kinetics of the reaction of ozone with propylene under real atmospheric environmental conditions. WU et al[9] studied the kinetics of decolorization of aqueous textile reactive dye by ozone. Some researchers[10–11] investigated the kinetics of the oxidation of cyanide to cyanate by ozone. But few reports introduced its usage in forming a precipitate for its strong oxidative especially in oxidation of cobalt().

In this study, the oxidation-precipitation of cobalt() in cobalt chloride solution by ozone is reported. Various factors affecting the oxidation rate are

investigated comprehensively, and the kinetics equation is established.

2 Experimental

The experimental apparatus, shown in Fig.1, has two main parts: ozone generator and sedimentation reactor. The ozone generator (OZOMJB-10B, OZOMAX, Inc) has a maximum ozone generation of 10 g/h. Ozone was produced from pure oxygen, and the volumetric flow rate at the outlet of the generator, controlled by regulation of electric current, can be measured by a flowmeter. Ozone was supplied to the bottom of 1 000 mL glass sedimentation reactor, which contained 500 mL of cobalt chloride solution. A replaceable porous glass ring pipe gas diffuser was located at the bottom. On the sides are ports to insert pH electrodes and thermometer. All sensors were connected to an analog-digital system to record data continuously. The dissolved ozone concentration was measured by the indigo method[12]. The concentration of cobalt ion was determined by potentiometric titration. The pH value was adjusted to the desired value with sodium hydroxide solution (1 mol/L) because a large amount of hydrogen ions were generated in the process.

The oxidation reaction using ozone as the precipitant is as follows:



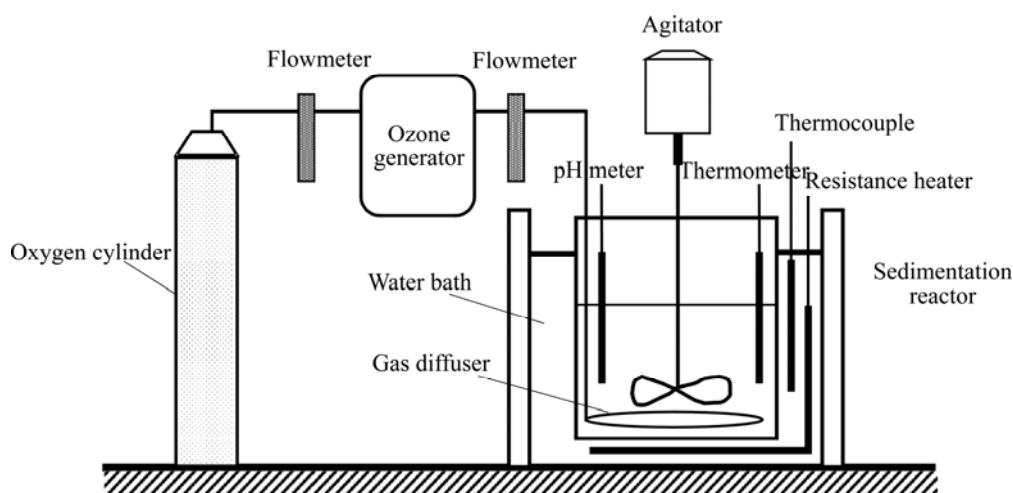


Fig.1 Experimental apparatus

3 Results and discussion

3.1 Effect of stirring speed

The stirring speed has an obvious effect on the oxidation rate by ozone. In this experiment, the conditions of 45 °C, ozone flow rate of 400 mL/min, ozone partial pressure of 4 435 Pa and pH 5.0 were kept constant. As shown in Fig.2, Co^{2+} concentration in solution decreases more quickly with the increase of stirring speed. That is to say, increasing stirring speed can enhance the oxidation rate obviously. The Co^{2+} concentration in the solution shows a linear decrease with reaction time increasing. It is indicated that the precipitation reaction is diffusion-controlled, and the reaction rate of cobalt precipitation is faster than the ozone mass transfer rate in the solution. With high agitation intensity, the reaction rate becomes fast with the acceleration of ozone diffusion rate, and the reaction time decreases. Simultaneously, as the ozone diffusion

rate keeps constant at a constant stirring speed, the concentration of Co^{2+} shows a linear decrease with the reaction time inevitably.

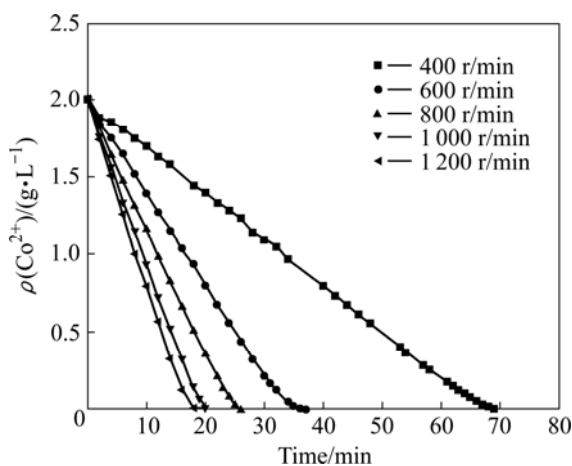
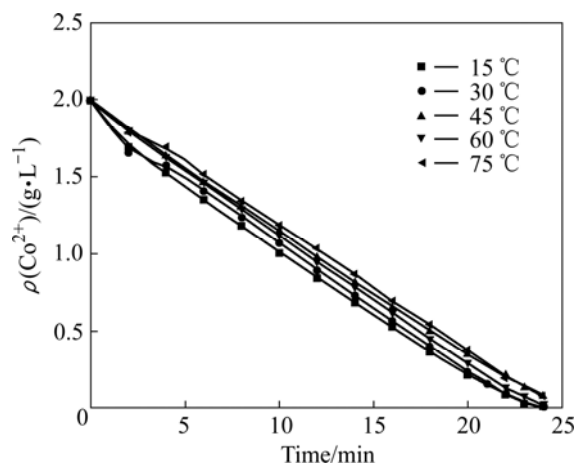
The relationship between the change rate of cobalt concentration in the solution and the stirring speed is obtained by calculating the slopes of all the reaction lines in Fig.2. It can be seen that the change rate of cobalt concentration in the solution tends to be steady with the increases of the stirring speed. The kinetic equation can be established as follows:

$$\frac{d\rho(\text{Co}^{2+})}{dt} = 5 \times 10^{-3} \omega^{0.8} - 0.0306 \quad (2)$$

where ω is the stirring speed.

3.2 Effect of temperature

The temperature is an important factor to the oxidation process. The mass transfer rate of ozone increases with the increase of temperature. In this experiment, the condition of 800 r/min, ozone flow rate

Fig.2 Co^{2+} concentration in solution with time at different stirring speedsFig.3 Co^{2+} concentration in solution with time at different temperatures

of 400 mL/min, ozone partial pressure of 4 435 Pa, pH=5 were kept constant. As shown in Fig.3, Co^{2+} concentration in solution kept constant with the temperature increasing at different time. That is to say, increasing temperature has no effect on the oxidation rate.

If the precipitation reaction is chemically controlled, the reaction rate will increase with increasing temperature obviously. It is suggested that the precipitation reaction is diffusion controlled. This can be explained by the ozone dissolution characteristics in water solution[13] as

$$\frac{dc(\text{O}_3)}{dt} = K(c_s - c_t) - c_d \quad (3)$$

where K is the mass transfer coefficient of ozone in the solution, c_s is the saturated solubility of ozone, c_t is the solubility of ozone at the specified time, and c_d is the concentration of ozone which is decomposed.

Under the diffusion controlled reaction, the ozone dissolved in the solution reacts with the cobalt immediately. So, c_t and c_d can be considered as 0. And the equation can be obtained as follows:

$$\frac{d\rho(\text{Co}^{2+})}{dt} = a_1 \frac{dc(\text{O}_3)}{dt} = a_1 K c_s \quad (4)$$

where a_1 is a constant. From Eq.(4), it is found that the oxidation rate depends on not only the mass transfer coefficient of ozone in the solution but also the solubility of ozone in the solution. As we know, the solubility of ozone in the water decreases with the temperature increasing, and the mass transfer coefficient of ozone in the water is reverse[14–15]. The reaction rate does not change with the temperature by the co-action of these two factors, and the change rate of cobalt concentration in the solution is also kept constant. The kinetic equation can be calculated and established as follows:

$$\frac{d\rho(\text{Co}^{2+})}{dt} = a_2 \quad (5)$$

where a_2 is a constant.

3.3 Effect of ozone partial pressure

The concentration of ozone in the mixed gas will be higher if the ozone partial pressure becomes higher. In diffusion controlled reaction, if more ozone can contact with cobalt ions, the reaction rate will increase. In this experiment, the condition of 45 °C, ozone flow rate of 400 mL/min, stirring speed of 800 r/min, pH 5 were kept constant. As shown in Fig.4, Co^{2+} concentration in solution decreases more quickly with the increase of ozone partial pressure.

The relationship between the change rate of cobalt concentration in the solution and the ozone partial pressure can be obtained by calculating the slopes of all

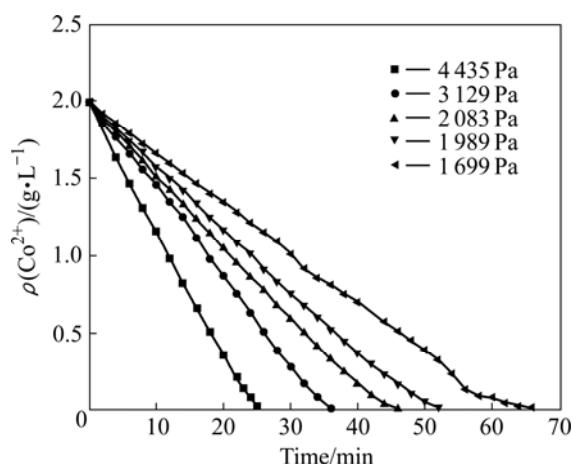


Fig.4 Co^{2+} concentration in solution with time at different ozone partial pressures

the reaction lines in Fig.4.

It is suggested that there is a direct proportion relation between the change rate of cobalt concentration and ozone partial pressure, and the kinetic equation can be established as follows:

$$\frac{d\rho(\text{Co}^{2+})}{dt} = a_3 p(\text{O}_3) \quad (6)$$

where a_3 is a constant; $p(\text{O}_3)$ is the ozone partial pressure.

3.4 Effect of gas-flow rate

In this experiment, the condition of 45 °C, pH 5, ozone partial pressure of 4 435 Pa, the stirring speed of 800 r/min were kept constant. As shown in Fig.5, Co^{2+} concentration in solution changes with the time. It is easy to find that it takes about 110 min for cobalt to precipitate completely when the O_2 flow rate is 100 mL/min. When the O_2 flow rate increases to 400 mL/min, it takes 25 min for cobalt to react completely. It is indicated that more

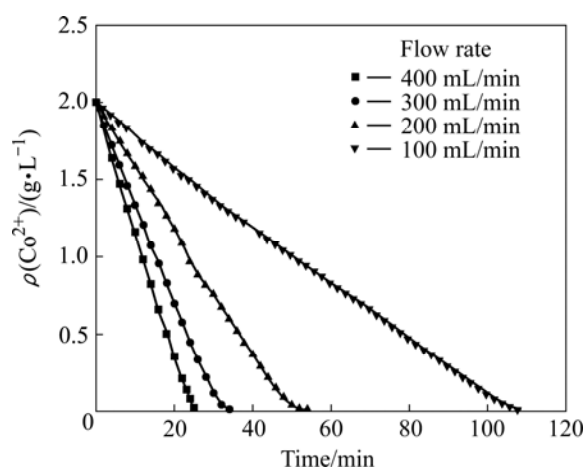


Fig.5 Co^{2+} concentration in solution with time at different flow rates

ozone molecules can diffuse into the solution to react with cobalt ions at a high flow rate of O_2 , and the oxidation rate increases.

By the slopes in Fig.5, it can be seen that there is also a direct proportion relation between the change rate of cobalt concentration and O_2 flow rate. The kinetic equation can be established as:

$$\frac{d\rho(Co^{2+})}{dt} = a_4 F(O_2) \quad (7)$$

where a_4 is a constant, $F(O_2)$ is the oxygen flow rate.

3.5 Effect of initial Co^{2+} concentration

In this experiment, the conditions of 45 °C, pH 5, ozone partial pressure of 4 435 Pa, the O_2 flow rate of 400 mL/min, and the stirring speed of 800 r/min were kept constant. The cobalt chloride solution with initial Co^{2+} concentration of 0.5, 1.0, 2.0 and 4.0 g/L was used. It can be seen from Fig.6 that the curves of the Co^{2+} concentration in solution with time are parallel at different initial Co^{2+} concentration. It is indicated that the changes of initial Co^{2+} concentration have no effect on the precipitation rate of cobalt by the oxidation of ozone.

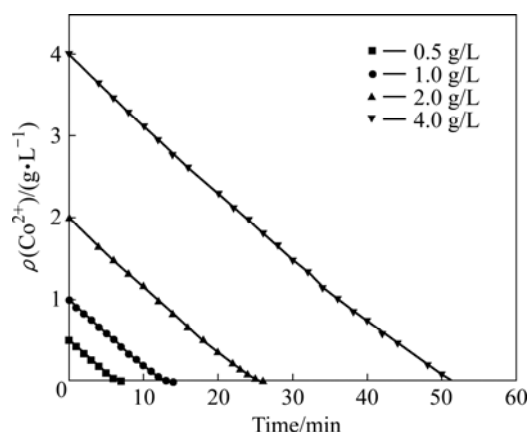


Fig.6 Co^{2+} concentration in solution with time at different initial Co^{2+} concentration

The relationship between the change rate of cobalt concentration in the solution and the initial Co^{2+} concentration is obtained by calculating the slopes of all the reaction lines in Fig.6. The kinetic equation can be established as:

$$\frac{d\rho(Co^{2+})}{dt} = a_5 \quad (8)$$

where a_5 is a constant.

By integrating all the factors studied above, the kinetic equation of the precipitation rate of cobalt by ozone oxidation is established as

$$\frac{d\rho(Co^{2+})}{dt} = a_6 \omega^{0.8} \cdot p(O_3) \cdot F(O_2) \quad (9)$$

where a_6 is a constant.

4 Conclusions

1) The use of ozone to precipitate cobalt() from cobalt chloride solution was demonstrated. The results from reaction kinetics indicate that the precipitation reaction is diffusion-controlled.

2) The oxidation rate increases obviously with the increase of stirring speed but the oxidation rate is independent of the initial concentration or solution temperature. And there is a linear relationship between ozone partial pressure or flow rate and oxidation rate.

3) The kinetic equation of the precipitation rate of cobalt by ozone oxidation is calculated and established.

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