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# A simple modeling study of the Ce(IV) regeneration in sulfuric acid solutions

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## ABSTRACT

The electrochemical regeneration of Ce(IV) for mediated electrochemical oxidation in sulfuric acid media was investigated in an electrolytic membrane reactor. A simple kinetic model was developed to analyze and simulate the regeneration of Ce(IV) in the electrolysis process. The model was based on the Faraday's law and the mass balance of components in the reactor. The key operating conditions of the initial electrolyte concentration and the regeneration time were analyzed. It was found that the simulating model agreed well with the experimental data for regeneration of Ce(IV). Experimental results showed that $Ce(SO_4)_2^-$ is the active species. The decomposition of surface complex of Ce(IV) at the anode surface is the rate determining step. Constant-current electrolysis shows that the high proton and Ce(III) concentrations are electrochemically favorable for the regeneration of Ce(IV). The current efficiency for regeneration of Ce(IV) decrease obviously with the increase of $SO_4^{2-}$ concentration from 0.8 to 2.4 mol/L.

## 1. Introduction

In recent decades, environmental pollution has become a global problem. The introduction of more stringent pollution regulations, coupled with financial and social pressures for sustainable development, has pressed to research and develop new and more efficient pollutant treatment technologies. The application of electrochemical oxidation methods for the treatment of pollutants has been attracted much more interest since it uses a clean reagent 'the electron'. The methods can be employed in oxidation of many different types of organic substrates [1–15], recirculation of spent Cr-etching solutions containing high concentrations of Cr(III) [16,17], removal of hydrogen sulfide from the atmosphere [18], removal of $SO_2$ and NOx from waste gases [19]. The electrochemical treatment of organic and inorganic substrates could be carried out by direct electrochemical oxidation (DEO) or mediated electrochemical oxidation (MEO), such as the degradation of phenol [1,3–5], β-dicarbonyl [6], aromatic derivatives [7], EDTA [10,11], pesticides [15] and removal of $H_2S/NO_2$ [18,19].

The disadvantage of the DEO processes is its low current efficiency: it is often impossible to make the anode reaction complete; the other disadvantage of the DEO processes is the reduced mass transfer of the pollutant from the bulk solution to the anode surface. In the MEO processes, the pollutant is destructed in the bulk solution by a mediate metal ion in the higher oxidation state. After the oxidation of the pollutant, the reduced mediate metal ion is reoxidized in situ at the anode and thus cycled infinitely. MEO is one of the most promising technologies for the destruction of the pollutant. In MEO processes, the metal ion in acid media is oxidized from its lower oxidation state to higher oxidation state and this oxidized species destructs the pollutant compounds, meanwhile, the higher oxidation of the metal ion is reduced to the lower oxidation by the pollutant compounds. Therefore, the metal ion acts as a powerful oxidant and destructs the pollutant. Cerium (IV) has often been selected as a well-known redox mediator for it has high redox potential and negligible rate of water oxidation comparing to silver and cobalt, and also cerium can be recovered and reused without much loss. Cerium belongs to the light lanthanoids and is about 100 times more abundant than cadmium in the earth's crust. Cerium is used in a variety of industrial fields as catalysts, lighters, glass additives, ceramics, magnets and abrasives, solar cells, fuel cells, phosphor/luminescence, gas sensors, oxygen pumps, and metallurgical and glass/ceramic applications. The wild usage of cerium as redox mediator is not only because their effectiveness but also due to the null toxicity for most of them [20]. The toxicity of the chemical products is classified according to the parameter lethal dose 50 (LD50). As an indicative result, lanthanide chlorides exhibit values for the LD50 similar to the sodium salt [21]. The kinetic and mechanistic of the oxidation of the pollutant by Ce(IV) in aqueous $H_2SO_4$ media have been extensively studied [22–27].

There is one common problem in using Ce(IV) to destruct different pollutants in MEO processes, which is the effective way of Ce(IV) regeneration. The factors involved in the regeneration of Ce(IV) influence the anodic mechanism of oxidizing Ce(III) to Ce(IV). However, the electrochemical processes of the regeneration of Ce(IV) on $PbO_2$ electrode are not completely understood yet because of

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discrepancies concerning the influence of variable parameters on the degradation rate of the pollutant. Since effective and economical means of the treatment of pollutants requires the appropriate electrolysis conditions, it is necessary to optimize the regeneration conditions of Ce(IV), and to establish the relationship between the partial current efficiency and the applied current density, concentrations of Ce(III), $H^+$ and sulfate ion in the filterpress-type cell. For these purposes, we have established the relationship between anode current density and concentrations of cerium (III), $H^+$, sulfate ion, and regeneration time.

## 2. Experimental

### 2.1. Materials

### 2.1.1. Reagents

Cerium (III) carbonate (99.99%, Terio Corporation, China), sulfuric acid (analytical reagent, China), magnesium sulfate (analytical reagent, China) were used without further purification. Cerium (III) sulfate was prepared by dissolution of cerium (III) carbonate in sulfuric acid and diluted to the desired concentration with doubly distilled water. Cerium (III) sulfate was titrated against a standard solution of EDTA, using methyl orange as an indicator. Concentration of Ce(IV) was titrated with ferrous ammonium sulfate using ferroin 1.10-phenanthroline-iron(II) as indicator. All other chemicals used were either analytical grade or chemically pure substances.

### 2.1.2. Anion-exchange membrane

The PE-203 (Shanghai Qiulong Chemical Co., Ltd.) was employed as an anion exchange membrane with polyethylene as substrate, $RN^+(CH_3)_3$ as functional ion, exchange capacity of $2 \pm 0.2$ mequiv./g (dry membrane), water content of about 35%, resistance of about $\leq 4.5\ \Omega/cm^2$, thickness of about 0.3 mm and selectivity of 96%. The membrane was equilibrated with sulfuric acid solution of 0.5 mol/L for one night and then rinsed with double distilled water before use.

### 2.1.3. Anode

The electrodeposition of $PbO_2$ on $Ti/RuO_2$ has been carried out in an electrochemical cell filled with a 0.5 M $Pb(NO_3)_2$ and 2.5 M $HNO_3$ solution at 65 °C[28]. The anode was a titanium mesh coated with a thin film of RuO2. The electrodeposition of $PbO_2$ was performed for 3 h, and $\beta$-$PbO_2$ is formed. The average mass of $PbO_2$ was $0.25\ g/cm^2$. The obtained deposit was mat grey, adherent, regular and uniform.

### 2.2. Methods

### 2.2.1. Electrochemical membrane reactor

The electrochemical oxidation of Ce(III) was carried out in a filterpress-type cell which was fabricated in our laboratory. This system featured an electrolytic membrane reactor, two storage tanks, two magnetic pumps and an adjustable DC power supply. $PbO_2$ was used as the anode, made of titanium plate coated with $PbO_2$ (Shanxi Elade New Material Technology Co., Ltd. China). Copper mesh was used as the cathode. Both the apparent geometrical surface areas of electrodes are of 100 mm × 115 mm (effective surface areas: $115\ cm^2$). The anode and cathode were separated by an anion exchange membrane. The anode and cathode compartments of the cell were coupled to the anolyte and catholyte vessels respectively. The DC current (WYK-3020 constant current regulator, 0–20 A, 0–30 V) was applied to the reactor, and the cell voltage was recorded at regular intervals. The solutions were circulated through the anodic and cathodic compartments continuously at a given flow rate using magnetic pumps. The temperature of the electrolyte was controlled to 25 °C with a variation of ±1 °C using a thermostatic control. All experiments were performed under constant current.

### 2.3. Data processing

During the experimental process, samples were collected at specified time intervals. Concentrations of Ce(IV) and Ce(III) were checked by redox titration with standard ferrous sulfate solution and EDTA respectively. From the concentrations of Ce(IV) and Ce(III), the current efficiencies of the anode and the conversion rate of Ce(III) to Ce(IV) were calculated. All current densities relate to the apparent surface areas of the electrodes. The current efficiencies were calculated using Eq. (1), which yield the ratio between the current effectively used for the Ce(III) oxidation to Ce(IV) and the total current supplied.

$$\eta_a = \frac{100\ z F V_a}{M_{Ce} I_{app} A_a} \left( \frac{\Delta C_{Ce}}{\Delta t} \right) \tag{1}$$

where: $\eta_a$ is the anode current efficiencies expressed as percentages, $\Delta C_{Ce}/\Delta t$ is the concentration drop for cerium (III) in the time interval $\Delta t$ ($g\,dm^{-3}\,s^{-1}$), $z$ are the number of electrons used in the electrolytic reactions ($z = 1$ for oxidation of Ce(III) to Ce(IV)), $F$ is the Faraday constant (96487 A s $mol^{-1}$), $V_a$ is the volume of anolyte (L), $A_a$ is the effective anode area ($m^2$), $I_{app}$ is the applied current density ($A/m^2$), $M_{Ce}$ is the molar mass (140.12 g/mol for cerium).

The partial current densities ($I_{Ce}$) used for the Ce(III) oxidation to Ce(IV) were calculated using Eq. (2),

$$I_{Ce} = \eta_a\ I_{app} \tag{2}$$

### 2.4. The electrolysis process

The cathode compartment was filled with a sulfuric acid solution of 1.0 mol/L, and the anode compartment contained a solution of different concentrations of $H_2SO_4$ and Ce(III) sulfate. The unlacquered face of the cathode was polished with fine silicon carbide paper and rinsed with double distilled water and acetone. The anode and cathode were activated together in a 0.5 M $H_2SO_4$ solution at selected constant current density until the cell voltage became stable. The anode and cathode were placed at a constant distance of 1.5 mm from the anion exchange membrane. The cell voltage was recorded at regular intervals. During the oxidation process, the anolyte and catholyte were recycled with a magnetic pump at the flow rate of 0.23 m/s. The anode current efficiency was calculated from the concentration of cerium (IV). The effects of concentration of Ce(III), $SO_4^{2-}$, $H^+$ and anode current density on the partial current efficiency were studied.

## 3. Results and discussion

### 3.1. Effect of different operating factors on current efficiency for the regeneration of Ce(IV)

The electro-regeneration of Ce(IV) involves four main electrode reactions, and sulfate ions migrate through the anion exchange membrane under an electric field. Ce(III) is oxidized at the anode and $H^+$ is reduced at the cathode, while $SO_4^{2-}$ permeates mainly through the anion exchange membrane from the cathode chamber to the anode chamber to balance charge.

The electro-regeneration of Ce(IV) and reduction of $H^+$ in the anion exchange membrane reactor, the main reactions and their standard electrode potentials ($E^\theta$) vs. standard hydrogen electrode are as follows:

At the cathode:

$$2H^+ + 2e \rightarrow H_2 \quad E^\theta_{H^+/H_2} = 0.00\,V \tag{3}$$