



# Manganese recovery and ammonia nitrogen removal from simulation wastewater by pulse electrolysis



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## ABSTRACT

Ammonia nitrogen- and manganese-contaminated water poses a considerable threat on the safety of water resources. In this work, pulse current (PC) electrolysis, a novel process, was developed to recover manganese and remove ammonia nitrogen from simulation wastewater simultaneously. Accordingly, the parameters of pulse electrolysis, and technological conditions, including temperature, initial pH, and concentration of addition NaCl, were investigated. The results showed that the concentration of manganese in simulation wastewater could be reduced from 160 mg L<sup>-1</sup> to 0.2 mg L<sup>-1</sup>, meanwhile, ammonia nitrogen could be removed from 80 mg L<sup>-1</sup> to 0.1 mg L<sup>-1</sup> for 2.5 h PC electrolysis at 30 mA cm<sup>-2</sup>, 1000 Hz, and duty cycle 50% where settled with Ti/SnO<sub>2</sub>–IrO<sub>2</sub>–RuO<sub>2</sub> electrodes, when the initial pH was 10.0 and NaCl addition was 0.008 mol L<sup>-1</sup> at room temperature. Moreover, XRD and SEM analysis showed that manganese dioxide was deposited on the anode, and manganese in simulation wastewater was mainly recovered in the form of manganese dioxide.

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## 1. Introduction

China has an important function in the global electrolytic metal manganese production [1,2], accounting for over 98.5% of the total world capacity in 2014. The non-sustainable development of electrolytic manganese produced a significant amount of contaminants mainly including manganese and ammonia nitrogen due to the incomplete pressure filtration of ore slurry with lots of manganese and ammonia nitrogen added to the ore slurry to adjust the pH during the manganese ore leaching [1]; NH<sub>4</sub>–N and Mn infiltrated into the soil and groundwater [3] and the situation has becoming worse as the increasing of electronic manganese residue [4]. In the most polluted period, concentrations of manganese and ammonia nitrogen respectively exceeded 500 and 70 times of the limit values specified in the 3rd class national standard for surface waters in certain rivers in areas where electrolytic metal manganese plants are concentrated. Intaking high concentrations of manganese causes manganese psychosis, an irreversible neurological disorder [5]; and too much ammonia nitrogen in the body can lead to the blue baby syndrome, liver damage, and gastric cancer [6,7]. Thus, water resource simultaneously contaminated by manganese and ammonia nitrogen has seriously damaged the ecology

and restricted the development of economy. In this work, the raw wastewater was simulated wastewater with ammonia nitrogen and manganese.

Most physical/chemical and biological methods applied to treat manganese and ammonia nitrogen pollution are separated; including the use of natural adsorbents [8–10], oxidation and precipitation of manganese [11], and biological treatments [12]. For ammonia nitrogen purification, the most commonly used methods are air stripping [13], biological [14], electrolysis [15], ion-exchange [16], break point chlorination [17], and chemical precipitation [18,19]. For manganese purification, natural adsorbents [9], oxidation and precipitation of manganese [11], and biological treatments [12] are commonly used. Calcined lime was generally used to remove manganese and ammonia nitrogen simultaneously in the electrolytic metal manganese wastewater, but it could produce large quantity of sediment preventing the manganese recovery, and cause severity secondary pollution creating a poor operating environment. However, simultaneously removing ammonia nitrogen and manganese is complicated, costly and can lead to undesirable by-products. Hence, developing an economical method for simultaneously removing manganese and ammonia nitrogen from wastewater is extremely urgent.

Electrolytic oxidation was used to remove ammonia nitrogen and recover manganese respectively [20–22], especially in wastewater treatment, where direct current (DC) is used in the

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power supply, for its advantages of lower operating costs and less usage of extra chemical reagents. However, the features of the power supply directly affected the driving force of the electrochemical reaction. Pulse electrolysis has been widely employed in electro-deposition, surface treatment, electro-crystallization, and anodic oxidation [23,24]; pulse electrolysis of water is a highly efficient method to produce hydrogen and hydrogen/oxygen gas mixtures [25,26]; the pulse current (PC) power supply determines the intrinsic electrochemical efficiency, and these technological conditions are considered important in the treatment of industrial electroplating wastewater [27]. Comparing to direct current PC power can generate a constant current during the pulse on-time ( $t_{on}$ ), following a pause during the pulse off-time ( $t_{off}$ ) which accelerates ion migration rate and reduces the concentration polarization and the over voltage of the electrodes.

This work aimed to use PC power and Ti/SnO<sub>2</sub>–RuO<sub>2</sub>–IrO<sub>2</sub> (as the anode material) in the simultaneous recovery of manganese and removal of ammonia nitrogen from simulation wastewater. The parameters of PC electrolysis were investigated in terms of their influences on simulation wastewater treatment. Meanwhile, the effects of temperature, initial pH, and concentration of NaCl addition in the PC electrolysis process were studied, and the precipitate of solution and anode plate precipitate were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

## 2. Materials and methods

### 2.1. Materials

The raw wastewater used in the work was simulated wastewater with ammonia nitrogen and manganese concentrations of  $(80 \pm 2)$  and  $(160 \pm 2)$  mg L<sup>-1</sup>, respectively, which was prepared by dissolving analytical-grade (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and MnSO<sub>4</sub>·H<sub>2</sub>O in distilled water. Meanwhile, Na<sub>2</sub>SO<sub>4</sub> (0.07 mol L<sup>-1</sup>) was supporting electrolyte. The chloride ion concentration varied from 0 to 0.01 mol L<sup>-1</sup> by adding NaCl. All reagents were of analytical grade and purchased from Chongqing Boyi Chemical Reagent Co., Ltd., China. Purified water was provided by Waters Purification System (HMC-WS10).

### 2.2. Electrolysis process

A cuboid organic glass (polymethyl methacrylate) cell with a free working volume of 500 mL was designed as the reactor. A Ti/IrO<sub>2</sub>–SnO<sub>2</sub>–RuO<sub>2</sub> plate (Baoji ZhiMing Special Metal Co., LTD, China) with a surface area of 90 cm<sup>2</sup> (9 cm × 10 cm) (anode) and a stainless plate with an identical area (cathode) were fixed at a distance of 80 mm. Herein, a high-frequency switching power supply (SMD-30, Handan Dashun Electroplating Equipment Co., Ltd., China) was used to offer a regular PC (peak current = 30 A,  $f = 5\text{--}5000$  Hz,  $r = 0\text{--}100\%$ ,  $U = 0\text{--}220$  V), where  $i_a$  was the average current,  $f$  and  $r$  denoted the frequency and duty cycle pulse current (PC) electrolysis, and voltage ( $U$ ) was monitored by an voltmeter (5135-LED, Shenzhen skill jing wei electronic co., Ltd, China). All experiments were conducted at room temperature unless otherwise specified. After the experiment, anode deposits and the precipitates of solution were dried at a certain temperature.

### 2.3. Analysis methods

The concentration of manganese ions was determined by atomic absorption spectrophotometry (AAS; HITACHI 180/80, Japan) in flame. Ammonia nitrogen concentration was obtained by Nessler's reagent spectrophotometry (National Standard of

China, HJ 535-2009) using a UV–vis spectrometer (UV-3802, China), which is a colorimetric method used to determine low concentrations of ammonia nitrogen. Surface morphology and elemental composition of manganese deposits were analyzed using Scanning Electron Microscopy (SEM, Tescan, Czech). Crystal structure was determined using X-ray diffraction (XRD, SHIMADZU-6000, Japan) with a Cu K $\alpha$  radiation source under the conditions of  $\lambda = 0.15418$  nm, 40 kV, and 40 mA at 10–90°.

Ammonia nitrogen removal efficiency ( $R_{\text{NH}_3\text{-N}}$ , %) and manganese recovery efficiency ( $R_{\text{Mn}}$ , %) are separately defined by Eqs. (1) and (2) as follows:

$$R_{\text{NH}_3\text{-N}} = \frac{C_{\text{NH}_3\text{-N},0} - C_{\text{NH}_3\text{-N},t}}{C_{\text{NH}_3\text{-N},0}} \cdot 100\% \quad (1)$$

$$R_{\text{Mn}} = \frac{C_{\text{Mn},0} - C_{\text{Mn},t}}{C_{\text{Mn},0}} \cdot 100\% \quad (2)$$

where  $C_{\text{NH}_3\text{-N}}$  (mg L<sup>-1</sup>) is the ammonia nitrogen concentration and  $C_{\text{Mn}}$  (mg L<sup>-1</sup>) is the manganese ion concentration. Subscripts 0 and  $t$  indicate the initial and sampling times, respectively.

## 3. Results and discussion

### 3.1. Investigation of parameters of pulse electrolysis

The main parameters of pulse electrolysis cell system, including current density, frequency, and pulse current (PC) electrolysis cycle, were investigated. The values of pulsating on-time ( $t_{on}$ ) and off-time ( $t_{off}$ ) were shown in Fig. 1.

Pulsating on-time ( $t_{on}$ ) and off-time ( $t_{off}$ ) are two independent variables that can be used to calculate duty cycle, frequency, and average pulsating current which are also determined by  $r$ ,  $f$ , and  $i_a$  according to Eqs. (3)–(5), respectively.

$$\text{Duty cycle } r = \frac{t_{on}}{T} = \frac{t_{on}}{t_{on} + t_{off}} \times 100\% \quad (3)$$

$$\text{Frequency } f = \frac{1}{T} = \frac{1}{t_{on} + t_{off}} \quad (4)$$

$$\text{Average current } i_a = i_p \times \frac{t_{on}}{t_{on} + t_{off}} = i_p \times \frac{r}{T} \quad (5)$$

The image in Fig. 2a displays the effect of current density on  $R_{\text{NH}_3\text{-N}}$ . The results indicate that  $R_{\text{NH}_3\text{-N}}$  significantly increased with increasing average current density ( $i_a$ ) and electrolysis time, and  $R_{\text{NH}_3\text{-N}}$  reached 99.9% when average current density was 30 mA cm<sup>-2</sup> for 2.5 h. Fig. 2b shows that the  $R_{\text{Mn}}$  increased with

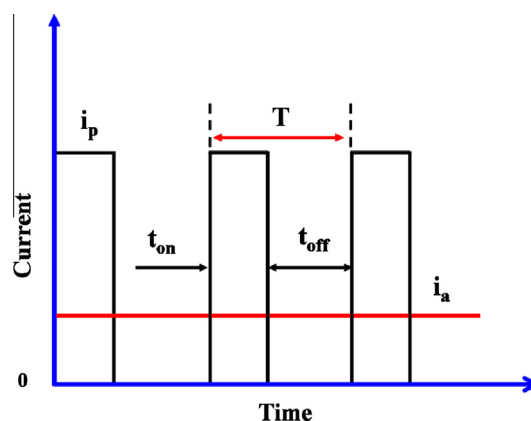


Fig. 1. A general concept of pulsating current technique.

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