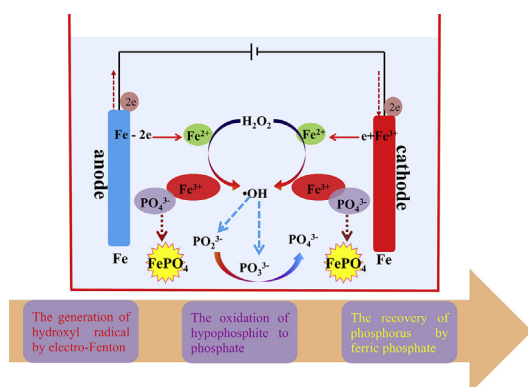


Regular Article

An electrochemical method through hydroxyl radicals oxidation and deposition of ferric phosphate for hypophosphite recovery

Wei Guan^{a,b}, Shichao Tian^c, Ning Ma^e, Xu Zhao^{b,d,*}^a Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing 402160, PR China^b Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China^c Shenzhen Environmental Science and New Energy Technology Engineering Laboratory, Tsinghua-Berkeley Shenzhen Institute, Shenzhen 518055, PR China^d University of Chinese Academy of Sciences, No.19 (A) Yuquan Road, Shijingshan District, Beijing 100049, PR China^e Beijing Key Laboratory of Water Environmental and Ecological Technology for River Basins, Beijing Water Science and Technology Institute, Beijing 100048, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 September 2017

Revised 15 January 2018

Accepted 16 January 2018

Available online 31 January 2018

Keywords:

Electroplating wastewater

Phosphorus recovery

Electro-Fenton

Hydroxyl radical

ABSTRACT

Phosphorus is an essential and irreplaceable element of the ecosystem. In this work, phosphorus has been recovered using an electro-Fenton process. The effects of current intensity, initial pH and H_2O_2 concentration on the recovery of hypophosphite were investigated. When the current intensity, pH value, and H_2O_2 concentration were 0.2 A, 3.0 and 90 mM, respectively, hypophosphite was completely oxidized to phosphate. Under such conditions, the phosphate was recovered through the generation of deposition. In order to determine the mechanism of hypophosphite recovery, the morphology and microstructure of the deposition were analyzed using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray, high resolution transmission electron microscopy, Fourier transform infrared and X-ray photoelectron spectra. The generation of hydroxyl radicals was confirmed using electron spin resonance technique. This method is a clean process for phosphorus recovery, and does not generate hazardous substances.

© 2018 Elsevier Inc. All rights reserved.

1. Introduction

Hypophosphite is commonly used as a reducing agent in metallurgical industries, especially in the processes of plating and surface finishing, which generate large amounts of hypophosphite

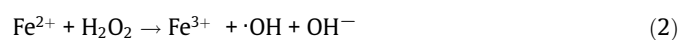
* Corresponding author at: P.O. Box 2871, 18 Shuangqing Road, Haidian District, Beijing 10085, PR China.

E-mail address: zhaoxu@rcees.ac.cn (X. Zhao).

wastewater [1,2]. The hypophosphite contaminated wastewater should be further treated before being discharged into the rivers or lakes, because it may stimulate the growth of algae and cause eutrophication [3,4]. In addition, phosphorus is a non-renewable resource used as a nutrient in agricultural production [5]. However, the reserves of high-grade phosphate rock are limited and the global demand for phosphorus resources is increasing, due to which, these reserves are anticipated to deplete in the next 50–100 years [6–8]. Due to these issues, phosphorus recovery from wastewater has attracted significant attention (see Table 1).

So far, several methods have been employed for the recovery of hypophosphite. Among them, the biological method for hypophosphite recovery is not very efficient, and the reaction system is also unstable [9]. For photoelectrocatalytic method, although the hypophosphite can be effectively oxidized to phosphate by hydroxyl radicals ($\cdot\text{OH}$), it needs another method to recover the phosphorus. Moreover, the utilization efficiency of the ultraviolet (UV) light is very low [10]. For ion-exchange method, some anion will influence the hypophosphite recovery, while the recovery efficiency is also low [11]. In short, these methods for the recovery of hypophosphite are limited, require long treatment time, and incur high cost.

Fenton reaction has been widely used to treat the contaminants in wastewater due to the generation of $\cdot\text{OH}$ radicals [12–14]. However, large amount of ferric hydroxide sludge is generated, which needs further treatment. Moreover, the utilization efficiency of hydrogen peroxide and ferrous is low. The Electro-Fenton (EF) process continuously generates $\cdot\text{OH}$ radicals, even at low dosage of ferrous ion, due to the regeneration of the catalyst. A small voltage is applied between the two iron electrodes, which leads to the electrolytic dissolution of the anode into aqueous Fe^{2+} ions (Eq. (1)). Then, the Fe^{2+} ions catalyze the H_2O_2 to generate homogeneous $\cdot\text{OH}$ radicals (Eq. (2)). In addition, Fe^{2+} is continuously electro-regenerated from the reduction of Fe^{3+} (Eq. (3)), thus creating a catalytic cycle, which accelerates the mineralization process [15,16]. It is an effective method to oxidize hypophosphite by the generation of $\cdot\text{OH}$ radicals.



As one of the important metal phosphates, ferric phosphate has attracted significant attention due to its extensive applications in various industries. Ferric phosphate is mainly used in garden pesticides, and as a coating on industrial metal surfaces. In recent years, it has also been used as a raw material in ceramic industry, and in lithium iron phosphate (LiFePO_4) battery industry. The LiFePO_4 battery has become the most competitive anode material for the next-generation lithium-ion batteries due to its low cost, long life cycle, low toxicity, environment friendliness, and charging/discharging voltage gentleness. However, because of the shortage in phosphorus resources and the complexity of the synthesis process, the price of ferric phosphate is high, which limits its fur-

ther application. Therefore, research focusing on the recovery of high purity ferric phosphate from wastewater is potentially very useful.

In this work, an efficient and environment-friendly method to recover high purity ferric phosphate was investigated. The method mainly consists of two processes, namely the oxidation and precipitation. The effects of current intensity, initial pH and H_2O_2 concentration on the recovery of hypophosphite were investigated. The depositions were analyzed using XRD, SEM, EDX, HR-TEM, FT-IR and XPS techniques. The generation of $\cdot\text{OH}$ radicals was detected using ESR technique, while the mechanism of hypophosphite recovery was proposed in detail.

2. Experimental

2.1. Materials

Sodium hypophosphite (NaH_2PO_2), hydrogen peroxide (H_2O_2 , 30.0 wt%), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), sodium sulfate (Na_2SO_4), and 5, 5-dimethylpyrrolidine-N-oxide (DMPO) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. DMPO was stored at -20°C . All the chemicals were analytical grade, and all the solutions were prepared using Milli-Q water (Millipore; $18.2\text{ M}\Omega\text{ cm}$). In addition, iron electrodes were purchased from Beijing Henglitai Co., Ltd., China.

2.2. Methodology

Electrochemical experiments were performed in a glass reactor with a capacity of 400 mL, while the initial concentration of hypophosphite was 248 mg/L. The electrochemical system included a direct-current (DC) power supply, an electrolytic cell, two iron electrodes, and a magnetic stirring apparatus. The electrochemical experiments were carried out at a constant current intensity, which was controlled by a DC power supply (DH1718E-6, Dahua Electronic, Co., Ltd., Beijing, China). Constant potentials of 1.0, 2.6, 3.8, and 5.3 V were applied successively for the current intensities of 0.05, 0.1, 0.2, and 0.3 A, respectively. The iron electrodes ($70\text{ mm} \times 40\text{ mm}$) were used as anode and cathode, which were directly connected to the direct-current (DC) power. The reaction solution was stirred magnetically at a speed of 300 rpm, while the reaction temperature was 20°C .

In the process of hypophosphite recovery, the reaction time was 30 min and the pH value of the solutions was adjusted by either H_2SO_4 (1.0 M) or NaOH (1.0 M). During the experiments, effects of current intensity (0.05, 0.1, 0.2 and 0.3 A), initial pH values (3.0, 5.0, 7.0 and 9.0) and H_2O_2 concentration (30, 60, 90 and 120 mM) on hypophosphite recovery were analyzed. The deposition was filtrated, and then, dried at 105°C , which was stored in a dryer and used for further analysis.

2.3. Analytical procedures

The concentrations of hypophosphite (NaH_2PO_2), phosphite (NaH_2PO_3) and phosphate (NaH_2PO_4) were measured using ion chromatography equipped with a 732 IC detector [17]. The total concentration of the phosphorus was measured using a spectrophotometer at a wavelength of 700 nm, which was based on the formation of a blue molybdenum complex and digestion using peroxodisulfate ($\text{K}_2\text{S}_2\text{O}_8$) [18]. The total concentration of iron ions was analyzed using a 700 series inductively coupled plasma optional emission spectrometry (ICP-OES; Agilent Technology, U.S.A.). The pH value was analyzed using a pH detector (310P-02, Thermo Fisher, U.S.A.). The phase composition of the deposition was determined within the range of 2θ from 5° to 80° using

Table 1
Energy consumption for phosphorus recovery under different current intensities.

Current intensity (A)	Voltage (V)	Recovered quantity (mg)	Energy (kWh/g)
0.05	1.0	91	0.08×10^{-3}
0.1	2.6	118	0.06×10^{-3}
0.2	3.8	176	0.04×10^{-3}
0.3	5.3	156	0.05×10^{-3}

Download English Version:

<https://daneshyari.com/en/article/6992221>

Download Persian Version:

<https://daneshyari.com/article/6992221>

[Daneshyari.com](https://daneshyari.com)