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Electrocoagulation of boron by electrochemically co-precipitated spinel ferrites

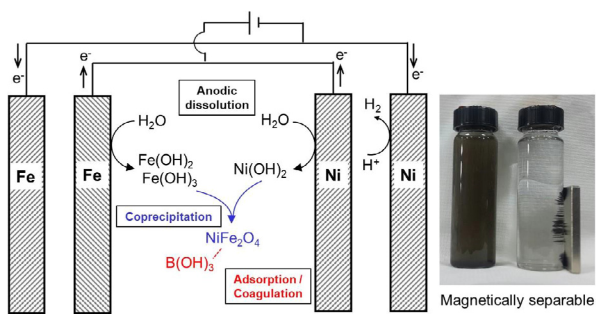
Fitri Widhiastuti[a], Jui-Yen Lin[a], Yu-Jen Shih[b,*], Yao-Hui Huang[a,c,*]

[a] Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan
[b] Institute of Environmental Engineering, National Sun Yat-sen University, Kaohsiung 804, Taiwan
[c] Sustainable Environment Research Center; National Cheng Kung University, Tainan 701, Taiwan

HIGHLIGHTS

- XRD evidenced the formation of spinel ferrites using iron anodes and transition metal electrolyte.
- Nickel ferrite has the highest adsorption capacity and saturation magnetization.
- EC using Fe/Ni anodes produces nickel ferrite in NaCl electrolyte.
- The kinetic of EC obeys pseudo first-order rate law.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnetically separable spinel ferrites were created in an electrocoagulation (EC) process for removing boron from aqueous solution. Coprecipitates of $NiFe_2O_4$, $CoFe_2O_4$ and $CuFe_2O_4$ were obtained using sacrificial iron anodes (EC-Fe) in an electrolyte that contained transition metal salts (Ni, Co, Cu). The use of nickel chloride ($NiCl_2$) as the supporting electrolyte yielded the highest boron removal since the maximum adsorption capacity of the resulting sludge was 28.9 mg-B/g. An EC that used iron and nickel as anodes (EC-Fe/Ni) in NaCl electrolyte was then employed to form nickel ferrite by electrochemical dissolution of ferrous (Fe(II)) and nickel (Ni (II)) ions, providing comparable removal efficiency but minimizing the residual level of Ni(II) in the treated water. The saturation magnetization of the precipitate that was produced in the EC-Fe/Ni system was 50.3 emu/g which exceeded that in the EC-Fe system with nickel chloride – 21.8 emu/g, indicating its outstanding magnetic separability. EC-Fe/Ni was optimized to remove 95% of boron from solution in 60 min with an initial boron concentration of 10 ppm at pH 8 and a current density of 3.75 mA/cm^2.

1. Introduction

Boron is an element that is naturally present in the environment. The majority of the earth's boron is in the ocean. In surface water systems, the natural weathering of sedimentary rocks mobilizes boron into soils and the aquatic environment [1]. The concentration of boron is normally low in soil and irrigation water, which could be easily contaminated by the discharge of boron-containing wastewater. Considering the negative effects of excess boron on the growth of plants and the health of humans, the Environmental Protection Administration

* Corresponding authors at: Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan (Y.-H. Huang); Institute of Environmental Engineering, National Sun Yat-sen University, Kaohsiung 804, Taiwan (Y.-J. Shih).
E-mail addresses: yjshih@mail.nsysu.edu.tw, mcdyessjin@gmail.com (Y.-J. Shih), yhhuang@mail.ncku.edu.tw (Y.-H. Huang).

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Nomenclature

$B_{1/2}$	full width at half maximum, FWHM (radian)	K_M	lumped kinetic constant ($M^{-1}s^{-1}$)
CD	current density (mA/cm^2)	K_s	dimensionless shape factor (-)
C_e	equilibrium concentration of boron (mg/L)	m	weight loss of anodes (g)
d	primary grain size (nm)	M_r	remanent magnetization (emu/g)
EC	electrocoagulation	M_s	saturation magnetization (emu/g)
EC-Fe	electrocoagulation using iron anodes	n	Freundlich isotherm constant
EC-Fe/Ni	electrocoagulation using iron and nickel anodes	Q_{cell}	amount of charges supplied (C)
H_c	coercivity (Oe)	$Q_{dissolution}$	amount of charges due to anode dissolution (C)
K_F	Freundlich isotherm constant	q_e	adsorption capacity of boron (mg/g)
K_L	Langmuir isotherm equilibrium constant (L/mg)	q_{max}	maximum adsorption capacity of boron (mg/g)
		θ	coverage of boron on precipitates (-)
		λ	wavelength of X-ray (nm)

(EPA) of Taiwan has set a standard of 1 mg/L for industrial effluent. The WHO guideline for boron in drinking water is 2.4 mg/L [2].

Electrochemical dissolution of metal ions from the sacrificial anodes enables aqueous pollutants to be coagulated instantly with metal hydroxides [3]. Electrocoagulation of boron in aqueous solution has been extensively studied. Yilmaz et. al. conducted a series of studies on treating boron-containing wastewater using aluminum anodes [4–8] and calcium chloride as an electrolyte. Empirical models were developed to describe energy consumption and kinetics [5–7]. A removal of 96% was achieved when applying a current density (CD) of 6 mA/cm^2 to treat geothermal wastewater that contained 24 mg/L of boron [8]. Isa et. al. demonstrated that more than 99% of boron could be removed from produced wastewater with an initial boron level of 15 mg/L using aluminum anodes at CD of 12.5 mA/cm^2; the flocs were recovered as calcium borate minerals after hydrothermal process [9]. Other metals have been also tested, including Fe, Zn, Mg, and Ni [10–13]. The feasibility of EC in a full pilot scale was demonstrated by Missaoui et al. [14].

Solid-liquid separation is a major part of coagulation processes. Electrocoagulation using iron anodes (EC-Fe) can produce magnetite (Fe_3O_4) as a coagulant that can be destabilized and separated from a liquid by applying a magnetic field [15–17]. The anodic reactions in EC-Fe system include dissolution of iron electrode as ferrous ion (Eq. (1)) and evolution of oxygen (Eq. (2)). In the presence of dissolved oxygen (DO), ferrous ion could be oxidized to ferric ion (Eq. (3)). Both ferrous hydroxide and ferric hydroxide are possible to precipitate when supersaturation is achieved (Eqs. (15)). Magnetite (Fe_3O_4) tends to form in the absence of carbonates [18]. When abundant DO is present, ferric oxyhydroxides, such as lepidocrocite (γ-FeOOH) and goethite (α-FeOOH), are preferred phases and they may transform to magnetite by dissolution/recrystallization (Eq. (6)) [18–20].

$$Fe = Fe^{2+} + 2e^- \qquad E^o = -0.447V(\text{vs. SHE}) \tag{1}$$

$$H_2O = 1/2O_2(g) + 2H^+ + 2e^- \qquad E^o = -1.229V(\textit{vs. SHE}) \tag{2}$$

$$Fe^{2+} + 1/2O_2(aq) + 2H^+ = Fe^{3+} + H_2O \tag{3}$$

$$Fe^{2+} + H_2O = Fe(OH)_2 + 2H^+ \tag{4}$$

$$Fe^{3+} + H_2O = Fe(OH)_3 + 3H^+ \tag{5}$$

$$Fe(OH)_2 + 2Fe(OH)_3 \rightarrow Fe_3O_4 + 4H_2O \tag{6}$$

Magnetite is a spinel ferrite with general formula $M^{(II)}Fe_2^{(III)}O_4$, where M can be Fe^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, or Mn^{2+}. Since spinel ferrites have outstanding magnetic properties and suitable band gaps, they have been applied in magnetic resonance image, electronic devices, drug delivery and catalyst for water splitting, photo chemistry and decomposition of toxic gas [21–23]. They have been regarded as promising water purification materials due to the high adsorption capacity toward aqueous pollutants, including dye, heavy metals, arsenate, fluoride and phosphate from wastewater [24–27]. Apart from sol–gel method, co-precipitation and solid-state reaction, bimetallic spinel ferrites have been successfully synthesized via electrochemical route using anodic dissolution of metals [28–30], which resembles EC process.

As aforementioned, the regular EC process adopted aluminum and other metallic anodes to treat the boron in aqueous solution with the

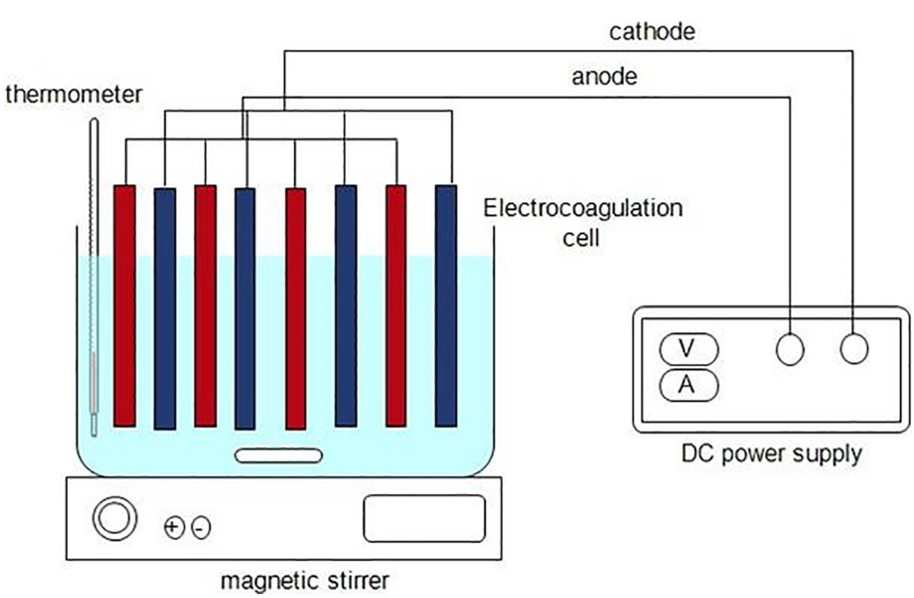

Fig. 1. Experimental apparatus for EC process.