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Boron removal by electrocoagulation and recovery

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ABSTRACT

This work investigated the removal of boron from wastewater and its recovery by electrocoagulation and hydrothermal mineralization methods respectively. The experimental design was developed using Box-Behnken Model. An initial study was performed based on four preselected variables (pH, current density, concentration and time) using synthetic wastewater. Response surface methodology (RSM) was used to evaluate the effect of process variables and their interaction on boron removal. The optimum conditions were obtained as pH 6.3, current density 17.4 mA/cm^2, and time 89 min. At these applied optimum conditions, 99.7% boron removal from an initial concentration of 10.4 mg/L was achieved. The process was effectively optimized by RSM with a desirability value of 1.0. The results showed that boron removal efficiency enhanced with increase in current density and treatment time. Removal efficiency also increased when pH was increased from 4 to 7 and subsequently decreased at pH 10. Adsorption kinetics study revealed that the reaction followed pseudo second order kinetic model; evidenced by high correlation and goodness of fit. Thermodynamics study showed that mechanism of boron adsorption was chemisorption and the reaction was endothermic in nature. Furthermore, the adsorption process was spontaneous as indicated by negative values of the adsorption free energy. Treatment of real produced water using electrocoagulation resulted in 98% boron removal. The hydrothermal mineralization study showed that borate minerals (Inyoite, Takadaite and Nifontovite) can be recovered as recyclable precipitate from electrocoagulation flocs of produced water.

1. Introduction

Boron is an essential compound for the manufacture of different products. Boron compounds are widely used in the manufacture of glass, ceramics, high quality steel, catalysts, cosmetics and flame retardants (Yilmaz et al., 2008a). Boron is also an essential micronutrient for plants and is readily present in the form of boric acid (H_3BO_3). Boron exists as undissociated boric acid and borate ions in aquatic environment. The functions of boron in plants include degradation of carbohydrates, sugar translocation, and hormonal action. Boron deficiency causes stunted growth, yield loss and even death of plant (Yilmaz et al., 2008b). High boron concentration in irrigation water, however, can cause severe environmental problem because boron compounds form complexes with heavy metals present in soil and increase the potential toxicity of these

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complexes when passed to groundwater (Seki et al., 2006). High boron concentration in surface water makes the water unfit for consumption because boron has been shown to induce male reproductive impediments in laboratory animals orally exposed to boric acid and borax (Linder et al., 1990). The World Health Organization (WHO, 2011) has set a guideline value for boron concentration in drinking water as 2.4 mg/L.

Presence of boron in various industrial wastewaters, such as produced water, can cause problems in wastewater reclamation and reuse. Produced water is water trapped in underground strata which is brought to the surface together with oil and gas during drilling. Produced water is reportedly the largest waste-stream of oil and gas exploration with an estimated 250 million barrels per day compared with about 80 million barrels per day of oil worldwide (Fakhruâul-Razi et al., 2009). The composition of produced water differs from other wastewater because produced water has been confined within underground formations for a very long time (Ezechi et al., 2012a). Produced water is being considered as a supplement to limited freshwater resource especially in arid areas because of its large production volume. One of the impediments to this usage is the presence of boron at higher than permissible concentrations. The large volumetric generation of produced water would also suggest the potential for high amount of boron recovery.

Boron removal from wastewater presents several challenges. Membrane process is a widely acceptable method for wastewater treatment. However, studies have shown that boron can diffuse through membranes in a non-ionic way, similar to that of carbonic acid or water (Hou et al., 2010). The use of selective ion exchange chelating resins has been shown to be effective in boron removal (Kabay et al., 2004). Disposal of the subsequently generated sludge and periodic regeneration of resin, however, remain as major challenges. On the other hand, conventional biological process only removes a small amount of boron from wastewater due to its antiseptic nature (Malakootian and Yousefi, 2009).

Electrocoagulation as a treatment process has been used in the removal of various water contaminants. Process versatility, sludge reduction, minimal operator attention and ease of operation are some of its advantages. The major action of electrocoagulation depends on the ability of water particles to respond to strong electric field in a redox reaction (Ezechi et al., 2010b). Electrocoagulation involves three major mechanisms; formulation of coagulants by electrolytic oxidation of sacrificial anodes, destabilization of the contaminants and particulate suspension, breaking of emulsions and aggregation of the destabilized phases to form a floc (Babu et al., 2007). The mechanism of aluminium oxidation during electrocoagulation is shown below (Balasubramanian et al., 2009).

Anode:

$$Al\ (s)\ \rightarrow Al^{3+}\ (aq) + 3e^- \quad (1)$$

Cathode:

$$2H_2O\ (l) + 2e^-\ \rightarrow H_2\ (g) + 2OH^-\ (aq) \quad (2)$$

Aluminum forms polymeric species during oxidation of the sacrificial anode. These polymeric species $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$, etc. transform finally into $Al(OH)_{3(s)}$ according to the following simplified equation (Ghosh et al., 2008).

$$Al^{3+}\ (aq) + 3H_2O\ (l) \rightarrow Al(OH)_3\ (s) + 3H^+\ (aq) \quad (3)$$

The formed $Al(OH)_3$ (s) appears as sweep flocs with large surface area which increases its adsorption capacity and aids in boron removal from solution. The formed flocs are separated from aqueous medium by sedimentation or flotation.

Considering that many landfill sites are filled up and finding new landfill sites is difficult. Recovery of boron will not only mitigate the adverse effect of boron in the environment but also provide a means of producing boron compounds for industrial use.

This study focuses on the use of electrocoagulation (EC) for boron removal from aqueous solution and its recovery. The specific objectives are: (a) to optimize EC removal of boron based on significant operating parameters using response surface methodology (RSM), (b) to study the boron adsorption kinetics and thermodynamics, and (c) to determine the potential recovery of boron by hydrothermal mineralization (HM).

2. Experimental method

2.1. *Characteristics of wastewater*

A preliminary study was conducted with synthetic wastewater prepared with appropriate amount of boric acid (H_3BO_3) and dissolved in 1 L distilled water to yield varying boron concentrations of 10, 20 and 30 mg/L. The produced water was collected from a local Crude Oil Terminal in Malaysia and was characterized with atomic absorption spectrometry (AAS) and ion chromatography (IC). A pH meter (Hach Sension 2 pH meter) and a conductivity meter (Myron L conductivity meter) were used to measure the pH and conductivity of the sample respectively. The produced water characteristics are shown in Table 1.

Table 1 – Produced water characteristics.

Parameter	Concentration[a]	Parameter	Concentration
Boron	15	Bromine	31.2
pH	7.84	Total phosphate	12
TSS	136	COD	1560
TDS	15,829	BOD	883
Conductivity	30,000 μS/cm	Nitrite	0.03
Turbidity	72 NTU	Copper	2.98
Aluminum	0.65	Ammonia nitrogen	16.5
Iron	1.66	TKN	60.7
Chloride	7546	Sulphate	168
Sodium	3952	Nitrate	1.9
Calcium	357	Sulphide	0.21
Magnesium	600	Phenol	15
Sulphate	168	Total alkalinity	1546
Potassium	284	Zinc	0.04
Hardness	957	Fluoride	0.61

[a] All concentrations are expressed in mg/L unless stated otherwise.