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Comparison of Chemical Coagulation and Electrocoagulation for Boron Removal from Synthetic Wastewater Using Aluminium

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***Abstract*—**Various techniques including conventional and advanced have been employed for the boron treatment from water and wastewater. The electrocoagulation involves an electrolytic reactor for coagulation/flotation with aluminium as anode and cathode. There is aluminium as coagulant to be used for removal which may induce secondary pollution in chemical coagulation. The purpose of this study is to investigate and compare the performance between electrocoagulation and chemical coagulation on boron removal from synthetic wastewater. The effect of different parameters, such as pH reaction, coagulant dosage, and initial boron concentration were examined. The results show that the boron removal using chemical coagulation was lower. At the optimum condition (e.g. pH 8 and 0.8 mol coagulant dosage), boron removal efficiencies for chemical coagulation and electrocoagulation were 61% and 91%, respectively. In addition, the electrocoagulation needs no chemical reagents and makes the boron treatment easy for application.

***Keywords*—**Electrocoagulation, chemical coagulation, aluminum electrode, boron removal.

I. Introduction

BORON is naturally present in the environment at low concentration. Boron bounds with oxygen to form borates in nature. Boron is one of micronutrient for plant's growth and metabolism of plant carbohydrates, hormonal action, sugar translocation, apical meristem function, and biological membrane structure. On the other hand, the deficiency of boron in plant gives result in yield loss, reduced growth, and even withered [1]. Boron is widely used in some industrials such as the manufacture of borosilicate glass, detergents, enamels, cosmetics, flame retardants, fertilizers, and dyestuff production [2]. Boron compounds passing into soil and ground water to form many complex compounds with heavy metals, such as Cd, Cu, Pb, and Ni. These compounds are more toxic than the heavy metals forming them [3]. Boron is also released from human activities, such as the use of borate-containing in fertilizers, the waste from borate mining and processing, and the use of borate in some industries. The main sources of the pollution come from boron mines and nuclear industries [4]. The toxicity of boron can cause some symptoms in humans, include nausea, vomit, dermatitis, diarrhea, and lethargy [5]. The recent World Health Organization (WHO) decides an upper limit of 2.4 mg B/L [6]. Therefore, waste containing boron solutions becomes a crucial problem and should be treated before discharge in the environment.

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The removal of wastewater containing boron solution becomes an important subject. Biological treatment cannot be used to remove boron from wastewaters due to inorganic boron compounds [7]. The previous studies for boron removal are adsorption [8], [9], ion exchange [10], [11], electrocoagulation [12]-[14], chemical coagulation [15], [16], nanofiltration and reverse osmosis [17], [18]. Ion exchange using selective two electrolytes has given good removal efficiency but the side effects are regeneration of resin and sludge disposal. Membrane fouling is the major problem in the nanofiltration and reverse osmosis system which causing decrease in flux. Adsorption is also unsuitable because of the need for backwashing and adsorbent loss during the treatment. These studies are concerned about affected parameters for removal efficiency and only few studies have compared between two or more mechanisms [19], [20].

Chemical coagulation is a wastewater treatment process by the addition of chemicals to alter the physical state of dissolved and suspended solids that involve van der Waals attractive forces and kinetic coagulation. Generally, a suitable coagulant such as aluminium or calcium salts have to added during intense agitation to coagulant disperse rapidly, followed by forming flocs in a slower mixing. Coagulation is usually used for wastewater removal in colloidal form. According to the stabilization mode, colloidal dispersion can be divided into two classes: hydrophilic colloids that gain stability by interface solvation and hydrophobic colloids that are stabilized by electrostatic repulsion [21]. In the coagulation, mixing conditions give a significant effect. The particles need to collide forming flocs by agitation. In general, flocs are formed by the cohesion between primary particles during flocculation in slow-mixing. The initial mixing conditions become the most important parameter due to rapid and uniform dispersion of coagulants affects the particles destabilization [22]. Destabilization of colloidal dispersions is generally carried out in the following mechanisms: double layer compression, adsorption and charge neutralization, sweep flocculation, and interparticle bridging [23].

Electrocoagulation for the wastewater treatment is proven a simple and efficient method [24]. Electrocoagulation is a process that based on responding of water particles to strong electric field by creating metalling hydroxide flocks as an effect of electrodissolution. The metal ions are generated in the anode and hydrogen gas is released in the cathode. The hydrogen gas gives an influence by help the flocculated particles to float going up to surface [25]. The main difference between electrocoagulation and chemical lies on the delivery of aluminium ions in the solutions. Coagulation and precipitation is conducted by delivering the dissolved electrodes in the system [26]. The appropriate selection of electrode materials is very important. The most common electrode materials are aluminium and iron because of cheap, readily available, and proven effective [27].

The mechanism of electrocoagulation depends on the conductivity of aqueous medium. In addition, the other parameters also give effects such as pH reaction, particle size, and solution concentrations in the electrocoagulation process. Based on previous studies [13], [28] the treatment process can be described by (1)-(3):

$$\text{At the cathode:} \quad 3H_2O + 3e \rightarrow 3/2H_2 + 3OH^- \qquad (1)$$

$$\text{At the anode:} \quad Al \rightarrow Al^{3+} + 3e \qquad (2)$$

$$\text{In the solution:} \quad Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \qquad (3)$$

The Al^{3+} and OH^- ions produced at the electrodes can react to form various mono-nuclear ($Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$) and poly-nuclear ($Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Al_{13}O_4(OH)_{24}^{7+}$) species, which are finally transformed into $Al(OH)_3$. The large specific area of aluminium hydroxide provides compound adsorption and traps the colloids [29].

The aim of this paper was to study the comparison of chemical coagulation and electrocoagulation in boron removal from synthetic wastewater. The experiment of chemical coagulation was investigated under different parameters of coagulant dosage (current density), pH reaction, and initial boron concentration. The obtained experimental data were compared between each process in order to determine optimum operating conditions.

II. Materials and Methods

A. Materials

The wastewater samples used in the experiments were prepared synthetically using $NaBO_3.4H_2O$ powder (97% purity) was purchased from Panreac Company. Sodium perborate tetrahydrate was dissolved in distilled water with 1 L volume to the required concentration (100 mg/L). The initial pH was adjusted to a desired value using NaOH or HCl. The parameters chosen in the chemical coagulation and electrocoagulation experiments were pH reaction, coagulant dosage, and initial boron concentration. The residual concentration of boron from each experiment was measured by ICP-OES (JY 2000-2, HORIDA). The crystal structure of by-products was analyzed using X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) JEOL JSM-6700F.

B. Chemical Coagulation Experiments

Chemical coagulation was carried using the standard jar testing technique. Synthetic wastewater with 500 mL volume was put into the reactor, then a desired aluminium chloride (Sigma Aldrich, 98%) was also added in the reactor. HCl and NaOH solutions were added into solution for pH adjustment. The procedures consisted of a 10 min rapid mix (100 rpm), 20 min slow mix (30 rpm), and 60 min settling period. After settling for 60 min, the pH values of solution were measured with a pH-meter. A solution of precipitates was withdrawn and filtered through a 0.45 um filter.

C. Electrocoagulation Experiments

A batch reactor, made of plexiglass was used in electrocoagulation experiments with 12 cm × 10 cm × 8 cm dimensions. The cathodes and anodes (by four pairs plates) with dimensions of 10 cm × 10 cm, made of aluminium were connected to a DC power supply characterized by the ranges 0-8 A for current and 0-7 V for voltage. The net spacing between electrodes was 1 cm. The desired concentration of boron solution was fed into the reactor in the beginning of each experiment. NaOH and HCl were used to control the pH of sample while NaCl (Showa, 99.5%) was added to the medium in order to increase the conductivity of solution. A magnetic stirrer was used to stir the solution with 300 rpm stirring speed. Each run was timed starting with the DC power supply switching on. During the experiments, pH and temperature of the synthetic wastewater were measured. Treated solution was collected for an interval time from reactor and collected samples were filtered by a 0.45 um filter before the analysis.

III. Results and Discussion

A. Effect of pH

The solution pH plays an important role in the chemical coagulation and electrocoagulation processes [24]. Therefore, the experiments were conducted to study the effect of pH on the boron removal. To investigate this effect, a series of experiments were performed using boron containing solution of 100 mg/L. The effect of pH on the boron solution was examined at 4.0, 6.0, 8.0, 10.0, and 12.0 pH. The coagulant dosage of 0.8 mol Al^{3+} and 10 min rapid mix (100 rpm), 20 min slow mix (30 rpm) were kept constant in chemical coagulation experiments. Current density of 6 mA/cm^2 (equal to 0.8 mol Al^{3+} dissolved) and stirring speed of 300 rpm were kept constant in electrocoagulation experiments. Boron removal increased with the increasing pH up to 8.0, and then decreased; the lowest removal efficiency occurred at pH 12.0. When removal efficiency reached up to 61% by chemical coagulation, then using electrocoagulation reached to 91%. The results in boron removal at different pH depend on the hydrolysis and polymerization reaction of dissolved Al^{3+} generated by electrochemical dissolution. Previous studies on the removal efficiency with aluminium electrodes, resulted to the $Al(OH)_3$ behaviour, leading to soluble become Al^{3+} cations (at acidic pH) and monomeric anions $Al(OH)_4^-$ (at alkaline pH) [30], [31]. Boron removal was quite low at very low pH due to competition between H_3O^+ ions from hydrolysis and the positively charged ions from polymeric aluminium hydroxide. On the other hand, the dominant species formed by dissolution of electrodes is $Al(OH)_4^-$ at pH >10 which can decrease coagulation effect because $Al(OH)_4^-$ in a dissolving form and no flocs formation [32]. In addition, borate ions are predominantly present as $B(OH)_4^-$ in alkaline solution. Thus the highest boron removal efficiency was obtained at pH 8 because the formation of $Al(OH)_3$ was high and boron was present as $B(OH)_3$ form. The results obtained are shown graphically in Fig. 1 for 100 mg/L boron concentration.

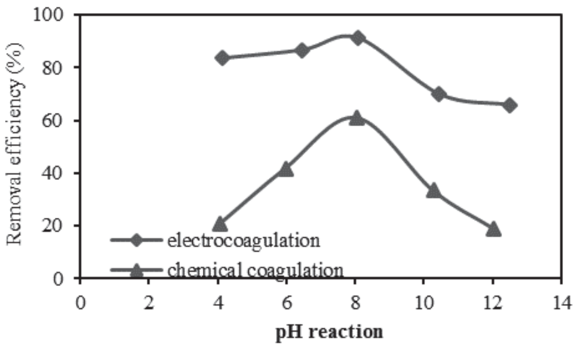

Fig. 1 The effect of pH reaction on boron removal by electrocoagulation and chemical coagulation (100 mg/L initial boron concentration, 0.8 mol coagulant dosage)

B. Effect of Initial Boron Concentration

To study the effect of initial boron concentration, experiments were examined at varying concentration of 10, 50, and 100 mg/L for each process. It was observed (Fig. 2) that as initial boron concentration increases, removal efficiency decreases.

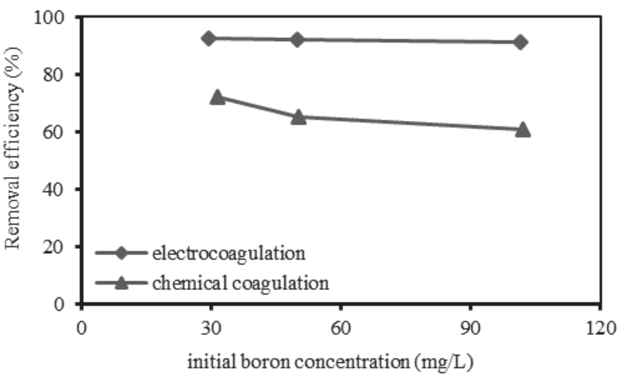

Fig. 2 The effect of initial boron concentration on boron removal by electrocoagulation and chemical coagulation (pH 8.0, 0.8 mol coagulant dosage)

Electrocoagulation experiments carried current density of 3.75 mA/cm^2 and pH 8 in constant conditions with following results 89% removal efficiency for 10 mg/L initial boron concentration, whereas 50 mg/L and 100 mg/L initial concentration gave 94% and 91% removal efficiencies.

Moreover, chemical coagulation experiments with coagulant dosage of 0.8 mol and pH 8 in constant conditions with following results 72% removal efficiency for 10 mg/L initial boron concentration, then the removal efficiency decreased to 65% for 50 mg/L and 60% for 100 mg/L, respectively. Although the same amount of Al^{3+} delivered into solution at the same coagulant dosage and current density for all boron concentrations, these metal ions were inadequate for higher boron concentration solutions. In addition, boron removal efficiency by chemical coagulation process was lower than that by electrocoagulation process.

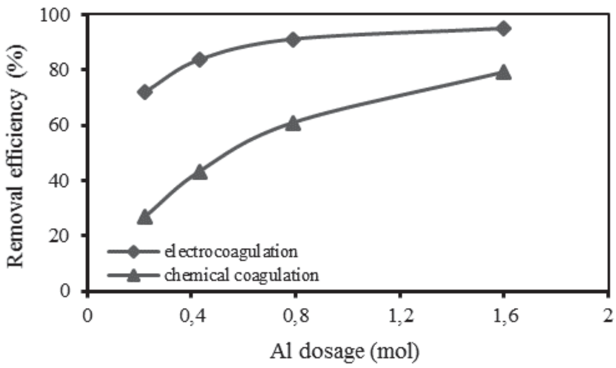

Fig. 3 The effect of coagulant dosage on boron removal by electrocoagulation and chemical coagulation (100 mg/L initial boron concentration, pH 8.0)

C. Effect of Coagulant Dosage

The current density affects performance of process and determines the dosage rate of coagulant in electrocoagulation process. Therefore, current density should have a significant effect on removal efficiency of boron. To examine the effect of current density on removal of boron, a series of experiments were carried out with current density varying from 1.25 to 5 mA/cm^2 (equal to 0.2-0.8 mol of total dissolved Al^{3+}) in the electrocoagulation process while pollutants loading, pH reaction, and electrolysis time remained constant. In the chemical coagulation, it is very important to consider the coagulant dosage which more pollutant reacts as coagulant dosage increases. To examine the effect of coagulant dosage on removal of boron, a series experiments were carried out amount coagulant varying from 0.2 to 0.8 mol Al^{3+} while pH reaction, pH reaction, and stirring speed remained constant. The results show that removal efficiency increases when current density is increased. This can be explained since increase in current density resulting in a greater amount of aluminium ions released into solution. The amount of metal ions generated from electrode can be calculated using the second Faraday's law [33].

$$m= ItM/zF \tag{4}$$

where *m* is amount of electrode material dissolved (g), *I* is current flow (A), t is reaction time (s), *M* is molecular weight of Al (g/mol), *n* is number of electrons passed in the system (n = 3), and *F* is Faraday's constant (96,486 C/mol). The results obtained are shown graphically in Fig. 3. The removal efficiency for chemical coagulation was lower than those of electrocoagulation. It was demonstrated that aluminium was more effective to remove pollutant by using electrocoagulation rather than using chemical coagulation as performed in this study.

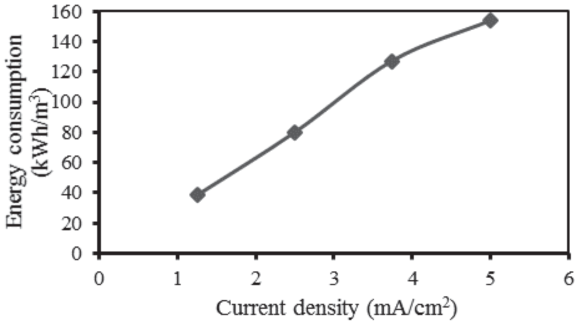

Fig. 4 The effect of current density on energy consumption (100 mg/L initial boron concentration, pH 8.0)

The relationship between current density and energy consumption was also investigated in electrocoagulation process. The electrical energy consumption can be explained with:

$$W= VIt/v \quad (5)$$

where W is electrical energy consumption (kWh/m^3), V is potential (V), I is current flow (A), t is time (h), and v is volume of solution (m^3). The obtained results for energy consumption were shown in Fig. 4. Increasing current density results in an increase of energy consumption. However higher current density could dissolve more metal ions from sacrificial anodes and remove more boron, this condition was not desired in electrical energy consumption regarding to economic evaluation.

D.Material Characterization

The solid phase formed as a result of electrocoagulation experiments was analyzed by SEM measurement. Fig. 5 shows the precipitates were formed by electrodes dissolution.

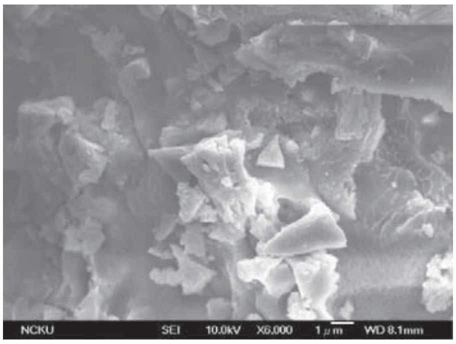

Fig. 5 The SEM image result of solid phase

The nuclei were formed on active sites of dissolution due to electricity passed into solution during electrocoagulation process. The collected precipitate was also characterized using XRD measurement. Formed solid has a crystallized construction formation. Fig. 6 shows the XRD pattern of the precipitate where the diffraction peaks for $Al(OH)_3$ with bayerite and doyleite type were identified. The presence of boron was not observed. This can be explained that the boron concentration was too low and masked in the noise of XRD base line.

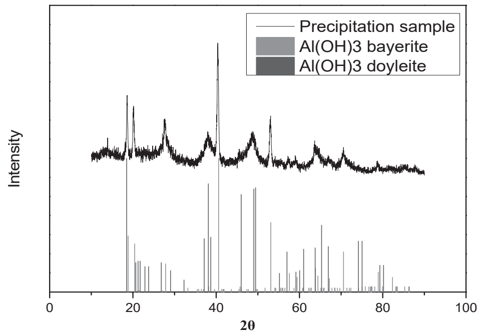

Fig. 6 The result of X-ray analysis of boron adsorbed aluminium hydroxide

IV. Conclusion

This study showed the applicability of electrocoagulation compared to traditional chemical coagulation to treat water contaminated by boron. The most effective boron removal was achieved at pH 8. The removal efficiency decreased as increasing boron concentration. The removal increased with increasing the current density within the range of experiments. The highest current density resulted in a greater amount of metal ions released through solutions and higher energy consumption obtained. It was found that high current density could increase total resistance formed in electrocoagulation cell. Although electrocoagulation and chemical coagulation were carried in the same operational parameters, the removal efficiency between each process was different. The results demonstrated the electrocoagulation process was better to use rather than chemical coagulation in terms of costs and effectiveness. For the same conditions applied, 8 mA/cm^2 current density (1.6 mol Al^{3+} total dissolved) and pH 8, boron removal efficiency was obtained at 95% for electrocoagulation and 79% for chemical coagulation. The nuclei formed on active sites of electrode dissolution were characterized by SEM. X-ray result identified the precipitate with $Al(OH)_3$ (bayerite and doyleite type).

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