



Effect of operating parameters on indium (III) ion removal by iron electrocoagulation and evaluation of specific energy consumption

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ABSTRACT

The aim of this study is to investigate the effects of operating parameters on the specific energy consumption and removal efficiency of synthetic wastewater containing indium (III) ions by electrocoagulation in batch mode using an iron electrode. Several parameters, including different electrode pairs, supporting electrolytes, initial concentration, pH variation, and applied voltage, were investigated. In addition, the effects of applied voltage, supporting electrolyte, and initial concentration on indium (III) ion removal efficiency and specific energy consumption were investigated under the optimum balance of reasonable removal efficiency and relative low energy consumption. Experiment results indicate that a Fe/Al electrode pair is the most efficient choice of the four electrode pairs in terms of energy consumption. The optimum supporting electrolyte concentration, initial concentration, and applied voltage were found to be 100 mg/l NaCl, 20 mg/l, and 20 V, respectively. A higher pH at higher applied voltage (20 or 30 V) enhanced the precipitation of indium (III) ion as insoluble indium hydroxide, which improved the removal efficiency. Results from the indium (III) ion removal kinetics show that the kinetics data fit the pseudo second-order kinetic model well. Finally, the composition of the sludge produced was characterized with energy dispersion spectra (EDS).

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1. Introduction

In the microelectronics industry, a number of semiconductor materials (particularly III–V intermetallic semiconductors) have replaced silicon in various applications. Indium is a metallic element in the IIIA column of the periodic table. It has been found that indium combines with elements, such as antimony or phosphorus, to produce compounds that exhibit semiconductor or optoelectronic characteristics. However, there is no discrete reserve of indium, and its global distribution is very sparse. This metal does not form any minerals of its own and one of its significant sources is zinc refinery residue [1]. It has been reported that indium phosphide (InP) has a high refractive index that allows for a small radius of curvature, resulting in components that are at least 10–100 times smaller than silicon technology [2]. Another characteristic of InP is its direct bandgap, allowing very easy and fast quantum transitions when photons are either absorbed or emitted. Meanwhile, indium and its compounds have numerous industrial applications; they are extensively used in the production of liquid crystal displays, semiconductors, low-temperature solders, and infrared photode-

tectors [3]. The three major applications use indium metal, its alloys, and indium tin oxide (ITO). More than one-half of the world's indium consumption is for indium–tin oxide (ITO) coatings. ITO, which is a sintered alloy containing a large portion of indium oxide and a small portion of tin oxide, is an optically transparent conductor and is used in the making of thin-film transistor liquid crystal displays (TFT-LCDs) for television screens, portable computer screens, cell phone displays, and video monitors. To meet the expanding demand for such displays, LCD production is rapidly increasing, especially in Asian countries, including Taiwan. Because of the demand for TFT-LCD, and semiconductor materials, the consumption of ITO and indium is also increasing. Indium and its compounds exhibit excellent semiconductor and optoelectronic properties, they have been found in the discharged etching wastewater from semiconductor or optoelectronic plants, and are suspected to be carcinogenic to human beings, damaging the heart, kidney, and liver [4]. Hence, the removal of this rare metal (indium) is an important issue.

One of the most general methods used for extracting metal ions from aqueous solutions is the reaction of a metal ion with a specific chelating agent to form a metal chelation followed by solvent extraction. Most studies related to the extraction of metal ions from solid and liquid samples have used chelation combined with solvent extraction [5,6]. However, these solvent extraction procedures are

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usually time-consuming and labor-intensive. In addition, solvent extraction requires many organic solvents and often creates environmental problems. Due to increased environmental legislation limiting the use of conventional solvents, some studies related to the removal and separation of indium ions used methods such as coprecipitation [7], electroanalytical techniques [8], nanofiltration membranes [9], solid phase extraction [10], and supercritical CO₂ extraction [11]. However, there is little research in the development of an electrochemical treatment (i.e., electrocoagulation) for the removal of indium (III) ions.

Electrochemical treatment techniques have attracted a lot of attention because of their versatility and environmental compatibility. Using electrons, which are a “clean reagent” [12], as the main reagent, an electrochemical treatment (i.e., electrocoagulation) method has been proposed to treat wastewater containing dispersed fine particles without chemical addition [13]. Belongia et al. [14] first investigated the particle removal phenomena of synthetic alumina and silica solution using electrodecantation and electrocoagulation. Electrocoagulation is an electrochemical method of treating polluted water whereby sacrificial anodes dissolve due to an applied voltage, producing active coagulant precursors (usually aluminum or iron ions). Furthermore, electrocoagulation offers the possibility of anodic oxidation and in situ generation of adsorbents (such as hydrous ferric oxides and hydroxides of aluminum).

When cathodic reactions occur, in many cases, the evolution of hydrogen gas is involved. Sacrificial anodic electrodes of iron and aluminum are commonly used to continuously supply metallic ions as the source of coagulation. These electrochemically generated metallic ions can hydrolyze near the anode to form a series of metallic hydroxides capable of destabilizing dispersed particles. Electrocoagulation is a complicated process with a multitude of mechanisms operating synergistically to remove pollutants in the vicinity of the anode from the suspended solution. The turbulence created by oxygen (generated as a secondary reaction in the anode) and hydrogen (produced due to water reduction in the cathode) generates a mixture that helps to destabilize particles, resulting in the coagulation of bigger particles. Pollutants are then removed by sedimentation and become the slurry. Electrocoagulation is an emerging water treatment technology that has been applied to treat potable water [15], urban wastewater [16], heavy metal laden wastewater [17], restaurant wastewater [18], colored water [19], mechanical cutting oil [20], wastewater containing phosphate [21], fluoride [22], arsenic [23], and dispersed fine particles from chemical mechanical polishing [13,24]. A remarkable removal efficiency of heavy metals from wastewater containing metals (Cr, Pb, Cu, Zn, Ni, etc.) using electrocoagulation has also been reported [25]. However, few studies have been conducted on treating wastewater containing indium (III) ions by electrocoagulation.

A technically effective process must also be economically feasible and practically applicable to environmental problems. Electrical energy consumption is a very important economical parameter in the electrocoagulation process like all other electrolytic systems. Parameters which are commonly explored in batch studies include synthetic wastewater characteristics, such as supporting electrolyte, initial concentration, and solution pH variation, and process variables, such as operating time, applied voltage, and electrode materials. The effect of three operational parameters (applied voltage, supporting electrolyte, and initial concentration) on specific energy consumption under the optimum conditions was evaluated in this study. In addition, the kinetic constants for indium (III) ion removal at various applied voltages were determined. Finally, the composition of the sludge produced was determined by energy dispersion spectra (EDS).

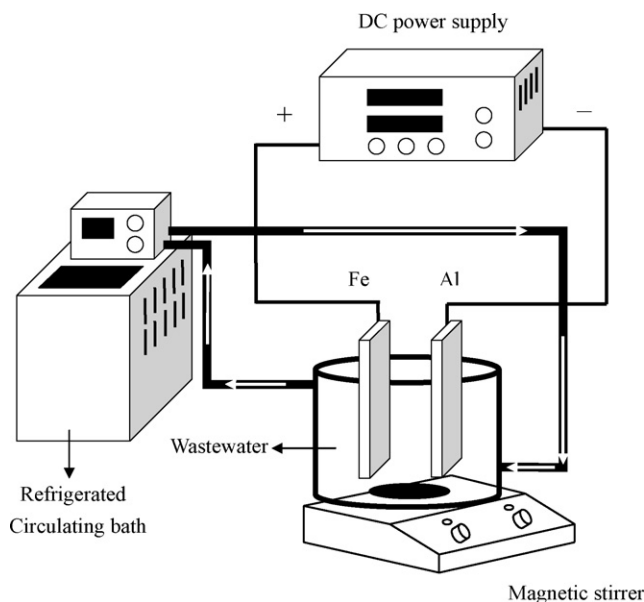


Fig. 1. Apparatus of the electrocoagulation process.

2. Experimental

2.1. Experimental device

A schematic diagram of the experimental apparatus and the electrode assembly for the electrocoagulation system is shown in Fig. 1. The electrolytic cell was a 1-l pyrex glass reactor which was equipped with a water jacket and a magnetic stirrer. The temperature of the electrolytic cell was controlled by continuously circulating water through the water jacket from a refrigerated circulating bath (Model BL-720, Taiwan). A magnetic stirrer bar (Corning, PC-420D, MALAYSIA) was rotated at the center of the bottom of the reactor. Cast iron (Fe) and aluminum (Al) plates (8 cm × 4 cm × 0.3 cm) were used in four different combinations as the anode/cathode pair. The electrode pair was dipped in synthetic wastewater to a depth of 4.5 cm, with the electrodes approximately 2 cm apart. The effective area of the electrode pair was 18 cm². Electrical voltage was provided by a manually controllable DC power supply (Model GC50-20D, Taichung, Taiwan) operating in the constant-voltage mode (range: 0–50 V). Characterization of the synthetic wastewater, such as pH (Y.S.I, pH 10, USA) and conductivity (EUTECH, cyberscan 510, Singapore), were determined using ROC EPA standard methods.

2.2. Chemicals and reagents

The standard reference material used in the experiments was the indium standard solution (from NIST, In(NO₃)₃ in HNO₃ 0.5 mol/l) from Merck (Darmstadt, Germany) with purity of at least 99%. The synthetic wastewater containing indium ions was prepared using deionized water. The conductivity of solutions was raised and adjusted by the addition of NaCl (Tedia Company, USA). Each sample concentration of indium (III) ion was measured three times with a flame atomic absorption spectrophotometer (AA-200, PerkinElmer). The wavelength was set at the 303.9 nm resonance line for indium. The calculation of indium (III) ion removal efficiency after electrocoagulation treatment was performed using this formula:

$$R(\%) = \frac{C_0V_0 - C_tV_t}{C_0V_0} \times 100 \quad (1)$$

where C_0 is the initial concentration in milligrams per liter, C_t is the concentration value at time t in milligrams per liter, V_0 is the initial volume of the treated wastewater in liters, and V_t is the volume of the treated wastewater at time t in liters. The sludge produced by the electrochemical process was analyzed by X-ray microanalysis. The analysis was performed on Phillips XL-30 microscope combined with energy dispersion spectra to determine the composition of the sludge.

2.3. Experimental procedure

Before each experiment, the electrodes were polished with sand paper to remove scale, then dipped in 3 M HCl to a depth of 6 cm for 10 min, and then cleaned with water. For each test run, the reactor was a circular container with 0.5 l of synthetic wastewater. The magnetic stirrer was turned on and set at 300 rpm. A steady temperature of 25 °C was maintained for all test runs. The stirrer speed was found to be sufficient to provide good mixing in the electrolytic cell and yet not strong enough to break up the flocs formed during the treatment process. A fixed amount of between 50 and 200 mg/l (NaCl) was added to the solution to increase the solution conductivity to facilitate the electrocoagulation treatment. The reaction was timed, starting from when the D.C. power supply was switched on. During electrocoagulation with an iron electrode, an oxide film was formed at the anode. In order to overcome electrode passivation at the anode, the electrodes were rinsed in diluted HCl solution after the each experiment. An electrocoagulation test run lasted 90 min in all experiments. Particulates of colloidal ferric oxyhydroxide were produced, making the aqueous solution yellow–brown after electrocoagulation. Samples were periodically taken from the reactor to deposit for 1 h in a 10 ml Pyrex glass column. After electrocoagulation treatment, the conductivity and pH of synthetic wastewater were measured with a multi-meter and pH meter, respectively. All samples were measured in duplicate to ensure data reproducibility, and an additional measurement was carried out if necessary.

2.4. A brief description of the iron electrocoagulation

Electrocoagulation requires only simple equipment. Its advantages include easy operation, brief reactive retention period, and a decreased amount of sludge. If iron electrodes are used, the generated Fe ions immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. Fe^{2+} ions are commonly produced during the dissolution of iron. In contrast, OH^- ions are generated at the cathode. By mixing the solution, hydroxide species are produced which cause the removal of waste by adsorption and coprecipitation. At a low pH, Fe^{2+} is easily converted to Fe^{3+} . The $\text{Fe}(\text{OH})_m$ (where $m=2$ or 3) formed remains in the aqueous solution as a gelatinous suspension, which can remove waste matter from wastewater either by complexation or by electrostatic attraction followed by coagulation. Ferric ions generated by the electrochemical oxidation of the iron electrode may form monomeric ions, $\text{Fe}(\text{OH})_3$, and hydroxyl complexes with hydroxide ions and polymeric species, namely, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+$, $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$, and $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{4+}$. Formation of these complexes strongly depends on the solution pH [26].

3. Results and discussion

3.1. Comparison of electrode pairs

In any electrochemical process, different electrode materials and the type of electrode pair are regarded as significant factors affecting the performance of the electrocoagulation process [27].

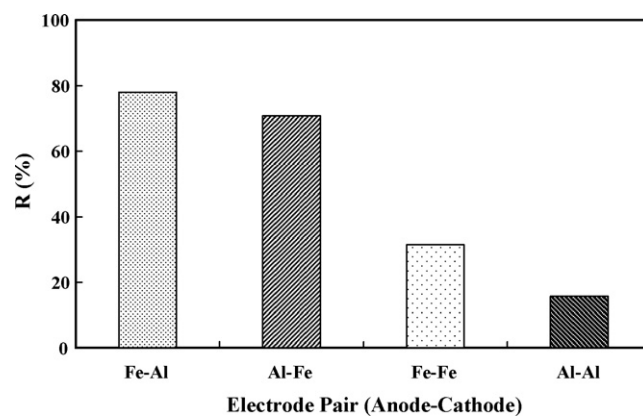


Fig. 2. Effect of different electrode pairs on the removal efficiency of indium (III) ion (initial pH 2.5, $C_0 = 20$ mg/l, $t = 90$ min, $V = 20$ V, $T = 25$ °C, $d = 2$ cm NaCl = 100 mg/l, agitation speed = 300 rpm).

Therefore, appropriate selection of the electrode pair is important. Iron and aluminum plates in four different combinations were investigated in this study to determine the optimum electrode pair. Fig. 2 illustrates the effect of different electrode pairs on the removal efficiency of indium (III) ions. As can be seen in this figure, relatively high removal efficiency indicated that the iron anode and aluminum cathode were the optimum electrode pair after 90 min of electrolysis. The removal efficiency of indium (III) ions was achieved in approximately 78.3, 70.1, 31.4, and 15.8% for Fe/Al, Al/Fe, Fe/Fe, and Al/Al electrode pairs, respectively. It also indicated that the Fe/Al pair yielded the best removal efficiency of indium (III) ions, followed by the Al/Fe, Fe/Fe, and Al/Al pairs. Fe/Al can be explained by the chemical reactions taking place at the aluminum anode and the iron anode as follows.

For Al anode:



For Fe anode:



The nascent aluminum and iron ions are very efficient coagulants for particulates to flocculate. From the above two reactions, we can calculate the electrochemical equivalent mass for Al and Fe. Consequently, for aluminum, the electrochemical equivalent mass is 335.6 mg/Ah. For iron, the value is 1041 mg/Ah, about three times that of aluminum. That is, more coagulants are theoretically produced for iron anodes when the same electric charge is passed. This is probably the reason for the iron anode removal efficiency being higher. All subsequent electrocoagulation experiments were conducted using the Fe/Al electrode combination.

3.2. Effect of supporting electrolyte concentration

In electrochemical processes which consist of heterogeneous ion transfer reactions, the conductivity of the solution to be treated is a significant parameter. Solution conductivity affects the current efficiency, applied voltage, and consumption of electrical energy in electrolytic systems, because the current passing through the circuit is a function of the conductivity under a certain applied voltage. The most common method used to overcome this problem is to add a small amount of electrolyte, which increases the electric conductivity of the solution and thus reduces the energy consumption during electrocoagulation. Conductivity of the solution increases as the supporting electrolyte concentration increases, so current passing through the circuit increases in potentiostatic mode [28].

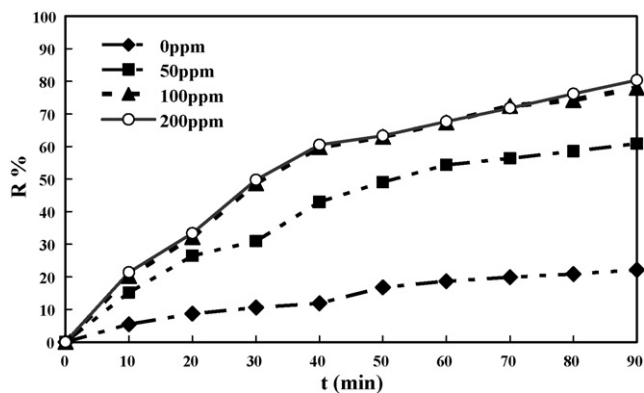


Fig. 3. Effect of supporting electrolyte concentration on the removal efficiency of indium (III) ion (initial pH 2.5, $C_0=20$ mg/l, $t=90$ min, $V=20$ V, $T=25$ °C, $d=2$ cm, agitation speed = 300 rpm).

In this study, sodium chloride (NaCl) was used as the supporting electrolyte for increasing the conductivity of the aqueous solution. The effect of various supporting electrolyte concentrations on the removal efficiency of indium (III) ion is demonstrated in Fig. 3. In general, after 90 min of electrolysis, the addition of the supporting electrolyte (NaCl) led to an increase in removal efficiency by a factor of 3–4, yielding around 60–80% indium (III) ion removal. This suggests that the presence of the supporting electrolyte makes indium (III) ion removal more efficient. When the concentration of supporting electrolyte increased from 0 to 50, 100, and 200 ppm, the removal efficiency improved markedly from 22.1 to 60.9, 78.3, and 80.3%, respectively. This was due to the Cl^- anions destroying the passivation layer and catalyzing the dissolution of the electrode material by pitting corrosion phenomenon, which is a type of localized corrosion caused by a high chloride concentration in the solution. Localized corrosion of iron, aluminum, and other similar metals [29] takes place through: (i) the adsorption of the aggressive anions such as Cl^- on the oxide layer due to ion–ion force of interaction; (ii) the chemical reaction of the adsorbed Cl^- with ions in the oxide layer; (iii) the dissolution or thinning of the layer; and (iv) the direct attack of the exposed metal, starting intense localized dissolution (localized corrosion). The de-passivation effect was more significant when more Cl^- anions were added to the solution. Therefore, it was expected that, electrocoagulation in the presence of NaCl might improve the removal efficiency of indium (III) ion by increasing the available metal coagulant in the solution due to the reduction of the oxides layer and the enhancement of anodic dissolution of the electrode material. In addition, the problem of electrode passivation was partially solved when NaCl was used as the supporting electrolyte. However, no significant improvement in the removal efficiency was observed when the concentration of the supporting electrolyte was above 100 ppm. When the concentration of the supporting electrolyte was increased from 100 to 200 ppm, the removal efficiency stayed at around 78.3–80.3%. Consequently, a value of 100 ppm concentration of the supporting electrolyte was chosen as the optimum concentration for the following electrocoagulation experiments.

3.3. Effect of initial concentration

The synthetic wastewater containing initial indium (III) concentrations in the range of 20–100 mg/l was treated and the removal efficiencies of metal ions were measured at different times of electrolysis by electrocoagulation. Fig. 4 indicates the effect of initial indium (III) ion concentration present in the aqueous solution on the removal efficiency for various durations of electrolysis. It can be seen evidently that increasing the initial indium (III) ion con-

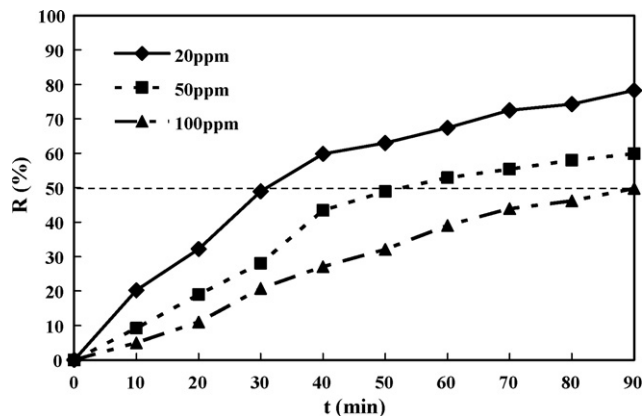


Fig. 4. Effect of initial concentration on the removal efficiency of indium (III) ion (initial pH 2.5, $t=90$ min, $V=20$ V, $T=25$ °C, $d=2$ cm, NaCl = 100 mg/l, agitation speed = 300 rpm).

centration from 20 to 100 mg/l led to a decrease in the removal efficiency of indium (III) ion after 90 min of electrolysis from 78.3 to 49.8%. As can be also seen in Fig. 4, the removal efficiency of indium (III) ions was achieved around 50% after 30, 50, and 90 min of electrocoagulation for initial concentrations of 20, 50, and 100 mg/l, respectively. This could be attributed to the constant amount of coagulant dissolving from the iron anode that passed to the solution at the same applied voltage and electrolysis time for all indium (III) ion concentrations. Consequently, the same amount of floc was produced in the aqueous solution. Therefore, this was probably because the hydroxyl and metal ions produced on the electrodes at high indium (III) ion concentrations were insufficient to absorb the entire indium (III) ion of the solution at a constant applied voltage.

3.4. Effect of applied voltage

Among the various operating variables, the applied voltage is an important factor which strongly influences the performance of electrocoagulation. The effect of applied voltage on the removal efficiency of indium (III) ions was studied at 10, 20, and 30 V. Fig. 5 illustrates the effect of the applied voltage on the removal efficiency of indium (III) ions for various durations of electrolysis. As the electrolysis time increases, comparable enhancements in the removal efficiency of indium (III) ion were observed. Fig. 5 shows that the removal efficiency of indium (III) ion was achieved to 50.4, 78.3, and 81.3% after 90 min of electrolysis 10, 20, and 30 V, respectively. As the applied voltage increased, the removal efficiency of indium

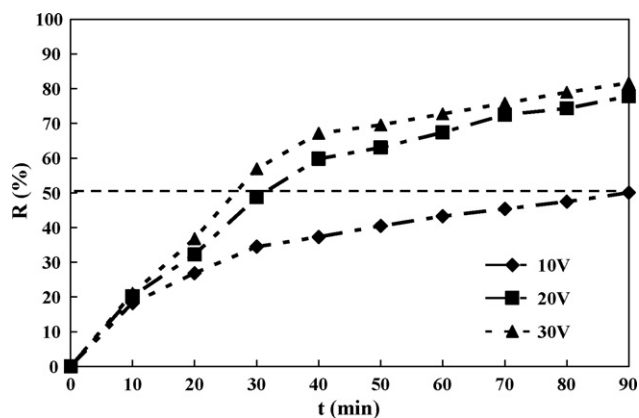


Fig. 5. Effect of applied potential on the removal efficiency of indium (III) ion (initial pH 2.5, $C_0=20$ mg/l, $t=90$ min, $T=25$ °C, $d=2$ cm, NaCl = 100 mg/l, agitation speed = 300 rpm).

(III) ions increased. Simultaneously, the sufficient current passing through the solution rose due to the increased applied voltage. Due to sufficient current through the solution, the metal ions generated by the dissolution of the sacrificial electrode were hydrolyzed to form a series of metallic hydroxide species. However, it took a longer time to reach over 50% indium (III) ion removal for an applied voltage of 10 V. This is due primarily to an insufficient amount of electric power supplied at 10 V for the complete destabilization of the suspended metallic hydroxide species in the solution. Therefore, both 20 and 30 V are suitable operating voltages for this electrocoagulation experiment, requiring treatment times to reach over 50% indium (III) ion removal of 30 min, and 25 min, respectively. As time progressed and dissolved coagulants at the iron electrode increased, there was an increase in the removal efficiency, which could be explained by a sufficient amount of coagulant dissolving from the iron electrode to effectively reduce the double layer of the suspended metallic hydroxide species to destabilize the metallic hydroxide species. However, slightly improvement in removal efficiency was observed when the applied voltage was increased from 20 to 30 V. In order to investigate the optimum applied voltage, the performance of the specific energy consumption at an applied voltage during electrocoagulation was evaluated, as shown in the following section.

3.5. Effect of the variation of pH during electrocoagulation

When dissolved in water, indium nitrate ($\text{In}(\text{NO}_3)_3$) solution indicates the pH at equilibrium from 2.4 to 2.6. As observed in previous investigations [23], electrocoagulation treatment induces a pH increase. Fig. 6 shows the variation of pH at applied voltages of 10, 20, and 30 V during electrocoagulation. As can be seen in this figure, initially the solution pH increases at a high rate and then the rate falls regardless of applied voltage value. The pH increases at higher applied voltages (20 or 30 V) were faster than at a lower applied voltage (10 V). After 40 min of electrolysis, the pH raised from 2.5 to 4.9, 6.5, and 6.7 when the applied voltage was adjusted to 10, 20, and 30 V, respectively. The corresponding indium (III) ion removal efficiencies were performed at 37.3, 59.8, and 67.2%, respectively, as shown in Fig. 5. These observations could be implied that the generation of coagulant iron hydroxides is higher for 20 and 30 V applied voltages, which induced that removal efficiency of indium (III) ion was increased at a faster rate due to such higher coagulant generate rate and the better removal efficiency was achieved in case of higher applied voltage (20 or 30 V), resulting in a higher solution pH. Therefore, higher pH at higher applied voltage (20 or 30 V) enhanced the precipitation of indium (III) ion as insoluble

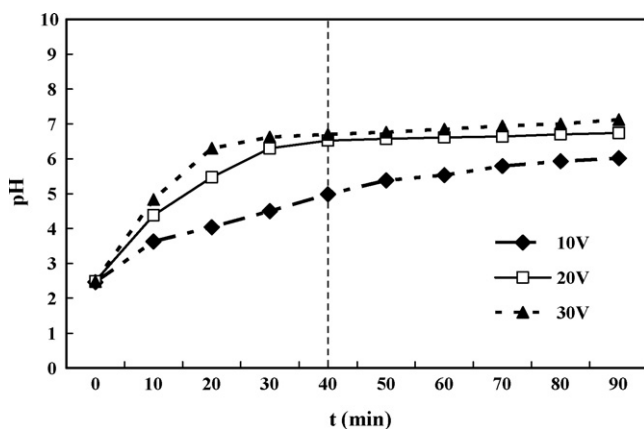


Fig. 6. Effect of applied voltage on the variation of pH during electrocoagulation process (initial pH 2.5, $C_0 = 20 \text{ mg/l}$, $t = 90 \text{ min}$, $T = 25^\circ \text{C}$, $d = 2 \text{ cm}$, $\text{NaCl} = 100 \text{ mg/l}$, agitation speed = 300 rpm).

indium hydroxide, which was a favorable factor in improving the removal efficiency of indium (III) ions. These observations agree with a previous report that showed that the formation of indium hydroxide and at high pH values ($\text{pH} > 6$) – induced hydrolysis of indium (III) ion solution, causing precipitation well before the $\text{OH}^-/\text{In}^{3+}$ ratio reached 3 [30].

3.6. Evaluation of specific energy consumption

Energy consumption is a very important economical parameter in the electrocoagulation process. Once the required voltages and the corresponding currents were obtained from the electrocoagulation experimental tests, it was possible to estimate the amount of energy consumed. Therefore, consider the initial and final concentrations of indium (III) ion in aqueous solution at different times. The specific energy consumption (SEC) was calculated as a function of 1 kg indium (III) ion removal during electrocoagulation in kWh/kg with constant applied voltage using the following equation:

$$\text{SEC} = \frac{\int U \times I dt}{(C_0 V_0 - C_t V_t) \times 216} = \frac{U \int I dt}{(C_0 V_0 - C_t V_t) \times 216} = \frac{U \times I_{\text{avg}} \times \Delta t}{(C_0 V_0 - C_t V_t) \times 216} \quad (4)$$

where U , I_{avg} , and Δt are the applied voltage (V), average current (A), and electrolysis time (min), respectively. In addition, C_0 is the initial concentration in milligrams per liter, C_t is the concentration value at time t in milligrams per liter, V_0 is the initial volume of the treated wastewater in liters, and V_t is the volume of the treated wastewater at time t in liters. In order to investigate the optimum balance with reasonable removal efficiency and relatively low energy consumption, the performance of the specific energy consumption on supporting electrolyte, applied voltage, and addition of supporting electrolyte during electrocoagulation were optimized in the subsequent section.

3.6.1. Effect of supporting electrolyte on removal efficiency and specific energy consumption

The concentration of supporting electrolyte was adjusted to the desired levels by adding a suitable amount of NaCl to the synthetic wastewater. Fig. 7 illustrates the effect of the supporting electrolyte on the removal efficiency and specific energy consumption during the electrocoagulation process. It can be seen evidently that increasing the concentration of the supporting electrolyte from 0 to 200 ppm leads to an increase in indium (III) ion removal efficiency, whereas with the concentration of the supporting elec-

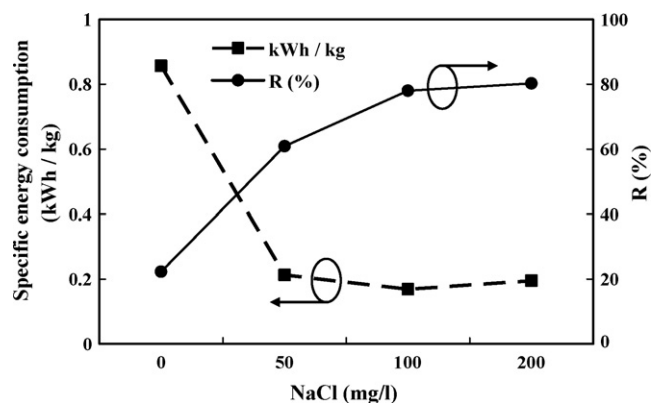


Fig. 7. Effect of supporting electrolyte on the removal efficiency of indium (III) ion and specific energy consumption (initial pH 2.5, $C_0 = 20 \text{ mg/l}$, $t = 90 \text{ min}$, $V = 20 \text{ V}$, $T = 25^\circ \text{C}$, $d = 2 \text{ cm}$, agitation speed = 300 rpm).

trolyte increasing, the specific energy consumption decreased by almost 80%. When the concentration of the supporting electrolyte increases, the solution ohmic resistance decreases, so the current required to reach the optimum applied voltage diminishes, decreasing the consumed energy. From the specific energy consumption shown in Fig. 7, 100 ppm NaCl was regarded as the optimum balance, with a reasonable removal efficiency at relatively low specific energy consumption.

3.6.2. Effect of applied voltage on removal efficiency and specific energy consumption

The synthetic wastewater with applied voltages in the range of 10–30 V was treated in terms of removal efficiency and the specific energy consumption by iron electrocoagulation. The effect of the applied voltage on the performance of removal efficiency and specific energy consumption is shown in Fig. 8. Apparently, it can be seen that an increase in the applied voltage from 10 to 30 V led to a corresponding increase in indium (III) ion removal efficiency from 50.1 to 81.7%. Fig. 8 also indicates that the specific energy consumption decreased from 0.182 to 0.159 kWh/kg when the applied voltage was increased from 10 to 20 V. There was an upward trend when the applied voltage was above 20 V. For example, by increasing the applied voltage from 20 to 30 V, the specific energy consumption increased from 0.159 to 0.192 kWh/kg. Consequently, when considering on the performance of the removal efficiency and specific energy consumption simultaneously, the applied voltage of 20 V seems to offer the best overall performance for the present electrocoagulation with reasonable removal efficiency and relatively low specific energy consumption.

3.6.3. Effect of initial concentration on removal efficiency and specific energy consumption

The synthetic wastewater with initial concentrations in the range of 20–100 mg/l was treated in terms of removal efficiency and specific energy consumption by iron electrocoagulation. Fig. 9 shows the effect of initial indium (III) ion concentration present in the solution on the performance of the electrocoagulation process. When the initial indium (III) ion concentration increased from 20 to 100 mg/l, the corresponding removal efficiency decreased from 78.3 to 49.8%, respectively. This observation may be attributed to more coagulant produced by the electrodes at high levels of concentration being inadequate to adsorb all of the indium (III) ions of the synthetic wastewater. Fig. 9 also demonstrates that the specific energy consumption increased from 0.169 to 0.435 kWh/kg when the initial indium (III) ion concentration increased from 20 to 100 mg/l.

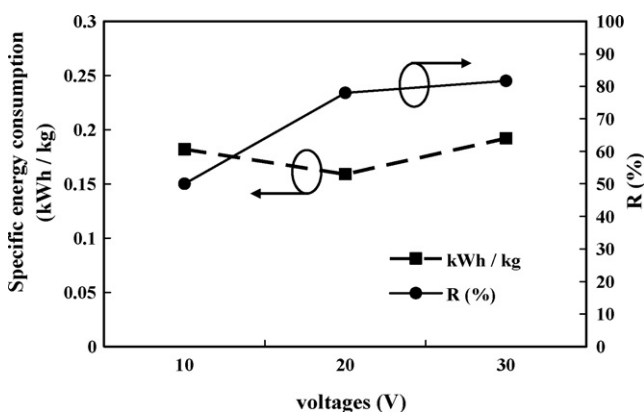


Fig. 8. Effect of applied voltages on the removal efficiency of indium (III) ion and specific energy consumption (initial pH 2.5, $C_0 = 20$ mg/l, $t = 90$ min, $T = 25$ °C, $d = 2$ cm, NaCl = 100 mg/l, agitation speed = 300 rpm).

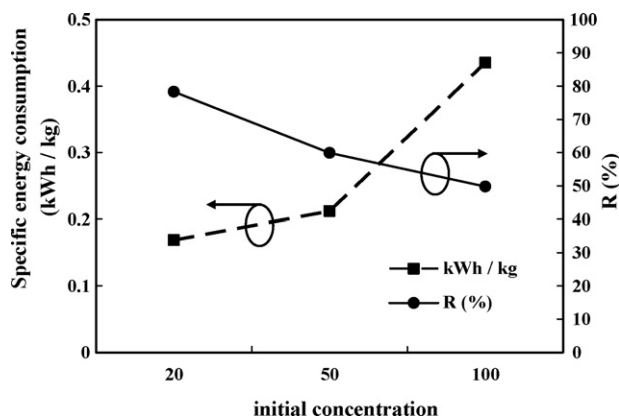


Fig. 9. Effect of the initial concentration on the removal efficiency of indium (III) ion and specific energy consumption (initial pH 2.5, $t = 90$ min, $V = 20$ V, $T = 25$ °C, $d = 2$ cm, NaCl = 100 mg/l, agitation speed = 300 rpm).

3.7. Indium (III) ion removal kinetics of the Fe electrocoagulation

The overall electrocoagulation process in indium (III) ion removal apparent kinetics is described by a macro-kinetics model in which the rate constant depends on the applied voltage (current density). This model provides preliminary data for evaluating the reaction rate constants. The kinetic rate equation for representing the removal rate in indium (III) ion concentration from the aqueous solution is described by the following m th order reaction kinetics:

$$\frac{dC}{dt} = -kC^m \quad (5)$$

where C represents the indium (III) ion concentration, m is the order of reaction, k is the reaction rate constant, and t is the time. For a first-order reaction, the above Eq. (5) becomes:

$$\ln\left(\frac{C_t}{C_0}\right) = -k_1 t \quad (6)$$

The slope of the plot of $\ln C_t/C_0$ versus time gives the value of the rate constant k_1 , min^{-1} . Here, C_0 is the initial concentration in milligrams per liter, C_t is the concentration value in milligrams per liter at time t , and t is the time.

For a second-order reaction, the above Eq. (6) becomes:

$$\frac{1}{C_t} - \frac{1}{C_0} = k_2 t \quad (7)$$

The slope of the plot of $1/C_t$ versus time gives the value of the rate constant k_2 , $1/(\text{mg min})$. The values of k with first-order and second-order models for indium (III) ion removal at various applied voltages were determined graphically and are shown in Table 1, respectively. The conformity between experimental data and the model values was evaluated by the correlation values (r^2). As can be seen in Table 1, regardless of the applied voltage, the r^2 value for the second-order model was relatively higher than that for the first-order model. The second-order kinetic model fits well with the observed data of the electrocoagulation process. With other exper-

Table 1
Kinetic rate constants with first-order and second-order models for indium (III) ion removal at various applied voltages.

Applied voltages	Parameters			
	First-order model		Second-order model	
	$k_1 \times 10^3$ (min^{-1})	r^2	$k_2 \times 10^3$ ($1/(\text{mg min})$)	r^2
10 V	4.4	0.94	0.3	0.98
20 V	14.2	0.96	1.7	0.99
30 V	16.2	0.94	2.2	0.99

Table 2
Characteristics of the sludge in atomic (%).

Element	Atomic (%)
O	51.44
Al	5.39
Si	0.76
Cl	2.60
Fe	39.40
In	0.41

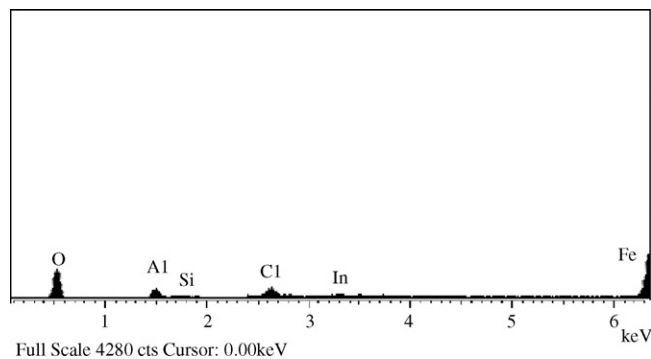


Fig. 10. Energy dispersive X-ray spectra of the sludge produced during the electrochemical process. Note that the iron is present in the sludge.

imental conditions fixed, when the applied voltage increased from 10 to 30 V, the second-order rate constant increased from 0.3 to 2.2 l/(mg min). It is very important to note that very fast indium (III) ion removal took place at a short electrolysis time; this is considered a great advantage of using the electrocoagulation process.

3.8. Sludge composition

The sludge production is another important parameter in characterizing the electrocoagulation process. Table 2 shows the composition of the sludge. The high concentration of Fe confirms that the iron was in the aqueous solution inducing particle destabilization and oxidation. This result was confirmed with energy dispersion spectra analysis. The composition analysis of the sample by energy dispersion spectra shown in Fig. 10 indicates that O, Al, Si, Cl, Fe and In are present in the sludge, confirming that the colloidal matter formed the sludge.

4. Conclusion

The electrochemical removal of indium (III) ion in synthetic wastewater was investigated in a batch electrocoagulation system. The removal efficiency of indium (III) ion was approximately 78.3, 70.1, 31.4, and 15.8% for Fe/Al, Al/Fe, Fe/Fe, and Al/Al electrode pairs, respectively. Due to its the superior removal efficiency of indium (III) ions, the Fe/Al electrode pair was deemed to be the best choice of the four electrode combinations verified in this study. The addition of NaCl as a supporting electrolyte at 100 mg/l was regarded as the optimum balance, with reasonable removal efficiency at relatively low specific energy consumption. It was found that increasing the initial indium (III) ion concentration from 20 to 100 mg/l led to a decrease in the removal efficiency of indium (III) ion after 90 min of electrolysis from 78.3 to 49.8%. In terms of the performance of the removal efficiency and specific energy consumption, the applied voltage of 20 V was found to be the optimum overall considerations for the present electrocoagulation, with reasonable removal efficiency and relatively low specific energy consumption. Our experiment results indicate that the kinetics of the indium (III) ion removal

can be described by the pseudo second-order model. Values of kinetic rate constants for indium (III) ion removal at various applied voltages were calculated. The kinetics results show that a pseudo second-order kinetic model was in good agreement with the experimental data. Finally, the element analysis of the sludge is revealed by energy dispersion spectra, and shows the presence of O, Al, Si, Cl, Fe and In as its constituents.

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