



Electrochemical removal of indium ions from aqueous solution using iron electrodes

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ABSTRACT

The removal of indium ions from aqueous solution was carried out by electrocoagulation in batch mode using an iron electrode. Various operating parameters that could potentially affect the removal efficiency were investigated, including the current density, pH variation, supporting electrolyte, initial concentration, and temperature. The optimum current density, supporting electrolyte concentration, and temperature were found to be 6.4 mA/cm², 0.003N NaCl, and 298 K, respectively. When the pH values lower than 6.1, the removal efficiencies of indium ions via electrocoagulation were up to 5 times greater than those by adding sodium hydroxide. The indium ion removal efficiency decreased with an increase in the initial concentration. Results for the indium ion removal kinetics at various current densities show that the kinetic rates conformed to the pseudo-second-order kinetic model with good correlation. The experimental data were also tested against different adsorption isotherm models for describing the electrocoagulation process. The adsorption of indium ions preferably fitting the Langmuir adsorption isotherm suggests monolayer coverage of adsorbed molecules.

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1. Introduction

Silicon is the predominantly used substrate in the microelectronics industry. In recent years, however, a number of other semiconductor materials (e.g., III–V semiconductors InAs, InP, GaAs, and GaP) have been used in place of silicon and been employed in many device applications such as light emitting diodes, semiconductor laser diodes, solar cells, optical computer, and liquid crystal displays [1]. Indium is a group IIIA metallic element and has emerged as an important strategic metal that is extensively used in high-tech industries. Indium is a crystalline, ductile, very soft, and malleable metal that retains its high plastic properties at cryogenic temperatures [2]. Indium and its compounds exhibit semiconductor or optoelectronic characteristics, which are used in the production of liquid crystal display, semiconductor, low-pressure sodium lamp, and infrared photo-detector [3]. 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 excellent transparent and conductive material that has been widely used in the making of thin-film transistor liquid crystal display (TFT-LCD) for television screens, portable computer screens, and cell phone displays. Because of the demand for TFT-LCD, and

semiconductor materials, the consumption of ITO and indium is increasing. Indium and its compounds have been found in the etching wastewater discharged from semiconductor or optoelectronic plants, and they are suspected to be carcinogenic to humans and damage the heart, kidney, and liver [4]. Therefore, there is a growing interest in the development of new method for the removal of indium. Most studies related to the extraction of metal ions from solid and liquid samples have employed chelation combined with solvent extraction [1,5–8]. However, these solvent extraction procedures are usually time-consuming and labor-intensive. This method is also unfavorable owing to the environmental contamination associated with the use of chemical solvents and its resulting health risks. In addition, strict new regulatory requirements on the use of organic solvents worldwide, motivated by health and environmental concerns, have prompted studies relating to the removal and separation of indium ions using methods such as electroanalytical techniques [9], coprecipitation [10], nanofiltration membranes [11], solid phase extraction [12], supercritical CO₂ extraction [13], and the use of extraction resin [1,14]. However, there is scant research on the development of an electrochemical treatment for the removal of indium ions aside from our earlier study [15].

Over the past 10 years, electrochemical techniques have been largely developed for their use in alternative wastewater remediation and their applications to environmental pollution abatement [16–18]. These methods can prevent pollution problems due to industrial discharges because of their versatility and environmen-

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tal compatibility. Electrons are considered as a clean reagent [19]; thus, an electrochemical treatment (e.g., electrocoagulation) is proposed for wastewater containing indium ions in the present study. Coagulation is a traditional treatment for the decontamination of wastewaters before discharge. This technique has advantages compared with conventional methods: high energy efficiency, easy operation, simple equipment, rapid sedimentation of the electrogenerated flocks, less sludge production, and safety. Electrocoagulation is the electrochemical production of destabilization agents that leads to charge neutralization for pollutant removal. This technology mainly uses an applied current to dissolve iron or aluminum sacrificial anodes immersed in the polluted water, giving rise to the corresponding metal ions and hydroxide ion, which yield different species such as hydrous ferric oxides and aluminum hydroxides. Electrochemically generated metallic ions can hydrolyze near the anode to form a series of metallic hydroxides capable of destabilizing dispersed particles. A coagulant species is believed to be the responsible for the aggregation as well as precipitation of dispersed particles and simultaneously the adsorption of dissolved pollutants. Pollutants can be removed by sedimentation to form slurry. In recent years, electrocoagulation has been proven to be a promising water treatment technology that has been used to treat potable water [20], urban wastewater [21], wastewater laden with heavy metals [22], restaurant wastewater [23], colored water [24], mechanical cutting oil [25], and wastewaters containing phosphate [26], fluoride [27], arsenic [28], and dispersed fine particles from chemical mechanical polishing [29,30]. A remarkable efficiency in removing heavy metals (e.g., Cr, Pb, Cu, Zn, and Ni) from wastewater using electrocoagulation has been reported [31]. To our knowledge, little information is available on treating wastewater containing indium ions by electrocoagulation.

An effective process must be economically feasible with regard to electric energy consumption and practically applicable to environmental problems. Electrical energy consumption is an important financial parameter in the electrochemical process. The effect of operational parameters (current density, supporting electrolyte, and temperature) on specific energy consumption under optimum conditions was evaluated in this study. Operational parameters such as current density, supporting electrolyte, pH variation, initial concentration, and temperature were also investigated in terms of the efficiency of indium ion removal. The kinetics of the electrocoagulation for indium ion removal at various current densities were determined using pseudo-first and second-order kinetic models. Finally, the equilibrium adsorption behavior was evaluated using Freundlich and Langmuir isotherm models.

2. Experimental

2.1. Materials and apparatus

The standard reference material used in the experiments was an indium standard solution (from NIST, 0.5 mol/L $\text{In}(\text{NO}_3)_3$ in HNO_3) from Merck (Darmstadt, Germany) with purity of at least 99%. Aqueous solutions containing indium ions were prepared by dissolving an appropriate quantity of indium nitrate in deionized water for electrocoagulation tests. The conductivity of the solutions was adjusted to desired values by adding NaCl (Tedia Company, USA). Fig. 1 is a schematic diagram of the experimental apparatus and the electrode assembly for the electrocoagulation system used in this work. The electrolytic cell equipped with a water jacket, having a dimension of 5 cm inner radius \times 12 cm depth was composed of Pyrex glass. A magnetic stirrer was used to agitate the solution. The agitation speed was 300 rpm. The temperature of the electrolytic cell was controlled by continuously circulating water

from a refrigerated circulating bath (BL-720, Taiwan) through the water jacket. The magnetic stirrer (Suntex, SH-301, Taiwan) was used in the reactor to maintain adequate mixing of the synthetic indium ion wastewater during the electrocoagulation process. From our previous studies on synthetic indium ion wastewater, we know that a cast iron (Fe)/aluminum (Al) electrode pair is the optimum choice for four electrode pair combinations [15]. Therefore, Fe plate of 8 cm \times 6 cm \times 0.3 cm was used as the anode and Al plate of 8 cm \times 6 cm \times 0.3 cm was used as the cathode. The connection of the electrodes was in a monopolar mode, in which there is an external electrical contact to each anode and cathode. The electrode pair was dipped in synthetic indium ion wastewater to a depth of 5.2 cm, with the electrodes positioned vertically 2 cm apart. The effective area of the electrode pair was 31.2 cm². The assembly was connected to a direct current power source (2400 Series Sourcimeter, Cleveland, OH, USA) to constitute an electrocoagulation cell with a galvanostatic mode for constant current supply (maximum source power of 22W). Characteristics of the indium ion aqueous solution, such as pH (Yellow Springs Instrument Co., pH 10, USA) and conductivity (Eutech, CyberScan 510, Singapore), were determined using the standard methods set out by the Republic of China Environmental Protection Administration [32].

2.2. Procedure and analysis

Before each experiment, the electrodes were abraded with sandpaper to remove scale, dipped in 3N HCl to a depth of 6 cm for 10 min, and finally cleaned with successive rinses of deionized water. During each test run, 0.5 L of aqueous solution containing indium ions was placed into the reactor. The magnetic stirrer stirred the wastewater at a speed of 300 rpm. The stirrer speed was found to be sufficient for proving good mixing in the electrolytic cell and yet was sufficiently low not to disrupt the flocks formed during the treatment process. A fixed amount (between 0.001 and 0.004N) of NaCl was added to the wastewater to increase the wastewater conductivity and thus facilitate the electrocoagulation treatment. The direct current power source was operated with constant current density of 3.2, 6.4, 9.6, or 12.8 mA/cm². A steady temperature of 288–318 K was maintained by circulating water from the refrigerated circulating bath through the water jacket. An electrocoagulation test run lasted 120 min in all experiments. Particulates of colloidal ferric hydroxide were produced, turning the aqueous solution yellow-brown after electrocoagulation. Samples were periodically taken from the reactor and allowed to settle for 24 h in a 10 ml Pyrex glass column. After electrocoagulation treatment, the conductivity and pH of synthetic wastewater were measured with a multimeter and pH meter, respectively. The concentration of indium ions in each sample was measured 3 times with a flame atomic absorption spectrophotometer (Perkin-Elmer, AA-200, USA). An indium hollow cathode lamp operated at 20 mA was used as the light source. The wavelength was set at the 303.9 nm resonance line for indium. The correlation coefficient of the calibration curves was generally 0.999. The calculation of the indium ion removal efficiency after electrocoagulation treatment was made using:

$$R(\%) = \frac{C_0 V_0 - C_t V_t}{C_0 V_0} \times 100 \quad (1)$$

where C_0 (mg/L) is the initial concentration, C_t (mg/L) is the concentration at time t , V_0 (L) is the initial volume of the treated wastewater, and V_t (L) is the volume of the treated wastewater at time t . All samples were measured in duplicate to ensure data reproducibility, and an additional measurement was carried out if necessary.

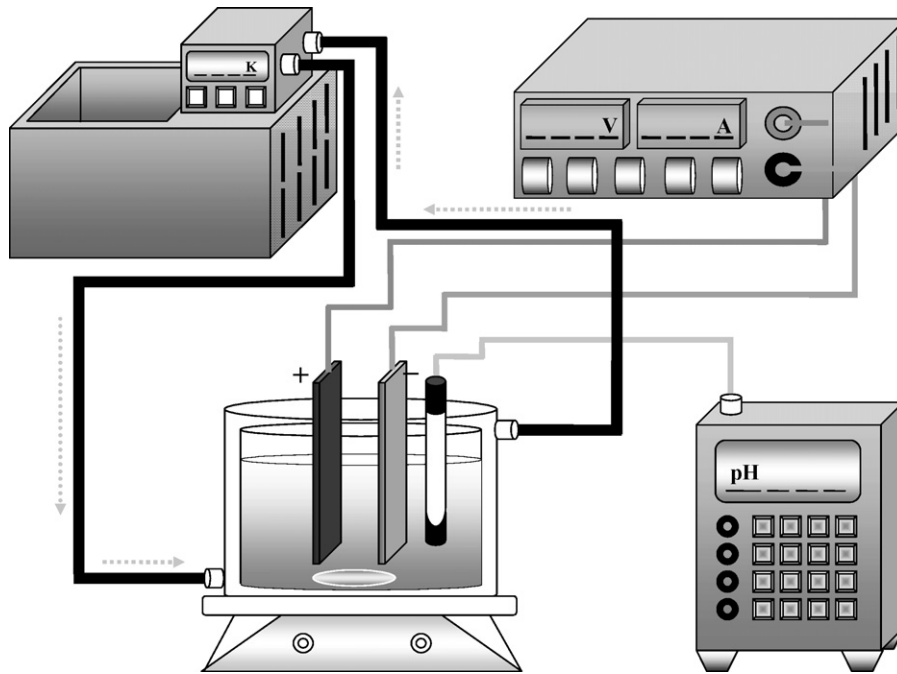


Fig. 1. Apparatus of the electrocoagulation process.

3. Results and discussion

3.1. Effect of current density

The current density strongly affects the performance of electrocoagulation. Current density was calculated as the applied current divided by the projected surface area of the studied electrode. The effect of current density on the removal efficiency of indium ions was studied at 3.2, 6.4, 9.6, and 12.8 mA/cm². Fig. 2 shows the effect of the current density on the removal efficiency of indium ions for various durations of electrolysis. As the duration of electrolysis increased, comparable enhancements in the removal efficiency of indium ions were observed for all current densities. It can be seen that the indium ion removal efficiency reached 61.2%, 90.4%, 94.7%, and 96.7% after 50 min of electrolysis at current densities of 3.2, 6.4, 9.6, and 12.8 mA/cm², respectively. As the current density increased, the removal efficiency of indium ions increased. With there being sufficient current flowing through the solu-

tion, the metal ions generated by the dissolution of the sacrificial electrode were hydrolyzed to form a series of metallic hydroxide species. The treatment times required to reach 90% indium ion removal were around 34, 39, 51, and 88 min for current densities of 12.8, 9.6, 6.4, and 3.2 mA/cm², respectively. However, it took longer to exceed 90% indium ion removal at a current density of 3.2 mA/cm². This is because the current density of 3.2 mA/cm² was insufficient to completely destabilize the suspended metallic hydroxides in the solution. As time progressed and the amount of dissolved coagulant at the iron electrode increased, there was an increase in the removal efficiency, which can be explained by a sufficient amount of coagulant dissolving from the iron electrode to effectively reduce the double layer of the suspended metallic hydroxides and destabilize the metallic hydroxides. However, a slight improvement in removal efficiency was observed when the current density was increased from 9.6 to 12.8 mA/cm². To investigate the optimum current density, the performance of the specific energy consumption at a certain current density during electrocoagulation was evaluated, with the results given in the following section.

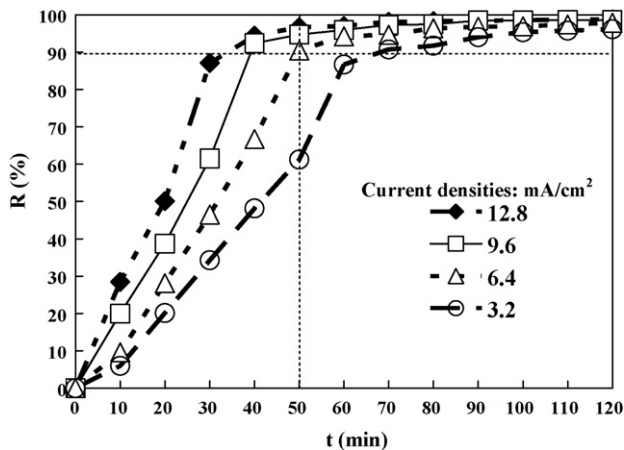


Fig. 2. Effect of current density on the removal efficiency of indium ions ($C_0=20$ mg/L, NaCl=0.003N, $t=120$ min, $T=298$ K, $d=2$ cm, and agitation speed=300 rpm).

3.1.1. Effect of current density on removal efficiency and specific energy consumption

It is critical to evaluate the electrical energy consumption in wastewater treatment to determine whether electrocoagulation is financially viable for the removal of indium ions from aqueous solution. Once the required currents and corresponding voltages were obtained from the electrocoagulation tests, the amount of energy used was estimated. The specific energy consumption SEC (kWh/kg) was calculated as a function of time for the removal of 1 kg of indium ions during electrocoagulation with constant applied current using:

$$SEC = \frac{\int I \times U dt}{(C_0 V_0 - C_t V_t) \times 3.6} = \frac{I \int U dt}{(C_0 V_0 - C_t V_t) \times 3.6} \quad (2)$$

where U , I , and t are the applied voltage (V), current (A), and electrolysis time (min), respectively. In addition, C_0 (mg/L) is the initial concentration, C_t (mg/L) is the concentration at time t , V_0 (L) is the initial volume of the treated wastewater, and V_t (L) is the volume of

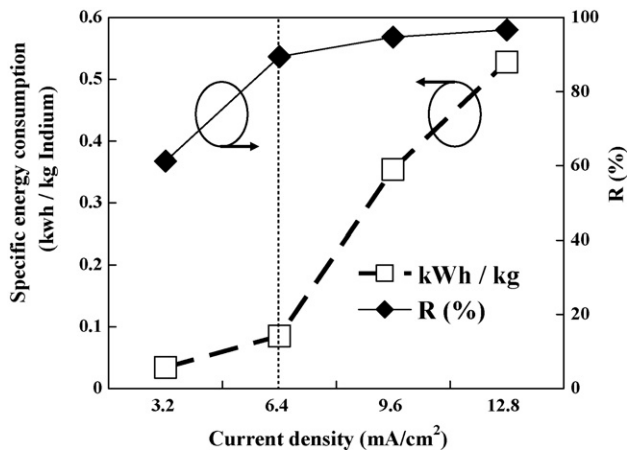


Fig. 3. Effect of current density on the removal efficiency of indium ions and specific energy consumption ($C_0 = 20$ mg/L, $\text{NaCl} = 0.003\text{N}$, $t = 50$ min, $T = 298$ K, $d = 2$ cm, and agitation speed = 300 rpm).

the treated wastewater at time t . A reasonable removal efficiency and relatively low energy consumption are determined below.

Indium ion solutions were treated by iron electrocoagulation at current densities in the range of 3.2–12.8 mA/cm² to determine the optimal removal efficiency and specific energy consumption. The effects of the current density on the performances of removal efficiency and specific energy consumption are shown in Fig. 3. It is seen that an increase in the current density from 3.2 to 12.8 mA/cm² led to a dramatic increase in the indium ion removal efficiency from 61.2% to 96.7%. When the current density was increased from 3.2 to 6.4 mA/cm², the indium ion removal efficiency increased appreciably from 61.2% to 90.4%, whereas the corresponding specific energy consumption increased only slightly. However, when the current density was increased from 6.4 to 12.8 mA/cm², the indium ion removal efficiency increased slightly from 90.4% to 96.7%, whereas the corresponding specific energy consumption increased significantly from 0.085 to 0.528 kWh/kg. Consequently, a current density of 6.4 mA/cm² provides the optimum performance for the present electrocoagulation system in that it results in reasonable removal efficiency and relatively low specific energy consumption.

3.2. Effect of the variation in pH during electrocoagulation

When dissolved in water, indium nitrate ($\text{In}(\text{NO}_3)_3$) solution has a pH at equilibrium from 2.2 to 2.4. As observed in previous investigations [28], electrocoagulation treatment induces a pH increase. Fig. 4 shows the variation in pH at current densities of 3.2, 6.4, 9.6, and 12.8 mA/cm² during electrocoagulation. As can be seen in the figure, initially the solution pH increased at a high rate and then the rate fell regardless of the current density. The pH increases at higher current densities were faster than those at lower current densities. After 50 min of electrolysis, the pH increased from 2.3 to 6.0, 6.3, 6.7, and 7.1 when the current density was 3.2, 6.4, 9.6, and 12.8 mA/cm², respectively. The corresponding indium ion removal efficiencies were 61.2%, 90.4%, 94.7%, and 96.7%, respectively, as shown in Fig. 2. These observations imply that the generation of coagulant iron hydroxides was greater at higher current densities, and thus the removal efficiency of indium ions was increased at a faster rate and better removal efficiency was achieved in the case of higher current density, resulting in a higher solution pH. Therefore, higher pH values enhanced the precipitation of indium ion as insoluble indium hydroxide, which was favorable in improving the removal efficiency of indium ions. As can be seen in Fig. 2, it was observed that the removal efficiency of indium ions increased as the duration of electrolysis progressed. The corresponding solution pH

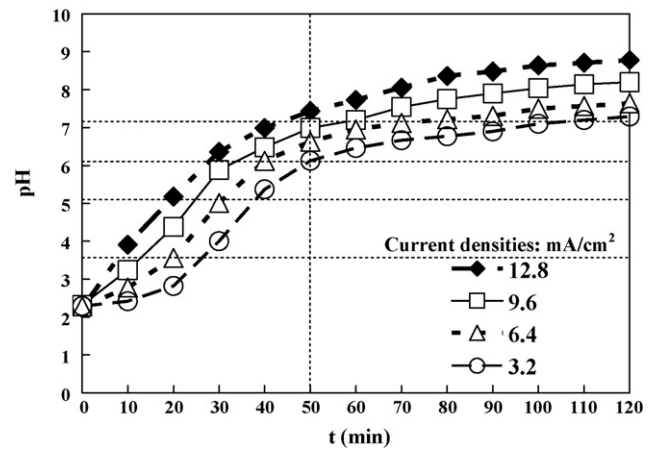


Fig. 4. Effect of current density on the variation of pH during electrocoagulation process ($C_0 = 20$ mg/L, $\text{NaCl} = 0.003\text{N}$, $t = 120$ min, $T = 298$ K, $d = 2$ cm, and agitation speed = 300 rpm).

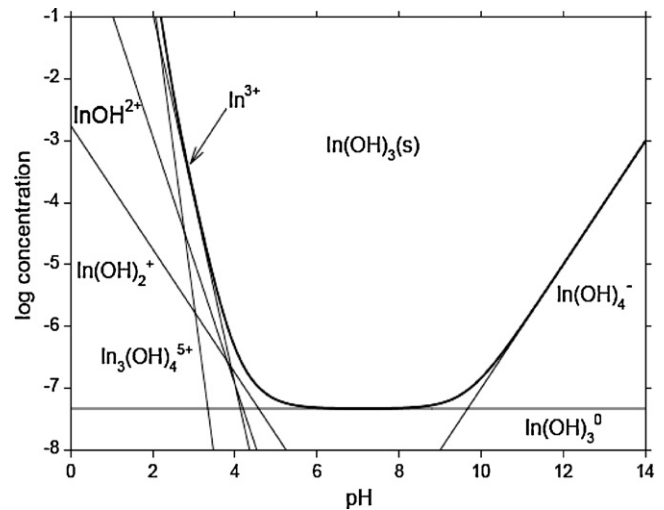


Fig. 5. Phase diagrams for In(III) chemical species in aqueous solution. The light lines show the concentrations of individual In(III) species in equilibrium with $\text{In}(\text{OH})_3(\text{s})$ and the heavy curve represents the total solubility [33].

increased for all current densities, as shown in Fig. 4. These observations agree with a previous report that showed the formation of indium hydroxide [33]. $\text{In}(\text{OH})_3$ is dominant species in the range of pH 5–10 according to predominance-zone diagrams for In(III) chemical species in aqueous solution, which is illustrated in Fig. 5 [33]. In the present study, $\text{In}(\text{OH})_3(\text{s})$ precipitated from the acidic solution of indium nitrate via OH^- generation at the cathode during electrolysis. A series of experiments were carried out to identify the dominant process for indium ion removal efficiency between electrogenerated OH^- at the cathode and OH^- by pH adjustment using sodium hydroxide. As can be seen in Table 1, the indium ion removal efficiencies were 4.7%, 9.9%, 43.5%, and 59.9% when the pH value of solution was adjusted to different values of 3.6, 5.1, 6.1, and 7.2, respectively. Under the same pH value of solution, the corre-

Table 1

Comparison of indium ion removal efficiencies between electrocoagulation and sodium hydroxide at various pH values of solution.

Parameters	pH values of solution			
	3.6	5.1	6.1	7.2
Sodium hydroxide	4.7%	9.9%	43.5%	59.9%
Electrocoagulation	28.5%	50.1%	76.1%	96.4%

sponding indium ion removal efficiency by electrocoagulation was approximately 28.5%, 50.1%, 76.1%, and 96.4%, respectively. Consequently, it was observed that the indium ion removal efficiencies by electrogenerated OH^- at the cathode were greater than those by indium hydroxide precipitation using sodium hydroxide at various values of solution pH. When the pH values lower than 6.1, the removal efficiencies of indium ions via electrocoagulation were up to 5 times greater than those by adding sodium hydroxide.

3.3. Effect of the supporting electrolyte concentration

Intentionally adding a small amount of electrolyte to the wastewater increases the solution conductivity and thus reduces the energy consumption during electrocoagulation. Solution conductivity increases as the supporting electrolyte concentration increases, so the current passing through the circuit increases in the potentiostatic mode [34]. In this study, NaCl was used as the supporting electrolyte for increasing the solution conductivity. The effect of various supporting electrolyte concentrations on the removal efficiency of indium ions is shown in Fig. 6. With increasing electrolysis time, appreciable increases in indium ion removal efficiency were observed regardless of the supporting electrolyte concentration. After 50 min of electrolysis, when the concentration of the supporting electrolyte increased from 0.001 to 0.002, 0.003, and 0.004N, the removal efficiency improved significantly from 53.4% to 67.5%, 90.4%, and 93.5%, respectively. This was due to the Cl^- anions destroying the passivation layer and catalyzing the dissolution of the electrode material via the pitting corrosion phenomenon, which is a type of localized corrosion caused by a high chloride concentration in the solution [35]. The depassivation effect was more significant when more Cl^- anions were added to the solution. Therefore, it is expected that electrocoagulation in the presence of NaCl might improve the removal efficiency of indium ions by increasing the availability of metal coagulant in the solution owing to the reduction of the oxide layer and the enhancement of anodic dissolution of the electrode material. Consequently, the problem of electrode passivation was partially solved when NaCl was used as the supporting electrolyte. The treatment times required to reach 90% indium ion removal efficiency were approximately 47, 50, 80, and 115 min for 0.004, 0.003, 0.002, and 0.001N, respectively. However, no significant improvement in the removal efficiency was observed when the concentration of the supporting electrolyte was above 0.003N. When the concentration of the supporting electrolyte was increased from 0.003 to 0.004N, the removal efficiency increased slightly from 90.4% to 93.5%. Consequently, a

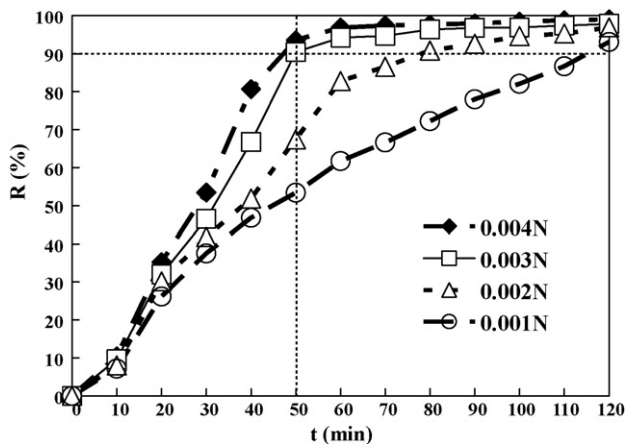


Fig. 6. Effect of supporting electrolyte on the removal efficiency of indium ions ($C_0 = 20 \text{ mg/L}$, current density = 6.4 mA/cm^2 , $t = 120 \text{ min}$, $T = 298 \text{ K}$, $d = 2 \text{ cm}$, and agitation speed = 300 rpm).

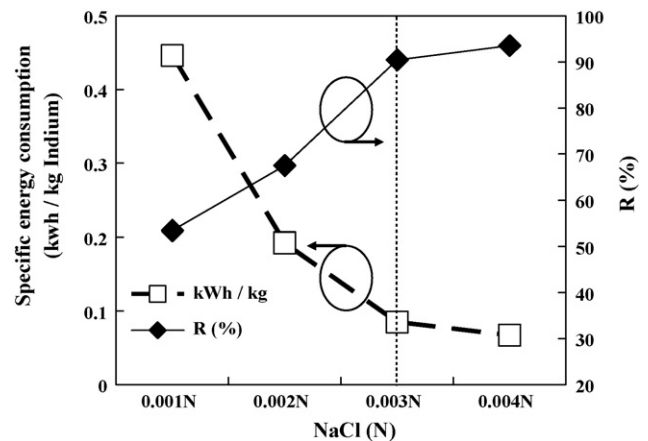


Fig. 7. Effect of supporting electrolyte on the removal efficiency of indium ions and specific energy consumption ($C_0 = 20 \text{ mg/L}$, current density = 6.4 mA/cm^2 , $t = 50 \text{ min}$, $T = 298 \text{ K}$, $d = 2 \text{ cm}$, and agitation speed = 300 rpm).

0.003N for the supporting electrolyte was chosen as the optimum concentration.

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

The concentration of supporting electrolyte was adjusted to the desire level by adding a suitable amount of NaCl to the solution. Fig. 7 shows the effect of the supporting electrolyte on the removal efficiency and specific energy consumption during electrocoagulation. Increasing the concentration of the supporting electrolyte from 0.001 to 0.004N led to an increase in the indium ion removal efficiency, whereas with the concentration of the supporting electrolyte increasing, the specific energy consumption decreased by almost 77%. The solution resistance decreases when the concentration of the supporting electrolyte in solution increases. The higher ionic strength generally decreases the cell voltage with increasing solution conductivity at constant current density. Accordingly, the necessary voltage for attaining a certain current density decreases and thus so does the consumed electrical energy [36]. However, when the concentration of the supporting electrolyte was increased from 0.003 to 0.004N, the removal efficiency increased slightly from 90.4% to 93.54%, while the corresponding specific energy consumption decreased from 0.085 to 0.067 kWh/kg. From the specific energy consumption shown in Fig. 6, 0.003N NaCl was regarded as the optimum balance, providing reasonable removal efficiency and relatively low specific energy consumption.

3.4. Effect of the initial concentration

Aqueous solutions with indium ion concentrations in the range of 20–80 mg/L were treated and the removal efficiencies for indium ions were measured at different times of electrolysis during electrocoagulation. Fig. 8 shows the effect of the initial indium ion concentration in the aqueous solution on the removal efficiency for various durations of electrolysis. It is seen that the indium ions removal efficiency reached 90.4%, 64.9%, 36.2%, and 26.1% after 50 min of electrolysis for 20, 40, 60, and 80 mg/L initial indium ion concentrations, respectively. When the initial concentration was increased, the removal efficiency for indium ions decreased. As also seen in Fig. 8, the treatment times required to reach 90% indium ion removal were approximately 50, 60, 88, and 107 min for 20, 40, 60, and 80 mg/L concentrations, respectively. This could be attributed to Faraday's law. According to Faraday's law, a constant amount of metal hydroxides dissolves from the iron anode and passes to the solution for the same current density and electrolysis time for

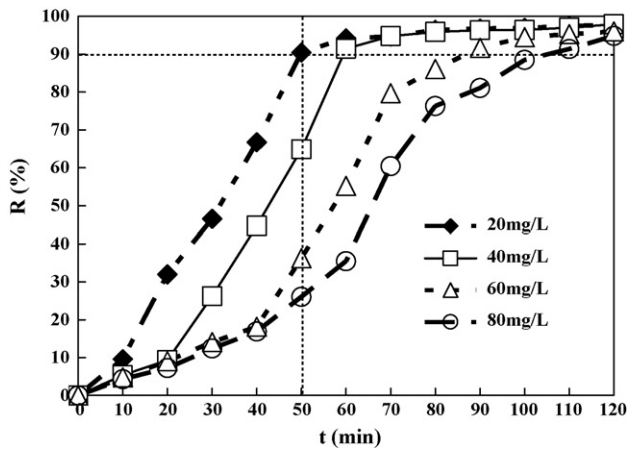


Fig. 8. Effect of initial concentration on the removal efficiency of indium ions (current density = 6.4 mA/cm², NaCl = 0.003N, $t = 120$ min, $T = 298$ K, $d = 2$ cm, and agitation speed = 300 rpm).

all indium ion concentrations. Consequently, the same amount of metal hydroxide was produced in the aqueous solution. This was probably because the amounts of hydroxyl and metal ion produced on the electrodes at high indium ions concentrations were insufficient for absorbing all indium ions in the solution at a constant current density.

3.5. Effect of temperature

The effect of temperature on electrocoagulation has rarely been investigated even though this technology has been used for more than 100 years. In the present study, the effect of temperature on the indium ion removal efficiency was studied at 288, 298, 308, and 318 K, as shown in Fig. 9. As the time of electrolysis increased, comparable increases in the indium ion removal efficiency were observed for the different temperatures. After 50 min of electrolysis, it seen that the indium ion removal efficiency reached 80.9%, 90.4%, 92.7%, and 94.1% for temperatures of 288, 298, 308, and 318 K, respectively. As also seen in Fig. 9, the treatment times required to reach 90% indium ion removal were approximately 46, 48, 50, and 70 min for temperatures of 318, 308, 298, and 288 K, respectively. The temperature influence can be attributed to the increased destruction of the iron oxide film on the anode surface and the increased rate of all reactions involved in the process

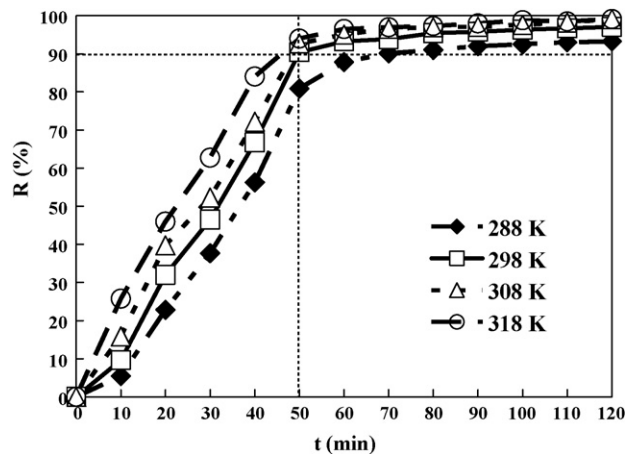


Fig. 9. Effect of temperature on the removal efficiency of indium ions ($C_0 = 20$ mg/L, current density = 6.4 mA/cm², NaCl = 0.003N, $t = 120$ min, $d = 2$ cm, and agitation speed = 300 rpm).

according to the Arrhenius equation. [18] Increased temperature promoted the generation of metal hydroxides formed in the electrocoagulation process, which led to greater mobility and more frequent collisions of species, resulting in an increased reaction rate of the metal hydroxides (i.e., iron hydroxides) with pollutants [37]. However, there is no significant improvement in the indium ion removal efficiency after 50 min of electrolysis when the temperature was beyond 298 K. This can be explained by the opposite effects that higher temperature possibly causes an increase in the solubility of the precipitates or the generation of unsuitable flocks [38]. In view of the present results it seems that within the temperature range of 288–298 K, the beneficial effects dominate over the adverse effects. For solution temperatures higher than 298 K, the beneficial effects are balanced by the adverse effects.

3.5.1. Effect of temperature on removal efficiency and specific energy consumption

To evaluate the temperature effects on the specific energy consumption and indium ion removal efficiency, a number of experiments were performed for 120 min of electrolysis with the Fe/Al electrode pair, 20 mg/L initial concentration, 0.003N NaCl, 6.4 mA/cm² current density, and 300 rpm agitation speed. The temperature of the indium ion solution was controlled to the desired level by water flowing in the water jacket from the refrigerated circulating bath. Fig. 10 shows the temperature effects on the performance of the indium ion removal efficiency and specific energy consumption after 50 min of electrolysis by iron electrocoagulation. The specific energy consumption decreased from 0.132 to 0.085 kWh/kg when the solution temperature was increased from 288 to 298 K, whereas the corresponding indium ions removal efficiency increased from 80.9% to 90.4%. However, beyond a temperature of 298 K, there was a steady tendency for the specific energy consumption. When the solution temperature was increased from 298 to 308 and 318 K, the specific energy consumption increased from 0.085 to 0.091 and 0.095 kWh/kg, respectively, whereas the corresponding indium ion removal efficiency increased slightly from 90.4% to 92.7% and 94.1%, respectively. Consequently, when considering both specific energy consumption and indium ion removal efficiency, a temperature of 298 K seems to offer the best overall performance, resulting in a reasonable indium ion removal efficiency and relatively low specific energy consumption.

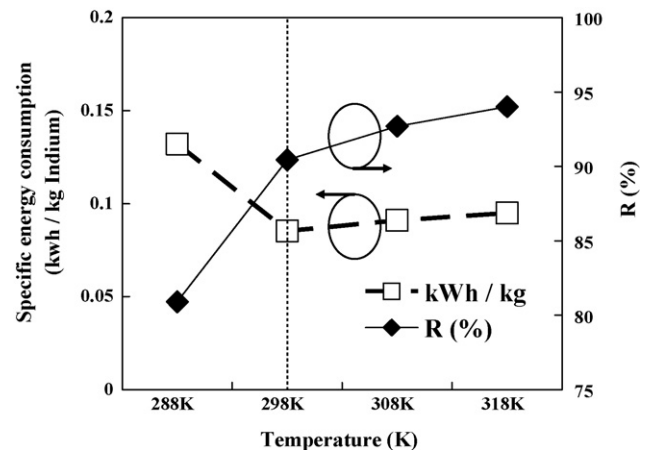


Fig. 10. Effect of temperature on the removal efficiency of indium ions and specific energy consumption ($C_0 = 20$ mg/L, current density = 6.4 mA/cm², NaCl = 0.003N, $t = 50$ min, $d = 2$ cm, and agitation speed = 300 rpm).

3.6. Indium ion removal kinetics in electrocoagulation

In the electrocoagulation process, the removal rate of indium ions is proportional to the amount of hydroxyl cationic complexes (e.g., $\text{Fe}(\text{OH})_3$), which can effectively remove indium ions. Further, the applied current density determines the rate of ferric hydroxide production. The overall electrocoagulation process in terms of the apparent kinetics of indium ion removal is described by a pseudo-kinetic model in which the rate constant depends on the current density.

For a first-order reaction, the kinetic rate equation becomes:

$$\ln\left(\frac{C_t}{C_0}\right) = -k_1 t \quad (3)$$

The slope of the plot of $\ln(C_t/C_0)$ versus time gives the value of the rate constant k_1 (1/min). Here, C_0 (mg/L) is the initial concentration and C_t (mg/L) is the concentration at time t .

For a second-order reaction, the kinetic rate equation becomes:

$$\frac{1}{C_t} - \frac{1}{C_0} = k_2 t \quad (4)$$

The slope of the plot of $1/C_t$ versus time gives the value of the rate constant k_2 (L/mg min). The values of the rate constants for first-order and second-order models for indium ion removal at various current densities were determined graphically and are shown in Table 2. The conformity between experimental data and the model values was evaluated using the correlation values R^2 . As shown in Table 2, regardless of the current density, R^2 value for the second-order model was higher than that for the first-order model. The second-order kinetic model fits the observed data for the electrocoagulation process well. With other experimental conditions fixed when the current density increased from 3.2 to 12.8 mA/cm², the second-order rate constant increased from 9.4 to 30.5 L/mg min. It is important to note that very fast indium ion removal occurred for a short electrolysis time; this is considered a great advantage of electrocoagulation.

3.7. Adsorption isotherms

The $\text{Fe}(\text{OH})_{n(s)}$ complexes formed remain in the aqueous stream as a gelatinous suspension. These gelatinous charged metal hydroxides can effectively remove pollutants by adsorption to produce charge neutralization by complexation, electrostatic attraction, and enmeshment in a precipitate [36]. $\text{Fe}(\text{OH})_3$ is the dominant species in the range of pH 6–9 according to predominance-zone diagrams for Fe(III) chemical species in aqueous solution [39]. The electrode consumption can be estimated according to Faraday's Law and the amount of flocks generated can be estimated stoichiometrically. Since the amount of coagulant can be estimated for a given time, the pollutant removal can be modeled by adsorption phenomenon. The two most commonly employed adsorption equilibrium models are the Langmuir and Freundlich equations. In this study, the adsorption characteristics for removal of indium ions from aqueous solution were tested with respect to both adsorption isotherms models.

Table 2
Pseudo-kinetic rate constants with first-order and second-order models for indium ion removal at various current densities.

Parameters	First-order model		Second-order model	
Current density (mA/cm ²)	$k_1 \times 10^3$ (min) ⁻¹	R^2	$k_2 \times 10^3$ (L/mg min)	R^2
3.2	31.3	0.93	9.4	0.95
6.4	34.5	0.89	15.9	0.97
9.6	37.0	0.86	29.8	0.96
12.8	33.7	0.79	30.5	0.96

Table 3

Langmuir and Freundlich isotherm constants for adsorption of indium ions on metal hydroxides.

Langmuir isotherm		Freundlich isotherm			
K_L (L/mg)	a_L (mg/g)	R^2	K_F ((mg/g)(L/mg) ^{1/n})	n	R^2
0.79	16.53	0.97	7.55	3.50	0.81

The Langmuir model was originally developed to represent chemisorption at a set of well-defined localized adsorption sites having the same adsorption energy, independent of the surface coverage and with no interaction between adsorbed molecules. This model assumes monolayer deposition on a surface with a finite number of identical sites. It is well known that the Langmuir equation is valid for a homogeneous surface. The mathematical expression for the Langmuir isotherm is [40]:

$$q_e = \frac{a_L K_L C_e}{1 + K_L C_e} \quad (5)$$

where a_L (mg/g) is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity; C_e (mg/L) is the equilibrium liquid-phase concentration; K_L (L/mg) is a direct measure of the intensity of adsorption; and q_e (mg/g) is the amount adsorbed at equilibrium. This equation can be linearized as:

$$\frac{1}{q_e} = \left(\frac{1}{K_L a_L}\right) \left(\frac{1}{C_e}\right) + \frac{1}{a_L} \quad (6)$$

From the data of $1/q_e$ versus $1/C_e$, K_L and a_L can be determined as the slope and intercept.

The Freundlich adsorption isotherm usually fits experimental data over a wide range of concentrations. This empirical model includes the surface heterogeneity and exponential distribution of the active sites and their energies. The isotherm is adopted to describe reversible adsorption and is not restricted to monolayer formation. The mathematical expression for the Freundlich mode is [40]:

$$q_e = K_F C_e^{1/n} \quad (7)$$

where K_F ((mg/g)(L/mg)^{1/n}) and n (dimensionless) are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. This equation can be linearized as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

The values of n and K_F are calculated from the slope and intercept of the plot of $\log q_e$ versus $\log C_e$.

The applicability of the isotherm equations was compared using the correlation coefficient R^2 . The model simulation constants of Langmuir and Freundlich isotherms are presented in Table 3. It can be seen that the Langmuir isotherm model has a better fit than the Freundlich isotherm model does. This suggests the adsorption of indium ions by metallic hydroxides is apparently with monolayer coverage of adsorbed molecules.

4. Conclusion

Experiments were carried out to remove indium ions from aqueous solution using electrocoagulation system. The following conclusions have been made based on the present investigation:

- (1) Considering the removal efficiency and specific energy consumption, a current density of 6.4 mA/cm², a temperature of

298 K, and a supporting electrolyte of 0.003N NaCl were found to be the optimum values for the present electrocoagulation.

- (2) It was observed that the indium ion removal efficiencies by electrogenerated OH^- at the cathode were greater than those by indium hydroxide precipitation using sodium hydroxide at various values of solution pH. When the pH values lower than 6.1, the removal efficiencies of indium ions via electrocoagulation were up to 5 times greater than those by adding sodium hydroxide.
- (3) It was found that increasing the initial indium ion concentration from 20 to 80 mg/L decreased the removal efficiency of indium ions.
- (4) Values of kinetic rate constants for indium ion removal at various current densities were calculated. The kinetic results show that a pseudo-second-order kinetic model matched satisfactorily with the experimental observations.
- (5) The gelatinous charged metal hydroxides generated in electrocoagulation can efficiently remove indium ions by adsorption. The electrocoagulation was modeled using Langmuir and Freundlich adsorption isotherm models. The predictions of Langmuir adsorption isotherm model are in good agreement with the experimental data for the adsorption of indium ions.

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