Arsenic Removal By Electrochemical Treatment Process

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Abstract: In the present study, electrocoagulation (EC) has been evaluated as a treatment technology for arsenic (As) removal from aqueous solutions. Iron plate electrode was used in experiments. The experiments was used were carried out in a batch reactor. The effects of operational parameters such as current density, initial pH, electrolysis time and initial arsenic concentration were investigated. The obtained experimental results showed that efficiency of arsenic removal increased with increasing current density and decreased with increasing arsenic concentration in the solution. It has been established that the pH has a considerable influence on the performance of electrocoagulation process. Under the optimum conditions of an initial pH of 4, current density of 1,07 mA/cm^2, stirring speed of 150 rpm, electrolysis time of 30 minutes, Arsenic was removed from aqueous solutions including arsenic concentration of 50 mg/L, at a rate of 99,50%.

Keywords: Arsenic removal, electrocoagulation, water treatment, iron electrode

1. Introduction

Arsenic, a toxic trace element present in natural waters (ground and surface water), has become a major unavoidable threat for the life of human beings and useful microorganisms. Arsenic concentration in water can become elevated due to several reasons like, mineral dissolution, use of arsenical pesticides, disposal of fly ash, mine drainage, and geothermal discharge [1]. Arsenic contamination in potable water supplies is a serious health problem in many countries around the world. As is a cause for skin, liver, lung and kidney or bladder cancer, it is a big headache to the nation. Due to carcinogenic nature of arsenic compounds, the purpose should now be to reduce the exposure of arsenic-contaminated water to a level as close to zero as possible [2.] . According to the World Health Organization (WHO), the maximum contamination level of arsenic in drinking water is 50 and 10 µg/L as a provisional guideline value [3]. This standard has been retained by the U.S. Environmental Protection Agency (USEPA) and is currently the maximum contaminant level. The range of values under consideration by USEPA is from 2 to 20 µg/L for total arsenic. Several methods have been investigated for removal of arsenic, including ion exchange [4, 5], coagulation and precipitation with iron and aluminum salts [6, 7], adsorption [8, 9], electrocoagulation [10, 11], membran techniques like ultrafiltration [12, 13], Nanofiltration [14] , electrodialysis, reverse osmosis [15].

EC (electocoagulation) is an emerging water treatment technology and could be a good choice to remove As (III) from water: the amount of required chemicals is much lower, a smaller amount of sludge is produced, no mixing of chemical is required, coagulant dosing as well required overpotentials can be easily calculated and controlled, operating costs are much lower when compared with most of the conventional technologies [16,17].

When iron is used as electrode material, the chemical reactions which occur on electrode and in the solution, are shown in Table 1. The following mechanisms describe the formation of the iron hydroxides $Fe(OH)_n$ where n = 2 or 3. The Fe(OH)n(s) formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation [18].

194

Mechanism		Reactions
Mechanism 1:	Anode :	$4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^-$
	In the solution	$4Fe^{2+}_{(aq)} + 10H_2O_{(1)} + O_{(2)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+_{(aq)}$
	Cathode:	$8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)}$
	Overall:	$4Fe_{(s)} + 10H_2O_{(1)} + O_{2\ (g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)}$
Mechanism 2:	Anode :	$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$
	In the solution	$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)}$
	Cathode:	$2H_2O_{(1)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$
	Overall:	$Fe_{(s)} + 2H_2O_{(1)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)}$

Table 1. The reactions occurred at iron electrode and in the solution

The H_2 produced as a result of the redox reaction may remove dissolved organics or any suspended materials by flotation.

The purpose of the present study is to assess the performance of EC on the treatment of arsenic, by exploring the effects of various operational parameters such as current density, initial pH and initial arsenic concentration on arsenic removal efficiency.
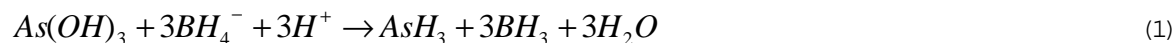

2. Experimental

2.1. Materials

All chemicals were of analytical grade. Stock arsenic solutions of 1.32 g/l were prepared according to the EPA standard method by dissolving arsenic oxide (As_2O_3) in 2N NaOH and then diluting the solution up to 1 liter with de-ionized water. Solutions of lower concentrations were prepared by proper dilution. The pH of the solution was adjusted by adding either sodium hydroxide or sulfuric acid.

2.2. Analytical methods

The concentration of As was determined by a Atomic Absorption Spectrophotometer model Shimadzu A-A 6800 equipped with a hydride generation. Hydride generation is, perhaps, the most popular sample derivatization method used for inorganic arsenic detection. Initially it was developed as a method for AAS, whereby sodium or potassium tetrahydroborate (III) is used for arsine production (Eq 4,5). The reduction reagents $NaBH_4$ and KBH_4 have proved to be exceptionally reliable reagents for the conversion of the sample to volatile forms [19]. The hydride generation procedure can be also used for differential determination of As (III) and As (V), based on the fact that As (III) reacts with tetrahydroborate at a higher pH than As (V).Thus tetrahydroborate is acting as a reductant for As (V) as well as a hydride source. The inclusion of on-line hydride generation generally increases the sensitivity of detection and reduces the possible interferences from the sample matrix. In this study sodium tetrahydroborate ($NaBH_4$) was of analytical grade and was dissolved in sodium hydroxide solution just before use.

$$As(OH)_3 + 3BH_4^- + 3H^+ \rightarrow AsH_3 + 3BH_3 + 3H_2O \tag{1}$$

$$3BH_3 + 3H_2O \rightarrow H_3BO_3 + 3H_2 \tag{2}$$

Electrocoagulation was conducted at different electrolysis time, different pH, different current density, and different initial concentrations, different stirring speed using Fe electrodes.

2.3. Electrocoagulation test

The experiments carried out in a 1600 mL^3 laboratory-scale batch reactor made of plexiglass. Two groups of alternating electrodes being cathodes and anodes (by six plates of each type) made of iron with total area of approximately 700 cm^2 were arranged vertically. The net spacing between the iron electrodes was 5 mm. They were treated with the solution of HNO_3 for cleaning prior to use. At the end of run, the electrodes were washed thoroughly with water to remove any solid residues on the surfaces, and dried. Electrodes were connected to a digital DC power supply characterized by the ranges 0.36–2.14 mA/cm^2 for current and 0–30V for voltage in monopolar mode. GW GPC –3060 D was used as a power supply. Cell current was measued using WTW Multiline 340i multimetre. During the experiments, the electrocoagulation unit was stirred at 150 rpm by a magnetic stirrer. (Heidolph MR-3004). The pH and conductivity were measured by a multimeter (WTW,

195

Multiline 340 i), which was freshly calibrated by 2 points (4.01, 7.00) before each test. The experimental apparatus is given in Fig. 1.

The reactor was fed with 1500 mL of arsenic containing solution at the beginning of each run performed at constant temperature (293 K). After each run was timed starting with switching the DC power supply on, the residual arsenic in the samples filtered and taken from the reactor was measured. Concentrations of arsenic were measured spectrophotometrically before and after electrolysis. The samples were analyzed by atomic absorption spectroscopy (Shimadzu A-A 6800) by the standard method (APHA).
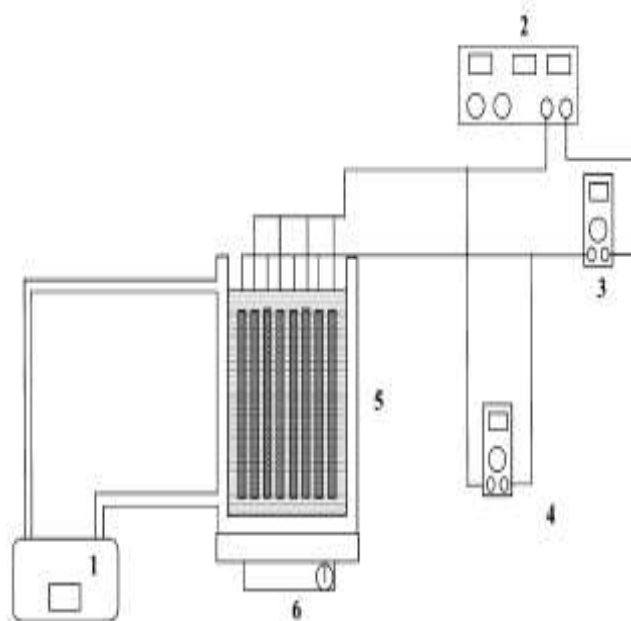
1. Water Circulator, 2. D.C. Power Supply, 3. Ampermeter, 4. Voltmeter, 5. Reactor, 6. Magnetic Stirrer
Fig. 1. Schematic diagram of the experimental setup.

3. Results and discussion

3.1. The effect of initial pH

The initial pH is one of the important factors in affecting the performance of electrochemical process. It has been established that the pH has a considerable influence on the performance of electrocoagulation process. To investigate this effect, a series of experiments performed using aqueous solution containing arsenic of 50 mg/L were carried out at initial pH of 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 8.0 under conditions in which current density of 1,07 mA/cm^2 and stirring speed of 150 rpm were kept constant during experiments. After the removal experiment, we observed 99% removal, in the water samples with initial Arsenic concentration at 50 mg/L and initial pH at 4.0, 3.0 and 5.0 respectively. In the study initial pH was chosen as 4 and other experiments were done at pH 4.
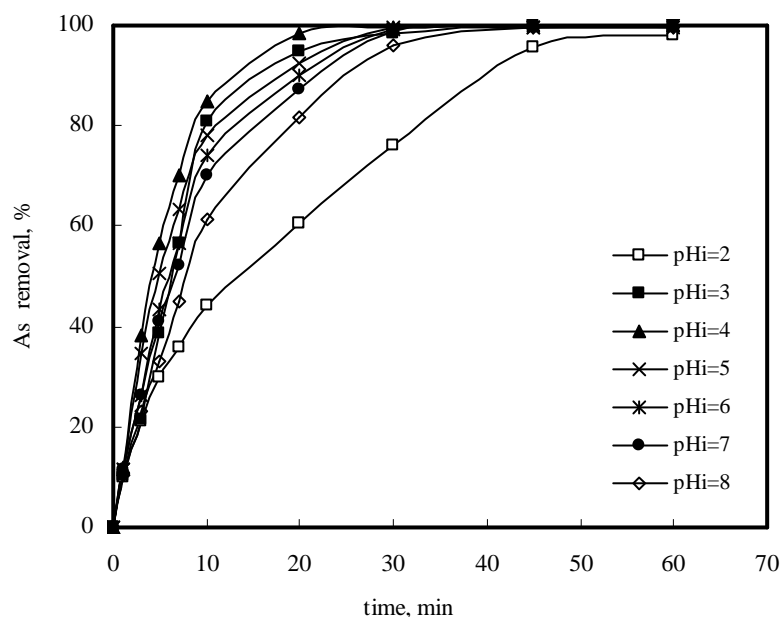
Figure 2. Effect of pH on arsenic removal

3.2. The effect of current density

The current density is defined as the ratio of current input to the electrolytic cell to the surface area of the electrode. It is well known that current not only determines the coagulant dosage rate but also the bubble production rate, size and the flocks growth, which can influence the treatment efficiency of the electrocoagulation. Thus, this parameter should have a significant impact on removal efficiencies of pollutants. To investigate the effect of current density on the energy consumption, a series of experiments were carried out under the experimental conditions of current density being varied from 0.36 to 2.14 mA/cm^2 solution pH of 4.0, temperature of 293 K and stirring speed of 150 rpm.
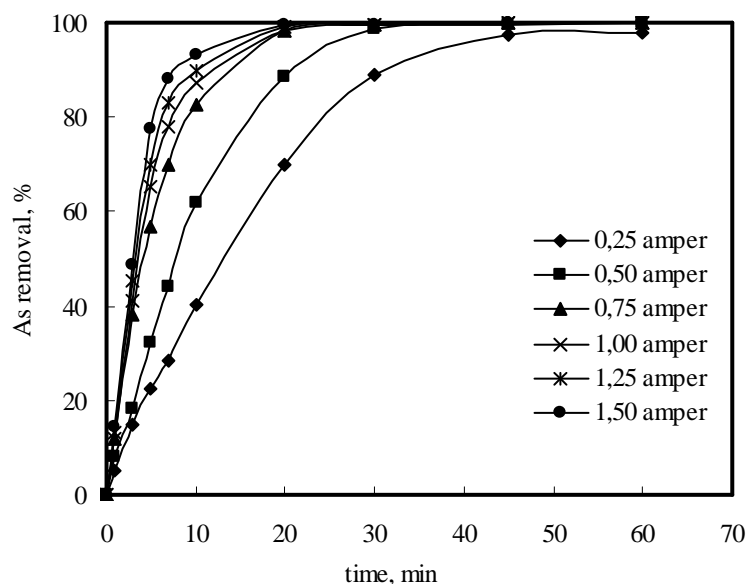

Figure 3. Effect of current density on arsenic removal

Increasing the current density 0.36 mA/cm^2 to 1.07 mA/cm^2 the removal efficiency is further improved. A higher current density means a higher Fe^{3+} and OH^- dosage, and a better removal should therefore be the result. On the other hand, increasing the current density to 2.14 mA/cm^2 no real difference in As removal.

3.3. The effect of initial arsenic concentration

The effect of initial arsenic concentration on the arsenic removal was examined with solutions including arsenic of 10, 25, 50 and 100 mg/L. Current density of 1.07 mA/cm^2, optimum pH of 4.0 and stirring speed of 150 rpm were kept constant in the experiments. The solution conductivity increased with increasing arsenic concentration. As a result of this situation, applied potential and energy consumption decreased. On the contrary, arsenic removal efficiency decreased with increasing arsenic concentration. This can be explained as following; although the same amount Fe^{3+} passed to solution at the same current density for all arsenic concentration, Fe^{3+} was insufficient for solutions including higher arsenic concentration. Because of increasing arsenic concentration, potential applied to solution and energy consumption decreased. The results obtained were shown graphically in Fig. 4.
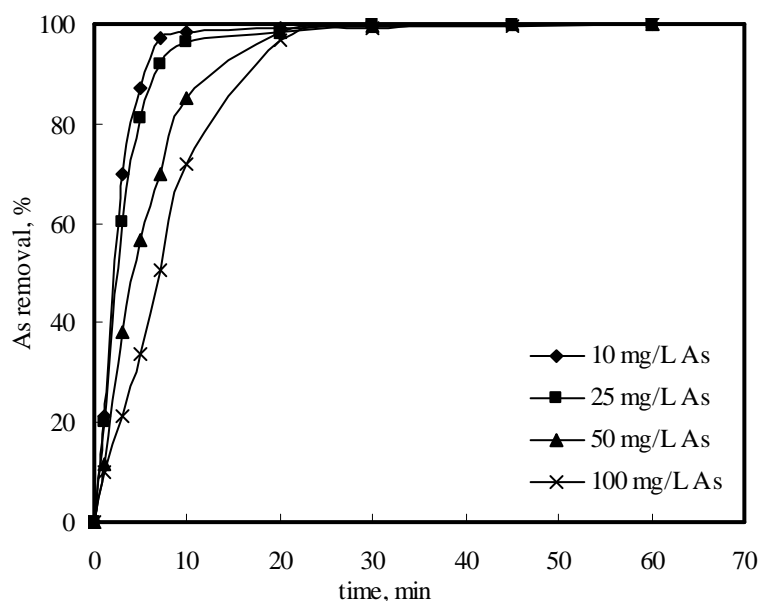

Figure 4. Effect of initial arsenic concentration on arsenic removal.

4. Conclusions

The present study clearly demontrated the applicability of electrocoagulation process using the iron electrode for arsenic removal. The effects of operational parameters such as current density, initial pH, electrolysis time, initial arsenic concentration on arsenic removal efficiency were studied in detail and explained as well.

It has been observed that the pH is an important operating factor influencing the performance of electrocoagulation process. Optimal initial pH was found as 4 in the use of iron as sacrificial electrode material in the treatment. Oxidation of As(III) to As(V) was occured as the first step and then subsequent adsorption on to hydrous ferric oxides. As(III) is more mobile and more toxic than As(V), so it is an advantage to convert As(III) to As(V). Increasing the current density 0,36 mA/cm^2 to 2,14 mA/cm^2, the Fe^{3+} and OH$^-$ dosage is increased too, and thereby favouring the removal of As. On the other hand, it seems that increasing the current density beyond a maximum value, the electrocoagulation process would not improve further. This could probably be explained by passivation of the anode. When effect of initial arsenic concentration on arsenic removal efficiency was investigated, the obtained results shown that increasing arsenic concentration increased conductivity of solution. Thus, solution with higher arsenic concentration had more ions at the same volume.

As a result under the optimum conditions of an initial pH of 4, current density of 1,07 mA/cm^2, stirring speed of 150 rpm, electrolysis time of 30 minutes, As was removed from aqueos solutions including arsenic concentration of 50 mg/L, at a rate of 99,50. It can be concluded from this study that electrocoagulation is a promising technique for arsenic removal.

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