

Influence of Operating Parameters on the Arsenic and Boron Removal by Electrocoagulation

¹Berrin Zeliha Can, ²Recep Boncukcuoğlu, ²Serkan BAYAR and ²Yalçın Kemal BAYHAN
¹8st Regional Directorate of State Hydraulic Works (DSİ), Erzurum 25100, Turkey.
² Ataturk University, Faculty of Engineering, Department of Environmental Engineering, 25240,
Erzurum-TURKEY.
rboncuk@atauni.edu.tr*

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Summary: Despite their high boron contents, some boron deposits contain considerable amounts of arsenic. Its toxicology and health hazard also has been reported for many years. In this work arsenic and boron removal from synthetic water was studied on laboratory scale by electrocoagulation using aluminum electrodes. The influence of main operating parameters such as current density, stirring speed, supporting electrolyte type and concentration on the arsenic and boron removal was investigated. Waste water sample was prepared with initial arsenic concentration of 50 mg L⁻¹ and boron concentration of 1000 mg L⁻¹. Current density was varied from 0.18 to 4.28 mA cm⁻², stirring speed was varied as 50, 150, 250, 350 rpm, NaCl, KCl and Na₂SO₄ were used as supporting electrolyte. The obtained experimental results showed that efficiency of arsenic and boron removal increased with increasing current density. As the current density increases, the potential difference applied to the system also increases the energy consumption. Increasing the supporting electrolyte concentration increased conductivity of solution and decreased energy consumption. The most favorable supporting electrolyte type was NaCl for arsenic and boron removal. The best stirring speed were 150 rpm for arsenic and boron removal.

Keywords: Aluminum electrode; Arsenic removal; Boron removal; Current Density; Electrocoagulation.

Introduction

The impact of arsenic compounds on human health and environment is known. 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]. The activities such as mine processing and the use of pesticide have increased arsenic concentrations in environmental compartments such as surface or underground waters over natural levels. Another source of naturally occurring arsenic is from borate mines.

Turkey has the richest boron reserve in the world. The important boron minerals of Turkey are tincal, colemanite and ulexite. Borat minerals observed in Turkey's reserves are mainly Ca; Ca- Na, and Na-Mg borats. It is known that there is rarely Sr-Borat in Kırka, and there are Ca-As and Sr borats in Emet region. The Emet borate mining district's abundance in As-bearing minerals realgar and orpiment makes it stand out among the various borate deposits in Turkey [3]. Arsenic minerals (realgar and orpiment) are spatially related to the borates, indicating a common genetic origin [4]. Kutahya-Emet area colemanites include roughly 0.1–5 % of arsenious compounds, primarily realgar and orpiment minerals [5]. After concentration by physical methods, colemanite is mainly used in the production of boric acid by sulphuric acid [2]. The arsenic both

is in borate deposits and occurs during the production of boric acid creates some problems in marketing and environment.

Boron and arsenic were the two important contaminants determined in the groundwaters around the borate mines. In underground waters, arsenic and boron reach at the values over normal standards depending on fast oxidization, high resonance and their mobility. They cause the changing of water quality, as regards agricultural irrigation and provision of fresh water, rather objectable results have been occurred. The toxicology and health hazard of arsenic has been reported for many years. According to US, EPA and WHO standards, the values more than 0.01 mg/L of Arsenic and 0.03 mg/L of boron in drinkable and portable waters is very dangerous for human health. [6]. So the control of arsenic and boron in water is vital and their removal is necessary.

In recent years, electrocoagulation has been extensively studied for arsenic and boron removal. Many studies have been done about boron removal by electrocoagulation [7-10]. And electrocoagulation has been successfully used to treat arsenic waste waters, with removal efficiencies as high as 90–99% [11-16]. But both arsenic and boron removal with electrocoagulation study is very limited [17].

*To whom all correspondence should be addressed.

Electrochemical application appear to be effective for the treatment of different effluents compared with conventional methods. The electrocoagulation process is one of the most commonly used electrochemical processes. Electrocoagulation is a process consisting of creating a floc of metallic hydroxides within the effluent to be cleaned, by electrodisolution of soluble anode. In electrocoagulation, coagulation and precipitation are not conducted by delivering chemicals – called coagulants – to the system, but via electrodes in the reactor [18,19]

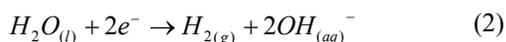
The electrocoagulation process is carried out in 3 stages. (1) the formation of coagulants by electrolytic oxidation of the “sacrificial electrode”, (2) destabilization of the contaminants, particulate suspension, and breaking of emulsions and (3) aggregation of the destabilized phases to form flocks [8, 20].

When using Al electrodes, main reactions are as:

At the anode:



At the cathode:



In the solution:



As seen in the reactions presented above, electrocoagulation is a process consisting of oxidation, flocculation and flotation [21, 22]

Amorphous $Al(OH)_3(s)$ flocs having large surface areas formed in aluminum anode are active in rapid adsorption of soluble organic compounds and trapping of colloidal particles and are easily separated from aqueous medium by sedimentation or H_2 flotation [23]. However, depending on the pH of the aqueous medium other ionic species, such as $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^{-}$ may also be present in the system [24].

In the present study, the removal of arsenic and boron from synthetic water was studied on

laboratory scale by electrocoagulation using aluminum electrodes. The influence of main operating parameters such as current density, stirring speed, supporting electrolyte type and concentration on the arsenic and boron removal and energy consumption were investigated.

Experimental

Materials

All chemicals were of analytical grade and supplied by Merck and Panreac. Wastewater samples used in the experiments were prepared synthetically using $Na_2B_4O_7$ and As_2O_3 . The solution with boron concentration of 1000 mg/L was prepared by dissolving 17.61 dimension is missing borax dried at 105 °C in distilled water and completed with distilled water to 2 L. The same operations were repeated for the solutions with boron concentrations of 250, 500, 2000 and 1000 mg L⁻¹ with different $Na_2B_4O_7$ weights. Stock arsenic solutions of 1.32 g L⁻¹ were prepared by dissolving arsenic oxide (As_2O_3) in 2M NaOH and then diluted the solution up to 1 liter with de-ionized water. Solutions of lower concentrations were prepared by proper dilution. For the solution with boron concentration of 1000 mg L⁻¹ and arsenic concentration of 50 mg L⁻¹; 17.61dimmesssion borax was by dissolved in 100 ml of 1000 mg L⁻¹ arsenic concentration and completed with distilled water to 2 L. The pH of the solution was adjusted by adding either concentrated how much? NaOH or H_2SO_4 .

Analytical Methods

The analytical determination of boron was done potentiometrically by means of mannitol, which forms a complex compound with boric acid. For this purpose, boron analysis was carried out as follows: solution pH was adjusted to 7.60. Then, 5 g mannitol was added to solution. The solution was titrated with 0.5 N KOH until solution pH became 7.60. Boron amount was calculated from KOH consumption. One milliliter 0.5 N KOH is equivalent to 17.41 mg B_2O_3 [25].

The concentration of arsenic was determined by Atomic Absorption Spectrophotometer model Shimadzu A-A 6800 equipped with a hydride generation. In this study sodium tetrahydroborate ($NaBH_4$) was of analytical grade (Merck) and was dissolved in sodium hydroxide solution just before use.

The removal efficiency of As and B in solution treated by electrocoagulation is calculated as follows:

$$\% \text{ efficiency} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (5)$$

where C_0 (mg L^{-1}) is the initial As or B concentration, C_t (mg L^{-1}) is the concentration of As or B in solution at time t .

The energy consumption was calculated by the following equation [26];

$$E = \frac{VxIx t}{v} \quad (6)$$

where, E is electrical energy consumption (kWh m^{-3}), V is potential (volt), I is current (ampere), t is electrolysis time (min) and v is volume of the solution (m^3).

Electrocoagulation Test

The experiments were carried out in a 1400 mL laboratory-scale batch reactor made of plexiglass. Two groups of alternating electrodes being cathodes and anodes (by six plates of each type) made of aluminum with total area of approximately 1400 cm^2 were arranged vertically. The net spacing between the aluminum electrodes was 0.5 cm. 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 0.54 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 measured using Brymen BM-810 multimeter. 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, Multiline 340i), 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 1400 mL of arsenic and boron containing solution at the beginning of each run. After each run was timed starting with switching the DC power supply on, the residual arsenic and boron in the samples filtered and taken from the reactor was measured. The analytical determination of boron was done potentiometrically

by means of mannitol, which forms a complex compound with boric acid. The analytical determination of arsenic was analyzed by atomic absorption spectroscopy with a hydride generation.

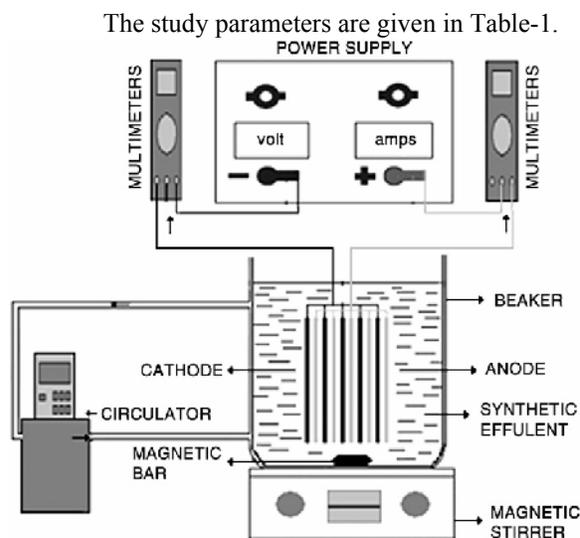


Fig. 1: Experimental set up.

Table-1: Experimental parameters.

Parameters	Chosen parameter ranges	Constant variables
Current density (mA cm^{-2})	0.18, 0.36, 0.54, 0.71, 0.89, 1.07, 2.14, 3.21, 4.28	initial pH:4, initial arsenic concentration: 50 mg L^{-1} and initial boron concentration: 1000 mg L^{-1} , stirring speed: 150 rpm
Stirring speed (rpm)	50, 150, 250, 350	initial pH:4, initial arsenic concentration: 50 mg L^{-1} , stirring speed: 150 rpm
Supporting electrolyte type	15 mM NaCl, 15 mM KCl, 10 mM Na_2SO_4	initial pH:4, initial arsenic concentration: 50 mg L^{-1} and initial boron concentration: 1000 mg L^{-1} , stirring speed: 150 rpm
Supporting electrolyte concentration (NaCl mM)	5,10,15,20	initial pH:4, initial arsenic concentration: 50 mg L^{-1} and initial boron concentration: 1000 mg L^{-1} , current density: 0.54 mA m^{-2} , stirring speed: 150 rpm

Initial pH was chosen as 4 because solution was adjusted to 4.0, 5.0, 6.0, 7.0 and 8.0 and high removal efficiencies were observed at initial pH of 4.0.

Experimental

Effect of Current Density

The current density is one of the most important parameters for the electrochemical

processes because it controls the reaction rate in the electrolytic cell. It is well known that current density 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 [29]. The removal efficiency values are presented in Fig. 2.

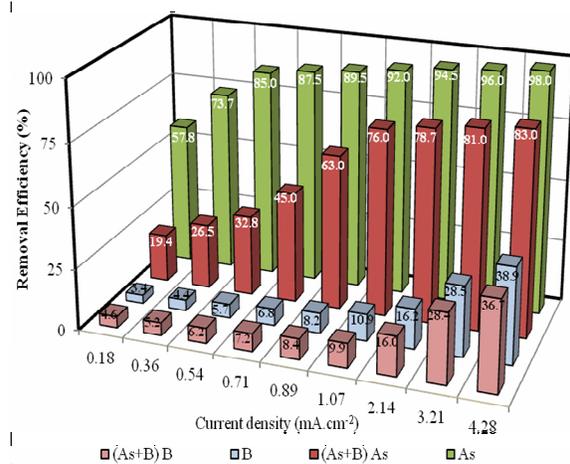


Fig. 2: Effect of current density on the arsenic and boron removal efficiency (initial pH:4, initial arsenic concentration: 50 mg L⁻¹ and initial boron concentration: 1000 mg L⁻¹, stirring speed: 150 rpm, time: 60 minute).

As shown in Fig. 2, arsenic and boron removal increased with increasing current density because the electrochemical solubility rate of aluminum increases and therefore more Al(OH)_{3(s)} reacts with constant pollutant amount, and more pollutant amount is removed from the medium. In the experiments performed under the conditions as initial pH of 4, 50 mg L⁻¹ of arsenic concentration, stirring speed of 150 rpm, arsenic removal efficiency was found as 98.00 % after 60 min reaction time at 4.28 mA cm⁻². In the experiments performed under the conditions as initial pH of 4, 1000 mg L⁻¹ of boron concentration, stirring speed of 150 rpm, boron removal efficiency was found as 38,89 % after 60 min reaction time at 4.28 mA cm⁻². The value of arsenic removal efficiency obtained from the experiments were done with a solution containing both arsenic and boron was found lower than the value of arsenic removal efficiency obtained from the experiments were done with a solution contains only arsenic. The value of boron removal efficiency obtained from the experiments were done with a solution containing both arsenic and boron was found approximately the same the value of boron removal efficiency obtained from the experiments were done

with a solution contains only boron. This situation is reflected in the values of energy consumption Fig. 3.

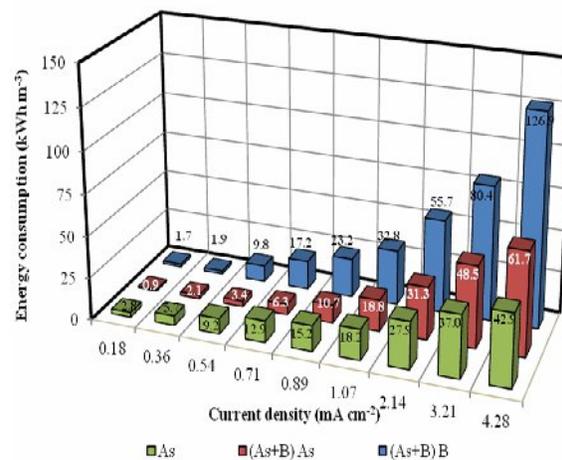


Fig. 3: Effect of current density on the energy consumption (initial pH:4, initial arsenic concentration: 50 mg L⁻¹ and initial boron concentration: 1000 mg L⁻¹, stirring speed: 150 rpm, time: 60 minute).

Current density and energy consumption are closely related. With the increased current density in the system, the electrochemical solubility rate of aluminum and the potential difference applied to the system increases thus both electrode consumption and energy consumption increased. The results are supported by the literature [12, 27].

Effect of Supporting Electrolyte Type and Concentration

The effect of supporting electrolyte type and concentration on the system performance were evaluated based on the removal efficiency and energy consumption under conditions in which are given in Table 1. Na₂SO₄, NaCl and KCl were used as supporting electrolyte. The results are presented in Fig. 4 and 5. Increasing the supporting electrolyte concentration were increased arsenic and boron removal. Because increasing the supporting electrolyte concentration increased amounts of ions in solution and the conductivity of solution. The highest arsenic and boron removal was observed with 15 mM NaCl.

Electrical energy consumption values were calculated from Eqn 6 and the data are shown in Fig. 6. The energy consumption values obtained from experiments carried out with the supporting electrolyte was lower than from experiments carried out without the supporting electrolyte. The reason for this is that the chemicals used in high resolution, they

well-ionized in the solution and the increment of electrical conductivity of the solution. Increment of the electrical conductivity of the solution caused a decrease of potential difference applied at constant current density and this provided low energy consumption. This approach is consistent with many studies [21, 28, 29].

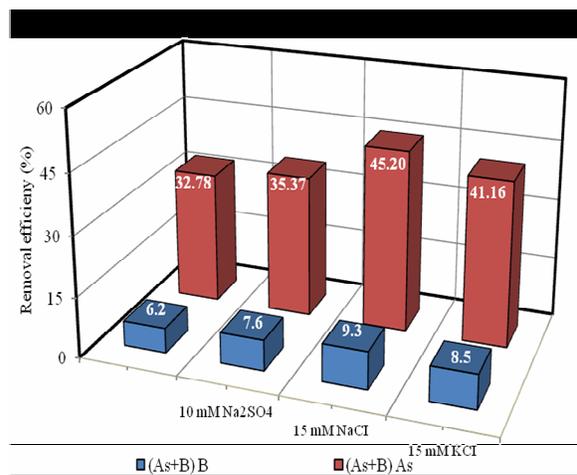


Fig. 4: Effect of type of supporting electrolyte on the arsenic and boron removal efficiency (initial pH:4, initial arsenic concentration: 50 mg L⁻¹ and initial boron concentration: 1000 mg L⁻¹, stirring speed: 150 rpm, time: 60 minute).

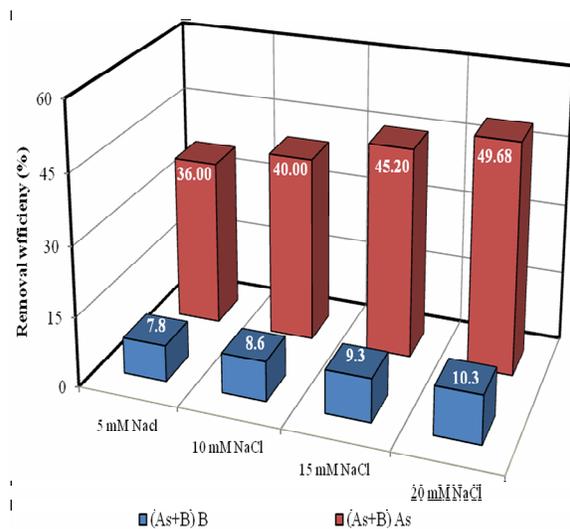


Fig. 5: Effect of concentration of supporting electrolyte on the arsenic and boron removal efficiency (initial pH:4, initial arsenic concentration: 50 mg L⁻¹ and initial boron concentration: 1000 mg L⁻¹, stirring speed: 150 rpm, time: 60 minute).

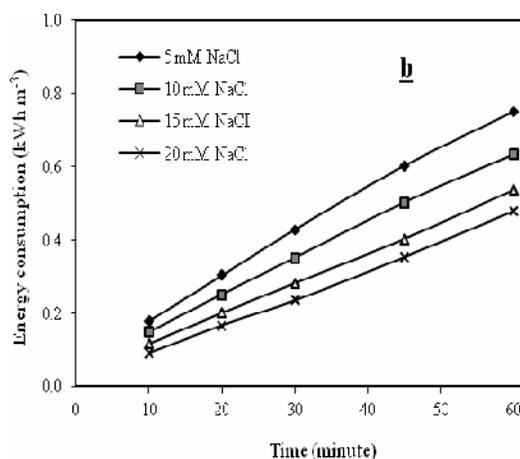
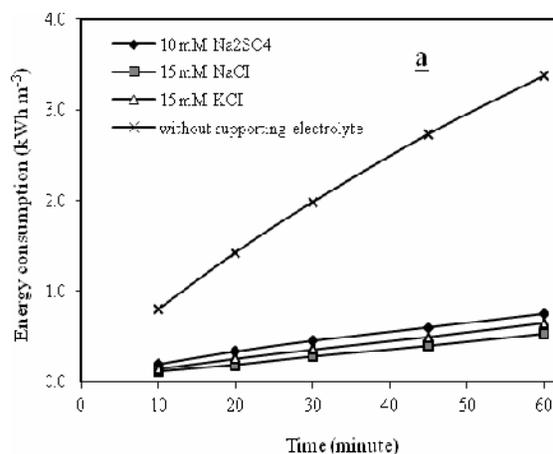


Fig. 6: Effect of supporting electrolyte type (a) and concentration (b) on the energy consumption (initial pH:4, initial arsenic concentration: 50 mg L⁻¹ and initial boron concentration: 1000 mg L⁻¹, stirring speed: 150 rpm).

Effect of Stirring Speed

To investigate the effect of stirring speed on the removal of arsenic and boron, a series of experiments was performed under conditions given in Table-1. Increasing stirring speed decreased cadmium removal efficiency increasing stirring speed decreased capability of flock formation of aluminum ions. The stirring speed, smaller than 150 rpm, decreased arsenic removal efficiency and this speed did not supply a homogeneous mixture in the reactor. The best arsenic and boron removal efficiency was seen at 350 rpm stirring speed. The results obtained are shown graphically in Fig. 7.

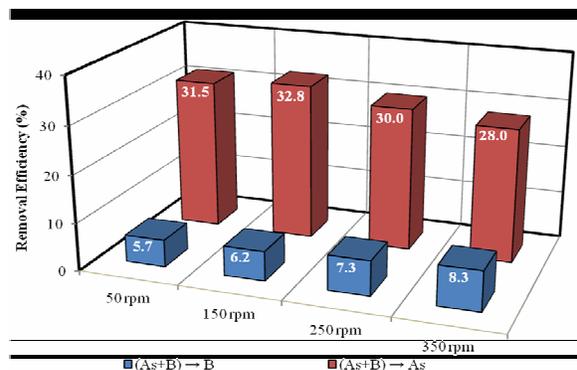


Fig. 7: Effect of stirring speed on the arsenic and boron removal efficiency (initial pH:4, initial arsenic concentration: 50 mg L⁻¹ and initial boron concentration: 1000 mg L⁻¹, time: 60 minute).

The energy consumption values were calculated and are shown in Fig. 8. The energy consumption values increased contrary to the arsenic removal efficiency in the stirring speed of both above 150 rpm (250, 350 rpm) and below 150 rpm (50 rpm). Graphical results showed that aluminum deposited between electrodes because of the electrochemically dissolution of aluminum couldn't mix homogeneously and this deposition caused the increment of cell resistance. The increase in the cell resistance causes the increase of potential value in the systems where constant current density applies and this causes the increase of the amount of energy consumption per unit volume. The reason for high stirring speed to increase energy consumption is slow electron flow or additional resistance due to negative pressure of high speed on electron flow in the reactor.

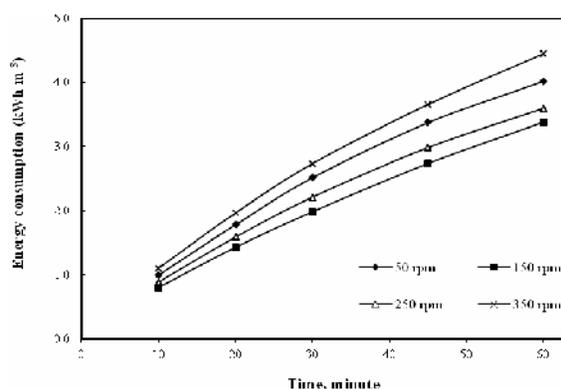


Fig. 8: Effect of stirring speed on the energy consumption (initial pH:4, initial arsenic concentration: 50 mg L⁻¹ and initial boron concentration: 1000 mg L⁻¹, stirring speed: 150 rpm).

Results and Discussion

In the present study, the removal of arsenic and boron from synthetic water was studied on laboratory scale by electrocoagulation using aluminum electrodes. The influence of main operating parameters such as current density, stirring speed, supporting electrolyte type and concentration on the arsenic and boron removal was investigated. According to the results obtained from the experiments, the removal efficiency has with by increasing current density (from 0,18 to 4,18 mA cm⁻²). But system energy consumptions increased with increasing current density. When the effect of supporting electrolyte type and concentration on the arsenic and boron removal and energy consumption was investigated, the obtained results showed that the most favorable supporting electrolyte type was NaCl for arsenic and boron removal. Increasing the supporting electrolyte concentration increased conductivity of solution. The higher conductivity values decreased energy consumption. Stirring speed affected arsenic and boron removal efficiency. The best stirring speed was found as 350 rpm for boron removal and 150 rpm for arsenic removal. Arsenic removal decreased when both stirring speeds under 150 rpm were not proved homogenization in the reactor. Stirring speed above 150 rpm prevented formation of Al(OH)₃ and to react between arsenic and Al⁺³ ions species.

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