Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Hansen, Henrik K. , Nuñez, Patricio and Jil, Cesar(2008) 'Removal of Arsenic from Wastewaters by Airlift Electrocoagulation. Part 2: Continuous Reactor Experiments', Separation Science and Technology, 43: 14, 3663 — 3675
To link to this Article: DOI: 10.1080/01496390802222533
URL: http://dx.doi.org/10.1080/01496390802222533

Separation Science and Technology, 43: 3663–3675, 2008

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802222533

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Abstract: Arsenic removal from wastewater is a key problem for copper smelters. Conventional methods either prove to be complicated, expensive, or not sufficiently effective. This work shows the results of electrocoagulation (EC) in aqueous solutions containing arsenic in a newly designed and constructed cylindrical continuous airlift reactor. The residence time distribution measurements showed that the reactor behaved as an ideal continuous stirred tank reactor (CSTR) with perfect mixing. Ten EC experiments were carried out in the continuous airlift reactor with sacrificial iron electrodes. The variables were: initial As(V) concentration, liquid flow rate, and electric current density. The results showed that the airlift EC process could reduce an initial As concentration from $1000\,mg\,L^{-1}$ to $220\,mg\,L^{-1}$ – corresponding to a reduction of 78%. In addition, a $100\,mg\,L^{-1}$ solution was reduced by 88%. The Fe-to-As (mol/mol) ratio, when EC was working properly, was in the range of 1.3–1.5, which is very promising for the future development of the reactor. The arsenic removal is proportional with the electric current, the electric charge and the CSTR residence time. On the other hand, when the flow rate is increased, the arsenic removal decreases.

Keywords: Airlift reactor, current, flow rate, iron electrodes, residence time distribution

Received 11 January 2008; accepted 6 April 2008.
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INTRODUCTION

Pyrometallurgic copper processing generates large amounts of arsenic that vaporize as arsenic trioxide. This compound is absorbed from the gas flow leading into the sulphuric acid plant together with a variety of heavy metals, creating a highly acidic contaminated wastewater. Wastewater from copper smelters is acidic and contains typically considerable amounts of copper, lead, cadmium, zinc, arsenic, and mercury (1). At the Codelco El Teniente copper smelter, heavy metals are precipitated as hydroxides but arsenic remains in the nearly pH-neutral wastewater (2). Combined $CaCO_3$ and $FeCl_3$ precipitation deals with the arsenic but since the arsenic concentration in the gas phase changes due to the batchwise operation of the smelter, it is difficult to predict and control the chemical dosage for the precipitation of the arsenic compounds. Typical arsenic concentrations in the wastewater during conventional processing are in the range of 100–1000 mg/L (after $CaCO_3$ addition) and 1–10 mg/L (after $FeCl_3$ addition).

Electrocoagulation, where sacrificial iron anodes are oxidized, has proven to be able to treat arsenic containing wastewaters (3–6). Arsenic is precipitated, and this precipitate can be removed from the solution by conventional methods. The dosage of the iron cations can be controlled by the electric current applied. Wastewaters with As concentration up to 5000 ppm can be treated by EC (7).

Two key factors have important influence on the efficiency of the EC to remove arsenic:

a) intense stirring to generate coagulates of Fe-oxides to co-precipitate with arsenate, and
b) oxidation of Fe^{2+} to Fe^{3+}. Hansen et al. (8)

showed that these effects could be obtained simultaneously in an airlift reactor, where either air or oxygen flow generated the stirring and the oxidizing conditions in a batch reactor.

On the other hand, often in industrial processes continuous wastewater treatment is needed, and therefore it would be of great importance if the airlift reactor could work in continuous operation.

The purpose of this work is to test an airlift reactor with continuous operation in synthetic wastewater solutions containing arsenic. First, the reactor will be analyzed hydrodynamically to have a description of the flow behavior in the reactor. This is done by determining the residence time distribution (RTD) of the reactor. Second, the arsenic removal

efficiencies will by analysed considering different operational parameters such as:

a) electric current,
b) EC time,
c) wastewater flow, and
d) initial arsenic concentration.

BACKGROUND

RTD of an EC Airlift Reactor

In order to be able to analyze the hydrodynamic characteristics of a reactor, one can determine the RTD. For this purpose, it is necessary that the reactor is at steady-state, transports at the inlet and the outlet takes place only by advection, and the fluid is incompressible. In a simple RTD experiment, a known tracer distribution is introduced into the inlet of a system, and the tracer concentration is recorded at the outlet after it has been modified by the system processes. Analysis of this convoluted output tracer distribution allows insight into the processes that brought those changes about. In addition to this simple case, tracer addition and detection may be performed at locations other than the system inlet and outlet, allowing for the isolation of particular flow phenomena of interest.

The flow behavior in a continuous reactor with a high degree of stirring is often approached to CSTR due to turbulent conditions. This approach could also be the case for the airlift EC cell first described by Hansen et al. (8). In this setup an air bubbling at the bottom of the cell together with the gas production at the electrodes creates the turbulence.

An ideal CSTR is based on the assumption that the flow at the inlet is completely and instantly mixed into the bulk of the reactor. The reactor and the outlet fluid have identical, homogeneous compositions at all times. An ideal CSTR has an exponential RTD:

$$E(t) = \frac{1}{\tau} e^{-t/\tau} \tag{1}$$

Where, E(t) is the exit age distribution, τ is the residence time of the reactor and t is the time.

τ is defined as the volume of the reactor divided by the flow rate. Introducing the concentration of the tracer at any time during the process the following expression is obtained:

$$C(t) = C_0 e^{-t/\tau} \quad (2)$$

where C(t) and C_0 is the tracer concentration at any time t and initially, respectively.

EXPERIMENTAL

Wastewater Characteristics

The arsenic containing wastewater was prepared by dissolving adequate amounts of Sodium Arsenate (Na_2HAsO_4 analytical grade) in distilled water to reach the wanted concentrations of 100 or 1000 mg L^{-1}. These concentrations were chosen to simulate the wastewater after $CaCO_3$ addition in conventional treatment. Four liters of solution were prepared for each experiment. The total arsenic and iron content in liquid samples was determined by an Atomic Absorbance Spectrophotometer (AAS). Detection limits were 2 mg L^{-1} and 1 mg L^{-1} for arsenic and iron, respectively. The pH of the solutions was in all cases initially around 7.

Experimental Setup

Figure 1 shows the experimental set-up used in this work. The cylindrical acrylic cell had a height of 20 cm and an inner diameter of 10 cm, and was open at the top. Two iron cylinders (each of 1 mm thickness) were placed inside the cell, and they were kept at approx. 3 cm from the bottom of the cell. The distance between the two cylinders was 2 cm. In the gap between the two iron cylinders at the bottom, a perforated PVC tube was placed in order to produce an airflow in between the cylinders. This airflow sucked liquid with it and when reaching the top, the air "lifted" the surface level of the liquid, and the generated liquid flow created turbulence in the reactor. Therefore, the main functions of the airflow are

a) the stirring in the cell and
b) the oxidation on Fe^{2+}.

The electrode surface area/volume (S/V) ratio for the reactor was estimated to be 16.7 m^2/m^3. The reactor was fed continuously from the

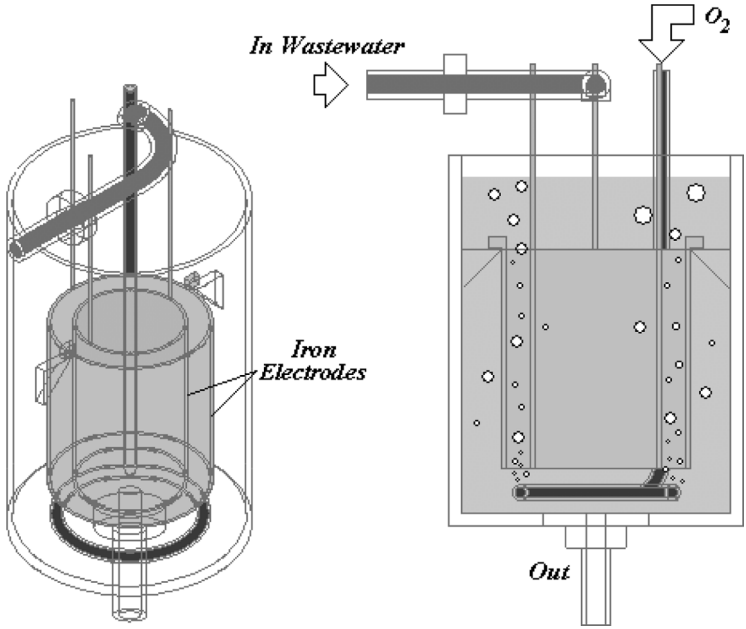

Figure 1. Experimental set-up. Cell height: 20 cm, Cell diameter: 10 cm, outer iron electrode diameter: 7 cm, inner iron electrode diameter: 5 cm, electrode height: 10 cm.

top, and the outlet was at the bottom. A valve connected to the tube at the outlet adjusted the flow so the volume inside the reactor was 1 L during the experiments.

An Extech power supply, a homemade devise to produce electric current reversal, a multimeter, and an oxygen gas container were used in the different experiments.

RTD Measurements

Three RTD experiments were carried out on the continuous EC reactor. 6 mg of methylene blue tracer was added to 10 mL of distilled water in all experiments. The cell was run with water flow rates of 0.06, 0.12 and 0.24 L min^{-1}, respectively. This correspond to the calculated CSTR residence times of 16.7, 8.3, and 4.2 min, respectively. The air flow was fixed at 1.7 L min^{-1}. The tracer was introduced at the inlet of the reactor. During the first 10 minutes, a sample at the outlet of the reactor was taken each minute. Hereafter, only every second minute 5 mL was

sampled. The concentration of the tracer in each sample was determined by UV spectrophotometry. For each flow rate a duplicate experimental run was done, and the average was taken.

EC Experiments

Ten series of EC experiments were carried out. See Table 1 for operational details. The experiments were done by preparing four liters of arsenic containing solution. An oxygen flow of 1.7 L min^{-1} was used in all experiments. The current was reversed each 2 minutes in order to minimize passivation of the iron anodes. Operational variables were: Initial As(V) concentration, applied electric current and wastewater flow. Either 100 or 1000 mg As L^{-1} solution was fed the EC reactor. Constant current was applied during experiments with current densities of 60 to 180 A m^{-2} (corresponding to 1–3 A). In order to avoid passivation of the anodes, the current was reversed each 60 seconds. Liquid flows from 0.06 to 0.24 L min^{-1} were used. Samples were taken from the outlet after 3 CSTR residence times (3 liters of solution had passed the cell) – except for experiment 3, where the samples were taken after 1, 2, 3 and 4 CSTR residence times. As and Fe concentrations were measured in the aqueous samples (after filtering through a 45 μm nuclepore filter).

RESULTS AND DISCUSSION

RTD Measurements

Figure 2 shows the reactor outlet concentration of the tracer as a function of time using different flow rates. From the figure it is seen that the reactor behavior is very close to ideal CSTR behavior for all flow rates. This makes scaling-up to industrial size of the reactor easy – assuming ideal CSTR. Based on the experimental data points, the true residence time τ can be calculated by rearranging the equation (2):

$$\tau = \frac{-t}{\log \frac{C(t)}{C_0}} \tag{3}$$

Now τ can be calculated at each sampling time, and the average can be estimated. For each of the three flow rates this gives: τ (0.060 L min^{-1}) = 16.8, τ (0.120 L min^{-1}) = 8.4, and τ (0.240 L min^{-1}) = 4.9. These values are very close to the calculated CSTR residence times, confirming that

Table 1. Continuous electrocoagulation. Experimental details and results. C_0: Initial arsenic concentration, $C_{f,i}$: Final concentration of element *i*

Exp.	C_0 mg/L	Liquid flow L/min	Electric current A	Residence time min	Electric charge[a] C	$C_{f,As}$mg/L	$C_{f,Fe}$mg/L	As removal %	Fe-to-As ratio mol/mol	Power usage Wh
1	100	0.06	3.0	16.67	3000	12	<1	88	13.2	8.3
2	1000	0.06	3.0	16.67	3000	220	<1	78	1.5	8.0
3	1000	0.06	3.0	16.67	3000	225[b]	<1	77.5	1.5	8.0
4	100	0.12	3.0	8.33	1500	20	<1	80	7.3	4.3
5	1000	0.12	3.0	8.33	1500	600	<1	40	1.5	4.1
6	100	0.24	3.0	4.17	750	50	<1	50	5.8	4.2
7	1000	0.24	3.0	4.17	750	770	<1	23	1.3	4.0
8	1000	0.06	0	16.67	–	980	8	2	–	–
9	1000	0.06	1.0	16.67	1000	700	<1	30	1.3	1.0
10	1000	0.06	2.0	16.67	2000	410	<1	59	1.3	2.8

[a]Electric charge during one CSTR residence time.
[b]An average of samples taken after 2, 3 and 4 CSTR residence times, respectively.

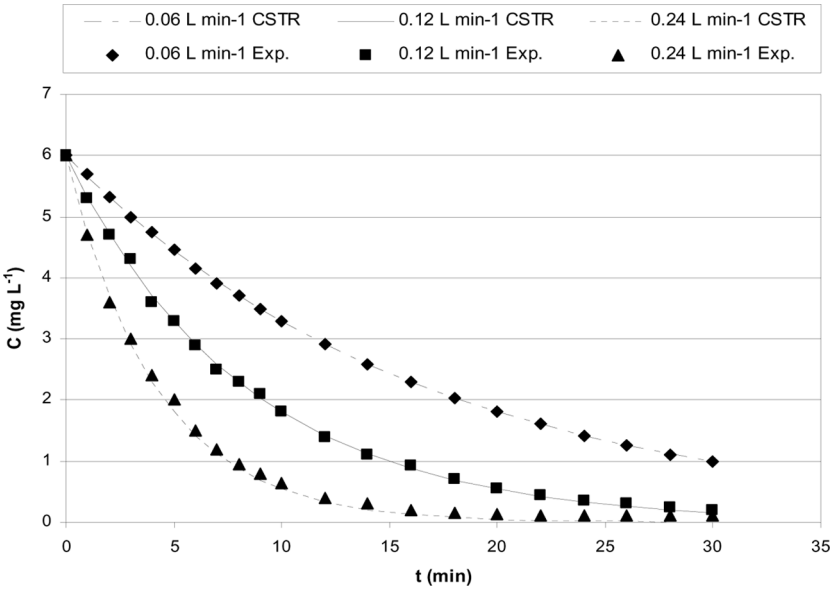

Figure 2. Methylene blue concentration with time for different flow rates. Experimental values and predictions considering a CSTR.

this particular airlift reactor is behaving very close to ideal CSTR. Only for the highest flow rate some deviation can be seen. This could be due to the detecting limit of the UV spectrometer ($0.1\,mg\,L^{-1}$) since all samples after 20 minutes for this flow rate were below the detection limit. Excluding these measurements, the average τ ($0.240\,L\,min^{-1}$) = 4.5.

EC Experiments

Table 1 shows a summary of the continuously operated EC results for all experiments. From the table it is noted that As can be removed from the wastewater solution in all EC experiments. Best arsenic removal is obtained in exp. 1, where a $100\,mg\,L^{-1}$ As solution is treated at a flow rate of $0.06\,L\,min^{-1}$. A red-orange precipitate was formed in all cases (except in exp. 8 without current). The majority of the precipitate was removed through the outlet of the reactor. The Fe-to-As ratio used in the table is defined as mol Fe^{2+} produced electrically (considering the only anode reaction to be $Fe \rightarrow Fe^{2+} + 2e^{-}$) divided by mol As removed as precipitate during one residence time. The Fe^{2+} is oxidized rapidly to Fe^{3+} by the introduced oxygen. When treating a $1000\,mg\,L^{-1}$ As solution, it can be seen that the EC reactor operates almost at a Fe-to-As

ratio of 1 (in the experiments between 1.3–1.5), which means that the main chemical reaction occurring during the process is $Fe^{3+} + AsO_4^{3-} \rightarrow FeAsO_4$. In addition, this low ratio assures only a small amount of final solid waste product in comparison to conventional treatment methods. The EC process seems very reproducible, which can be seen when comparing the arsenic removal for experiments 2 and 3. The removal is almost identical with exactly the same operational parameters. Furthermore, it can be seen that no residual iron is present in the outlet solution, insuring a high As removal efficiency of the produced ferric cations. pH was followed in some of the experiments, e.g. in experiment 1 the pH raised from initially 7.0 to around 7.8 after one CSTR residence time and stayed at that level during the rest of the experiment. This could indicate that OH^- is produced at the cathode and is promoting the arsenic precipitation.

In addition, the electrode loss during one CSTR residence time can be estimated from Table 1. The initial weight of the inner iron cylinder was 123 g. Taking exp. 1–3 as examples and assuming that the only anode reaction is: $Fe \rightarrow Fe^{2+} + 2e^-$, with a current reversal frequency of 60 seconds, one can estimate the loss of the electrode to 0.43 g for a residence time of 16.67 min. In other words, during each residence time around 0.35% of the electrode is corroded. This is an important issue when running the EC in a continuous way, since electrode substitution has to be carried out after a certain while.

Figure 3 shows the arsenic concentration at the outlet of the continuous EC cell with time passing a 1000 mg L^{-1} As solution through the cell at a flow rate of 0.06 L min^{-1} (exp. 3). The time was transferred to CSTR residence time units (the residence time for this experiment was 16.67 min). This was done in order to estimate when a steady state would be reached. From the figure it can be seen that after 2 residence times the concentration has reached a constant level. For the rest of the experiments, it was considered that after 3 residence times steady state should be reached, and therefore the As concentration was measured at this stage only.

Figure 4 shows the arsenic concentration in the outlet after steady state was reached as a function of the applied electric current. As expected, the outlet concentration is lower when applying a higher current. In this case the highest amount of iron is dissolved electrolytically, and therefore enhancing the arsenic precipitation. There is a small tendency indicating that at the highest current used (3A) the As removal efficiency is decreasing a little. This can be explained by the mass transfer limitation in the solution and possible presence of competing anode reactions. Even though, at even higher currents further As removal could be expected since the curve on the figure has not reached a constant level yet. On the other hand, no As removal is obtained after 3 residence times

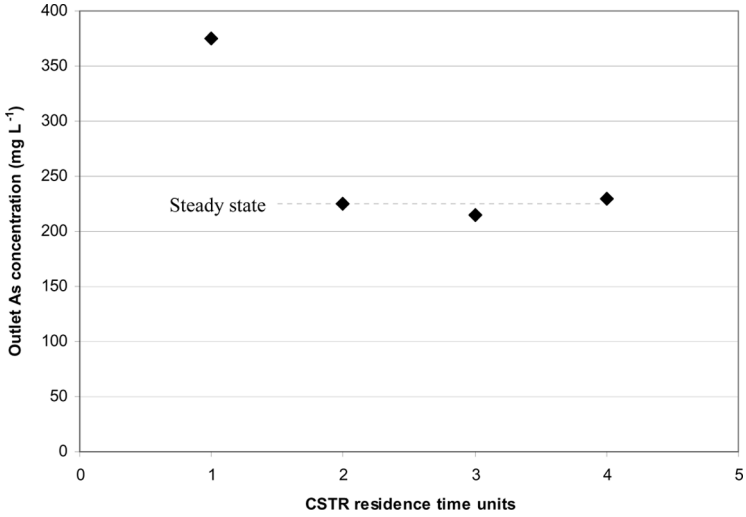

Figure 3. The arsenic concentration at the outlet of the EC reactor as a function of CSTR residence time units.

without applying current (exp. 8). This indicates that if any dissolution of the iron electrode is occurring it is to slow to have any influence on the EC results.

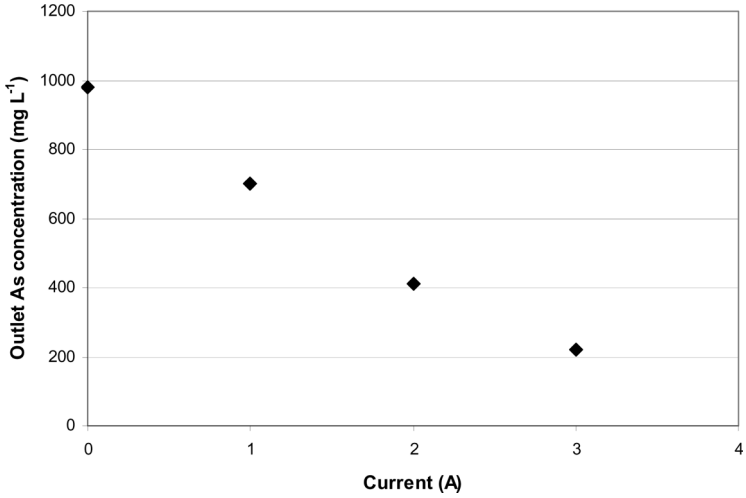

Figure 4. The arsenic concentration at the outlet of the EC reactor as a function of applied current.

Figure 5 shows the arsenic concentration at the outlet of the EC reactor as a function of the residence time. It can be noted that at lower flow rates less arsenic is present in the outlet – meaning a better As removal is obtained. This is not surprising, since the electric current is the same in all experiments (3A) and therefore when the flow rate is lower, more Fe^{2+} (and consequently Fe^{3+}) is produced per treated solution. A tendency is seen from Fig. 5 that the arsenic concentration in the outlet is approximately inverse proportional with the residence time. In other words this means that the arsenic removal is proportional with the residence time.

Figure 6 shows the arsenic removal as a function of electric charge. The electric charge is calculated as the applied current multiplied by the residence time. It can be seen that the arsenic removal is proportional with the electric charge in a large charge range. Only when treating 100 mg L^{-1} As, the curve for the arsenic removal flattens above 80%. This is also expected since less amount of As is remaining. So, relatively more Fe^{3+} has to be added at this low concentration to remove the rest of the arsenic. Mass transfer could be the limiting step for this concentration, and it could be hindered by the increased gas production when applying higher current. Another reason could be that the stress on the lower edges of two electrodes together with relative much higher electric field around them will make them corrode much faster than other parts of the electrodes. This could lead to waste of iron and electricity due to a

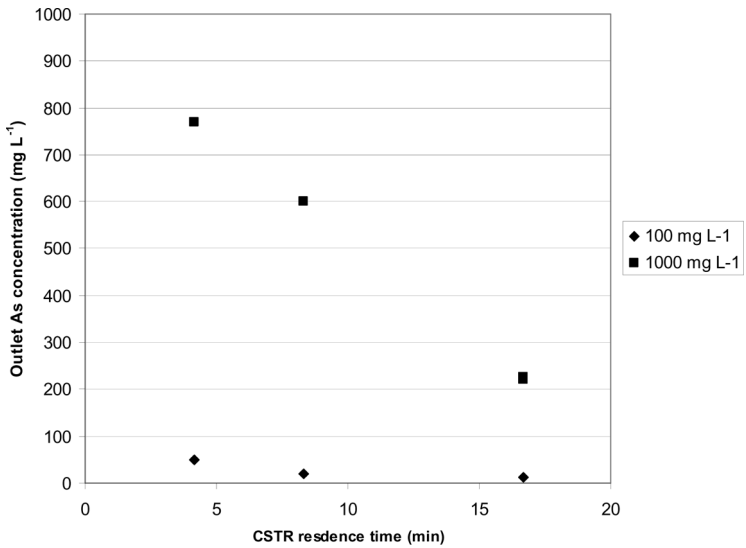

Figure 5. The arsenic concentration at the outlet of the EC reactor as a function of residence time.

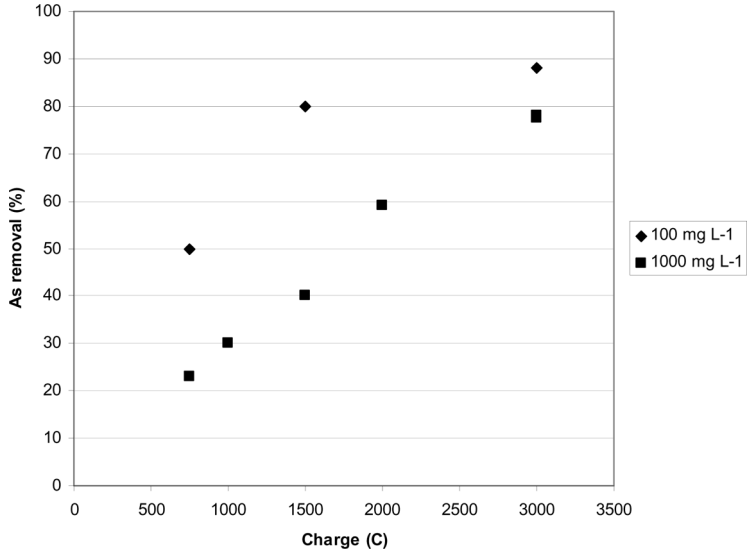

Figure 6. Arsenic removal as a function of applied electric charge.

loss of the dissolved iron at the outlet leading to a lower slope in Fig. 6. It has been shown by Hansen et al. (8) using batch airlift EC that the Fe-to-As ratio had to be high to reduce the concentration of arsenic below 10 ppm – around 20–28. On the other hand, for effective arsenate removal due to chemical precipitation, the Fe-to-As ratio should be higher than 4 (9). A question left for future investigation is until which level the continuous EC reactor can reduce the arsenic concentrations in wastewater solutions.

CONCLUSIONS

A continuous airlift EC reactor has been tested for the removal of arsenic from aqueous solutions. The residence time distribution measurement of the cylindrical reactor showed that the reactor behaves very close to an ideal CSTR reactor with complete mixing.

During the EC process Fe^{2+} is produced anodically and is oxidized by O_2 to Fe^{3+}, which precipitates with the arsenate present in the solution. The arsenic removal was seen to be efficient – 88% of arsenic was removed from a 100 mg L^{-1} solution applying 3 A with a flow rate of 0.060 L min^{-1}. Even when treating 1000 mg As L^{-1} solutions considerable arsenic reduction could be obtained.

The arsenic removal is proportional with the electric current, the electric charge and the CSTR residence time. On the other hand, when the flow rate is increased, the arsenic removal decreases.

A very promising finding was that the reactor operates with theoretical Fe-to-As mol ratios of about 1.3–1.5 when treating 1000 mg L^{-1} solutions. This is very low compared to conventional arsenate precipitation processes.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the FONDECYT Project No 1085118 and the UTFSM Project No 24.07.28.

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