REMOVAL OF ARSENIC FROM WASTEWATERS BY BATCH AIRLIFT ELECTROCOAGULATION

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ABSTRACT

Arsenic removal from wastewater is a key problem for copper smelters. This work shows results of electrocoagulation in aqueous solutions containing arsenic in a newly designed and constructed batch airlift reactor using iron electrodes. A series of electrocoagulation experiments were carried out in the reactor focussing on: initial As(V) concentration, use of either a pure oxygen or an air flow, remediation time, and electric current density. The results showed that the airlift electrocoagulation process could reduce an initial As concentration from 1000 mg L^{-1} to 40 mg L^{-1} – corresponding to a reduction of 96 %.

When the electrocoagulation process was working efficiently, the arsenic removal rate in the cell was found to be around 0.08 – 0.1 mg As/C and the Fe-to-As (mol/mol) ratio was in the range of 4-6.

Keywords: Electro-chemical Treatment, Coagulation, Arsenic, Iron, Water Treatment, Air Bubbles, Oxidation

1. 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]. Heavy metals are precipitated as hydroxides but arsenic remains in the nearly pH-neutral wastewater. Combined $CaCO_3$ and $FeCl_3$ precipitation can deal with most of the arsenic but since the arsenic concentration in the gas phase changes due to the batch wise operation of the smelter, it is difficult to predict and control the chemical dosage for the precipitation of the arsenic compounds.

Electrocoagulation is by now proven to be able to treat wastewaters from different industrial sources[2-3]. Typically, aluminium or iron plates are used as electrodes in the electrocoagulation process. When DC voltage is applied, the anodes sacrifice themselves to produce Al^{3+} or Fe^{2+} ions, which precipitate with the arsenic. Hansen *et al*.[4-5] found analysing preliminarily the electrocoagulation process in a rectangular reactor with cylindrical electrodes, that upto 99% of arsenic could be removed (from 5000 mg As/L solutions) using iron sacrificial electrodes. Here it was also shown that introduction of air was necessary to assure oxidation of dissolved iron. The effect of air bubbling not only oxidized Fe2+ to Fe3+ but also promoted the coagulation/flocculation process due to turbulence.

The purpose with this work is to evaluate the As(V) removal from aqueous solutions by a newly developed airlift process. The airlift produces the necessary turbulence in the reactor. Parameters studied are: a) initial arsenic concentration, b) the use of either oxygen or air as an oxidant, c) electric current density, and d) remediation time.

2. Methods

2.1. 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 5000, 1000 or 100 mg L^{-1}. The total arsenic and iron content in liquid samples was determined by an Atomic Absorbance Spectrophotometer (AAS).

2.2. Experimental setup and electrocoagulation experiments

Figure 1 shows the experimental set-up used in this work. The cylindrical acrylic cell had a total volume of approximately 1.5 L. Two iron cylinders were placed inside the cell at approx. 3 cm from the bottom of the cell. 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 generated turbulence in the reactor. The cell was filled with 1 L solution in each experiment. An Extech power supply, a homemade devise to produce electric current reversal, a multimeter, and an air compressor/oxygen gas container were used in the different experiments. Ten series of electrocoagulation experiments were carried out. See Table 1 for operational details. Operational variables were: Initial As(V) concentration, applied electric current and either an air or pure oxygen flow to produce the combined oxidation/airlift effect. The same air or oxygen flow was used in all experiments: 5 L/min. The current was reversed each 2 minutes in order to minimize passivation of the iron anodes. Constant current was applied during experiments – either 1, 2 or 3 A, corresponding to a current density of 60, 120 and 180 A/m2, respectively. The experiments were run for either 60, 120, 300 or 420 minutes depending on initial concentration and current strength. During and after experiments the As (all experiments) and Fe (only exp. 3-6 and 8) concentrations were measured in the solution.

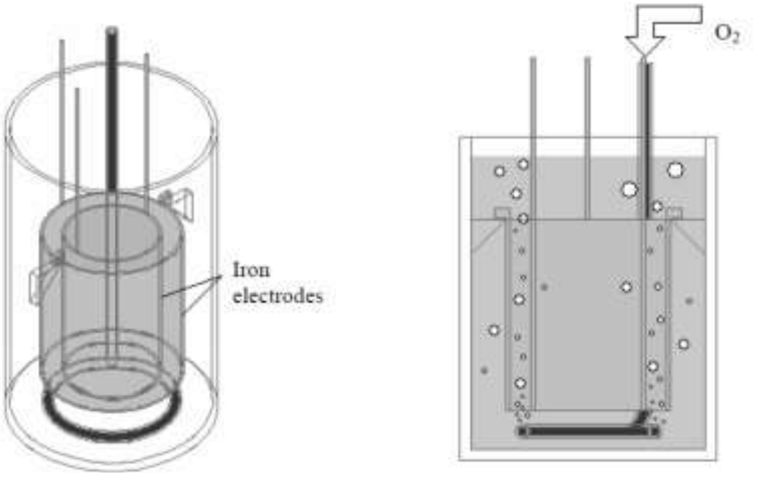


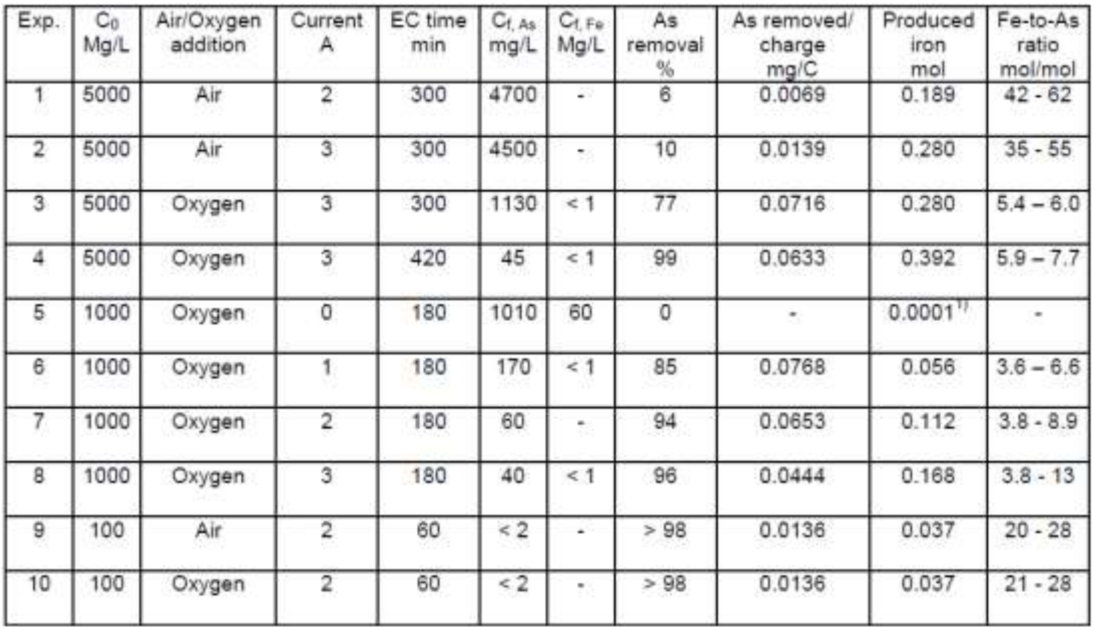
Figure 1: Experimental setup.

3. Results and discussion

In Table 1 electrocoagulation results for all experiments in terms of final As and Fe concentration, removal efficiency, removed arsenic/charge and Fe-to-As ratio are given. Initial concentrations were measured before all experiments and the standard deviations were: 5000 ± 25 mgL^{-1}, 1000 ± 15 mgL^{-1}, 100 ± 2 mgL^{-1}. In general it can be said that the airlift reactor is working successfully. A red-orange precipitate formed during most experiments (except exp. 1 and 5) indicating formation of ferric hydroxide. In the experiments with pure oxygen addition, the amount of precipitate was larger than with air bubbling. The cell potential was nearly constant during experiments. The overall arsenic removal as a function of applied electrical charge is also given in the table as an indication if the electrocoagulation process is working at an acceptable level.

It seems that for treating 5000 mgL^{-1} solutions efficiently, the arsenic removal rate would be around 0.06-0.07 mgC^{-1}. Higher rates could be possible but the reaction kinetics and mass transfer determining steps should be evaluated. When treating a 1000 mgL^{-1} solution, higher removal rates can be achieved (around 0.07-0.08 mgC^{-1}). The soluble iron content in the experiments was in all cases (except exp. 5) lower than the detection limit of the AAS – meaning all electrochemically dissolved iron is precipitated during the process. No residual Fe should therefore be removed from the cleaned wastewater.

Table 1: Electrocoagulation experiment details and results. C0: Initial arsenic concentration, Cf,i: Final concentration of element i, EC time: Electrocoagulation time.



Exp.	C_0 Mg/L	Air/Oxygen addition	Current A	EC time min	$C_{f, As}$ mg/L	$C_{f, Fe}$ Mg/L	As removal %	As removed/ charge mg/C	Produced iron mol	Fe-to-As ratio mol/mol
1	5000	Air	2	300	4700	-	6	0.0069	0.189	42 - 62
2	5000	Air	3	300	4500	-	10	0.0139	0.280	35 - 55
3	5000	Oxygen	3	300	1130	< 1	77	0.0716	0.280	5.4 – 6.0
4	5000	Oxygen	3	420	45	< 1	99	0.0633	0.392	5.9 – 7.7
5	1000	Oxygen	0	180	1010	60	0	-	$0.0001^{1)}$	-
6	1000	Oxygen	1	180	170	< 1	85	0.0768	0.056	3.6 – 6.6
7	1000	Oxygen	2	180	60	-	94	0.0653	0.112	3.8 - 8.9
8	1000	Oxygen	3	180	40	< 1	96	0.0444	0.168	3.8 - 13
9	100	Air	2	60	< 2	-	> 98	0.0136	0.037	20 - 28
10	100	Oxygen	2	60	< 2	-	> 98	0.0136	0.037	21 - 28

Considering that the only reaction at the anode is $Fe \rightarrow Fe^{2+} + 2e^-$ (which would be the case when no passivation of the anode is occurring), then the theoretical amount of produced Fe^{2+} can be calculated using Faraday`s law. The amount of As removed is measured, and then the ratio Fe-to-As in mol/mol can be estimated (see Table 1). The Fe-to-As is given as a range observed during the whole period of electrocoagulation. From Table 1 it is seen that electrocoagulation with 1000 and 5000 mgL^{-1} As with oxygen flow generally functions well showing Fe-to-As ratios around 4-6 mol/mol. This is quite low in comparison with conventional iron hydroxide/arsenate precipitation. Hansen *et al*.[3] presented Fe-to-As ratio in an airlift reactor around 14 mol/mol, when carrying out electrocoagulation on a 100 mgL^{-1} solution – compared to 20-28 mol/mol in this present work using the same current density. The configuration of the cells was somehow different. The higher Fe-to-As ratio with 100 mgL^{-1} could be due to mass transfer being the limiting step. Figure 2 shows the effect of the Fe^{2+}-to-Fe^{3+} oxidizing agent – either air or pure oxygen. The As concentration is given as a function of electrocoagulation time for experiments with 5000 mgL^{-1} solution applying different current strengths and oxidant.

Figure 2 shows the effect of the Fe^{2+}-to-Fe^{3+} oxidizing agent – either air or pure oxygen. The As concentration is given as a function of electrocoagulation time for experiments with 5000 mgL^{-1} solution applying different current strengths and oxidant. It is clearly seen, that the arsenic removal is better when adding oxygen than air at this arsenic concentration level. When using air only small amounts of arsenic are precipitated indicating that the Fe^{2+} oxidation step could be the limiting step in the process. Therefore, stronger oxidants (such as pure oxygen) should be considered to remove arsenic. For conventional arsenate/iron hydroxide precipitation purposes, several oxidants have been suggested, e.g. permanganate or ozone. The Fe^{2+} oxidation by air is enhanced at alkaline pH, therefore with time the oxidation could be faster, since pH rises during the electrocoagulation process. The low arsenic removal per charge (see Table 1) can be contributed to other rate determining steps such as mass transfer and diffusion.

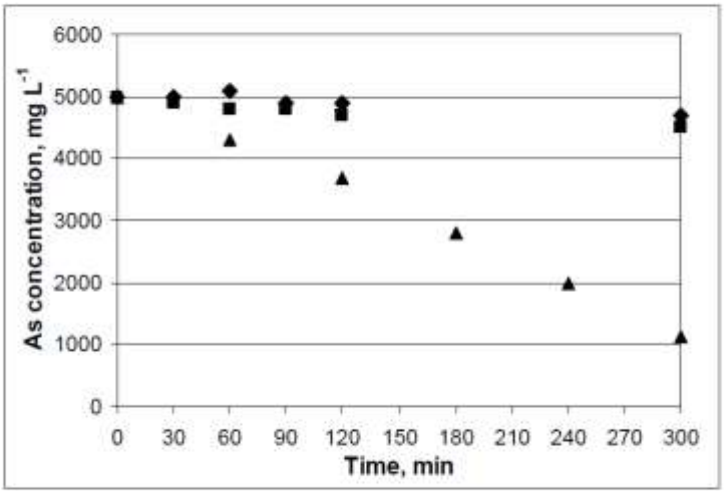


Figure 2: Arsenic removal by electrocoagulation with time. Initial concentration 5000 mg L-1. Legend ◆: 2 A, air; ■ : 3 A, air; ▲ : 3 A, oxygen.

Figure 3 shows the arsenic concentration in the solution as a function of time for exp. 5-8 when applying 0, 1, 2 or 3 A. Initial As concentration was 1000 mgL^{-1}. In the figure the effect of the current can be evaluated. It looks like the arsenic removal is almost proportional with the applied current - at least until around 90% of the arsenic is removed. Figure 3 indicates that the current could be raised even further, if faster arsenic removal is desired. The limiting current density has not yet been reached at 180 Am^{-2} (3 A).

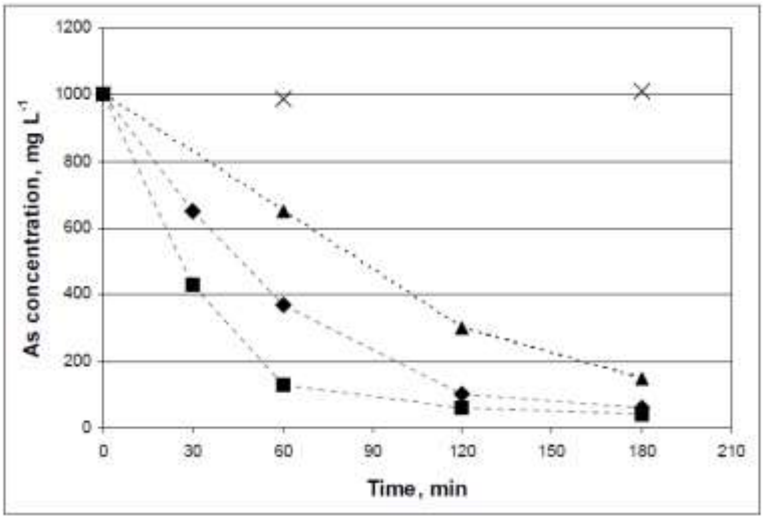


Figure 3: Arsenic removal by electrocoagulation with time. Initial concentration 1000 mg L-1. Legend: X: 0 A, oxygen; ▲ : 1 A, oxygen; ◆: 2 A, oxygen; ■ : 3 A, oxygen.

4. Conclusions

Electrocoagulation of As(V) in wastewaters is a promising remediation tool to remove arsenic by precipitation or adsorption. In a newly developed batch airlift reactor As removal efficiencies higher than 98 % were obtained in 100 mgL^{-1} As(V) solutions. In more concentrated arsenic solutions electrocoagulation functioned well, too. Oxidation of Fe^{2+} to Fe^{3+} seems to be a limiting step when treating concentrated arsenic solutions. Only small amounts of arsenic was removed from a 5000 mgL^{-1} solution by electrocoagulation in the batch airlift reactor using air as an oxidant. On the other hand, when using pure oxygen the removal rate increased remarkably.

The arsenic removal seems to be proportional with the charge, when working with current densities in the range 120 – 180 Am^{-2}. Around 0.1 mg As is removed per Coulomb. When the electrocoagulation process is working properly, the Fe-to-As ratio lies around 4 to 6. This low value makes the electrocoagulation process very competitive to conventional precipitation techniques.

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