This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

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

Removal of Arsenic from Wastewaters by Airlift Electrocoagulation: Part 3: Copper Smelter Wastewater Treatment

Henrik K. Hansen[a]; Lisbeth M. Ottosen[b]
[a] Departamento de Ingeniería Química y Ambiental, Universidad Técnica Federico Santa Maria, Avenida España, Valparaíso, Chile [b] Department of Civil Engineering, Technical University of Denmark, Lyngby, Denmark

Online publication date: 02 June 2010

To cite this Article Hansen, Henrik K. and Ottosen, Lisbeth M.(2010) 'Removal of Arsenic from Wastewaters by Airlift Electrocoagulation: Part 3: Copper Smelter Wastewater Treatment', Separation Science and Technology, 45: 9, 1326 — 1330

To link to this Article: DOI: 10.1080/01496391003697432

URL: http://dx.doi.org/10.1080/01496391003697432

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Separation Science and Technology, 45: 1326–1330, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496391003697432

Removal of Arsenic from Wastewaters by Airlift Electrocoagulation: Part 3: Copper Smelter Wastewater Treatment

Henrik K. Hansen[1] **and Lisbeth M. Ottosen**[2]
[1]*Departamento de Ingeniería Química y Ambiental, Universidad Técnica Federico Santa Maria, Avenida España, Valparaíso, Chile*
[2]*Department of Civil Engineering, Technical University of Denmark, Lyngby, Denmark*

The arsenic content in wastewater is of major concern for copper smelters. A typical complex wastewater treatment is needed with a combination of chemical and physical processes. Electrocoagulation (EC) has shown its potential for arsenic removal due to the formation of ferric hydroxide-arsenate precipitates. This work evaluates the feasibility of EC as a treatment process at various stages during conventional copper smelter wastewater treatment – with a focus on arsenic. The reactor used is a batch airlift electrocoagulator. The results showed that raw copper smelter wastewater was difficult to treat for arsenic and heavy metals with EC, mainly due to the very low pH. On the other hand, after a preliminary $Ca(OH)_2$ treatment for sulphate and heavy metal removal, arsenic could be removed totally by EC. In addition, EC could also be applied as a final remediation control tool for arsenic since the national threshold value for wastewater discharge could rapidly be reached when the conventional method did not clean the wastewater sufficiently.

Keywords airlift reactor; current density; electric field; heavy metals; iron electrodes

INTRODUCTION

The pyrometallurgic copper processing generates large amounts of arsenic that vaporize as arsenic trioxide. This compound is absorbed from the gas flow, creating a highly arsenic contaminated wastewater flow. Typically, a complex wastewater treatment is needed with a combination of chemical and physical processes. Wastewater from copper smelters is acidic and contains typically considerable amounts of copper, lead, cadmium, arsenic, and mercury (1).

At the Codelco El Teniente copper smelter, the wastewater treatment is generally as shown in Fig. 1 (2). Indicated on the figure is an initial oxidation step with H_2O_2 to oxidize all species, in particular arsenic, in the wastewater. Metals such as copper and zinc are mainly precipitated as hydroxides together with calcium sulphate in the first precipitation step but a large amount of arsenic remains in the slightly alkaline wastewater. Combined $Fe_3(SO_4)_2$ and $FeCl_3$ addition in acid 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 $5000-15000\,mg\,L^{-1}$ (raw wastewater), $100–1000\,mg\,L^{-1}$ (after $Ca(OH)_2$ addition) and $0.1–5\,mg\,L^{-1}$ (after $Fe_3(SO_4)_2/FeCl_3$ addition). Since the Chilean norm for wastewater discharge in rivers is $0.5\,mg\,L^{-1}$ and the internal Codelco norm for wastewater reuse as process water is $1\,mg\,L^{-1}$, in some cases the wastewater has to be recirculated back into the treatment process or reused with a higher content of arsenic. Both these options are undesirable for the copper smelter.

Electrocoagulation is by now a well known process and has treated a variety of different wastewaters (3–6). Lately electrocoagulation has shown to be efficient for arsenic removal from different water streams (7–11). Treatment of arsenic containing wastewater is a high priority environmental necessity. Hansen et al. (10) proposed a newly designed airlift electrocoagulation cell. Cylindrical iron plates were used as sacrificial electrodes to produce Fe^{2+} cations in the electrocoagulation process with frequent current reversal to avoid passivation of the anodes. Turbulence (and mixing) was achieved by both the air flow (produced by the airlift principle) and the gases from the electrode reaction. The oxygen in the airflow also oxidized Fe^{2+} to Fe^{3+}, which promoted the precipitation of $FeAsO_4$ and adsorption of arsenic onto Fe(OH)O colloids. Arsenic removal efficiencies in batch experiments were found to be higher than 98%—starting with concentration of $100\,mg\,L^{-1}$ of As(V). Even with a concentration in synthetic wastewater samples as high as $5000\,mg\,L^{-1}$ of As(V) efficient arsenic removal was found (10). Still it

---

Received 23 October 2009; accepted 11 January 2010.

Address correspondence to Henrik K. Hansen, Departmento de Ingeniería Química y Ambiental, Universidad Técnica Federico Santa Maria, Avenida España, Valparaíso 1680, Chile. E-mail: henrik.hansen@usm.cl

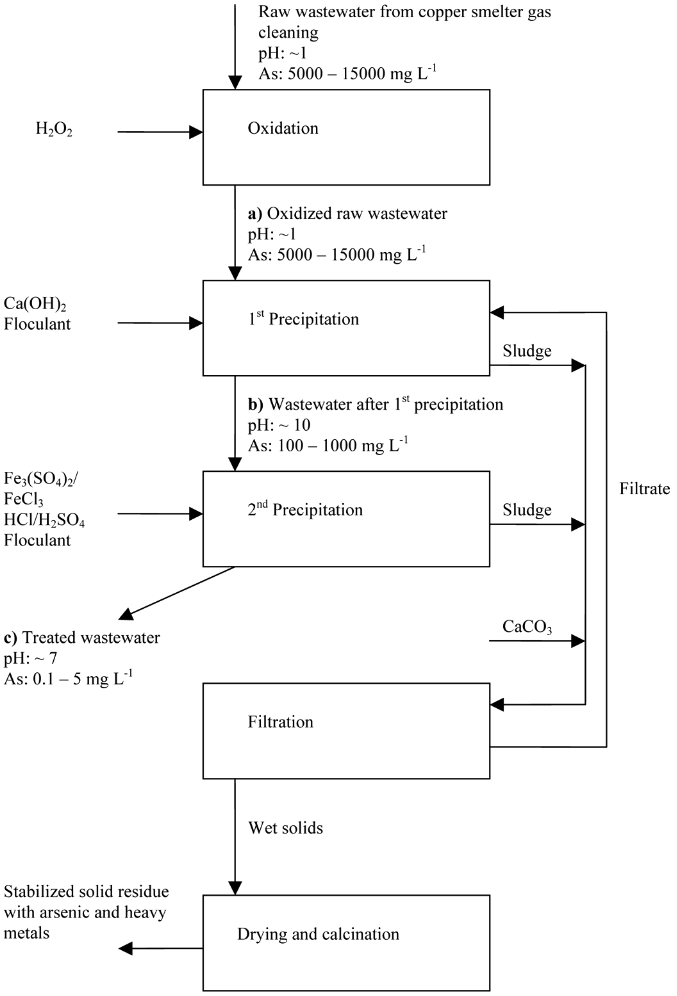


FIG. 1. Actual copper smelter treatment scheme.

had to be analyzed if real copper smelter wastewater could be treated for arsenic by the method.

This work focuses on the treatment of real copper smelter wastewater with an airlift batch electrocoagulation reactor. The efficiency of the process will be tested for the raw wastewater and wastewater from different stages in the actual wastewater treatment plant. Parameters that would be analyzed are the treatment time and the applied electric current. The results are evaluated in terms of arsenic removal efficiency.

EXPERIMENTAL

Analytical

Before and after the experiments each solution was filtered (paper filter grade 131), and As, Cu, Pb, and Cd contents were determined by an Atomic Absorbance Spectrophotometer (AAS).

The pH was measured by a standard combination pH electrode connected an ORION, model 370, pH-meter.

Wastewater Characteristics

The arsenic containing wastewater was sampled at the Codelco El Teniente copper smelter, VI Region, Chile. Three different samples were taken:

a. oxidized raw wastewater – WW1,
b. wastewater after $Ca(OH)_2$ precipitation – WW2, and
c. treated wastewater – WW3.

These samples correspond to the points a, b, and c, respectively, on Fig. 1. Table 1 gives specific details on these wastewater samples. Each sample was initially measured for As, Cu, Pb, Cd, and Zn in triplicate. More than 99% of the arsenic was found to be As(V) for all three wastewater samples.

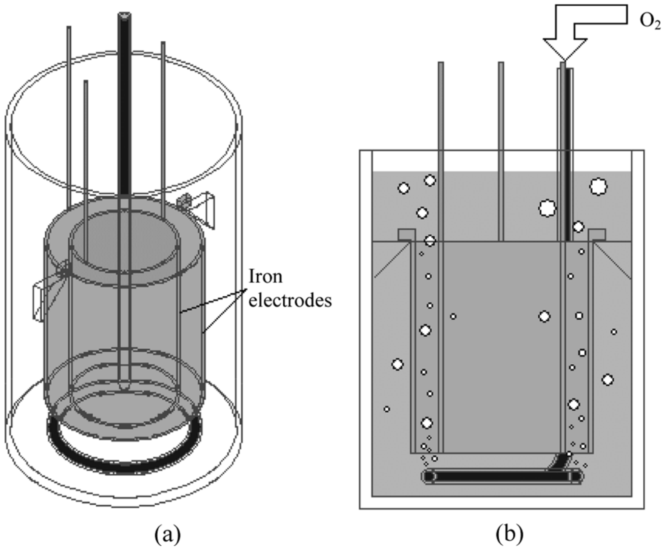
Experimental Setup

Figure 2 shows the experimental setup used in this work. The cylindrical acrylic cell (thickness 2.5 mm) had an inner height and diameter of 20 cm and 10 cm, respectively. The total volume (without electrodes) was approximately 1.5 L. Inside the cell were placed two iron cylinders – one of 7 cm diameter (outer cylinder) and one of 5 cm diameter (inner cylinder). The height of the cylinders was 10 cm, and they were maintained 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 oxygen flow in between the cylinders. This oxygen flow sucked liquid with it and when reaching the top, the oxygen "lifted" the surface level of the liquid, and the generated liquid flow created turbulence in the reactor. The electrode surface area/volume (S/V) ratio for the reactor was estimated to $16.7\,m^2/m^3$.

An Extech power supply, a homemade electric current reverser, a multimeter, and an air compressor/oxygen gas container were used in the different experiments.

TABLE 1
Characteristic data of the different wastewater samples

Sample type	Sample code	C_{As} mg L^{-1}	C_{Cu} mg L^{-1}	C_{Pb} mg L^{-1}	C_{Cd} mg L^{-1}	pH
a) Raw wastewater	WW1	5250 ± 150	720 ± 30	450 ± 25	4.0 ± 1.0	0.7 ± 0.3
b) After $Ca(OH)_2$ treatment	WW2	910 ± 40	6.0 ± 0.3	5.0 ± 0.3	<0.1	9.9 ± 0.1
c) Treated wastewater	WW3	4.38 ± 0.22	0.20 ± 0.10	<0.2	<0.1	7.0 ± 0.1



(a) (b)

FIG. 2. 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.

Electrocoagulation Experiments

A total of thirty-two electrocoagulation experiments were carried out on the three wastewater samples:

1. oxidized raw wastewater (WW1),
2. wastewater treated with calcium hydroxide (WW2), and
3. final treated wastewater (WW3).

See Table 2 for operational details. Since the arsenic concentration in the final treated wastewater still was too high for discharge, this wastewater sample was tested with electrocoagulation too.

The experiments were done by treating 1 L wastewater samples in batch; each experiment lasted a pre-determined period of time. After the experiment, the sample was filtered and element concentration was measured. The initial and final pH was recorded too. The same oxygen flow was used in all experiments: 5 L min^{-1}. The constant current was reversed every second minute in order to minimize passivation of the iron anodes.

TABLE 2
Experimental plan

Sample type	Sample code	Time	Current
a) Raw wastewater	WW1	60–300 min	2–5 A
b) After 1st precipitation	WW2	15–120 min	2–5 A
c) Treated wastewater	WW3	2–20 min	0.8–5A

TABLE 3
Electrocoagulation results for raw wastewater (WW1)

Time (min)	I (A)	Final pH	C_{As} (mg L^{-1})	C_{Cu} (mg L^{-1})	C_{Pb} (mg L^{-1})	C_{Cd} (mg L^{-1})
60	2	0.7	5100	710	430	4.5
120	2	0.7	5150	690	440	3.9
300	2	0.9	5300	700	450	4.2
60	3	0.7	5050	710	440	3.8
120	3	0.8	5400	710	430	4.2
300	3	1.1	5200	730	440	3.9
60	5	0.7	5400	700	440	4.5
120	5	0.8	5320	730	460	3.7
180	5	1.0	5300	700	440	4.0
240	5	1.4	4990	660	425	3.6
300	5	1.8	4750	610	410	3.0

RESULTS AND DISCUSSION

From Table 1 it can be seen that all elements analyzed are found in elevated concentrations in the raw wastewater but after the calcium hydroxide treatment only arsenic is the real concern. In the final treated wastewater arsenic is still found in too high a concentration—in contrast to the other elements—and arsenic has to be removed from this solution before discharge. In this work, the focus is on arsenic removal—only when treating the raw wastewater, the removal of the other elements is followed too.

Tables 3–5 show the electrocoagulation results for WW1, WW2, and WW3, respectively. When first analyzing the oxidized raw wastewater (WW1) in Table 3 it can be noted that the arsenic and heavy metal removal

TABLE 4
Electrocoagulation results for raw wastewater after $Ca(OH)_2$ precipitation (WW2). Initial arsenic concentration: 910 mg L^{-1}

Time (min)	I (A)	Final pH	C_{As} (mg L^{-1})	Arsenic removal (%)	Fe-to-As ratio (mol mol^{-1})
30	2	9.9	600	34.1	4.5
60	2	9.9	320	64.8	4.7
90	2	10.3	170	81.3	5.7
120	2	10.3	70	92.3	6.6
180	2	10.4	17	98.1	9.4
240	2	10.5	<0.02	>99.9	12.3
30	5	10.0	330	63.7	6.0
60	5	10.0	150	83.5	9.2
90	5	10.4	49	94.6	12.2
120	5	10.6	9.7	98.9	15.5
180	5	10.7	<0.02	>99.9	23.0
240	5	10.9	<0.02	>99.9	30.7

TABLE 5
Electrocoagulation results for treated wastewater (WW3). Initial arsenic concentration: 4.38 mg L^{-1}

Time (min)	I (A)	Final pH	C_{As} (mg L^{-1})	Arsenic removal (%)	Fe-to-As ratio (mol mol^{-1})
2	0.8	7	0.08	98.2	8.7
5	0.8	7	<0.02	>99.5	21.3
20	0.8	7	<0.02	>99.5	85.1
2	2	7	<0.02	>99.5	21.3
5	2	7	<0.02	>99.5	53.2
20	2	7	<0.02	>99.5	213
2	5	7	<0.02	>99.5	53.2
5	5	7	<0.02	>99.5	133
20	5	7	<0.02	>99.5	532

seems very slow. Only for the experiments carried out at 5A and longer than 240 min duration some indication of removal was observed. In fact, only in these two experiments some amounts of orange/brown solids were formed during the EC process. In these experiments the final pH reached 1.4 and 1.8, respectively. Probably the pH was too low in the other experiments to form the necessary ferric hydroxides or hydrous ferric oxides (HFO), which are known to adsorb arsenic and heavy metals efficiently (12). Therefore, the EC process should have been carried out for a longer time in order to first neutralize the wastewater to a certain pH level before any arsenic removal could be an option. For practical implementation at this stage of the wastewater scheme shown in Fig. 1, it would be convenient with first a neutralization step with reagent addition, such as $Ca(OH)_2$, in small amounts to reach a pH of around 2 to 4 followed by electrocoagulation.

Another option could be the implementation of the EC process after the actual $Ca(OH)_2$ addition – at point b on Fig. 1. This specific treatment has several objectives:

a. to remove sulphates,
b. to increase the pH to around 10 in order to precipitate heavy metal cations, and
c. to precipitate some arsenic as $Ca_3(AsO_4)_2$.

The clarified solution from the sedimentation was sampled and called WW2 in this work. From Table 4 it can be observed that arsenic could be removed to less than the detection limit after 240 minutes with 2A when treating WW2 with EC. Increasing the current to 5A, complete removal was obtained after 180 minutes. In this work the behavior of the heavy metals during EC of WW2 was not followed due to the relative low concentration in this sample (see Table 1).

Figure 3 shows the arsenic removal from the WW2 sample with time together with an identical series of experiments recently published in this journal (10) with a synthetic wastewater sample of 1000 mg L^{-1}. As it can be seen from the figure, the removal tendencies are similar with time for the real and the synthetic wastewater. Therefore, the behavior of the real wastewater could be simulated well by the synthetic wastewater sample. Arsenic would also be expected to be the main species in this sample, since the $Ca(OH)_2$ treatment has removed considerably the heavy metals, sulphates, and acidity. Increasing the current, the arsenic removal increases with time too, meaning that the current could be an efficient Fe^{3+} dosage mechanism. For both currents investigated in this work on $Ca(OH)_2$ treated copper smelter wastewater, arsenic could be removed completely.

From Table 5 it can be seen that arsenic is removed rapidly from the treated wastewater WW3. For a 2 min treatment, using the lowest current (0.8 A), already 98% of the arsenic has been removed. For higher currents, at 2 min the arsenic concentration is below the detection limit. The same is the case for longer treatment at all applied current densities. For all experiments, the arsenic concentration after treatment was below the Chilean norm for discharge. During EC of WW3, iron hydroxides were formed in all experiments and the amounts produced were in proportion with the applied current and treatment time. This means that the EC process could be a very efficient control option for the treated wastewater. Therefore, the $Fe(OH)_3$ dosage could be controlled with the applied current as shown above.

Considering that the only reaction at the anode is $Fe \rightarrow Fe^{2+} + 2\ e^-$(which would be the case when no passivation of the anode is occurring), then the theoretical amount of produced Fe^{2+} can be calculated when knowing the total electrical charge passed through the system:

$$Fe = \frac{C}{2F}$$

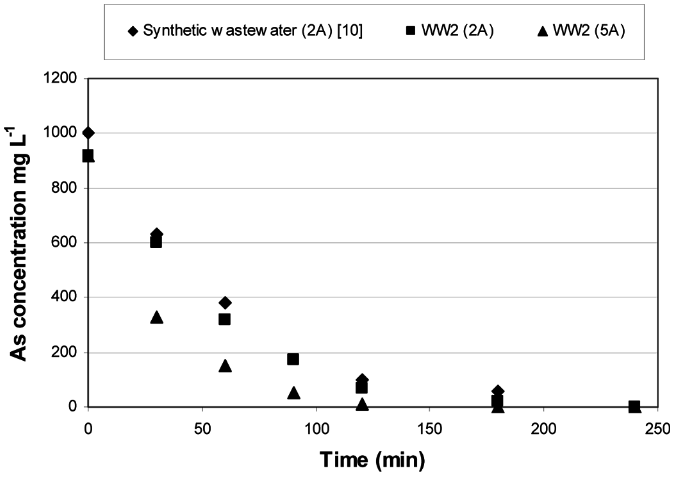


FIG. 3. Results for the EC treatment of WW2 and synthetic wastewater with 1000 mg L^{-1} (10).

where Fe is mol Fe^{2+} produced, C are the coulombs passed through the system and F is Faradays constant.

It must be stated that the theoretical amount of dissolved iron due to Faraday's law does not take into account any chemically dissolved iron. The amount of As removed is measured, and then the ratio Fe-to-As in mol/mol can be estimated (see Tables 4 and 5). It can be seen from Table 4 (WW2) that the Fe-to-As ratio is quite low (around 4 to 6) in the beginning of the EC process. It is here where most of the As is removed. When the concentration of arsenic is getting lower, e.g., after some EC time, a considerably larger amount of iron is needed to reach the threshold value. The Fe-to-As ratios are in the same order than previous experiments done on synthetic arsenic wastewater (10). At any rate, a Fe-to-As ratio of 12 to remove all arsenic is not high compared with conventional ferric ion treatment (13,14). Here values of 5 up to 100 are reported considering a lower initial arsenic concentration in the wastewater. From Table 5 it can be noted that the Fe-to-As ratio is much higher when treating WW3. In other words, the majority of the experiments with WW3 have been producing an excess of cationic iron, and all the arsenic has been removed long before the end of the experiments. In fact, only exp. 1 can be used to evaluate correctly the effect of the ratio, since the EC process is still active. Here the Fe-to-As ratio is comparable with the WW2 treatment.

CONCLUSIONS

This work evaluates the feasibility of EC as a treatment process at various stages during conventional copper smelter wastewater treatment with the focus on arsenic. The reactor used is a batch airlift electrocoagulator.

The results showed that raw oxidized copper smelter wastewater was difficult to treat for arsenic and heavy metals with EC, mainly due to the very low pH.

On the other hand, after a preliminary $Ca(OH)_2$ treatment for sulphate and heavy metal removal, arsenic could be removed totally by EC. Therefore, for a new treatment plant this would be the most convenient option.

In addition, EC could also be applied as a final remediation control tool for arsenic since the national threshold value for wastewater discharge could rapidly be reached when the conventional method did not clean the wastewater sufficiently. In an actual wastewater plant, this option would be interesting since it could be a feasible add-on process to the existing treatment scheme.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the FONDECYT Project N° 1100440. Ana Gonzalez, Sandra Aguirre, Cristian Maureira, Cesar Jil, and Alejandro Jeria are acknowledged for help with the experimental work.

REFERENCES

1. The World Bank Group. (1999) *Pollution Prevention and Abatement Handbook, 1998*; World Bank: Washington D.C., USA.
2. Codelco, Chile. (2009) Internal information.
3. Kobya, M.; Can, O.T.; Bayramoglu, M. (2003) Treatment of textile wastewaters by electrocoagulation using iron and aluminium electrodes. *Journal of Hazardous Materials*, B100: 163–178.
4. Beck, E.C.; Giannini, A.P.; Ramirez, E.R. (1974) Electrocoagulation clarifies food wastewater. *Food Technology*, 22: 18–19.
5. Mills, D. (2000) A new process for electrocoagulation. *Journal of American Water Works Association*, 92: 34–43.
6. Chen, X.; Chen, G.; Yue, P.L. (2000) Separation of pollutants from restaurant wastewater by electrocoagulation. *Separation and Purification Technology*, 19: 65–76.
7. Balasubramanian, N.; Madhavan, K. (2001) Arsenic removal from industrial effluent through electrocoagulation. *Chemical Engineering & Technology*, 24: 519–521.
8. Kumar, P.R.; Chaudhari, S.; Khilar, K.C.; Mahajan, S.P. (2004) Removal of arsenic from water by electrocoagulation. *Chemosphere*, 55: 1245–1252.
9. Hansen, H.K.; Nuñez, P.; Raboy, D.; Schiappacasse, I.; Grandon, R. (2007). Electrocoagulation in wastewater containing arsenic: Comparing different process designs. *Electrochimica Acta*, 52(10): 3464–3470.
10. Hansen, H.K.; Nuñez, P.; Jil, C. (2008). Removal of arsenic from wastewaters by airlift electrocoagulation. Part 1: Batch reactor experiments. *Separation Science and Technology*, 43(1): 212–224.
11. Hansen, H.K.; Nuñez, P.; Jil, C. (2008). Removal of arsenic from wastewaters by airlift electrocoagulation. Part 2: Continuous reactor experiments. *Separation Science and Technology*, 43(14): 3663–3675.
12. Streat, M.; Hellgardt, K.; Newton, N.L.R. (2008) Hydrous ferric oxide as an adsorbent in water treatment: Part 3: Batch and mini-column adsorption of arsenic, phosphorus, fluorine and cadmium ions. *Process Safety and Environmental Protection*, 86: 21–30.
13. Krause, E.; Ettel, V.A. (1989) Solubilities and stabilities of ferric arsenate compounds. *Hydrometallurgy*, 22(3): 311–337.
14. Harper, R.; Kingham, N.W. (1992) Removal of arsenic from wastewater using chemical precipitation methods. *Water Environment Research*, 64: 200–203.