J Appl Electrochem (2010) 40:1031–1038
DOI 10.1007/s10800-009-0045-6

ORIGINAL PAPER

Electrochemical peroxidation as a tool to remove arsenic and copper from smelter wastewater

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Received: 31 August 2009 / Accepted: 25 November 2009 / Published online: 11 December 2009

Abstract Electrochemical peroxidation (ECP) is a method that recently has been applied in the treatment of heavy metal polluted wastewater. This method is based on the anodic dissolution of iron to ferrous ions that reacts with H_2O_2 to produce tiny particles of ferric oxides. These oxides adsorb metals efficiently from aqueous solutions. In the present study, the technique was tested experimentally on copper smelter wastewaters with high concentrations of copper and arsenic. A completely mixed airlift batch reactor was used, and the copper and arsenic removal was measured both for synthetic and real wastewater samples. The concentric iron electrodes acted as ferrous ion source when applying a constant direct current with current reversal every minute and the H_2O_2 was added dropwise. Initial pH was fixed at 3.5, 5.0 and 6.5, respectively. The best results with the synthetic wastewater showed >99% removal of copper and 80% removal of arsenic (at pH 6.5). When treating the real wastewater samples, both arsenic and copper could be removed more than 99% for all pH levels studied. It can be concluded that presence of other substances in the real wastewater favours the arsenic adsorption and/or precipitation. The copper and arsenic removal velocity was found to be dependent of pH—with the fastest removal at pH 3.5. The ECP could be regarded as a promising remediation method for treating highly contaminated wastewaters since arsenic (from 1000 mg L^{-1}) and copper (from 300 mg L^{-1}) was removed nearly completely from copper smelter wastewaters.

Keywords Hydrated ferric oxides · Adsorption · Precipitation · Electrochemical processes · Peroxidation

1 Introduction

Mining activities have importance for the Chilean economy since Chile is one of the principal copper manufacturers in the world. During the processing and concentration of the minerals considerable amounts of residues and wastewaters are produced, and especially acidic wastewaters is causing concern since their heavy metal and arsenic concentration is by far over the Chilean threshold value for discharge in the nearby aquatic environment.

At present, the wastewaters are treated with $Ca(OH)_2$ to increase the pH, which favours the precipitation of heavy metals as hydroxides that are separated by settling and filtration. These solids have high water content and needs a posterior treatment of drying and calcination to stabilize the residue. This treatment requires large amounts of $Ca(OH)_2$ and results in large amount of solids to be separated and treated including high energy consumption.

Several technologies are available based on the use of ferric hydroxides, also known as hydrous or hydrated ferric oxides (HFOs), to remove heavy metals from wastewater. HFOs are highly insoluble solids ($K_{sp} \approx 10^{-38}$) that form orange-brown jelly flocs when suspended in water with a large surface area (around 600 $m^2\ g^{-1}$). They have a high adsorption capacity for several heavy metals, and therefore often used in wastewater treatment [1–3].

Between the methods using and forming HFOs one can mention electrochemical peroxidation (ECP) [4, 5]. This

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method was originally invented for oxidation of organic contaminants in wastewater since the process uses the reactions resulting when applying Fenton's reagent [6]. Fenton's reagent uses a ferrous catalyst together with hydrogen peroxide to produce highly oxidative hydroxyl radicals ($OH^\bullet$). Along with the reaction of Fe^{+2} with hydrogen peroxide, also HFOs are obtained as a secondary product. This last reaction can be intensified for heavy metal removal.

In the original Fenton reactions the ferrous ions are added as salts (typically $FeCl_2$ or $FeSO_4$), which increases the concentration of chloride or sulphate in the wastewater, creating a secondary contamination. In the ECP process steel electrodes are used and when applying a DC current between them, Fe^{2+} is produced and released to the solution by the anode process. Hydrogen peroxide is added simultaneously—creating Fenton's reagent. At the cathode, OH^- is produced—favouring further the formation of small hydroxides [7]. The heavy metal and arsenic removal mechanisms are several, and these include ion exchange, cementation, specific adsorption and precipitation [3, 4, 8].

The objectives with this work are: (i) to evaluate the arsenic and copper removal efficiency when applying ECP to synthetic wastewaters, (ii) to evaluate the arsenic and copper removal efficiency when applying ECP to real copper smelter wastewater samples, (iii) to compare the removal behaviour from synthetic and real wastewater, respectively, and (iv) to evaluate the influence of pH on the ECP process.

2 Theoretical background

When using ECP, the heavy metal and arsenic removal occurs due to the formation of HFOs as mentioned above followed by an adsorption and/or co-precipitation. The total removal process consists of a series of reactions:

(i) Generation of ferrous ions by anodic dissolution

At the anode, iron at oxidation state zero is oxidised and released to the solution as iron(II):

$$Fe_{(s)} \rightarrow Fe^{+2}_{(ac)} + 2e^- \tag{1}$$

(ii) Cathodic reactions

At the cathode, the main reaction is the water reduction. This is in neutral to basic conditions observed by hydrogen evolution and production of hydroxyl ions, which are released to the solution:

$$2H_2O + 2e^- \rightarrow H_{2(gas)} + 2OH^- \tag{2}$$

In acidic conditions the following reaction occurs:

$$2e^- + 2H^+ \rightarrow H_{2(gas)} \tag{3}$$

(iii) Oxidation reactions

- Ferrous to ferric iron oxidation (Fenton's Reagent)

The total reactions occurring due to Fenton's Reagent are complex [9]. The main reactions when applying the Fenton reactions during ECP are given here:Oxidation of ferrous iron to ferric iron is caused by hydrogen peroxide:

$$H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^\bullet + OH^- \tag{4}$$

In addition, the free hydroxyl radical produced during reaction (4) also oxidises Fe(II) to Fe(III):

$$OH^\bullet + Fe^{+2} \rightarrow Fe^{+3} + OH^- \tag{5}$$

- Arsenite to arsenate oxidation

When arsenic is present in aqueous solution as As(III), the hydrogen peroxide acts as oxidant forming As(V) as indicated by reaction (6):

$$H_2O_2 + H_3AsO_3 \rightarrow H_3AsO_4 + H_2O \tag{6}$$

This reaction occurs simultaneously with the ferrous to ferric iron oxidation.

(iv) Formation of HFOs when ferric iron is present

The formation of HFOs can by represented as:

$$Fe^{+3} + 3OH^- \rightarrow Fe(OH)_3\downarrow \tag{7}$$

and

$$Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3H^+ \tag{8}$$

depending on the local conditions.

(v) Adsorption of heavy metals and arsenic by iron hydroxides

Arsenic adsorption could be represented as:

$$\alpha Fe(OH)_{3(s)} + \beta As \rightarrow \alpha Fe(OH)_3 * \beta As \tag{9}$$

Metal cations such as Cu^{2+} are equally adsorbed efficiently by the HFOs, and the process could be represented as:

$$\lambda Fe(OH)_{3(s)} + \delta Cu^{+2} \rightarrow \lambda Fe(OH)_3 * \delta Cu^{+2} \tag{10}$$

When other metals are present as is the case of copper smelter wastewater then these also tend to adsorb to or precipitate with the HFOs, and the process could be represented as:

$$\gamma Fe(OH)_{3(s)} + \phi M^{+\omega} \rightarrow \gamma Fe(OH)_3 * \phi M^{+\omega} \tag{11}$$

3 Experimental

3.1 Reagents

The synthetic wastewaters was prepared by dissolving the calculated amount of either $CuSO_4{\cdot}5H_2O$ or $NaAsO_2$ (both analytical grade) in distilled water. The calculated amounts were based previous copper smelter wastewater sampled at Codelco Chile.

The copper smelter wastewater was sampled from the treatment plant at Codelco Chile, División El Teniente, VI Region of Chile. The wastewater was diluted 10 times during the adjustment of the original pH (lower than 0) to the experimental value in the range of 3.5–6.5. For the pH adjustment NaOH was used. After the dilution/pH-adjustment the wastewater sample was filtered.

In order to increase and obtain similar electrical conductivity in all wastewaters, 4 g L^{-1} NaCl was added to the solutions. The addition of NaCl did not affect the removal efficiency of the ECP process. If NaCl was not added, the voltage drop when treating synthetic wastewater was higher than in real wastewater treatment.

H_2O_2 (30% w/w) was using during ECP experiments.

3.2 Analytical

After the experiments each solution was filtered (paper filter grade 131), and the arsenic (As^{+3}, As^{+5} or total As), copper and iron content in the solid and liquid was analysed by the Chilean standard methods NCh 2313/9 Of. 96 and NCh 2313/10 Of. 96. These were based on for As^{+3} by the Vogel quantitative analysis, total As and Cu by Atomic Absorption, and Fe by the Kolthoff inorganic quantitative analysis. As^{+5} was estimated as the difference between total As and As^{+3}.

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

3.3 Experimental setup

Figure 1 shows the experimental ECP setup. The ECP process was tested in the cylindrical acrylic cell with an external diameter of 10.1 cm, a height of 20 cm, and a thickness of the cell wall of 2.5 cm. The volume of the reactor was 1.6 L, and the reactor used the injection of air (airflow 5 L min^{-1}) as stirring mechanism. This stirring created turbulent conditions, and the reactor behaved as a perfectly stirred reactor. The ferrous ions were added by anodic dissolution of steel (A37-ES) electrodes placed concentrically within the cell. The current polarity was reversed each 60 s in order to achieve an equal dissolution of both electrodes and to avoid passivation. The height and thickness of the electrodes were 85 and 2.5 mm, respectively, and the exterior diameter was 59 mm for the external electrode and 33.3 mm for the internal electrode. The distance between the electrodes was 1 cm. H_2O_2 solution was added to the wastewater dropwise from a burette, and the liquid flow was fixed at around 0.5–1 mL min^{-1}.

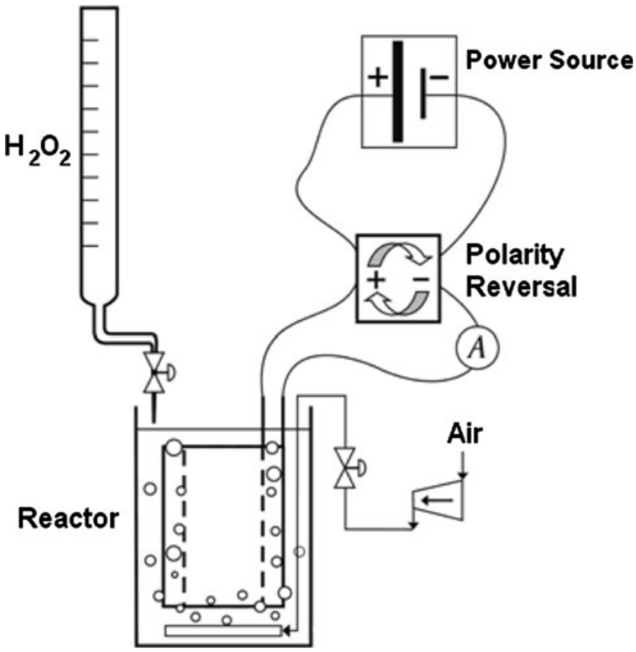

Fig. 1 Experimental ECP setup

An Extech, model 382285, power supply, a homemade current reversal device, a UNI-TREND International Limited, UT60 Series multimeter, and an air compressor completed the experimental setup.

3.4 Experimental plan

Table 1 shows the experimental conditions of a total of five ECP experimental series carried out on either synthetic or real wastewater samples. Each series consisted of 4 separate experiments of different duration. Durations were 30, 60, 120 and 180 min—meaning that a total of 20 experiments were carried out. In each experiment within a series, initial concentration, current density and initial pH were the same. A stock volume of 5.0 L of each solution to be treated was prepared, and the solution volume used in each experiment was 1.0 L. Initial pH was fixed at 3.5, 5 or 6.5 depending on experiments. The current was fixed at 2 A in all experiments—giving a current density of 171.7 A m^{-2}, when considering an average surface area of the two electrodes as 116.5 cm^2. All experiments were carried out at ambient air temperature (20–25 °C).

4 Results and discussion

Table 2 shows the arsenic, copper and iron concentration with time together with the overall removal from the solution and pH in five ECP experimental series. The arsenic concentration in the synthetic wastewater was

Table 1 Experimental ECP conditions

Parameter	Experiments with synthetic copper wastewater	Experiments with synthetic arsenic wastewater	Experiments with real wastewater, diluted 1:10
Initial concentration (mg L^{-1})	$\approx$1000	$\approx$3000	As: $\approx$1000 Cu: $\approx$300
Time (min)	30, 60, 120 and 180	30, 60, 120 and 180	30, 60, 120 and 180
Current (A)	2	2	2
Current density (A m^{-2})	171.7	171.7	171.7
NaCl concentration (g L^{-1})	4	4	4
Solution pH	6.5	6.5	3.5, 5.0 and 6.5

Table 2 Iron (C_{Fe}), copper (C_{Cu}) and arsenic (C_{As}) concentrations, pH and contaminant removal results during ECP experiments

Time (min)	C_{Fe} (mg L^{-1})	C_{Cu} (mg L^{-1})	Cu removal efficiency (%)	C_{As} (mg L^{-1})	As removal efficiency (%)	pH
Synthetic wastewater, pH 6.5—copper removal						
0	–	1001	0.0	–	–	6.5
30	<1	56	94.4	–	–	4.8
60	<1	1.0	99.9	–	–	5.7
120	<1	1.1	99.9	–	–	7.9
180	<1	0.3	>99.9	–	–	7.7
Synthetic wastewater, pH 6.5—arsenic removal						
0	–	–	–	2.868	0.0	6.5
30	<1	–	–	2.157	24.8	2.1
60	<1	–	–	1.622	43.4	2.2
120	<1	–	–	501	82.5	2.9
180	<1	–	–	457	84.1	2.7
Copper smelter wastewater, pH 3.5						
0	–	292.0	0.0	1007.0	0.0	3.5
30	<1	165.0	43.5	18.3	98.2	3.9
60	<1	30.0	89.7	<0.5	>99.9	4.2
120	<1	0.4	99.9	<0.5	>99.9	5.6
180	<1	0.4	99.9	<0.5	>99.9	6.0
Copper smelter wastewater, pH 5.0						
0	–	291.0	0.0	974.0	0.0	5.0
30	<1	70.0	75.9	<0.5	>99.9	4.0
60	<1	56.0	80.8	<0.5	>99.9	4.6
120	<1	36.0	87.6	<0.5	>99.9	4.4
180	<1	12.0	95.9	<0.5	>99.9	4.9
Copper smelter wastewater, pH 6.5						
0	–	294.0	0.0	1026.0	0.0	6.5
30	<1	138.0	53.1	544.0	47.0	4.5
60	<1	2.5	99.1	6.6	99.4	6.1
120	<1	2.1	99.3	4.4	99.6	6.2
180	<1	0.8	99.7	2.6	99.7	6.9

chosen to be 3 times higher than the copper concentration. This was based on As/Cu ratios found in real wastewater samples. The wastewater treated was either synthetic wastewater with copper or arsenic, or real wastewater with pH adjusted to different values. The pH of the crude wastewater was around 0, and HFO-based treatment are not likely to work at that low pH [10]. Therefore, pH was increased to different levels.

In all experiment an orange-brown precipitate was formed indicating the presence of HFO [11]. In case of copper removal from synthetic wastewater, the precipitate was brown during all experiment and the quantity increased with time as expected. When treating arsenic wastewater, the colour of the precipitate was orange in the beginning, and then turning dark orange-brown with time. For real wastewater treatment experiments the colour was something in between the two cases mentioned.

Figure 2 shows the copper and arsenic concentration at different times when treating synthetic wastewater. As can be seen from the Fig. 2 and Table 2, after 30 min the copper removal is around 90%, and after 60 min the copper removal is almost complete. Therefore, the ECP could be an efficient tool when treating copper containing wastewaters. On the other hand, it seems that arsenic cannot be removed totally from a synthetic prepared wastewater solution. The arsenic removal is almost proportional with the treatment time, until it stabilizes at a level corresponding to 84% removal. From Table 2 is seen that after 30 min only 25% of the arsenic is adsorbed, which is much lower than the copper removal at the same time (>90%) but it seems that the removal rate is almost the same since the initial concentration of the two solutions are different. From Fig. 2, where the concentrations of the solutions are shown with time, it can be noted that the slope of the curves are approximately the same in the initial stadium—indicating a similar removal rate.

From Table 2 it can also be observed that pH drops from 6.5 to around 5 after 30 min in the experiments with synthetic copper wastewater, and thereafter raises to around 8 with time. This pH lowering can be explained by the fact that initially only a small amount of OH^- has been produced at the cathode, and all are being used fast in the reaction with Fe^{+3}, along with the reaction of Cu^{2+} in the solution with OH^- to form $Cu(OH)_2$ precipitates. Fe^{3+} in excess will react with water to form H^+ and pH is lowered. Later during the experiment, OH^- will be in excess and pH is raised a little. When treating synthetic arsenic wastewater, it can be observed that pH drops to around 2 after 30 min from initially 6.5. This is due to an even more pronounced initial acidification effect as mentioned above, and the oxidation of As^{+3} to As^{+5} (see below). Hereafter, pH is slowly increasing to 3 as an effect of the OH^- production at the cathode. The same tendency is observed when treating real wastewater, independent of the initial pH: first a slight pH decrease followed by an increase in pH.

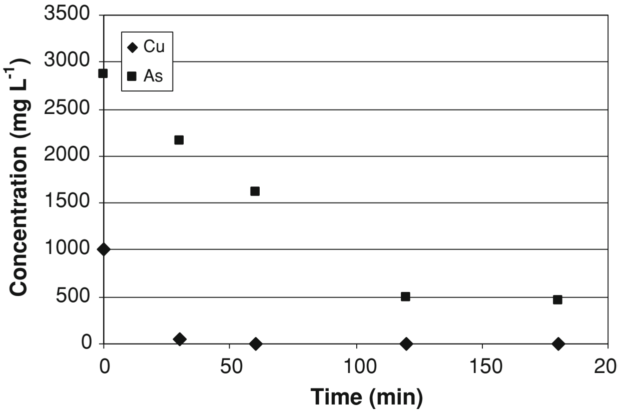

Fig. 2 Concentration of copper and arsenic with time treating synthetic wastewater with the ECP process

It is important to mention that the solution prepared dissolving As_2O_3 in distilled water and adjusted to pH 6.5 was nearly colourless. When initiating the ECP process, a fine white precipitate was formed and deposited on the electrodes (during the first 10–15 min). After this time, the precipitate turned orange/brown—the typical colour of HFOs. This phenomenon can explain the drastic lowering of pH in the experiments with synthetic arsenic wastewater. In acidic environments, the dissolution of As^{+3} containing species (such as sodium arsenite) forms the cation AsO^+, and when the acidity decreases, AsO^+ is transformed into H_3AsO_3, which coexists at high As^{+3} concentrations with the white solid, As_2O_3 [12]. This explains the white solid formed initially (initial pH 6.5). If an oxidant is added, such as H_2O_2, the following As^{+3} to As^{+5} oxidation reactions occur:

$$\begin{aligned} & H_2O_2 + H_3AsO_3 \rightarrow H_2AsO_4^- + H^+ + H_2O \\ & H_2O_2 + H_3AsO_3 \rightarrow HAsO_4^{-2} + 2H^+ + H_2O \end{aligned} \tag{12}$$

These reactions would explain the pH lowering in the solution in the beginning since arsenates tend to be present rather as anions at low pH. On the other hand, $H_2AsO_4{}^-$ coexists with arsenic pentoxide, As_2O_5, which is a soluble white species. This can explain the pale white colour of the solution at the beginning (the first HFOs produced are covered by these white solids). With time the solution turned into orange since the HFOs now were in excess compared to the white arsenic oxides.

Table 3 shows the chemical analysis of the solids produced during ECP of synthetic copper wastewater. It can be observed that the copper percentage in the solids decreases and the iron content increases with time. This corresponds well with the fact that in the beginning of the experiment

Table 3 Detailed ECP results when treating synthetic wastewater with copper

Time (min)	0	30	60	120	180
C_{Cu} liquid phase (mg L^{-1})	1001	56	1.0	1.1	0.3
(g Cu/100 g of sample) solid phase	–	41.3	37.8	21.5	17.6
(g Fe/100 g of sample) solid phase	–	29.6	24.7	42.0	46.9
(g (Fe + Cu)/100 g of sample) solid phase	–	70.9	62.5	63.5	64.5
g Cu/g Fe in the solid	–	1.4	1.5	0.5	0.4

less iron is present, and after a time, when the copper content in the solution is reduced, iron will be in excess, since it is liberated from the anodes with a constant rate (the electric current is constant). On the other hand, the sum of iron and copper is almost the same—around 60%—in all experiments. Only after 30 min the sum is higher—around 70%—but this is due to the initial precipitates that are formed with more iron due to the lower concentration of OH^- at that stage (pH is lowered in the solution). One can observe that the copper/iron fraction (g Cu/g Fe) in the solids, when still considerable adsorption/precipitation is occurring ($t \leq 60$ min), is in the range of 1.4–1.5 corresponding to more than 1 mol copper per mol iron in the precipitate. This indicates the minimum iron necessary for an adsorption of copper to the HFOs. Lower copper/iron fraction values indicates excess of iron that are not used optimal.

Table 4 shows the chemical analysis of the solids produced during ECP of synthetic arsenic wastewater. The table shows that more than 99% of the arsenic adsorbed is found as As^{+5}. This indicates that arsenic in the solution is present as As^{+5} too. Therefore, the initial As^{+3} is oxidised during the process. In fact it is known that As^{+5} is adsorbed/precipitated more efficiently than As^{+3}, when producing HFOs in chemical manner [13]. Furthermore, it would not be necessary to include a separate arsenic oxidation step in the overall wastewater treatment as is the case in other technologies [14, 15]. On the other hand, the total arsenic plus iron content in the solid is maintained around 55% in all experiments. In addition, the arsenic/iron fraction in the solid is around 1.1–1.2 g As/g Fe in the experiments where still considerable arsenic adsorption to the HFOs is observed ($t \leq 60$ min). This value can be taken as a guideline for necessary iron amount in the solution for arsenic adsorption. From Table 2 it can be observed that all iron dissolved at the anodes is precipitated since the iron concentration in the solution in all experiments is almost zero.

Table 4 Detailed ECP results when treating synthetic wastewater with arsenic

Time (min)	0	30	60	120	180
C_{As} liquid phase (mg L^{-1})	2868	2157	1622	501	457
(g As total/100 g of sample) solid phase	–	27.7	28.9	30.64	29.96
(g As^{+3}/100 g of sample) solid phase	–	ND	ND	0.14	0.16
(g As^{+5}/100 g of sample) solid phase	–	27.7	28.9	30.5	29.8
% As adsorbed as As^{+5} on HFO	–	100	100	99.54	99.47
(g Fe/100 g of sample) solid phase	–	25.0	27.5	25.3	25.9
(g (Fe + As)/100 g of sample) solid phase	–	52.7	56.4	55.94	55.86
g As/g Fe in solid	–	1.1	1.1	1.2	1.2

ND not detected (lower than detecting limit)

Three series of four separate experiments were carried out with pH-adjusted real copper smelter wastewater. Initial pH was varied between the series to find an optimum pH level for applying ECP in practise. Table 5 gives the concentrations of copper and speciation in the original and diluted wastewater samples. From the table it is important to note that the arsenic speciation is almost the same in all samples. Therefore, no As^{+3} is oxidised to As^{+5} during the pH adjustment/dilution.

In the experiment with wastewater at pH 6.5, the solution turned green in the beginning. This is explained by that the arsenite anion hinders the precipitation of Cu^{+2} as copper hydroxide, and the green colour indicated formation of the green species named as Scheele's Green or copper arsenite (AsO_3HCu, $(AsO_3)_2Cu_3$). This compound is formed in neutral to light acidic conditions [12].

Figures 3 and 4 show the copper and arsenic concentration, respectively, at different times when treating real copper smelter wastewater with adjusted pH. As can be seen from Fig. 4 (and Table 3), already after 60 min the arsenic removal is more than 99% for all 3 pH levels when treating real wastewaters. For copper, the picture is a little different since the efficiency seems to be better at neutral pH than acidic (Fig. 3). This could be explained by the formation of copper hydroxide for pH > 5. In general, since the arsenic and copper concentrations in the treated wastewater after 120 min are very low, the ECP process could be a promising method in treating copper smelter wastewater.

Table 5 Cu, As^{+3} and As^{+5} concentrations in the original and diluted wastewater samples

	Cu (mg L^{-1})	Total As (mg L^{-1})	As^{+3} (mg L^{-1})	As^{+5} (mg L^{-1})	As^{+3}/As^{+5}
Original wastewater	2870	9980	8160	1820	4.48
Wastewater diluted 1:10; pH: 3.5	292	1007	825	182	4.54
Wastewater diluted 1:10; pH: 5	291	974	797	177	4.51
Wastewater diluted 1:10; pH: 6.5	294	1026	838	188	4.46

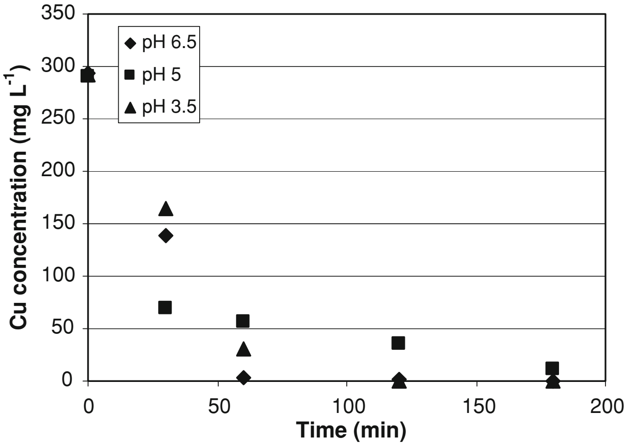

Fig. 3 Concentration of copper with time treating copper smelter wastewater with the ECP process. pH initially adjusted to different levels

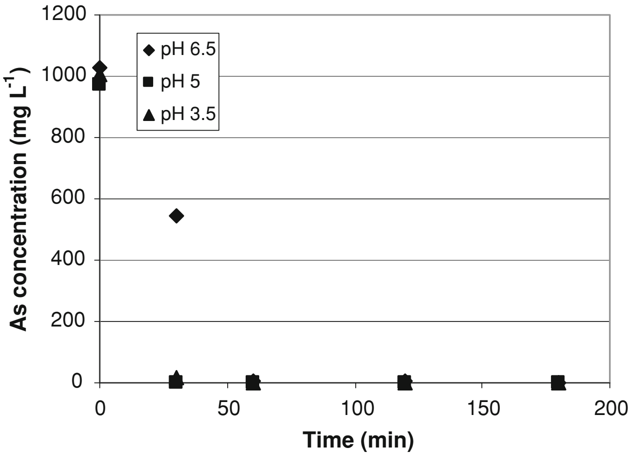

Fig. 4 Concentration of arsenic with time treating copper smelter wastewater with the ECP process. pH initially adjusted to different levels

Table 6 shows detailed results from the ECP of real wastewater adjusted to pH 6.5. From the table it is seen that practically all arsenic is adsorbed as As^{+5} (more than 99.7%). The copper smelter wastewater does not need a separate As^{+3} to As^{+5} oxidation process, since to oxidation during ECP is very efficient. In addition, the percentage that iron, copper and arsenic occupies in the solid is almost constant with time (for initial pH 6.5 wastewater). As in the case with synthetic wastewater the As/Fe and Cu/Fe ratios give indication of how efficiently the ECP process works. In the case of real wastewater, the presence of other heavy metal species would compete with the elements studied in this work. Anyway, the As/Fe is still very high and comparable with synthetic arsenic wastewater (1.2–1.4 g As/g Fe).

5 Conclusions

The ECP technique has been proven to remove arsenic and copper from copper smelter wastewater with a very high efficiency. In a laboratory scale batch reactor both copper and arsenic was removed more than 99%, and to levels that fulfil the Chilean legislation for treated wastewater discharge.

Arsenic was removed more efficiently from real wastewater samples than synthetic wastewater—this confirms even more the potential of the method as an arsenic removal process. Copper was both efficiently from both real and synthetic waste water. On the other hand, a synthetic single element wastewater could not fully simulate the real wastewater both when comparing removal rates and pH development.

When treating real wastewater adjusted to different pH of 3.5, 5.0 and 6.5, nearly 100% removal was obtained in all cases and for both elements. There was a tendency showing that arsenic is removed faster from a wastewater with lower pH and copper from a solution with higher pH—which correspond well with additional $Cu(OH)_2$ formation and higher arsenic solubility at higher pH.

Table 6 Detailed ECP results treating copper smelter wastewater adjusted to pH 6.5

Time (min)	0	30	60	120	180
C_{Cu} liquid phase (mg L^{-1})	294	138	2.5	2.1	0.8
C_{As} liquid phase (mg L^{-1})	1026	544	6.6	4.4	2.6
(g Cu/100 g of sample) solid phase	–	5.4	4.1	4.1	3.8
(g As total/100 g of sample) solid phase	–	26.79	21.8	20.2	18.2
(g As^{+3}/100 g of sample) solid phase	–	0.09	ND	ND	ND
(g As^{+5}/100 g of sample) solid phase	–	26.7	21.8	20.2	18.2
% As adsorbed as As^{+5} on HFO		99.66	100	100	100
(g Fe/100 g of sample) solid phase	–	14.3	18.7	19.2	28.0
(g (Fe + Cu + As)/100 g of sample) solid phase	–	46.49	44.6	43.5	50
g Cu/g Fe in solid	–	0.4	0.2	0.2	0.1
g As/g Fe in solid	–	1.9	1.2	1.1	0.7

ND not detected (lower than detecting limit)

Acknowledgements The authors would like to acknowledge the financial support of the FONDECYT Project No 1085118. Ana Gonzalez is acknowledged for help with the experimental work.

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