Chemosphere 83 (2011) 21–28

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Influence of organic matter on arsenic removal by continuous flow electrocoagulation treatment of weakly mineralized waters

Virginie Pallier [a], Geneviève Feuillade-Cathalifaud [a,*], Bernard Serpaud [b]

[a] Université de Limoges – Groupement de Recherche Eau Sol Environnement (GRESE), ENSIL, Parc d'Ester Technopôle, 16 rue Atlantis, 87068 Limoges Cedex, France
[b] Université de Limoges – Groupement de Recherche Eau Sol Environnement (GRESE), Faculté des Sciences et Techniques, 123 avenue Albert Thomas, 87060 Limoges Cedex, France

ARTICLE INFO

Article history:
Received 23 July 2010
Received in revised form 12 January 2011
Accepted 17 January 2011

Keywords:
Arsenic
Speciation
ECF
CF
Iron
Zeta potential

ABSTRACT

The aim of this study is to evaluate and understand the electrocoagulation/flocculation (ECF) process to remove arsenic from both model and natural waters with low mineral content and to compare its performances to the coagulation/flocculation (CF) process already optimized. Experiments were thus conducted with iron electrodes in the same specific treatment conditions ($4 \leqslant$ current density (mA cm^{-2}) $\leqslant 33$) to study the influence of organic matter on arsenic removal in conditions avoiding the oxidation step usually required to improve As(III) removal. The process performance was evaluated by combining quantification of arsenic residual concentrations and speciation and dissolved organic carbon residual concentrations with zeta potential and turbidity measurements. When compared to CF, ECF presented several disadvantages: (i) lower As(V) removal yield because of the ferrous iron dissolved from the anode and the subsequent negative zeta potential of the colloidal suspension, (ii) higher residual DOC concentrations because of the fractionation of high molecular weight compounds during the treatment leading to compounds less prone to coagulate and (iii) higher residual turbidities because of the charge neutralization mechanisms involved. However, during this process, As(III) was oxidized to As(V) improving considerably its removal whatever the matrix conditions. ECF thus allowed to improve As(III) removal without applying an oxidation step that could potentially lead to the formation of toxic oxidation by-products.

1. Introduction

The removal of arsenic from natural water has been the subject of many studies because drinking water is considered as the main source of exposure to inorganic arsenic (Villaescusa and Bollinger, 2008). Different treatment processes including adsorption, precipitation/coprecipitation, membrane filtration and ion exchange resins were thus developed and optimized by studying the influence of arsenic speciation and concentration, pH and competitive ions on arsenic removal (Bissen and Frimmel, 2003; Garelick et al., 2005; Mondal et al., 2006; Mohan and Pittman, 2007). These processes showed a medium to low As(III) removal efficiency and also required pH regulation as it influences arsenic speciation and surface charge of adsorbents. Authors thus usually recommended to oxidize As(III) to As(V). However in the presence of organic matter, the oxidation step applied prior to As(III) removal could lead to the formation of toxic oxidation by-products especially when chlorine is used as oxidative reagents. We thus developed in a previous study the coagulation/flocculation (CF) process with high coagulant availability ($9 \leqslant [Fe^{3+}]$ (mg L^{-1}) $\leqslant 55$) to improve As(III) removal without applying an oxidation step (Pallier et al., 2009). When initial As(III) concentration in model water was 100 μg L^{-1}, these conditions meet the maximum contaminant level of 10 μg L^{-1} for $[Fe^{3+}] \geqslant 18$ and 36 mg L^{-1} in the absence and presence of organic matter respectively.

Literature results on arsenic removal by electrocoagulation/flocculation (ECF) showed high As(III) removal efficiency without any pH regulation (Kumar et al., 2004; Balasubramanian et al., 2009). ECF is also characterised by ease of operation, reduced production of sludge and no need to handle chemicals (Emamjomeh and Sivakumar, 2009).

Electrocoagulation (EC) is an alternative process to CF. Instead of adding a chemical reagent as ferric chloride, metallic cations are directly generated in the effluent to be treated by applying a current between iron electrodes to dissolve soluble anodes. Metallic cations and hydroxides formed thus neutralize negatively charged colloids allowing them to coagulate (Matteson et al., 1995). The main reactions taking place during EC with iron electrodes are well known. During EC with iron electrodes, the amount of iron cations experimentally dissolved from the anode corresponds to the value predicted by the second Faraday's law (Vik et al., 1984; Pretorius et al., 1991) that is used to calculate the treatment dose to apply.

* Corresponding author. Tel.: +33 555 423695; fax: +33 555 423662.
E-mail address: genevieve.feuillade@ensil.unilim.fr (G. Feuillade-Cathalifaud).

0045-6535/$ - see front matter
doi:10.1016/j.chemosphere.2011.01.038

The existing studies on arsenic removal by EC highlighted several conclusions synthesized in Emamjomeh and Sivakumar (2009). However, although the influence of several parameters on arsenic removal has been studied, few studies used continuous flow reactors but rather batch reactors differing from those used for drinking water production. Besides, in a drinking water production plant, CF and ECF are mainly use for colloids and organic matter removal and actually no study deals with the removal of arsenic in the presence of organic matter.

The objective of the present study was thus to evaluate the removal of arsenic from both model and natural waters with low mineral content by ECF with iron electrodes using a continuous flow reactor. Specific treatment conditions were applied to compare the efficiency of ECF and CF using ferric salts as coagulant (Pallier et al., 2009). Organic matter influence on arsenic removal by ECF was also studied and zeta potential measurements were used to understand and compare arsenic removal mechanisms during these treatments.

2. Materials and methods

All the reagents used were of the purest grade available with the lowest arsenic and iron content and the solutions were prepared in ultrapure grade water (Milli-Q system: resistivity 18.2 MΩ cm, TOC < 10 μg L^{-1}).

2.1. Experimental electrolyte: model and natural water samples

EC experiments were performed on a low mineral content model water spiked with 100 μg L^{-1} As(III) or As(V) which corresponds to the maximum arsenic concentration acceptable before drinking water production (European Council Directive 98/83/EC). This model water was previously developed by Lenoble et al. (2004). Its characteristics are listed in Table 1. Experiments were conducted on model water to maintain a constant composition in the matrix. In order to increase its mineral suspended solids concentration (*i.e.*, turbidity) and to reproduce natural surface water characteristics, 2 mL of 10 g L^{-1} kaolinite suspension was added. Batch experiments with a contact time up to 8 h were conducted to evaluate arsenic adsorption on kaolinite surface. It was found that neither 100 μg L^{-1} As(III) nor 100 μg L^{-1} As(V) sorbed onto 20 mg L^{-1} kaolinite suspension. In these conditions, arsenic speciation was maintained (Pallier et al., 2009). Previous literature studies underlined pH, matrix composition and arsenic concentration and speciation influence on its adsorption onto kaolinite. In our study, the ratio [kaolinite]/[arsenic] was 200 whereas in previous literature studies, it was around 30 000 and 800 000 (kaolinite concentration between 2.5 and 40 g L^{-1} and arsenic concentration between 0.005 and 2750 μg As_{Total} L^{-1}). The absence of adsorption in our study could thus be explained by a too small kaolinite concentration compared to that of arsenic minimizing the influence of pH.

Table 1
Chemical and physico-chemical initial characteristics of model and natural water samples.

Parameter	Model water	Natural water
pH	6.0 ± 0.2	5.7 ± 0.1
Conductivity (μS cm^{-1})	70 ± 1	80 ± 2
Turbidity (NTU)	0.6 ± 0.1	6.5 ± 0.1
Turbidity after kaolinite addition (NTU)	17.3 ± 0.9	15.2 ± 0.6
DOC (mg L^{-1})	<0.2	3.9 ± 0.2
DOC after humic substances addition (mg L^{-1})	10 ± 0.2	3.9 ± 0.2
Total iron (μg L^{-1})	<10	130 ± 3
Ferrous iron (μg L^{-1})	<10	80 ± 2
Alkalinity (mg $CaCO_3$ L^{-1})	9 ± 2	13 ± 1
Natural contamination: As(V) (μg L^{-1})	⩽0.78	101 ± 2
Spiking with As(III) or As(V) (μg L^{-1})	100	–
Inorganic species (mg L^{-1})[a]		
Cl^-	8.1	4.3
NO_3^-	9.9	2.8
SO_4^{2-}	3.4	1.8
Na^+	6.9	7.8
K^+	0.8	3.4
Mg^{2+}	1.3	0.7
Ca^{2+}	3.2	3.0
SiO_2	9.0	ND[b]

[a] Anions and cations concentrations (±5%) were measured with a Dionex DX-120 ionic chromatography, after sample filtration on 0.2 μm cellulose nitrate filters.
[b] ND: not determined.

The influence of organic matter on arsenic removal by ECF was evaluated by spiking model water with humic acids extracted from peat humic substances (humic acid sodium salt from Aldrich), according to the Schnitzer and Khan protocol (1972). The final dissolved organic carbon (DOC) concentration in the model water was 10 mg L^{-1}. In our experimental conditions, arsenic adsorption onto kaolinite was not affected by the presence of humic acids (Pallier et al., 2009).

The process was applied to a water sample collected in the Limousin region (France). This was a weakly mineralized surface water (Table 1) spiked with kaolinite to achieve a turbidity similar to the one of model water.

2.2. Electrocoagulation/flocculation experimental setup

A Plexiglas laboratory scale electrocoagulation reactor designed by Brizard (2001) with a total volume of 1.25 L was used (Fig. 1). Plexiglas electrodes spacers allowed holding two different kinds of electrodes (active area = 241 and 255 cm^2 for type 1 and type 2 respectively) composed of at least 99% of iron at a fixed 3 mm inter-electrode distance in bipolar connection (Fig. 1). This layout of the electrodes in the reactor promoted a sinusoidal movement of the effluent and as a consequence its mixing without a mechanical tool.

A DC source generator from Blanc Meca Electronique EA PS 3016-10 providing at the most 10 A (±0.2) under 16 V (±0.5) was used. A 10 V potential was applied. The current intensity delivered between electrodes was controlled by a Metrix MX20 ampermeter. The effluent's conductivity was increased till around 1000 μS cm^{-1} by adding NaCl (Fluka) to allow the current to pass through the electrodes because a conductivity between 1000 and 4000 μS cm^{-1} did not affect the decrease in turbidity and also because such a conductivity allowed to reach the maximum required treatment dose. Harif and Adin (2007) set conductivity values upper than 1000 μS cm^{-1}.

The effluent's flow rate was fixed at 150 L h^{-1} by a centrifugal pump (Iwaki France, model MD-30RZM-200N). These design and operation conditions fixed the residence time at 27 s. For residence times between 7 and 45 s, Brizard (2001) showed that this EC reactor behaved like a series of 10 perfectly mixed reactors without any short circuit or dead zones. Such experimental conditions were chosen to obtain treatment doses between 9 and 55 mg Fe L^{-1} which were reached by varying the current intensities between approximately 1 and 8 A. In these conditions, current densities ranged from 4 to 33 mA cm^{-2}.

Flocculation (30 rpm (35 s^{-1}) for 15 min) and decantation (30 min) steps were carried out after EC by using a jar test device (Numeric Flocculater 10409 from Fischer Bioblock Scientific) equipped with stainless steel paddles (7.5 × 2.5 cm).

2.3. Physico-chemical and chemical analysis

Sample pH was measured under magnetic stirring with a Cyberscan 510 pHmeter from Eutech Instruments equipped with a com-

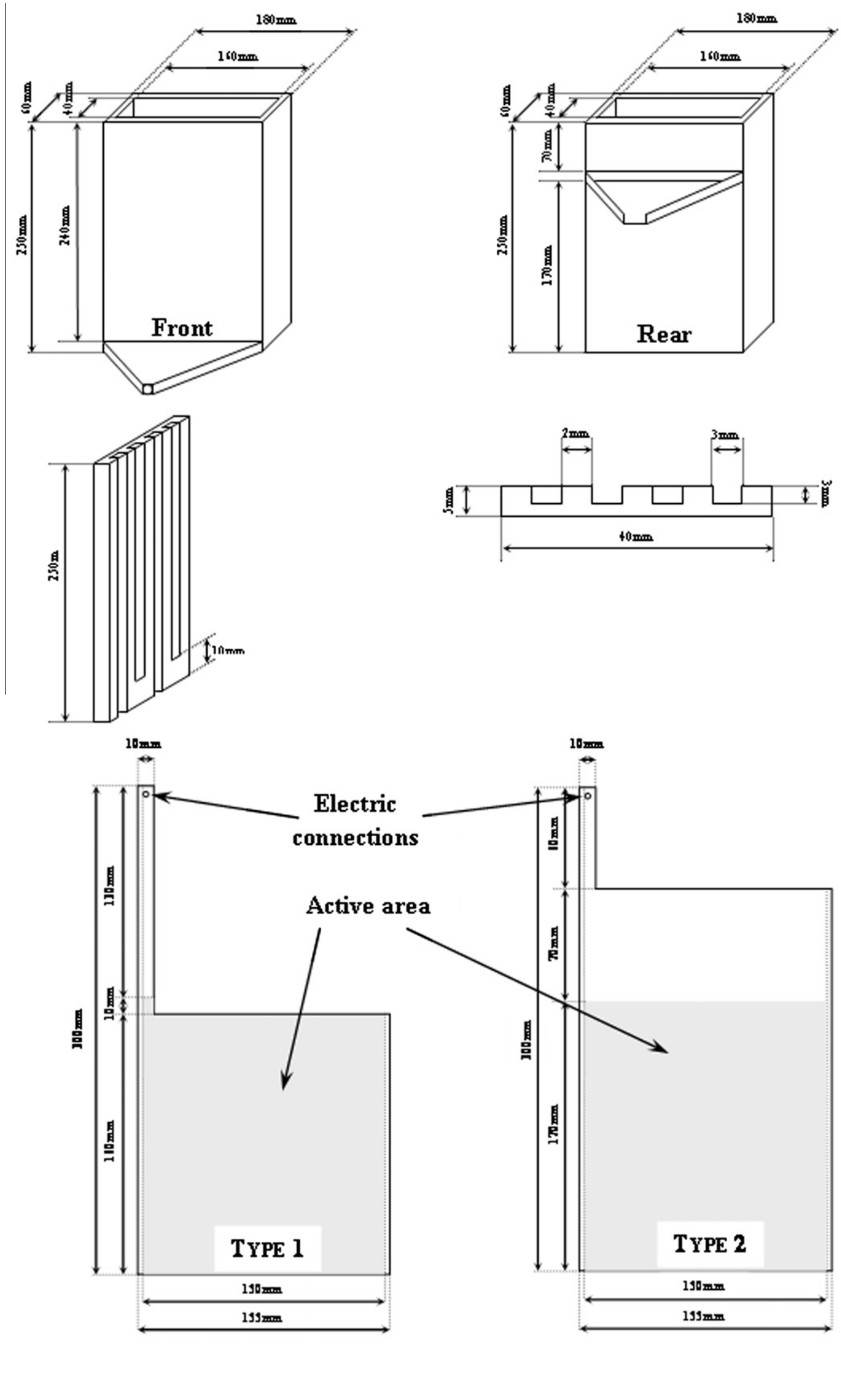

Fig. 1. Schematic representation of electrocoagulation reactor and dimensional characteristics of Plexiglas electrodes spacers and electrodes.

bined Ag/AgCl/KCl 4 M glass electrode and with a platinum temperature probe, turbidity with a HI 98703 turbidimeter from HANNA Instruments and conductivity with a LF 538 conductimeter from WTW equipped with a Tetracon 325 measuring cell. The temperature was systematically measured to correct conductivity (reference temperature: 25 °C).

Table 2
Analytical methods applied for the quantification of As(III), As_{Total}, Fe(II) and Fe_{Total} and for the determination of DOC and zeta potentials in water samples.

Analysis	Method	Analytical apparatus	QL[a]	Source
As(III)	HG-AAS	Varian SpectrAA 220 flame AAS Varian VGA-77 Varian SpectrAA 880Z AAS	0.6 µg L^{-1}	Pallier et al. (in press)
As_{Total}	GF-AAS	GTA 100Z graphite furnace with Zeeman background correction	0.78 µg L^{-1}	Michon et al. (2007)
Fe(II) Fe_{Total}	NF T 90-017	UV-1700 Shimadzu spectrophotometer	5 mg L^{-1}	–
DOC	–	Tekmar–Dohrmann Phoenix 8000 TOC analyzer	0.1 mg L^{-1}	–
Zeta potential	–	Zetaphoremeter IV model Z4000 from CAD Instrumentation	–	–

[a] QL: quantification limit.

Analytical methods for As(III), As_{Total}, Fe(II) and Fe_{Total} and zeta potential and DOC measurements are described in Table 2. Iron analysis required a 1 vol.% acidification of the sample with 2 M HCl. As(III) and As_{Total} analysis required a sample filtration on 0.45 µm cellulose–acetate filters and a conservation with 500 mg EDTA L^{-1} and 8.7 M acetic acid to adjust pH between 3.3 and 3.5 (Gallagher et al., 2004).

Organic matter was fractionated before and after ECF treatment by ultrafiltration using a frontal ultrafiltration cell with magnetic stirring and a membrane (YM type, Amicon, diameter 76 mm) and a molecular cut-off of 30 kDa. The tests were carried out by using the diafiltration method (Berthe et al., 2008).

3. Results and discussion

3.1. Electrolysis time

In batch EC experiments, the increase in residence time improved the arsenic removal efficiency (Gomes et al., 2007; Balasubramanian et al., 2009; García-Lara and Montero-Ocampo, 2009). Indeed, as the experiment proceeded, the aqueous phase arsenic concentration continued to be reduced as the iron (hydr)oxides concentration increased (Kumar et al., 2004). In continuous flow EC experiments, EC systems will be operated continuously ultimately reaching steady state (Lakshmanan et al., 2010). According to these authors, theoretically, current of 28 mA, flow rate of 245 mL min^{-1} and residence time of 2 min should attain an iron concentration of 2.0 mg L^{-1} at steady state based on Fe^{2+} generation. In this study, the effect of electrolysis time on pH evolution and As(III), turbidity and iron removal was studied for a current density of 22 mA cm^{-2}. pH stabilised at 7.8 ± 0.1 after 10 min of EC treatment. As(III) residual concentration was 1.2 ± 0.2 µg L^{-1} whatever the electrolysis time and residual turbidity and iron concentration stabilised after 5 min of treatment. Thus, in these experimental conditions, the EC process worked as a continuous reactor after 10 min. The electrolysis time was fixed to 15 min to allowing system regeneration and achievement of a steady state. The high current density certainly contributed to the more rapid development of steady state conditions. Same results were obtained by Lakshmanan et al. (2010).

3.2. Electrocoagulation flocs characteristics

For 6 < pH < 9, Fe(III) hydroxides and Fe(II) hydroxides begin to precipitate with a yellowish color and a dark green color respectively (Moreno-Casillas et al., 2007). Flocs generated in the EC reactor presented a green color characteristic of ferrous oxide. The mixing conditions of the flocculation step promoted the oxidation of ferrous oxide to hydrous ferric oxide or ferric hydroxide (Moreno-Casillas et al., 2009). Their quantity and size increased as the current density increased till 22 mA cm^{-2}. Then, for current densities ⩾ 22 mA cm^{-2}, flocs size and quantity were stable. Flocs were generally smaller than after CF treatment and even if more flocs were generated compared to the chemical process, the volume of sludge was lower. Thus the effective density of the flocs was probably higher.

The presence of humic acids affected EC floc characteristics as flocs were smaller than in absence of humic acids. This result was attributed to both the coagulation mechanisms and the more negative zeta potential because the mechanism of coagulant removal is governed by the particle size of coagulant species (Yan et al., 2008). In the presence of humic acids, the zeta potential of the colloidal suspension decreased $(-35 \pm 5 \leqslant \zeta\ (\mathrm{mV}) \leqslant 17 \pm 1)$ and thus a charge neutralization mechanism occurred rather than sweep flocculation that generally occurred in absence of humic acids $(-7 \pm 1 \leqslant \zeta\ (\mathrm{mV}) \leqslant 11 \pm 1)$. Indeed, the specific mechanism of charge neutralization involves charge reversal indicated by the change in zeta potential towards more positive values (Harif and Adin, 2007).

3.3. pH evolution during electrocoagulation treatment

EC does not require pH control unlike CF because of the cathodic reduction of water and the subsequent formation of hydroxide ions. It has been reported that the electrolyte pH plays an important role on the EC process. According to Balasubramanian et al. (2009), arsenic removal increased when the electrolyte pH increased from 4 to 7 whereas an electrolyte pH from 7 to 11 did not improve arsenic removal like in the study of Kumar et al. (2004). Model water's initial pH was 6.0 ± 0.2. Thus, no pH adjustment before treatment was carried out to improve arsenic removal.

During EC treatment of model water, pH increased immediately from 6.0 ± 0.2 to 8.6 ± 0.3 and 8.3 ± 0.3 respectively in the absence and presence of humic acids because of the reduction of water at the cathode. In absence of humic acids, for [Fe] ⩾ 18 mg L^{-1}, pH stabilized at 7.4 ± 0.1 because the OH^- produced were consumed during the rapid oxidation of Fe(II) to Fe(III) (Sasson et al., 2009), Fe(III) hydrolysis and $Fe(OH)_3$ precipitation (Lakshmanan et al., 2009). In the presence of humic acids, it stabilized at 8.2 ± 0.1 for [Fe] ⩾ 18 mgFe L^{-1}. The presence of humic acids could slow down Fe(II) oxidation and $Fe(OH)_3$ precipitation.

3.4. As(V) removal by electrocoagulation/flocculation

During ECF treatment of model water, increasing the iron dose controlled by the current density improved As(V) removal. Similar results were obtained by Kumar et al. (2004) and García-Lara and Montero-Ocampo (2009) on underground water. On the contrary, during CF treatment, As(V) residual concentrations were independent of the coagulant dose in these high coagulant concentrations tested (Pallier et al., 2009). CF and ECF treatments thus presented different As(V) removal performances (Table 3).

As(V) residual concentrations respected the maximum concentration level of 10 µg L^{-1} whatever the treatment dose for the two processes. However, the treatment dose required to reach As(V) complete removal was higher for ECF treatment ([Fe] = 27 mg L^{-1}) compared to CF treatment ([Fe] = 18 mg L^{-1}) in specific pH conditions. This complete As(V) removal coincided with a positive zeta potential of the colloidal suspension (Table 3) which was controlled either by pH or by the concentration and speciation of iron species involved in the treatment. An increase in treatment pH de-

Table 3
Comparison of the performances of CF and ECF to remove As(V) from model water spiked or not with humic acids.

Treatment dose ($mgFe\ L^{-1}$)		9	18	27	37	46	55
Current density ($mA\ cm^{-2}$)		5.4	10.8	16.6	22	27.5	32.8
Coagulation	As(V) ($\mu g\ L^{-1}$)	0.9 ± 0.1			⩽QL		
Flocculation	ζ (mV)	−8 ± 2			⩾0 ± 1		
pH = 6.9 ± 0.2	Turbidity (NTU)	0.6 ± 0.1			0.6 ± 0.1		
Electrocoagulation	As(V) ($\mu g\ L^{-1}$)	⩾3.2 ± 0.4			⩽QL		
Flocculation	ζ (mV)	⩽−5.1 ± 0.8			⩾7.1 ± 0.5		
	Turbidity (NTU)	1.1 ± 0.1–2.4 ± 0.2			⩽0.8 ± 0.1		
	pH	⩾7.6 ± 0.3			7.3 ± 0.1		
Coagulation	As(V) ($\mu g\ L^{-1}$)	31 ± 2			⩽QL		
Flocculation	ζ (mV)	−28 ± 2	−15.5 ± 0.8 ⩽ ζ ⩽ 25 ± 2				
pH = 6.1 ± 0.1	DOC ($mg\ L^{-1}$)	5.8 ± 0.3			0.8 ± 0.1		
DOC = 10 $mg\ L^{-1}$							
Electrocoagulation	As(V) ($\mu g\ L^{-1}$)	94 ± 3 ⩽ [As(V)] ⩽ 3.0 ± 0.3					1.2 ± 0.1
Flocculation	ζ (mV)	−35 ± 5 ⩽ ζ ⩽ −9.3 ± 0.6					⩾11 ± 2
DOC = 10 $mg\ L^{-1}$	DOC ($mg\ L^{-1}$)	9.8 ± 0.5 ⩽ [DOC] ⩽ 2.4 ± 0.1					1.7 ± 0.2

creased the zeta potential of hydroxide ferric flocs which became negative from pH > 7.3 (Cathalifaud et al., 1993) and increased the concentration of hydroxyl ions specifically adsorbed on the Stern layer. As a consequence, the adsorption of As(V) decreased because it exists in anionic species from pH > 2 and because hydroxyl ions competed with As(V) for adsorption (Ghurye et al., 2004).

Residual turbidities were higher after ECF than after CF (Table 3). During CF, the high coagulant dosage and pH conditions promoted sweep coagulation as the main mechanism for turbidity removal (Pallier et al., 2009). During ECF, residual turbidity decreased with increasing treatment dose. It met the quality requirements for waters entering the distribution network of 1 NTU when [Fe] = 22 $mg\ L^{-1}$ and ζ = 0 mV (isoelectric point). Charge neutralization was thus identified as the predominant removal mechanism because of the ferrous species electrodissolved from anode during ECF.

3.5. Influence of organic matter on As(V) removal by electrocoagulation/flocculation

Humic acids negatively influenced As(V) removal as no coagulant dose applied during ECF allowed a complete removal of As(V) (Table 3). For [Fe] = 9 $mg\ L^{-1}$, As(V) removal percentage only reached 6 ± 3% in model water spiked with humic acids whereas 94 ± 3% of 100 μg As(V) L^{-1} were removed in absence of humic acids. This result could be explained by a decrease in zeta potential of the colloidal suspension induced by humic acids (ζ = −25 ± 3 and −47 ± 3 mV in the absence and presence of humic acids respectively). The negative zeta potential obtained after treatment by ECF could be explained by the matrix conditions (pH after treatment = 8.2 ± 0.1) and the ferrous iron species involved in the treatment. Thus, during CF, for [Fe] ⩾ 18 $mg\ L^{-1}$, As(V) was completely removed whereas during ECF, for [Fe] ⩾ 46 $mg\ L^{-1}$, As(V) removal reached a steady state (Table 3). CF was thus more efficient than ECF to remove As(V) from model water.

In the presence of humic acids, an isoelectric point (ζ = 0 mV) was reached for [Fe] = 41 $mg\ L^{-1}$. This isoelectric point corresponded to a stable state for which turbidity = 29 ± 2 NTU. After CF treatment, residual turbidities ranged from 23 ± 2 to 0.9 ± 0.2 NTU.

Organic matter removal should coincide with turbidity removal because they were removed by the same mechanisms (Dennett et al., 1996; Exall and vanLoon, 2000). However, while residual turbidity increased with the treatment dose applied, residual DOC concentration decreased and stabilized at 1.7 ± 0.2 $mg\ L^{-1}$ for [Fe] ⩾ 37 $mg\ L^{-1}$ (Table 3). As shown in Fig. 2, the less negative the zeta potential, the lower the residual DOC concentration and when zeta potential became positive, residual DOC concentration stabilized at 1.7 ± 0.1 $mg\ L^{-1}$. This steady state highlighted the refractoriness of organic matter towards EC treatment. According to Sharp et al. (2006), this refractory fraction was composed of hydrophilic compounds because they coagulated less than hydrophobic ones due to the size of the molecules and of their specific surface.

After CF treatment, residual DOC concentrations were 43 ± 15% lower than after ECF treatment. The distribution of apparent molecular weight of the organic molecules before and after ECF treatment showed that the fraction >30 kDa decreased after treatment (31% towards 76% before treatment) underlining a fractionation of the organic matter during treatment. Same results were obtained by Brizard (2001) who showed that high molecular weight compounds were transformed into low molecular weight and more hydrophilic compounds during EC, decreasing their removal by coagulation mechanisms.

3.6. Influence of organic matter on As(III) removal by electrocoagulation/flocculation

ECF showed better results than CF for the treatment of As(III). Whatever treatment dose applied during ECF, As(III) residual concentration respected the maximum contaminant level of 10 $\mu g\ L^{-1}$ whereas during CF, a 18 mgFe L^{-1} concentration was required to reach such results (Pallier et al., 2009). However, in Fig. 3, unlike CF, ECF promoted As(III) oxidation in As(V), increasing the treatment dose to meet the maximum As_{total} concentration of 10 $\mu g\ L^{-1}$ to 11 mg Fe L^{-1}. ECF still removed As(III) more efficiently than CF and residual As(III) concentrations were 73 ± 8% lower after ECF than after CF.

The efficiency of EC towards As(III) was attributed to the dissolution of Fe(II) from the anode. Indeed, the oxidation of As(III) to As(V) followed generated ferrous iron oxidation to ferric iron (Hug and Leupin, 2003). According to Roberts et al. (2004), ferrous iron improved As(III) removal by adsorption if compared to ferric iron because ferrous iron oxidation by dissolved oxygen led to the formation of oxidizing intermediates (H_2O_2, $^{\cdot}O_2^-$, $^{\cdot}OH$, Fe(IV)) responsible for the oxidation of As(III). Leupin and Hug (2005) described this phenomenon in two stages:

Oxidation of Fe(II) to Fe(III) by dissolved oxygen

$$\mathrm{Fe(II)} + 1/4\mathrm{O_2} + \mathrm{H_2O} = \mathrm{Fe(III)} + 1/2\mathrm{H_2O} + \mathrm{OH^-} \quad (1)$$

Oxidation of As(III) to As(IV) by oxidizing intermediates

$$\mathrm{As(III)} + \text{oxidizing intermediates}(^{\cdot}\mathrm{OH}, \mathrm{Fe\ (IV)}) = \mathrm{As(IV)} \quad (2)$$

$$\mathrm{As(IV)} + \mathrm{O_2} = \mathrm{As(V)} + {}^{\cdot}\mathrm{O_2^-} \quad (3)$$

The subsequently formed As(V) was more efficiently removed by adsorption onto ferric hydroxide (Leupin and Hug, 2005). The more the ferrous iron generation, the more the oxidizing intermediates when Fe(II) is oxidized in Fe(III) by dissolved oxygen.

In Fig. 3a, As(III) removal percentage increased with treatment dose until [Fe] = 37 $mg\ L^{-1}$ and then reached 100%. Simultaneously, As(V) formation decreased until [Fe] = 18 $mg\ L^{-1}$ and for higher treatment doses, no As(V) could be quantified in samples after treatment while zeta potential ranged from 3 ± 1 to 9.9 ± 0.6 mV. Thus, when current intensity increased, As(III) oxidation in As(V) increased and the positive zeta potential favoured As(V) removal by adsorption. For [Fe] ⩽ 18 $mg\ L^{-1}$, As(V) was

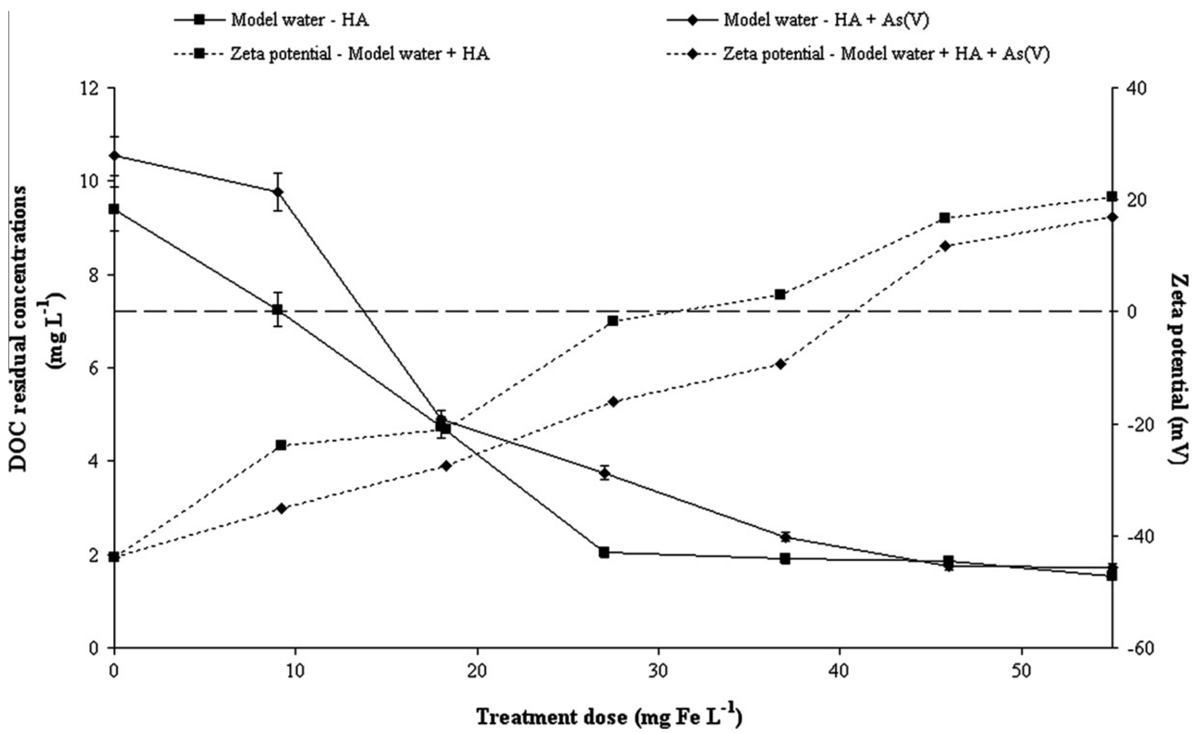

Fig. 2. Matches between residual DOC concentrations and zeta potential of colloidal suspension during treatment of model water spiked with humic acids by ECF.

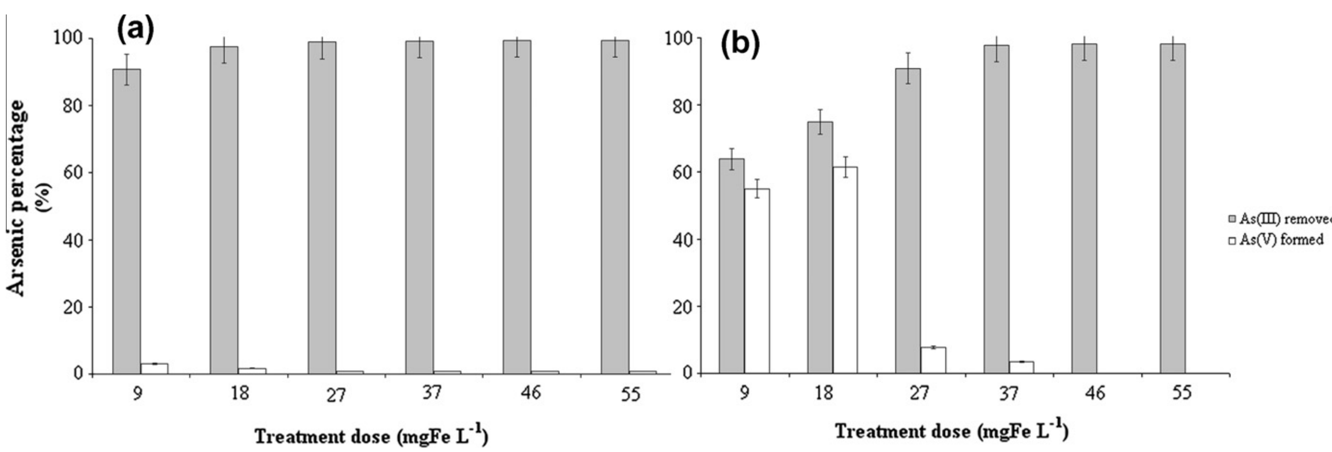

Fig. 3. As(III) removal percentage and As(V) formation percentage function of treatment dose after ECF treatment of model water (a) and model water spiked with humic acids (b).

quantified in the sample after treatment because the negative zeta potential decreased As(V) adsorption.

Organic matter negatively influenced As(III) removal by ECF (Fig. 3b). Indeed, As_{total} removal percentage ranged from 8 ± 2 to $99 \pm 1\%$ and from 88 ± 3 to $99 \pm 1\%$ after ECF treatment of As(III) in model water spiked or not with humic acids respectively. For [Fe] = 9 and 18 mg L^{-1}, As(III) removal percentage increased from 64 ± 3 to $75 \pm 2\%$ respectively while As(V) formation percentage was 55 ± 4 and $61 \pm 3\%$ respectively. In these conditions, the main reaction taking place in the reactor was the oxidation of As(III) to As(V) while Fe(II) was oxidized to Fe(III) by dissolved oxygen. Indeed, the [Fe(II)]/[Fe(III)] ratio was lower than 0.2 underlining low Fe(II) concentration and high Fe(III) concentration. Besides, high As(V) concentrations were quantified after treatment because $\zeta = -21 \pm 1$ and -18 ± 3 mV disfavoring As(V) adsorption on flocs. Then, as current intensity increased, As(III) removal percentage increased and As(V) formation percentage decreased as zeta potential increased from -11 ± 1 to 21 ± 2 mV for $27 \leqslant [Fe]\ (mg\ L^{-1}) \leqslant 55$. The treatment dose required to respect the maximum As_{total} concentration of 10 μg L^{-1} was still lower than during CF treatment ([Fe] = 34 and 37 mg L^{-1} during ECF and CF respectively).

3.7. Electrocoagulation/flocculation performances for the treatment of natural water

During CF treatment of natural water, As(V) was completely removed whatever the coagulant concentration whereas during ECF, for [Fe] = 9 mg L^{-1}, As(V) = 19.2 ± 0.1 μg L^{-1}. For $[Fe] \geqslant 18$ mg L^{-1}, As(V) residual concentrations were under the quantification limit of the spectrometric method.

During the treatment by ECF, the zeta potential of the colloidal suspension was negative as it ranged from -29 ± 2 to

-10.1 ± 0.7 mV. This result could be explained by the matrix's composition. In natural water, the DOC concentration was 3.9 ± 0.2 mg L^{-1} and was composed of around 80% of natural fulvic acids and 20% of humic acids whereas model water was spiked with commercial humic acids ([DOC] = 10.0 ± 0.2 mg L^{-1}) which were more hydrophobic compounds (around 90% of humic acids and 10% of fulvic acids). These hydrophobic compounds are generally easily coagulated (Sharp et al., 2006) and could thus improve the coagulation step and the formation of iron hydroxide flocs. In these conditions, sweep coagulation could occur favouring the removal of colloidal particles by entrapment and the decrease of the zeta potential of the colloidal suspension consequently. In natural water, more hydrophilic and soluble and as a consequence less coagulated compounds were present favouring charge neutralization instead of sweep coagulation. The zeta potential of the colloidal suspension was thus lower after treatment.

Residual DOC concentrations obtained after treatment of natural water correlated with residual As(V) concentrations as adsorption is the main mechanism occurring during their removal (Pallier et al., 2009). For [Fe] = 9 mg L^{-1}, the ferrous iron species generated during EC did not destabilize the colloidal suspension and did not allow flocs formation. As a consequence, As(V) residual concentration was 19.2 ± 0.1 μg L^{-1} and DOC residual concentration was 1.7 ± 0.1 mg L^{-1}. Then, for [Fe] $\geqslant$ 18 mg L^{-1}, As(V) was completely removed and DOC concentrations stabilised at 1.0 ± 0.1 mg L^{-1}. Thus, as during CF, as soon as the coagulation step was effective, As(V) and organic matter were removed by adsorption. The initial turbidity of the natural water was 6.5 ± 0.1 NTU. After treatment by ECF, for [Fe] = 9 mg L^{-1}, residual turbidity increased to 31 ± 1 NTU because this treatment was insufficient to destabilize the colloidal suspension. The residual soluble total iron concentration obtained ($[Fe_{Total}] = 364 \pm 22$ μg L^{-1}) confirmed this result. For $18 \leqslant$ [Fe] (mg L^{-1}) $\leqslant 55$, residual turbidity decreased from 23 ± 2 to 12 ± 1 NTU and the zeta potential of the colloidal suspension increased from -29 ± 2 to -11 ± 2 mV.

4. Conclusions

The evaluation of ECF for As(III) and As(V) removal from both model and natural water with low mineral content in high treatment doses conditions and in the presence of organic matter underlined several conclusions:

(i) Flocs generated during ECF treatment were smaller than those generated during CF treatment. Indeed, the presence of humic acids negatively influenced the size of flocs because of the more negative zeta potential involved influencing coagulation mechanisms.
(ii) The treatment dose required to completely remove As(V) was 1.5 times higher during ECF ([Fe] = 27 mg L^{-1}) than during CF treatment ([Fe] = 18 mg L^{-1}) because of ferrous iron dissolved from the anode and the lower zeta potential measured consequently. In presence of humic acids, no treatment dose applied during ECF allowed to reaching an As(V) complete removal whereas during CF, As(V) was completely removed for [Fe] $\geqslant$ 18 mg L^{-1}.
(iii) Organic matter was refractory to the treatment at high treatment doses ([Fe] $\geqslant$ 37 mg L^{-1}) and lower DOC concentrations were obtained after CF because ECF fractionated high molecular weight compounds into hydrophile ones, less prone to coagulate.
(iv) Residual turbidities were higher after ECF compared to CF because sweep coagulation was substituted by charge neutralization removal mechanisms
(v) As(III) was more efficiently removed by ECF ([Fe] = 11 mg L^{-1} in ECF towards 18 mg L^{-1} in CF) because of its oxidation to As(V) following ferrous iron oxidation to ferric iron. The presence of humic acids negatively influenced As(III) removal because of the more negative zeta potential disadvantaging subsequent formed As(V) removal by adsorption.

The results obtained for the treatment of natural water by ECF matched well with the ones obtained for the treatment of model water. ECF thus presents the advantages to oxidize As(III) in As(V) and improve its removal without applying the usually required oxidation step and to allow the respect of the maximum contaminant level of 10 μg L^{-1} whatever arsenic speciation. The higher residual turbidities obtained after treatment would be decreased by the sand filtration step commonly used after coagulation treatment.

Acknowledgments

The authors thank the "Regional Council of the Limousin" for the grants assigned to the development of this project, Prof. J.C. Bollinger (GRESE) for useful discussions. This paper was a part of the Ph.D. thesis by V.P., whose work was distinguished by the "Prix de Thèse 2009" from Association Scientifique et Technique pour l'Eau et l'Environnement (ASTEE).

References

Balasubramanian, N., Kojima, T., Basha, C.A., Srinivasakannan, C., 2009. Removal of arsenic from aqueous solution using electrocoagulation. J. Hazard. Mater. 167, 966–969.
Berthe, C., Redon, E., Feuillade, G., 2008. Fractionation of the organic matter contained in leachate resulting from two methods of landfilling: an indicator of waste degradation. J. Hazard. Mater. 154, 262–271.
Bissen, M., Frimmel, F.H., 2003. Arsenic – a review. Part II: oxidation of arsenic and its removal in water treatment. Acta Hydrochim. Hydrobiol. 31, 97–107.
Brizard, Y., 2001. L'Electrocoagulation Appliquée à la Production d'Eau Potable au Moyen d'Electrodes de Fer. Thèse de doctorat, Université de Limoges.
Cathalifaud, G., Wais Mossa, M.T., Mazet, M., 1993. Preformed ferric hydroxide flocs as adsorbents of humic substances. Water Sci. Technol. 27 (11), 55–60.
Dennett, K.E., Amirtharajah, A., Moran, T.F., Gould, J.P., 1996. Coagulation: its effect on organic matter. J. Am. Water Works Assoc. 88 (4), 129–141.
Emamjomeh, M.M., Sivakumar, M., 2009. Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. J. Environ. Manage. 90, 1663–1679.
EU Council Directive 98/83/EC of 3 November 1998 Relative to the Quality of Drinking Water, Official Journal of European Union L330, p. 32.
Exall, K.N., VanLoon, G.W., 2000. Using coagulants to remove organic matter. J. Am. Water Works Assoc. 92 (11), 93–102.
Gallagher, P.A., Schwegel, C.A., Parks, A., Gamble, B.M., Wymer, L., Creed, J.T., 2004. Preservation of As(III) and As(V) in drinking water supply samples from across the United States using EDTA and acetic acid as a mean of minimizing iron–arsenic precipitation. Environ. Sci. Technol. 38, 2919–2927.
García-Lara, A.M., Montero-Ocampo, C., 2009. Improvement of arsenic electro-removal from underground water by lowering the interference of other ions. Water Air Soil Pollut. 205, 237–244.
Garelick, H., Dybowska, A., Valsami-Jones, E., Priest, N.D., 2005. Remediation technology for arsenic contaminated drinking waters. J. Soils Sediments 5, 182–190.
Ghurye, G., Clifford, D., Tripp, A., 2004. Iron coagulation and direct microfiltration to remove arsenic from groundwater. J. Am. Water Works Assoc. 96 (4), 143–152.
Gomes, J.A.G., Daida, P., Kesmez, M., Weir, M., Moreno, H., Parga, J.R., Irwin, G., McWhinney, H., Grady, T., Peterson, E., Cocke, D.L., 2007. Arsenic removal by electrocoagulation using combined Al–Fe electrode system and characterization of products. J. Hazard. Mater. 139, 220–231.
Harif, T., Adin, A., 2007. Characteristics of aggregates formed by electroflocculation of a colloidal suspension. Water Res. 41, 2951–2961.
Hug, S.J., Leupin, O., 2003. Iron-catalyzed oxidation of As(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. Environ. Sci. Technol. 37, 2734–3742.
Kumar, P.R., Chaudhari, S., Khilar, K.C., Mahajan, S.P., 2004. Removal of arsenic from water by electrocoagulation. Chemosphere 55, 1245–1252.
Lakshmanan, D., Clifford, D.A., Samanta, G., 2009. Ferrous and ferric ion generation during iron electrocoagulation. Environ. Sci. Technol. 43, 3853–3859.
Lakshmanan, D., Clifford, D.A., Samanta, G., 2010. Comparative study of arsenic removal by iron using electrocoagulation and chemical coagulation. Water Res. 44, 5641–5652.
Lenoble, V., Chabroullet, C., Al Shukry, R., Serpaud, B., Deluchat, V., Bollinger, J.C., 2004. Dynamic arsenic removal on a MnO_2-loaded resin. J. Colloid Interface Sci. 280, 62–67.

Leupin, O.X., Hug, S.J., 2005. Oxidation and removal of arsenic(III) from aerated groundwater by filtration through sand and zero-valent iron. Water Res. 39, 1729–1740.
Matteson, M.J., Dobson, R.L., Glenn Jr., R.W., Kukunoor, N.S., Waits III, W.H., Clayfield, E.J., 1995. Electrocoagulation and separation of aqueous suspensions of ultrafine particles. Colloids Surf. A 104, 101–109.
Michon, J., Deluchat, V., Al Shukry, R., Dagot, C., Bollinger, J.C., 2007. Optimization of a GFAAS method for determination of total inorganic arsenic in drinking water. Talanta 71, 479–485.
Mohan, D., Pittman, C.U., 2007. Arsenic removal from water/wastewater using adsorbents – a critical review. J. Hazard. Mater. 142, 1–53.
Mondal, P., Majumber, C.B., Mohanty, B., 2006. Laboratory based approaches for arsenic remediation from contaminated water: recent developments. J. Hazard. Mater. 137B, 464–479.
Moreno-Casillas, H.A., Cocke, D.L., Gomes, J.A.G., Morkovsky, P., Parga, J.R., Peterson, E., 2007. Electrocoagulation mechanism for COD removal. Sep. Purif. Technol. 56, 204–211.
Moreno-Casillas, H.A., Cocke, D.L., Gomes, J.A.G., Morkovsky, P., Parga, J.R., Peterson, E., Garcia, C., 2009. Electrochemical reactions for electrocoagulation using iron electrodes. Ind. Eng. Chem. Res. 48, 2275–2282.
Pallier, V., Feuillade-Cathalifaud, G., Serpaud, B., Bollinger, J.C., 2009. Effect of organic matter on arsenic removal during coagulation/flocculation treatment. J. Colloid. Interface Sci. 342, 26–32.
Pallier, V., Serpaud, B., Feuillade-Cathalifaud, G., Bollinger, J.C., in press. Comparison of voltammetric and AAS methods for As(III) quantification in presence of iron species in model water samples with a low mineral content. Int. J. Environ. Anal. Chem. doi: 10.1080/03067310902977534.
Pretorius, W.A., Johannes, W.G., Lempert, G.G., 1991. Electrolytic iron flocculant production with a bipolar electrode in series arrangement. Water SA 17, 133–138.
Roberts, L.C., Hug, S.J., Ruettimann, T., Billah, M., Khan, A.W., Rahman, M.T., 2004. Arsenic removal with Iron(II) and Iron(III) in waters with high silicate and phosphate concentrations. Environ. Sci. Technol. 38, 307–315.
Sasson, M.B., Calmano, W., Adin, A., 2009. Iron-oxidation processes in an electroflocculation (electrocoagulation) cell. J. Hazard. Mater. 171, 704–709.
Schnitzer, M., Khan, S.U., 1972. Humic Substances in the Environment. Dekker, New York.
Sharp, E.L., Parsons, S.A., Jefferson, B., 2006. Impact of fractional character on the coagulation of NOM. Colloids Surf. A 286, 104–111.
Vik, E.A., Carlson, D.A., Eikum, A.S., Gjessing, E.T., 1984. Electrocoagulation of potable water. Water Res. 18, 1355–1360.
Villaescusa, I., Bollinger, J.C., 2008. Arsenic in drinking water: sources, occurrence and health effects: a review. Rev. Environ. Sci. Biotechnol. 7, 307–323.
Yan, M., Wang, D., Ni, J., Qu, J., Chow, C.W.K., Liu, H., 2008. Mechanism of natural organic matter removal by ployaluminum chloride: effect of coagulant particle size and hydrolysis kinetics. Water Res. 42, 3361–3370.