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Study on mechanism of electrocoagulation with iron electrodes in idealised conditions and electrocoagulation of humic acids solution in batch using aluminium electrodes

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ABSTRACT

This work consists to use distilled water as a solution in electrocoagulation (EC) tests using iron electrodes in order to bear witness to EC mechanisms and concerns EC of humic acids (HA) solution (10 mg L^{-1}) in batch using aluminium electrodes with pH modification and magnetic agitation. The pH of the distilled water is adjusted to three representative values: 2 (acid), 7 (neutral) and 12 (alkaline). Based on the current intensity as a function of applied voltage variation and the pertinent literature, three mechanisms are proposed for acid, neutral and alkaline pH. For pH 2, *Mechanism* 1 explains $Fe(OH)_{2(s)}$ formation; for pH 7, *Mechanism* 2 concerns both the varieties $Fe(OH)_{2(s)}$ and $Fe(OH)_{3(s)}$ production; and for pH 12, *Mechanism* 3 is characterised by $Fe(OH)_{3(s)}$ apparition. From these results, it can be seen that there is an extremely high dependence of iron species on pH in EC system. Finally, EC process using aluminium electrodes (better than iron ones) is proved highly efficient for HA removal (more than 70%) by charge neutralisation and adsorption (current density 16.6 A m^{-2} during 30 min at pH 7).

Keywords: Electrocoagulation; Mechanism; Iron; Humic acids; Aluminium

1. Introduction

The interest in electrochemical methods for wastewater treatment such as EC is permanently growing [1–3]. Electrochemical methods are also considered as promising methods for water treatment [4–6]. EC process consists to generate in water metallic cations by electrodissolution of soluble anodes (e.g. in iron or aluminium). The *in situ* formed cations (Fe^{2+} and/or Fe^{3+} or Al^{3+}) destabilise finely dispersed particles by charge neutralisation and conduct near the anodes to hydroxide forms ($Fe(OH)_{n(s)}$, $n = 2$ or 3, or $Al(OH)_{3(s)}$) which adsorb the dissolved matter by constitution of large and stable flocs containing less bound water [7]. The flocs can be separated by flotation (transport to the surface by fixation on the $H_{2(g)}$ bubbles produced at the cathode), sedimentation, or filtration [3,6,8–17]. Indeed the greater part of $H_{2(g)}$ bubbles combine additively because hydrogen is a hydrophobic gas [18], and iron is dense to settle out at the recipient bottom [4,11]. It has been demonstrated [9,19] that $Fe(OH)_{n(s)}$ has alkaline properties and a very high adsorption capacity 100 more important than chemical $Fe(OH)_{n(s)}$.

On the other hand, several EC process mechanisms have been proposed mostly without specifying solution pH or it was supposed neutral [1,4,6,19–24]. Due

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to the large different conditions, such as organic and inorganic solutions, a great confusion exists about iron hydroxides $Fe(OH)_{2(s)}$ and/or $Fe(OH)_{3(s)}$ production in EC systems.

Brown and black biopolymers associated with soil, sediment and particulates in water consist of material derived from the degradation of animals and plants are called humic substances. Humic acids (HA) are one of the main components of the humic substances in water [25]; they are soluble in dilute alkaline solution but precipitate from an acidified solution (pH < 2) [26]. The presence of organic matter (OM) in surface water potabilised by classical physicochemical treatment has several problems such as disinfection by-products [27].

In this work, to get appropriate EC mechanisms explaining the Fe(II) and Fe(III) formation and depending on pH, the pH of distilled water was adjusted to three representative values: 2 (acid), 7 (neutral) and 12 (alkaline). Then, these solutions were electrocoagulated as witness tests during evolution of applied voltage *E* increase as function of current intensity *I*. This work is enclosed in an overall study concerning EC feasibility as water treatment process. Thus, HA in synthetic solution are electrocoagulated to define optimal conditions of their removal and to understand implicated mechanisms and electrochemical phenomena.

2. Experimental

2.1. Iron EC tests in distilled water

2.1.1. Experimental Procedure

The EC tests have been realised using equipment that is composed of two ordinary steel electrodes (99.8%: iron and 0.2%: carbon). These electrodes are of the same dimensions (1.9 cm × 20 cm) and are plunged in a device of 0.5 L as volume. For each electrode, the immerged (active) surface is 19.95 cm^2 (1.9 cm × 10.5 cm) and the distance *d* between them is 4 cm. These two parameters are maintained constant. The anode and the cathode are connected to a DC power supply (Enyl1 Elektrolyser) with 15 V as maximal voltage and 10 A as maximal current intensity. The applied voltage and the current intensity are measured by a voltammeter and an ammeter connected in parallel and in series, respectively, as shown in Fig. 1.

The EC tests consist to raise the applied voltage *E* gradually from 0 to 15 V and to note the corresponding value of current intensity *I* on a distilled water sample. The phenomena which are producing in the EC device are observed (this operation will take 30 min as Holt et al. [14] state that EC was efficient only for 30 min for clay suspension removal).

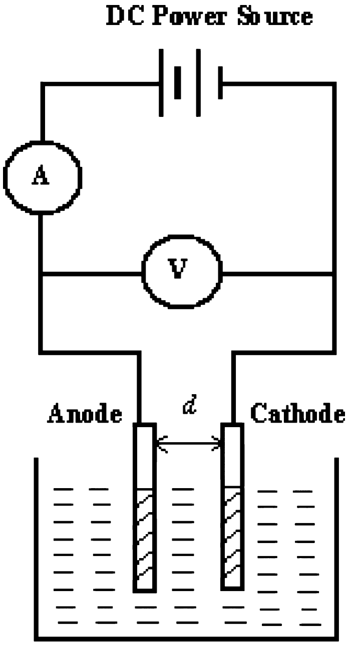

Fig. 1. Experimental set-up for iron EC process, *d* (*d* = 4 cm) is the distance between the anode and the cathode.

In order to study only EC phenomena, no agitation was applied. Moreover, the solutions after EC tests are submitted to sedimentation during 30 min before their analyses. Thus, the influence of the EC treatment time and the iron hydroxides precipitation time on the process has not been studied in this work.

Before EC tests, the pH was adjusted using NaOH and HCl (2 N) solutions. In order to avoid any interference, the electrodes are prepared as follows: (1) skim with solution composed of: NaOH, 25 g; Na_2CO_3, 25 g; K_2CO_3, 25 g; distilled water, q.s.p. 1000 mL; (2) rinse with distilled water and polish using abrasive paper; (3) clean in sulphuric acid solution (H_2SO_4 at 20%) at 40 °C during 5 min; and (4) rinse with distilled water. All used chemicals are of reagent grade and the temperature was maintained constant.

2.1.2. Analytical techniques

The performed analyses concerned turbidity in NTU (2100N Hach turbidimeter), conductivity in µS cm^{-1} at 25 °C (EC215 Hanna Instruments conductimeter), and pH (CG820 Schott Geräte pH-meter).

2.2. Aluminium EC tests in HA solution

2.2.1. Experimental procedure

The used HA are a commercialised product by Across Organics Company (USA). This product is like a brown powder. A concentrated solution at 1 g L^{-1} is prepared by dissolving 1 g of HA in 62.5 mL of NaOH (2 N) solution in 1 L phial and then completed to 1 L with distilled water. This solution is submitted to magnetic agitation during 48 h and then conserved at 4 °C in the absence of light. From this solution, diluted solutions (10 mg L^{-1}, $Ab_i = 0.286$) are prepared for EC tests.

EC tests have been realised using equipment which is composed of two commercialised aluminium electrodes. Both the electrodes are of the same dimensions and plunged in a device with 0.5 L as volume and 8 cm as diameter. For each electrode, the immerged (active) surface is 18 cm^2 (2 cm × 9 cm) and the distance d between them is varied from 2.5 to 5.5 cm. Electrodes are connected to direct current power supply (Stell Trafo) with 30 V as maximal voltage and 10 A as maximal intensity. Applied voltage E (V) and current intensity I (A) are measured by voltammeter and ammeter connected in parallel and in series respectively. Before EC test and in order to avoid any interference, aluminium electrodes are prepared as follows: (1) rinse with distilled water, (2) clean in sodium hydroxide solution (10%) (3) rinse with distilled water. They are then dried with absorptive paper and weighted (A_m and C_m are their masses, respectively). After introduction of solution to treat in the reactor, pH is adjusted at its selected initial value using H_2SO_4 or NaOH (2 N) solutions. Electrodes are plunged in the reactor and fixed before their connection to power supply. When current is applied, the magnetic agitation is started at 300 rpm for 4 min and then fixed at 120 rpm to the test end. After 30 min sedimentation, a 50 mL sample is taken from the settled solution by pipetting. Conductivity and pH measures are immediately realised. Before UV absorbance at 254 nm measure, pH is adjusted at 12. Finally, electrodes are dried and weighted again. All used chemicals are of analytical grade.

2.2.2. Analytical techniques

The performed analyses concerned turbidity in NTU (Turb 550 (wtw) turbidimeter), conductivity in mS cm^{-1} at 25 °C (EC215 Hanna Instruments conductimeter), and pH (Inolab pH level 1 pH-meter). UV absorbance at 254 nm of HA contained in synthetic solution is measured using Shimadzu 1601 spectrophotometer with 1 cm cell quartz. The pH of solutions is adjusted at 12 prior absorbance measure to enhance HA absorbance. The removal of HA is calculated using the following relation:

$$R\ (\%) = \frac{Ab_i - Ab_f}{Ab_i} \times 100 \qquad (1)$$

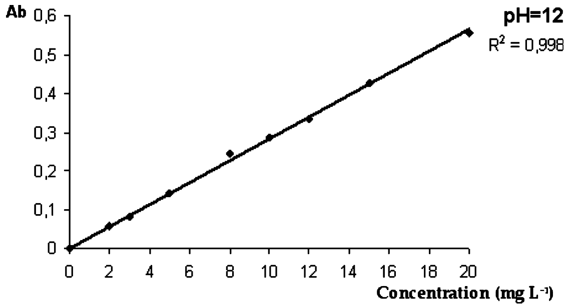

Fig. 2. Calibration curve expressing UV absorbance (254 nm) at pH 12 as a function of HA concentration.

where Ab_i and Ab_f are initial and final UV absorbances, respectively. A calibration curve expressing UV absorbance at pH 12 as a function of HA concentration is established (Fig. 2). This curve shows that UV absorbance is an accurate method to measure HA concentration.

3. Results and discussion

3.1. Iron EC tests in distilled water

The variation of intensity I (mA) as a function of the applied voltage E (V) for EC of distilled water at acid, neutral and alkaline pH is shown in Fig. 3. The initial and final conditions of these variation experiments are presented in Table 1:

Acid pH (pH 2): When E is 1 V, there is an intense $H_{2(g)}$ bubbles emanation from the cathode and less intense $O_{2(g)}$ production from the anode. When E is 5 V, the cathode at the side of the anode starts to blacken. When E is 8 V, the surface of cathode which

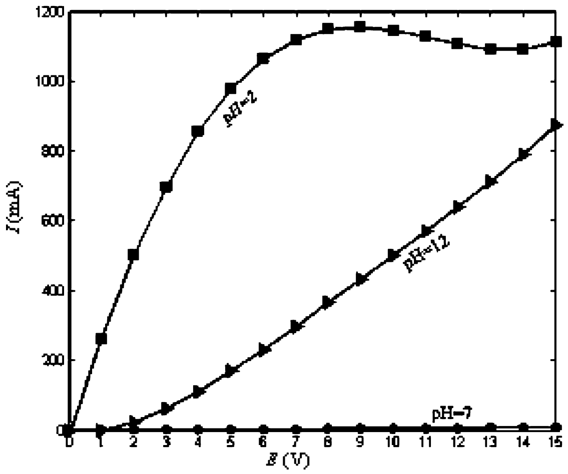

Fig. 3. Variation of the intensity I (mA) as a function of applied voltage E (V) for iron EC of distilled water at acid (■), neutral (●) and alkaline (▲) pH.

was previously blackened starts to decay giving black flocs. A fraction of these flocs deposits under the cathode and the other fraction remains fixed at the cathode base. The anode surface at the side of the cathode starts to blacken. When *E* is 10 V, the cathode surface at the side of anode is entirely black. The other surface of cathode at the side of recipient starts to blacken from the base to the top. When *E* is 11 V, the flocs coming from the cathode remain in its surroundings. When *E* is 15 V, the solution is limpid and the cathode becomes green.

Neutral pH (pH 7): When *E* is 2 V, the distilled water starts to be green. When *E* is 8 V, clouds of red-brown flocs appear especially near the cathode at the side of anode with few $H_{2(g)}$ bubbles.

Alkaline pH (pH 12): Just when the electrodes were introduced in the device, the solution becomes yellow-red-brown with flocs apparition. The emanation of $H_{2(g)}$ bubbles is less intense at the cathode.

These observations can be explained as follows:

Acid pH (pH 2): The intense emanation of $H_{2(g)}$ bubbles at the cathode, the less intense emanation of $O_{2(g)}$ bubbles at the anode and the apparition of blue-green to black flocs ($Fe(OH)_{2(s)}$, according to [19,25]) are explained by these reactions:

■ *Mechanism 1* (pH 2)

Anode:

$$2Fe_{(s)} - 4e^- \rightarrow 2Fe^{2+}_{(aq)} \quad (E^\circ = +0.447\ V) \tag{2}$$

$$2H_2O_{(l)} - 4e^- \rightarrow O_2(g) + 4H^+_{(aq)} \quad (E^\circ = +1.229V) \tag{3}$$

Solution:

$$2Fe^{2+}_{(aq)} + 4OH^-_{(aq)} \rightarrow 2Fe(OH)_{2(s)} \tag{4}$$

Cathode:

$$8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)} \quad (E^\circ = 0.000V) \tag{5}$$

Total:

$$2Fe_{(s)} + 6H_2O_{(l)} \rightarrow O_{2(g)} + 4H_{2(g)} + 2Fe(OH)_{2(s)} \tag{6}$$

Mechanism 1 (reaction (6)) accounts for the observed productions of oxygen at the anode and hydrogen at the cathode and green-black colour apparition ($Fe(OH)_{2(s)}$) in the solution. The cathode at the side of anode that started to blacken: it is a ferrous oxide which deposits [28]. The anode surface at the side of cathode which started to blacken: it is the start of its passivation.

Neutral pH (pH 7): The observed green colour when *E* was 2 V indicates ferrous Fe^{2+} and/or bihypoferrite $HFeO_2^-$ ions presence [28]. The observed red-brown colour indicates ferric hydroxide $Fe(OH)_{3(s)}$ and/or hematite Fe_2O_3 presence [28]. For Kovacheva-Ninova [19], yellow-orange-red-brown colour indicates $Fe(OH)_{3(s)}$ presence:

Mechanism 2 (pH 7)

Anode:

$$2Fe_{(s)} - 4e^- \rightarrow 2Fe^{2+}_{(aq)} \quad (E^\circ = +0.447V) \tag{7}$$

$$Fe^{2+}_{(aq)} - e^- \rightarrow Fe^{3+}_{(aq)} \quad (E^\circ = -0.771V) \tag{8}$$

$$Fe_{(s)} - 3e^- \rightarrow Fe^{3+}_{(aq)} \quad (E^\circ = +0.037V) \tag{9}$$

Solution:

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)} \tag{10}$$

$$2Fe^{3+}_{(aq)} + 6OH^-_{(aq)} \rightarrow 2Fe(OH)_{3(s)} \tag{11}$$

Cathode:

$$8H_2O_{(l)} + 8e^- \rightarrow 4H_{2(g)} + 8OH^-_{(aq)} \quad (E^\circ = -0.828V) \tag{12}$$

Total:

$$3Fe_{(s)} + 8H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + 2Fe(OH)_{3(s)} + 4H_{2(g)} \tag{13}$$

Mechanism 2 (reaction (13)) accounts for the apparition in solution of green ($Fe(OH)_{2(s)}$) and then red-brown ($Fe(OH)_{3(s)}$) flocs and hydrogen production at the cathode. For ferrous to ferric ions conversion, Muruganathan et al. [29] talk about auto-oxidation and Kovacheva-Ninova [19] proposes a series of reactions going from metallic to ferric iron:

$$\begin{aligned} Fe \xrightarrow{H_2O} Fe(OH)_{ads} \xrightarrow{H_2O,O_2} Fe(OH)_{2(s)} \\ + Fe^{2+} \cdot nH_2O \xrightarrow{H_2O,O_2} Fe(OH)_{3(s)} \end{aligned} \tag{14}$$

Alkaline pH (pH 12): When the electrodes were introduced in the recipient, the solution becomes yellow-red-brown with flocs apparition because of ferric ions spontaneous discharge. The ferric ions in intense presence of OH^- give birth to the ferric hydroxide following this mechanism:

? Mechanism 3 (pH 12)

Anode:

$$2Fe_{(s)} - 6e^- \rightarrow 2Fe^{3+}_{(aq)} \quad (E^\circ = +0.037V) \tag{15}$$

Table 1
Initial and final conditions of the variation of intensity I (mA) as function of applied voltage E (V) for iron EC of distilled water at acid, neutral, and alkaline pH (minus signs in brackets indicate percentage increase for the turbidity because the conductivity and anode mass percentages are for their reduction)

Parameter	Initial state	Final state
Acid pH with $Fe(OH)_{2(s)}$, *Mechanism 1*	2	2.62
Turbidity (NTU)	2.1	3.1 (−47%)
Conductivity (μS cm^{-1})	9450	2910 (69%)
Cathode mass (g)	91.36	91.36
Anode mass (g)	91.68	91.41 (0.29%)
Neutral pH with $Fe(OH)_{2(s)}$ and $Fe(OH)_{3(s)}$, *Mechanism 2*	7	6.59
Turbidity (NTU)	2.1	3.6 (−71%)
Conductivity (μS cm^{-1})	47.5	12.5 (74%)
Cathode mass (g)	91.37	91.37
Anode mass (g)	91.71	91.70 (0.01%)
Alkaline pH with $Fe(OH)_{3(s)}$, *Mechanism 3*	12	12.1
Turbidity (NTU)	3.6	4.3 (−19%)
Conductivity (μS cm^{-1})	5880	5290 (10%)
Cathode mass (g)	91.34	91.34
Anode mass (g)	91.39	91.37 (0.02%)

Solution:

$$2Fe^{3+}_{(aq)} + 6OH^{-}_{(aq)} \rightarrow 2Fe(OH)_{3(s)} \tag{16}$$

Cathode:

$$6H_2O_{(l)} + 6e^{-} \rightarrow 3H_{2(g)} + 6OH^{-}_{(aq)} \quad (E^\circ = -0.828V) \tag{17}$$

Total:

$$2Fe_{(s)} + 6H_2O_{(l)} \rightarrow 2Fe(OH)_{3(s)} + 3H_{2(g)} \tag{18}$$

Mechanism 3 (reaction (18)) reflects the red-brown flocs ($Fe(OH)_{3(s)}$) apparition in the solution and the hydrogen production at the cathode.

At the end of the current intensity as function of applied voltage variation for all pH, the cathode mass did not change (Table 1) but the anode mass decreased even slightly (EC time t_{EC} was fixed at only 30 min) as follows: 0.29% (acid pH), 0.02% (alkaline pH) and 0.01% (neutral pH). These results indicate clearly that EC is essentially a process using sacrificial anodes.

The adjustment of pH at 2 and 12 conducted to an increase of the conductivity of the solutions (from 47.5 μS cm^{-1} at pH 7 to 9450 (~200 times) and 5880 (~120 times) μS cm^{-1} at pH 2 and 12, respectively). These results prove that H^+ and OH^- ions have a great role in EC phenomena.

The final turbidity increased as follows: 71% (neutral pH with both forms $Fe(OH)_{2(s)}$ and $Fe(OH)_{3(s)}$), 47% (acid pH with $Fe(OH)_{2(s)}$) and 19% (alkaline pH with $Fe(OH)_{3(s)}$) indicating that EC in neutral and acid conditions produce more flocs which are particularly convenient for adsorption.

The final conductivity decreased as follows: 74% (neutral pH), 69% (acid pH) and 10% (alkaline pH) showing that EC is better realised when a neutral pH is used.

On the other hand, Fig. 3 shows that the electrical current passes through the solution better when pH is acid and alkaline. When pH is neutral, the electrical conduction becomes less important ($Fe(OH)_{2(s)}$ and $Fe(OH)_{3(s)}$ flocs constitute an electrical resistance by steric effect). This is also an obvious fact of the most essential effect of pH on EC process which can be considered as an accelerated corrosion process (Fig. 3).

For pH 2 (*Mechanism 1*), two reactions are at the anode: ferrous dissociation and anodic hydrolysis (reactions (2) and (3) respectively). In the solution, a synthesis reaction of $Fe(OH)_{2(s)}$ (reaction (4)) progresses. At the cathode, a consummative reaction of $H^+_{(aq)}$ ions in large excess (reaction (5)) progresses. These anodic and cathodic reactions constitute an important driving force for ionic transport in the solution (Fig. 3).

For pH 12 (*Mechanism 3*), a ferric dissociation reaction is at the anode (reaction (15)). In the solution, a synthesis reaction of $Fe(OH)_{3(s)}$ (reaction (16)) progresses. At the cathode, a cathodic hydrolysis reaction (reaction (17)) progresses. This cathodic hydrolysis reaction (17) seems to be less consummative of electrons than the cathodic reaction (5) for acid pH (Fig. 3).

For pH 7 (*Mechanism 2*), two ferrous and ferric dissociation reactions (reactions (7) and (8)) and a third

Table 2
Effect of pH in Al EC of HA solution (10 mg L^{-1}, $Ab_i = 0.286$) for $i = 16.6$ A m^{-2} ($t_{EC} = 30$ min, $d = 2.5$ cm)

Initial stage				Final stage				
pH	C (μS cm^{-1})	A_m (g)	C_m (g)	pH	C (μS cm^{-1})	A_m (g)	C_m (g)	Ab_i
4	165	14.3595	13.0236	6.61	158	14.3567	13.0175	0.089 (68.88%)
5	156	13.3353	12.7901	6.74	140	13.3328	12.7846	0.091 (68.18%)
6	150	13.3386	12.7965	7.52	140	13.3360	12.7906	0.088 (69.23%)
7	151	13.3418	12.8024	8.06	140	13.3389	12.7974	0.080 (72.03%)
8	156	13.3169	12.7724	8.26	149	13.3145	12.7657	0.095 (66.78%)
9	158	14.3558	13.0169	8.44	143	14.3537	13.0114	0.096 (66.43%)

reaction of ferrous ferric transformation (reaction (9)) are at the anode. In the solution, two synthesis reactions of $Fe(OH)_{2(s)}$ and $Fe(OH)_{3(s)}$ (reactions (10) and (11)) exist. These two synthesis reactions for neutral pH instead of only one reaction (reaction (16)) for alkaline pH seem clutter ionic circulation in solution ($Fe(OH)_{2(s)}$ and $Fe(OH)_{3(s)}$ in suspension in comparison with $Fe(OH)_{3(s)}$ alone). At the cathode, a cathodic hydrolysis reaction (reaction (12)) progresses (Fig. 3).

3.2. Aluminium EC tests in HA solution

The aim of these experiments is to study the influencing parameters on HA removal by EC using aluminium electrodes at a fixed concentration 10 mg L^{-1} such as pH, interelectrode distance, duration and current density. Aluminium electrodes are chosen here because they are proved better than iron ones for HA removal. In fact, humic macromolecules are easily removed from solution by flotation with $Al(OH)_{3(s)}$ flocs than decantation with iron flocs (Al is less dense than Fe). In this way, to investigate the influence of one parameter it is varied and all the others are fixed.

3.2.1. Preliminary observations

During EC tests, these observations are noticed: hydrogen and oxygen bubbles are produced at the cathode and the anode, respectively, and anode mass A_m and cathode mass C_m are both decreased as shown in Tables 2–5. To explain these observations, the following mechanism, at pH 7 (which is proved optimal (Table 2)), can be proposed:

Anode:

$$Al_{(s)} - 3e^- \rightarrow Al^{3+}_{(aq)} \quad (E^\circ = +1.66V) \tag{19}$$

$$2H_2O_{(l)} - 4e^- \rightarrow 4H^+_{(aq)} + O_{2(g)} \quad (E^\circ = -1.23V) \tag{20}$$

Solution:

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Al(OH)_{3(s)} \tag{21}$$

$$Al(OH)^-_{4(aq)} \rightarrow OH^-_{(aq)} + Al(OH)_{3(s)} \tag{22}$$

Cathode:

$$4H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)} + 2H_{2(g)} \quad (E^\circ = -0.83V) \tag{23}$$

$$Al_{(s)} + 4OH^-_{(aq)} - 3e^- \rightarrow Al(OH)^-_4(aq) \tag{24}$$

Total:

$$2Al_{(s)} + 8H_2O_{(l)} \rightarrow 5H_{2(g)} + 2Al(OH)_{3(s)} + O_{2(g)} \tag{25}$$

Table 3
Effect of interelectrode distance in Al EC of HA solution (10 mg L^{-1}, $Ab_i = 0.286$) for pH 7, $i = 16.6$ A m^{-2} and $t_{EC} = 30$ min

Initial stage				Final stage				
D (cm)	C (μS cm^{-1})	A_m (g)	C_m (g)	pH	C (μS cm^{-1})	A_m (g)	C_m (g)	Ab_f
2.5	151	13.3418	12.8024	8.06	140	13.3389	12.7974	0.080 (72.03%)
3.5	188	14.0280	12.5940	7.52	184	14.0185	12.5832	0.101 (64.69%)
4.5	177	14.0353	12.6059	8.08	174	14.0289	12.5955	0.120 (58.04%)
5.5	165	14.0580	12.6245	7.88	159	14.0523	12.6150	0.153 (46.50%)

Table 4
Effect of current density in Al EC of HA solution (10 mg L^{-1}, $Ab_i = 0.286$) for pH 7, $d = 2.5$ cm and $t_{EC} = 30$ min

Initial stage				Final stage				
i (A m^{-2})	C (μS cm^{-1})	A_m (g)	C_m (g)	pH	C (μS cm^{-1})	A_m (g)	C_m (g)	Ab_f
5.50	150	14.2726	12.8950	8.63	145	14.2661	12.8895	0.090 (68.53%)
11.1	146	14.3140	12.9530	7.73	137	14.3117	12.9469	0.085 (70.28%)
16.6	151	13.3418	12.8024	8.06	140	14.0185	12.5832	0.080 (72.03%)
22.2	139	14.3039	12.9340	8.59	136	14.2955	12.9227	0.078 (72.73%)
27.7	143	14.2940	12.9230	8.82	139	14.2831	12.9101	0.077 (73.08%)
33.3	133	14.2819	12.9100	9.20	125	14.2727	12.8956	0.074 (74.13%)

Aluminium dissolution at anode (reaction (19)) and cathode (reaction (24)) produces $Al^{3+}_{(aq)}$ and $Al(OH)_4{}^{-}{}_{(aq)}$, respectively. On the other hand, $Al^{3+}_{(aq)}$ neutralises negative humic macromolecules to constitute neutral colloids and contributes with $Al(OH)_4{}^{-}{}_{(aq)}$ to produce white-grey flocs ($Al(OH)_{3(s)}$) (reactions (21) and (22)). These flocs adsorb humic macromolecules during their carrying away by hydrogen and oxygen bubbles to the surface of solution constituting brown froth layer (Figs. 4 and 5). This mechanism takes in account aluminium dissolution at cathode (reaction (24)) which was also observed by several authors [12,30].

3.2.2. Effect of initial pH

It is well known that pH is both significant in aluminium species formation and humic macromolecules configuration so we studied initial pH effect in EC of HA. Initial pH is varied from 4 to 9 and all the other parameters are maintained constant for $i = 16.6$ A m^{-2} and $d = 2.5$ cm during 30 min. The obtained results (Table 2) show that optimal pH for EC of HA is near to 7 (72%). These results can be explained by the fact that HA removal is by charge neutralisation and adsorption:

- For pH < 5, charge neutralisation predominates; this is attributed to the aluminium cationic species presence such as Al^{3+} (reaction (19)), $Al(OH)^{2+}$ and $Al(OH)_2{}^{+}$ [4].
- For pH comprised between 5 and 7, adsorption predominates; this is attributed to the aluminium hydroxide formation (reactions (21) and (22)). Several authors have shown at this pH range, EC is more efficient [6,31]. For water treatment production by EC without adjusting pH, this pH is convenient since surface water's pH is generally around 7.
- For pH > 7, HA disprotonation increase its negative charge [32] and its dissolution (HA solution is moreover prepared in alkaline condition and pH is adjusted at 12 before UV absorbance measure). On the other hand, $Al(OH)_4{}^{-}{}_{(aq)}$ presence restricts adsorption by charge repulsion.

3.2.3. Effect of interelectrode distance and current density

Interelectrode distance is varied from 2.5 to 5.5 cm for pH 7 and $i = 16.6$ A m^{-2} during 30 min. The

Table 5
Effect of duration in Al EC of HA solution (10 mg L^{-1}, $Ab_i = 0.286$) for pH 7, $d = 2.5$ cm and $i = 33.3$ A m^{-2}

Initial stage				Final stage				
t (min)	C (μS cm^{-1})	A_m (g)	C_m (g)	pH	C (μS cm^{-1})	A_m (g)	C_m (g)	Ab_f
5	154	13.1880	12.6650	8.48	140	13.1760	12.5950	0.261 (08.74%)
10	121	13.1755	12.5747	8.97	120	13.1706	12.5693	0.152 (46.85%)
15	121	13.9453	12.4928	9.25	117	13.9403	12.4851	0.124 (56.64%)
20	124	13.1841	12.5804	9.07	120	13.1766	12.5754	0.104 (63.63%)
25	189	13.9386	12.4845	9.22	184	13.9217	12.4713	0.096 (66.43%)
30	133	14.2819	12.9100	9.20	125	14.2727	12.8956	0.074 (74.13%)
35	154	13.9266	12.4703	9.70	140	13.9163	12.4523	0.073 (74.47%)
40	185	13.1553	12.5537	9.76	159	13.1385	12.5332	0.073 (74.47%)
45	185	13.9675	12.5185	9.70	135	13.9465	12.4932	0.072 (74.82%)
50	170	13.2036	12.6110	9.85	122	13.1852	12.5860	0.072 (74.82%)

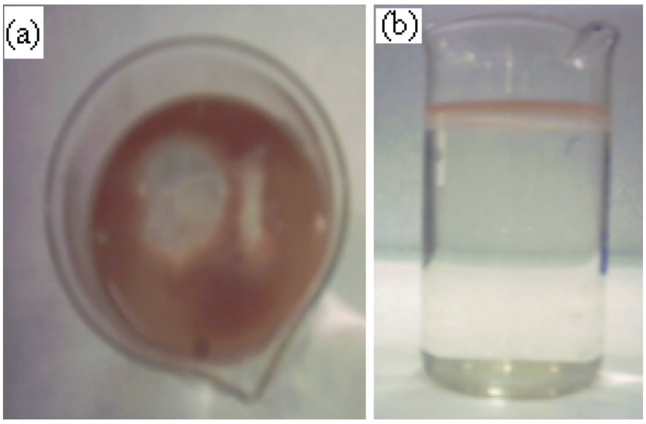

Fig. 4. Froth at the surface after Al EC test (photo (a), above view; photo (b), full-face view).

obtained results (Table 3) show that when interelectrode distance increases HA removal is decreased indicating electrical field significance in charge neutralisation and gas bubbles collision with formed flocs. Current density is varied from 5.5 to 33.3 A m^{-2} for pH 7 and $d = 2.5$ cm during 30 min. The obtained results (Table 4) show that when current density increases HA removal is increased indicating charge neutralisation significance.

3.2.4. *Effect of duration*

Duration is varied from 5 to 50 min for pH 7 and $d = 2.5$ cm. The obtained results (Table 5) show that HA removal increase with duration until 30 min where it becomes nearly constant (74%). Similar results are obtained by Holt et al. [14]. On the other hand, HA removal by EC is higher than chemical coagulation which does not exceed 60% in most cases [33].

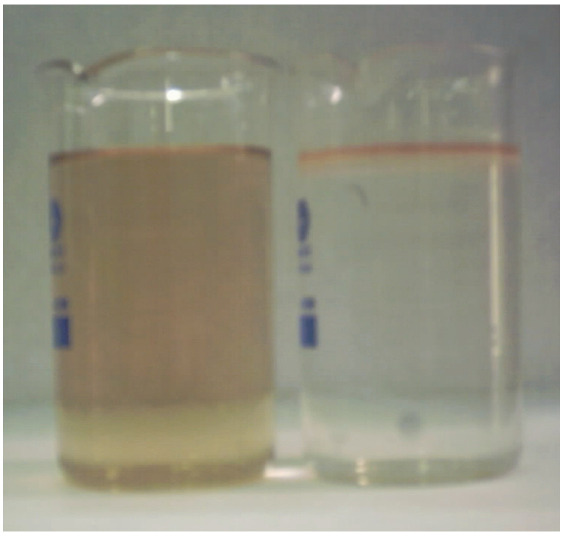

Fig. 5. Initial and final stages of HA solution before and after Al EC test at optimal conditions ($i = 33.3$ A m^{-2}, pH 7, $t_{EC} = 30$ min, $d = 2.5$ cm).

4. Conclusion

Three pH dependent mechanisms are proposed using distilled water as solution for EC process with iron electrodes. When pH is 2, $Fe(OH)_{2(s)}$ occurs, when pH is 12, $Fe(OH)_{3(s)}$ appears and when pH is 7, both species are produced. These suggested mechanisms are a contribution to understand EC process in idealised conditions. On the other hand, the laboratory tests show also that EC process using aluminium electrodes is highly efficient for HA removal. The *in situ* formed cations (Al^{3+}) neutralise humic macromolecules and contribute with $Al(OH)^{-}_{4(aq)}$ to the formation of hydroxides ($Al(OH)_{3(s)}$) which adsorb OM at optimal pH 7. Electrical field and current density are most essential in HA removal by EC which is proved once more as promising process for water treatment.

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References

[1] C. Barrera-Díaz, F. Ureña-Nuñez, E. Campos, M. Palomar-Pardave and M. Romero-Romo, A combined electrochemical-irradiation treatment of highly colored and polluted industrial wastewater, Radiat. Phys. Chem., 67 (2003) 657-663.
[2] H. Bergmann, A. Rittel, T. Iourtchouk, K. Schoeps and K. Bouzek, Electrochemical treatment of cooling lubricants, Chem. Eng. Process., 42 (2003) 105-119.
[3] W. Den and C. Huang, EC for removal of silica nano-particles from chemical–mechanical-polarization wastewater, Colloids Surf. A, 254 (2005) 81-89.
[4] M.Y.A. Mollah, R. Schennach, J.R. Parga and D.L. Cocke, Electrocoagulation (EC)—science and applications, J. Hazard. Mater., B84 (2001) 29-41.
[5] M.I. Kerwick, S.M. Reddy, A.H.L. Chamberlain and D.M. Holt, Electrochemical disinfection, an environmentally acceptable method of drinking water disinfection? Electrochim. Acta, 50 (2005) 5270-5277.
[6] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11-41.
[7] N.P. Barkley, C. Farrell and T. Williams, Electro-Pure Alternating Current EC, SITE, USEPA EPA/540/S (1993) 93/504.
[8] V.K. Kovatcheva and M.D. Parlapanski, Sono-electrocoagulation of iron hydroxides, Colloids Surf. A, 149 (1999) 603-608.
[9] A. Gürses, M.Yalçin and C. Doğar, Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables, Waste Manag., 22 (2002) 491-499.
[10] X. Chen, G. Chen and P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, Sep. Purif. Technol., 19 (2000) 65-76.

[11] X. Chen, G. Chen and P.L. Yue, Investigation on the electrolysis voltage of electrocoagulation, Chem. Eng. Sci., 57 (2002) 2449-2455.

[12] O.T. Can, M. Bayramoglu and M. Kobya, Decolorization of reactive dye solutions by electrocoagulation using aluminium electrodes, Ind. Eng. Chem. Res., 42 (2003) 3391-3396.

[13] M. Kobya, O.T. Can and M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminium electrodes, J. Hazard. Mater., B100 (2003) 163-178.

[14] P.K. Holt, G.W. Barton, M. Wark and C.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloids Surf. A, 211 (2002) 233-248.

[15] P. Ratna Kumar, S. Chaudhari, K.C. Khilar and S.P. Mahajan, Removal of arsenic from water by electrocoagulation, Chemosphere, 55 (2004) 1245-1252.

[16] N. Bektaş, H. Akbulut, H. Inan and A. Dimoglo, Removal of phosphate from aqueous solutions by electrocoagulation, J. Hazard. Mater., B106 (2004) 101-105.

[17] S.-H. Shin, Y.-H. Kim, S.-K. Jung, K.-H. Suh, S.-G. Kang, S.-K. Jeong and H.-G. Kim, Combined performance of electrocoagulation and magnetic separation processes for treatment of dye wastewater, Korean J. Chem. Eng., 4 (2004) 806-810.

[18] C.Y. Hu, S.L. Lo, W.H. Kuan and Y.D. Lee, Removal of fluoride from semiconductor wastewater by electrocoagulation–flotation, Water Res., 39 (2005) 895-901.

[19] V. Kovacheva-Ninova, Electrochemical treatment of mine wastewaters containing heavy metal ions, Annual Mining and Mineral Processing (part II), vol. 46, Sofia (Bulgaria) (2003) 215-220.

[20] J.G. Ibáñez, M.M. Singh and Z. Szafran, Laboratory experiments on electrochemical remediation of the environment. Part 4: color removal of simulated wastewater by EC-electroflotation, J. Chem. Educ., 8 (1998) 1040-1041.

[21] A.S. Koparal, U.B. Öğütveren, Removal of nitrate from water by electroreduction and electrocoagulation, J. Hazard. Mater., B89 (2002) 83-94.

[22] N. Daneshvar, H. Ashassi-Sorkhabi and A. Tizpar, Decolorization of orange II by electrocoagulation method, Sep. Purif. Technol., 31 (2003) 153-162.

[23] N. Daneshvar, H. Ashassi-Sorkhabi and M.B. Kasiri, Decolorization of dye solution containing Acid Red 14 by EC with a comparative investigation of different electrode connections, J. Hazard. Mater., B112 (2004) 55-62.

[24] M. Bayramoglu, M. Kobya, O.T. Can and M. Sozbir, Operating cost analysis of electrocoagulation of textile wastewater, Sep. Purif. Technol., 37 (2004) 117-125.

[25] A.G.S. Prado and C. Airoldi, Humic acid–divalent cation interactions, Thermochim. Acta, 405 (2003) 287-292.

[26] A.K. Camper, Involvement of humic substances in regrowth, Int. J. Food Microbiol., 92 (2004) 355-364.

[27] D. Bursill, Drinking water treatment – understanding the processes and meeting the challenges, Water Sci. Technol. Water Supply, 1 (2001) 1-7.

[28] M. Pourbaix, J. Van Muylder, N. de Zoubov, Atlas d'equilibres électrochimiques à 25°C, Gauthier-Villars & Cie, Paris, 1963 (French).

[29] M. Murugananthan, G. Bhaskar Raju and S. Prabhakar, Removal of sulfide, sulfate and sulfite ions by electrocoagulation, J. Hazard. Mater., B109 (2004) 37-44.

[30] J.-Q. Jiang, N.J.D. Graham, C. André, G.H. Kelsall and N. Brandon, Laboratory study of electro-coagulation–flotation for water treatment, Water Res., 16 (2002) 4064-4078.

[31] A.B. Paul, Electrolytic treatment of turbid water in package plant, 22nd WEDC Conference, New Delhi, India, 1996.

[32] Y.Lu, J. Liu, J. Tang, B. Wei and X. Zhang, The removal of humic acids from water by solvent sublation, J. Colloid Interface Sci., 283 (2005) 278-284.

[33] V. Kazpard, B.S. Lartiges, C. Frochot, J.B. d'Espinose de la Caillerie, M.L. Viriot, J.M. Portal, T. Gorner and J.L. Bersillon, Fate of coagulant species and conformational effects during the aggregation of a model of a humic substance with Al13 polycations, Water Res., 40 (2006) 1965-1974.