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Humic acid removal by electrocoagulation using aluminium sacrificial anode under influencing operational parameters

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ABSTRACT

Humic acids (HA) in water can react with active chlorine to produce carcinogenic compounds and their presence is, therefore, considered as a serious problem in water purification plants throughout the world. The present study was undertaken with the aim of investigating the efficiency of using an electrocoagulation (EC) process based on aluminium electrodes at a laboratory scale as a complementary treatment step for HA removal from surface water. A series of experimental assays were performed to determine the optimal operating conditions (electrolysis time, pH, current intensity and initial concentration) involved in the EC mechanism during the HA removal process. The findings revealed that under optimum conditions HA could be removed by up to 72%. Further, high performance liquid chromatography and Fourier transform infrared spectroscopy analyses showed the non-forming products and non-attack points of the HA molecules, respectively. Overall, the results yielded in a pH range (6–7) and low current density (1.78–7.14 mA/cm^2) were promising and indicated that the EC method was effective for the achievement of HA removal from surface waters.

Keywords: Electrocoagulation; Humic acids; Aluminium electrodes; Surface waters; Mechanisms

1. Introduction

Humic substances (HS) are the most abundant natural organic materials in terrestrial and aquatic environments and represent the major portion of soil organic matter [1,2]. They constitute a physically and chemically heterogeneous mixture of biogenic and relatively high-molecular-mass compounds with mixed aliphatic and aromatic natures [3,4]. They are also organic polyelectrolytes that consist of the greatest natural proportion of dissolved organic matter in the watery systems which are usually subdivided into three distinct classes: humic acids (HA), fulvic acids and humins. Those classes still remain not fully

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defined particularly because of their highly complex polymeric structures [5].

HA can be found everywhere in nature and, through their structural and chemical characteristics, exert strong influences on the environment. Accordingly, in-depth assumptions on its structure still remain incomplete [6]. These compounds are characterized by low O/C atomic ratio (approximately 0.5) and as negatively charged complex aggregates, brown to black colour **[7]**. Further, they are generally recognized as complex macromolecules that are dependent on amino acids, glucosamines, aromatic peptides and aliphatic compounds that carry the carboxylic, phenolic and aloxyl groups consolidated by hydrogen bonds, forces of Van der Waals and interactions between the electrons π of close aromatic nuclei [8]. Grinhut et al. [9] proposed a new model for HA structure based on the available data in the literature and on related information drawn from various techniques used for the analysis of NMR (GC–MS) and fluorescence spectroscopy.

One of the main challenging concerns disturbing current water management and distribution systems throughout the world is the lack of in-depth knowledge and understanding of those complex macromolecules. Several reports point to the increasingly alarming impacts of HA with respect to the quality of distributed water. During the process of disinfection, those compounds react with chlorine and generate intermediary products called trihalomethanes, the formation of which poses severe carcinogenic and mutagenic effects on humans [10]. When present in surface waters, HA (contents of HS) are also reported to entail the following equally serious problems: (i) the presence of colourings or bad tastes that lead to negative consumer responses, the absorption of other organic molecules, such as pesticides, which inhibits their degradation, and the formation of undesirable soluble or insoluble complexes through the interaction with certain metals (ii) the use of additional costly devices and reagents, which makes the treatment process more expensive; (iii) the emergence of serious diseases, such as stomach cancer, particularly when present at high concentrations in drinking water; (iv) to provoke and facilitate the microbiological and chemical corrosion of conduits of flows and water reservoirs [11,12]; and (v) the relegation of the effectiveness of the water treatment systems which use membranes or microporous adsorbents [13] through a the increase in ΔP in the membrane processes, which entails pumping with high pressure and, consequently, the deterioration of the membranes [13].

Conventional treatment systems often manage to partially remove HA from raw water, such as the coagulation/flocculation, through the use of sulphate of aluminium or ferrous. Those techniques, known as the adsorption and the membrane techniques, do not lead to the adequate removal of dissolved and recalcitrant HA. Several reports have, therefore, pointed to a pressing need for the exploration of new alternative water treatment techniques that can help overcome the limitations of the conventional ones [14,15].

The literature indicates that electrochemical processes are increasingly gaining momentum as effective substitutes [16,17]. The latter have often been reported to be more efficient in the removal of a broad range of pollutants, such as heavy metals, solids in suspension and emulsified organic materials and microorganisms.

In their essence, electrochemical processes are based on the use of electricity and various types of electrodes that differ according to the technique being recommended (Table 1) [18,19]. Of particular interest, electrocoagulation (EC) processes have recently found reception in the water treatment industry. They proved effective and reliable, though their exploitation to the full requires greater technical command. In fact, recent research provides ample quantitative data on a variety of mechanisms using EC for the removal of pollutants [20]. EC technology is considered amongst the most effective electrochemical processes used for the removal of several types of organic pollutants and heavy metals in surface water as well as a variety of industrial effluents [21]. More importantly, this process has limited sludge production, does not require the use of chemicals and is easy to operate [22]. Owing to its promising attributes, EC has been successfully applied in various industries and processes related to the treatment of industrial wastewater, such as textile wastewaters [23], landfill leachate [24], floor-wash wastewater [25], mechanical polishing wastewater [26] and raw water for potable supply [27]. This technology has also been employed for the removal of phenols and surfactants [28–29].

Overall, EC is the electrochemical production of destabilization agents that create a charge neutralization needed for the removal of pollutants [30]. In this process, the coagulant is produced *in situ* by the electrolytic oxidation of an anode following the passage of a current through the use of iron or aluminium electrodes, two metals that are commonly used in the conventional treatment of water in salt forms. Power runs through the metal electrodes, generating the following two processes [31]:

- Oxidizing metal (M) at anode in its cation (Mn+) according to:

Table 1
Removal of HA by different electrochemical processes

Process	Type of water	Type of electrodes	Range of pH	Reaction time (min)	Percentage of removal (%)	Reference
Electrocoagulation	Ground water	Aluminium	3–9	50	97.8	[14]
Electrochemical	Natural water	$Ti/Ir_{0.3}Ti_{0.7}O_2$ $Ti/Ru_{0.3}Ti_{0.7}O_2$ $Ti/Ir_{0.2}Ru_{0.2}Ti_{0.6}O_2$	5.24	120	87–99	[12]
Photoelectrochemical	Drinking water	$(TiO_2)_{0.7}(RuO_2)_{0.3}$	5.24	180	65	[11]
Photocatalytic	Saline waters	$(TiO_2)_{0.7}(RuO_2)_{0.3}$	4.50–8.15	80	95	[13]

$$M \rightarrow M^{n+} + ne^- \quad (1)$$

and:

$$H_2O \rightarrow 1/2\ O_2 + 2H^+ + 2e^- \quad (2)$$

and, at the same time, water is reduced out of the hydrogen gas and the hydroxyl ion at cathode according to:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (3)$$

The main reactions for the aluminium electrodes used are as follows:

At anode:

$$Al \rightarrow Al^{3+}_{(aq)} + 3e^- \quad (4)$$

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+ \quad (5)$$

$$nAl(OH)_{3(s)} \rightarrow Al_n(OH)_{3n} \quad (6)$$

The electrolytic dissolution of the aluminium anode produces cationic monomeric species, such as Al^{3+} and $Al(OH)_2^+$, at acidic pH which, at the outset and with suitable values of pH, would be transformed into $Al(OH)_{3(s)}$ and be ultimately polymerized into $Al_n\ (OH)_{3n}$. Both of those metal hydroxides are known to possess high abilities for adsorption [32].

Moreover, if the current density is sufficient and the medium conditions lead themselves to it, the anode can also be predisposed to water oxidation (reaction 2) [33].

However, and according to the pH of aqueous media, other ionic species, such as $Al(OH)_2^+$, $Al_2(OH)_2^+$ and $Al(OH)_4^-$, can also be present in the system [31,34,35]. The flocs formed in the water are transported to the surface by gas bubbles (O_2, H_2) produced in the electrolysis process. In EC using aluminium as anode, the pollutants are removed by the bubbles, capturing the coagulated pollutants and floating at the surface where they can be removed easily.

The present study was undertaken to investigate and evaluate the effectiveness in EC in the reduction of HA using two aluminium electrodes. In the process, the study explores the individual and synergistic effects of various parameters, such as the initial pH of the solution, current intensity, electrolysis time and initial concentration of HA. This work also seeks to demonstrate a number of phenomena, such as flocs' apparition and/or desperation and other advanced interaction mechanisms, involved in EC treatment. It also aims to determine the effect of EC on HA molecular structures.

2. Materials and methods

2.1. Experimental setup

The experimental setup used for the EC experiments is presented in Fig. 1(a). The volume of HA wastewater was 1 L. A magnetic agitator system (model Fisher Scientific FB 15010) was used to achieve good mass transfer and to maintain the continuity of the solution homogeneity in the reactor (150 rpm). A DC power source was employed to supply regulated cell currents of 0–15.0 V, 0.0–10.0 A (Matrix MPS - 30039). An electrochemical cell made from Plexiglas (6 × 10 × 20 cm) was used. A pH-Meter (EUTECH, resolution and accuracy: ± 0.01) was connected to the EC cell. Aluminium plates (electrodes) having the size of 15 × 4 × 0.2 cm were used, and the distance between the electrodes was set at 4 cm. The electrodes were rinsed with distilled water, scoured with NaOH and re-rinsed with distilled water. The essential element of this laboratory-based reactor was the material of the

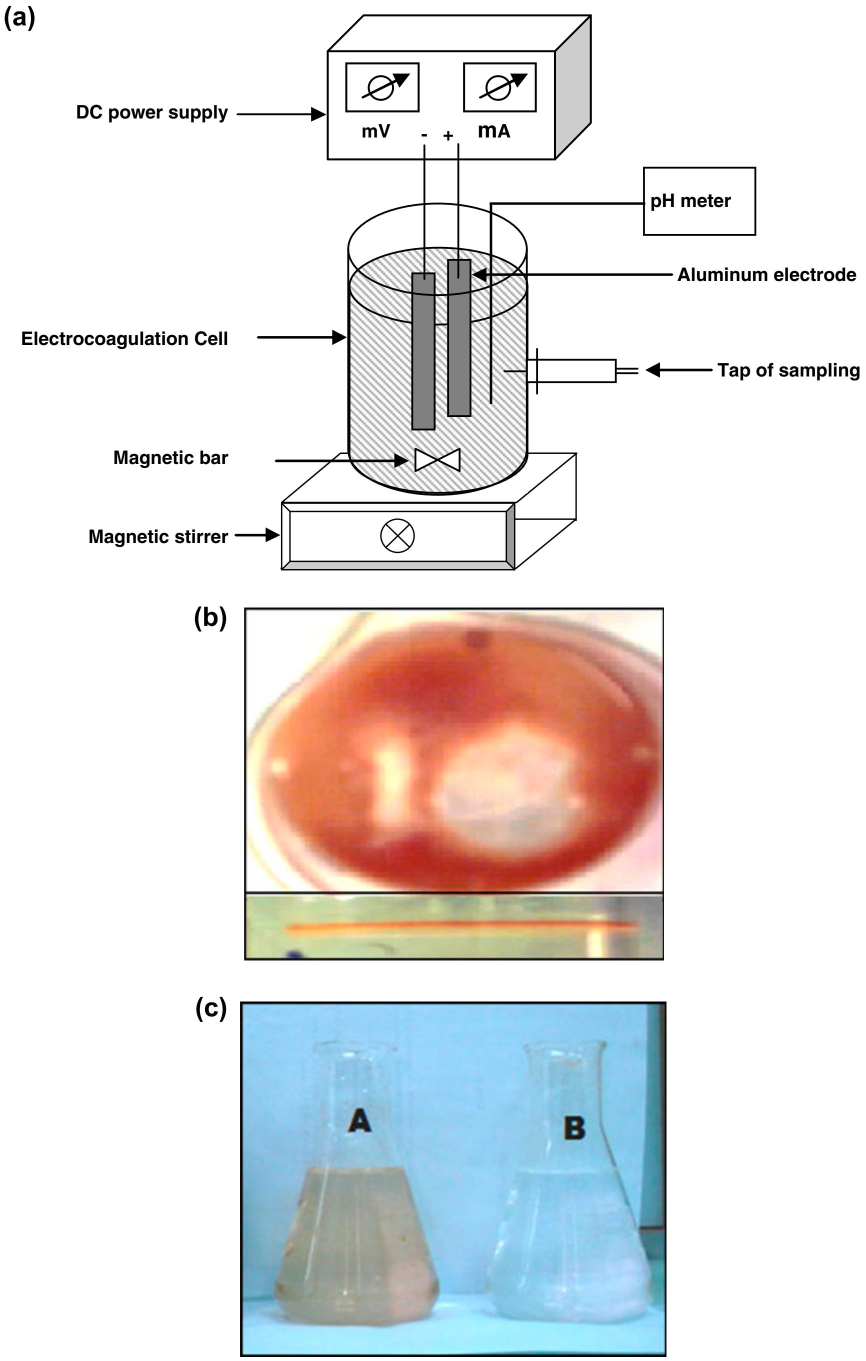

Fig. 1. (a) Experimental setup for the treatment of HA substances by EC. (b) Flocs accumulate on the surface of the HA solution during EC treatment. (c) HA solution before (A) and after (B) the EC treatment.

electrodes, which plays an important role in the improvement of the EC efficiency process.

2.2. Preparation of the HA solution

HA used in all experiments are commercial products (provided by the ACROS Company, USA). HA purified step required a solubilization of 5% HA in 0.1 N NaOH and then agitated under a nitrogen environment for 20 min. To precipitate HA, the pH of solution is adjusted to 1 ± 0.2 by HCl (1 N) and the precipitate is dried at temperature of 60°C. A stock solution of 1,000 mg/L is prepared by dissolving 1 g of HAs (dried HA) in 62.5 mL of NaOH (2 N) and then supplement until 1L with distilled water and agitated for 48 h. This solution is preserved at a temperature of +4°C in the dark.

2.3. Experimental procedure

All the experiments involved in the present work were carried out in a batch system and were performed sequentially as follows: (i) the HA solution (1 L) was introduced to the electrochemical cell at a known concentration; (ii) the initial pH was adjusted to a desired value by 0.5 N NaOH or 1 N H_2SO_4 under moderate agitation; (iii) electrolysis was started under an agitation system (150 rpm) to homogenize the solution mixture; (iv) sampling (5 mL liquid volume from reactor) was performed at different time intervals and the analyses were then conducted.

2.4. Analytic procedures

The properties of the HA wastewater were analysed at regular time intervals throughout the treatment so as to obtain good quality of water.

2.4.1. Measurements of HA reduction

Samples of HA treated solutions were analysed using a double-beam UV–vis spectrophotometer (Shimadzu UV-1700, Japan) equipped with a 10-mm quartz cell used for absorbance measurements at 254 nm [35,36]. The goodness of fit of the model was determined by calculating the ratio $R(\%)$ of HA removal using the following equation [14]:

$$R(\%) = \left(\frac{(C_0 - C_t)}{C_0}\right) \times 100 \tag{7}$$

where C_0 refers to initial concentration and C_t to concentration at time t.

2.4.2. Measurements in the treated solution

The concentrations of $Al^{3+}_{(aq)}$ generated by the EC cell were analysed using an atomic absorption spectrophotometer (SOLAAR M6).

2.4.3. Fourier transform infra red spectroscopy analysis

The change in the structure of the HA molecule during the treatment was monitored by Fourier transform infra red spectroscopy (FTIR). After complete treatment, the sample was centrifuged at 5,000 rpm for 15 min. FTIR spectra were recorded from KBr pellets using a Shimadzu FTIR 9800 spectrophotometer over a range of 4,000–400 cm^{-1} and at a rate of 16 nm/s (1 µl of sample containing the rest of HA was spread on pellets and then quickly dried).

2.4.4. High performance liquid chromatography analysis

The products formed after the treatments were analysed by high-erformance liquid chromatography (HPLC) using a UV–Visible detector set at 254 nm. Chromatographic analyses were conducted using a 125 × 4.6 mm RP-C18 column with an isocratic mobile phase of acetonitrile: deionized water 0.3:0.7 (v/v) at a flow rate of 0.6 mL min^{-1}. Data were analysed using class VP Shimadzu software. Before injection in the column, the samples were filtered by syringe filters specific for HPLC (diameter 0.45 µm of porosity) to avoid the clogging of the column.

3. Results and discussion

3.1. Phenomena that accompanied HA removal in EC cell

The hydrogen (H_2) gas bubbles released on the surface of cathode and the oxygen (O_2) gas bubbles released on the surface of the anode are translated as indicated by reactions 2 and 3 (see above), respectively. At the same time, $Al^{3+}_{(aq)}$ ions were generated by the oxidation of the anode (reaction 4). Flocs, formed during electrolysis, were noted to accumulate rapidly on the surface, forming a layer of foam as illustrated in Fig. 1(b). The latter was recuperated by filtration (Fig. 1(c)). The HA macromolecules were adsorbed on the aluminium hydroxide formed under those pH conditions. A decrease in the HA concentration which was removed from the solution was, therefore, reasonably observed. The flocs were also noted to be relatively bulky and with low densities [37,38].

3.2. Effect of initial pH as a function of electrolysis time

The pH is a significant operating factor for, as is often reported in the literature, it influences the performance of electrochemical process [35,39,40]. In fact, the formation and stability of aluminium hydroxide during electrolysis, as well as their solubility products, are primarily dependent on the initial pH. To investigate this effect, the initial pH of the sample was adjusted to a desired value for each experiment. The HA solutions (initial concentration, $C_{i=}15$ mg/L), adjusted to different values of pH (3.5–9), were electrolysed under a current density fixed at 1.78 mA/cm^2. Figure 2(a) and (b) shows the efficiency of HA removal as a function of the time of electrolyses and as a function of the initial pH. With the pH values of 5, 6, 7 and 8, the removal was noted to go fast during the first 20 min reaching over 40%, to undergo a subsequent slow progress till 120 min of treatment and to stabilize beyond this time. For pH 4, however, the removal rate was observed to be slower during the first 20 min reaching less than 35% and to continue to increase up to 50% after 120 min. As to pH 3.5, the removal reached up to 25% after 10 min of treatment and then remained almost stable. With pH 9, on the other hand, the HA removal speed was initially weak, not exceeding 10% (for 10 min) and then namely beyond 20 min and up to 60 min, became fast. The findings indicated that the maximum HA removal rate, which reached up to 72%, was attained at pH 6 after 120 min of electrolysis.

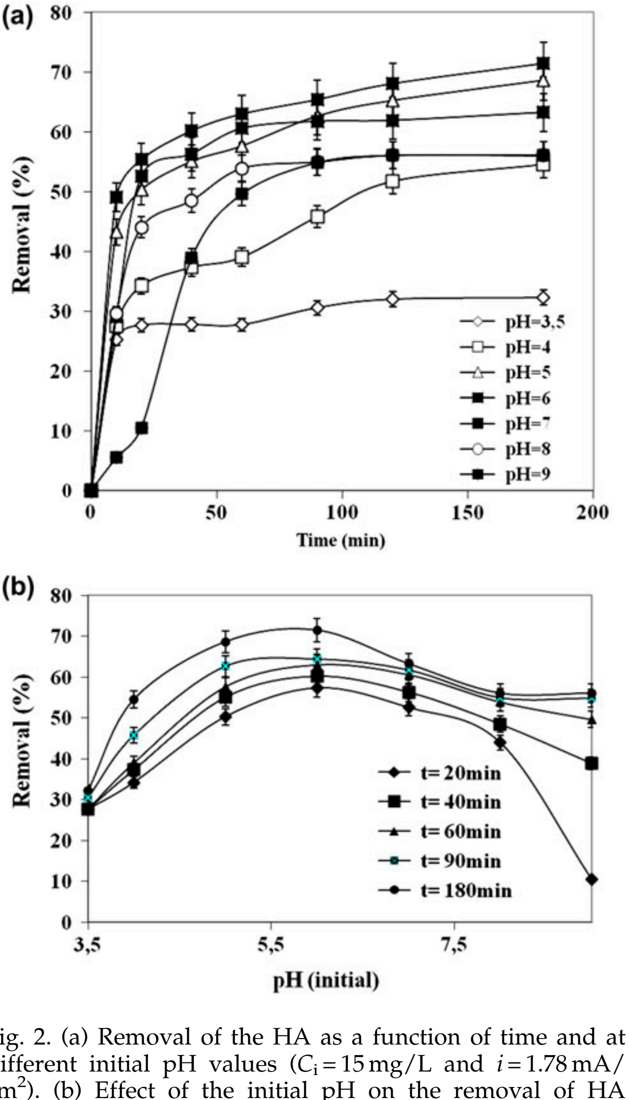

Fig. 2. (a) Removal of the HA as a function of time and at different initial pH values ($C_i = 15$ mg/L and $i = 1.78$ mA/cm^2). (b) Effect of the initial pH on the removal of HA $[HA]_0 = 15$ mg/L and $i = 1.78$ mA/cm^2).

Taken together, the results strongly support the assertion that the pH exerts a significant effect on HA removal, which, translating the maximum removal rates, was noted to be optimal at pH 6. At pH 3.5, 4 and 9, on the other hand, the treatment was observed to be less effective, with the removal reaching 27.6, 34.2 and 10.5% after 20 min of electrolysis, respectively. Moreover, this ratio was noted to reach 27.7 and 39% and not to exceed 49% for pH 3.5, 4 and 9, respectively. After 20 min of electrolysis, pH 5, 6 and 7 were also noted to yield into the maximum removal rates of 50.3, 57.3 and 52.5%, respectively.

Overall, the results revealed that the maximum removal rate of 71.4% was obtained with pH 6 after 180 min of treatment. In comparison, however, the work of Bayramoglu et al. [41] reported that EC was most effective at a pH range between 6 and 8. Other reports [19] indicated that the HA removal by EC was most effective in the vicinity of a neutral pH. In fact, the latter results could be attributed to the fact that HA removal was performed through neutralization of charge and/or adsorption.

The phenomena described above, which primarily depend on the form of aluminium in the medium, can explain the various removal ratios as a function of the pH. In fact, in the pH interval $3 < pH < 5$, the HA molecules would have less negative charges, and the carboxylic and hydroxyl groups occur in the chemical form of –COOH and –OH, respectively [14]. The most dominant aluminium forms are the $Al^{3+}_{(aq)}$ ions and the aluminium species, which, having a valence raised, such as $Al(OH)^{2+}_{(aq)}$and $Al(OH)^{+}_{2}(aq)$, were used to destabilize the HA molecules by neutralizing their negative charges via complexation according to the mechanism proposed in Fig. 3(a) and thus supporting the aggregation of the flocs. Also, the destabilization of HA in this range of pH may occur by double layer compression where the layer of positively charged H^+ (in abundantly produced due to acidic pH) is compressed by high valence Al species such as Al^{3+} following adsorption of destabilized HA on solid Al hydroxide species or floc formation due to Van der Waals forces [42].

For the interval of $5 < pH < 7$, on the other hand, the treatment is apparently most effective, and this is attributed to the adsorption phenomena which is prevalent by the formation of the $Al(OH)_{3(s)}$ species according to reaction (5) given above. Most reports [35,43] showed that for pH between 5 and 8, the prevalent species is $Al(OH)_{3(s)}$ and that the increase in aluminium hydroxide concentration would bring about a strong adsorption capacity, which would in turn lead to a higher reduction ratio of HA. The

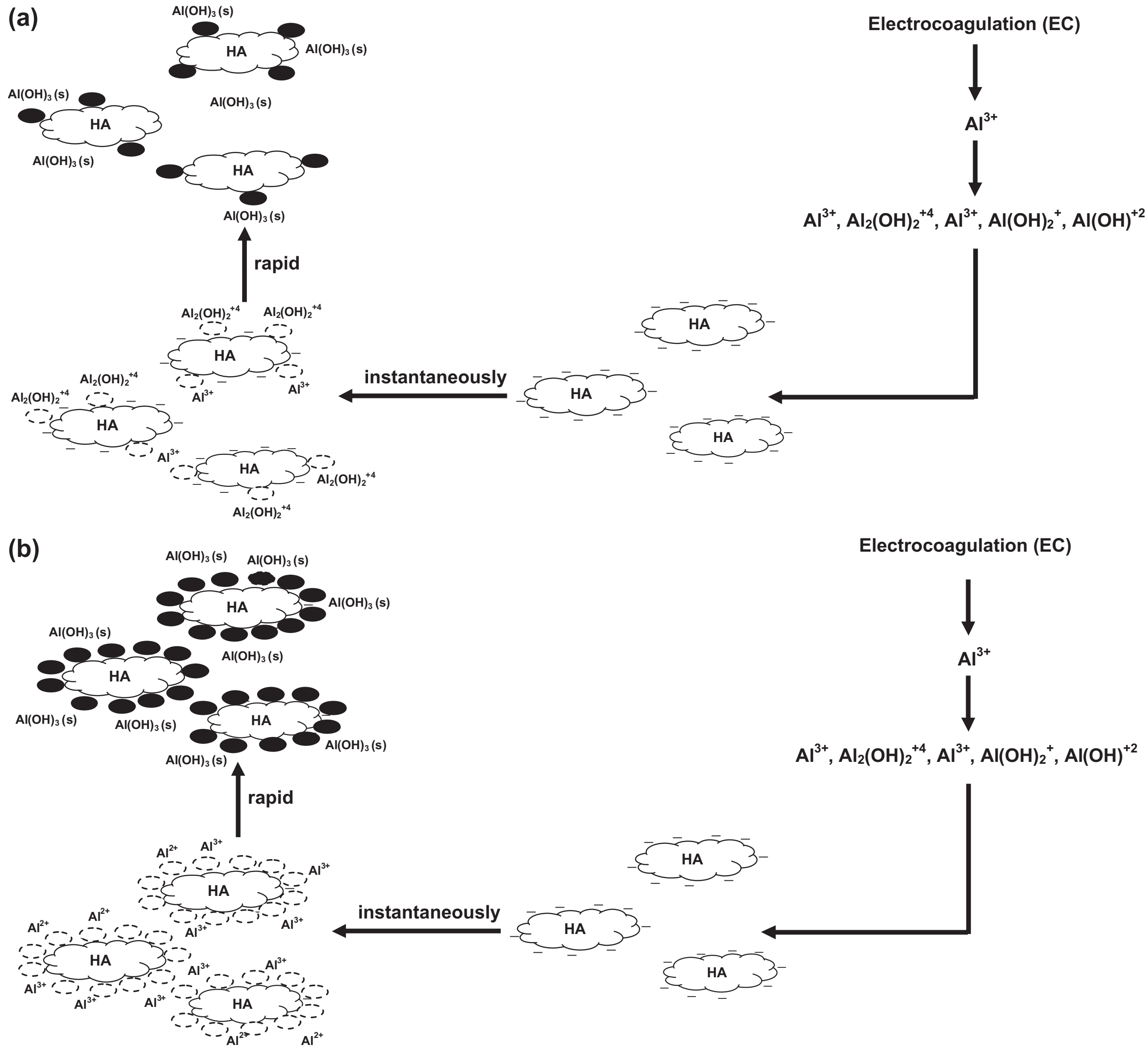

Fig. 3. (a) A mechanism proposed to explain the neutralization–precipitation of HA in the solution during EC treatment. (b) Sweep coagulation causing floc formations during EC treatment.

change of the surface quality of HA would support the precipitation of HA on the aluminium hydroxides $Al(OH)_{3(s)}$ by sweep coagulation, which is illustrated in Fig. 3(b).

For a pH value equal 9, removal of HA is substantially higher than that at pH 3.5 although the situation is almost identical to that at pH 3.5 (in case of acidic initial pH, HA and Al species both are positively charged whilst at basic alkaline pH, the deprotonation of the HA molecules increases their negative charges [44]; the carboxylic and hydroxyl radicals occur in the chemical form of $-COO^-$ and $-O^-$ [14,36]). These results can be due, on the one hand, to generation of insoluble Al species (such as $Al(OH)_3$), which removes HA simply by adsorption on its vast surface area. On the other hand, the $Al(OH)^{4-}_{(aq)}$ forms would become prevalent and would presumably limit the adsorption phenomenon (the forces of repulsion arise in this case).

3.3. pH variation during EC treatment

Fig. 4(a) shows the results obtained during all the EC experimental assays. Overall, a significant increase in terms of pH was noted as a function of time. It was noted to be unchangeable at pH 3.5 and to undergo almost identical variations (2–2.5 pH point) from 4 to 8. In fact, several previous reports [45,46] attribute this increase in pH to the consumption of the protons H^+ on the surface of the cathode to liberate H_2 bubbles and thus the release of OH^-. Kobya et al. [47] noted an exceptional decrease in this value from 9 to 7.5 with pH 9 after 10 min of treatment and attributed this decline to the consumption of ions OH^- by $Al(OH)_{3(s)}$ to produce $Al(OH)_4^-$ as illustrated in the following reaction:

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^- \qquad (8)$$

3.4. Effect of current density

Several previous studies [47,48] on the parameters affecting the EC process concluded that the current density applied has a determining impact on the amount of the coagulant that passes in the solution and even on the lifespan of the electrodes. Accordingly, a series of experiments were performed using different current densities with the same HA initial concentration (15 mg/L) and with maintained optimal pH (pH 6 in our case).

The findings revealed that the percentages of HA removal increased as a function of electrolysis time and passed through two phases. Whilst in the first phase, which covered the first moments and up to 20 min of treatment, the rate of HA removal was fast, in the second phase, which covered the time following the first 20 min, the removal rate became slower. It was also noted that when the current density increased, the removal speed and percentages increased only slightly. The latter were recorded to be 62.9% after 60 min with 1.78 mA/cm^2, to pass to 67.8% at 5.35 and to reach 69.2% for a density of 7.14 mA/cm^2 (Fig. 4b). This slow increase is presumably linked to the increase in the initial pH to values that disadvantaged the adsorption of HA molecules on the aluminium hydroxides as well as to the adhesion of the $Al(OH)_3$ hydroxides to the gas bubbles with weak concentration by decreasing the probability of contact between the humic molecules and $Al(OH)_3$. According to Kobya et al. [47] and Ihan et al. [48], the dissolution of the anode through the generation of $Al^{3+}_{(aq)}$ ions from ($Al(OH)_3$) complexes is proportional to the increase in the current intensity. Moreover, other reports [19,49] showed that the reduction in the size of the gas bubbles occurs with the increase in the current density and that the bubbles of small sizes provide a large surface for the fixing of particles, which would, therefore, have better opportunities for separation by electroflotation. However, the power consumption becomes highly significant by increasing the electrical current and the duration of electrolysis, which would consequently add to the cost of the treatment [47]. The results of the present study demonstrated the increase in the residual concentration of aluminium after 30 min of EC treatment at different current densities (the current densities applied were

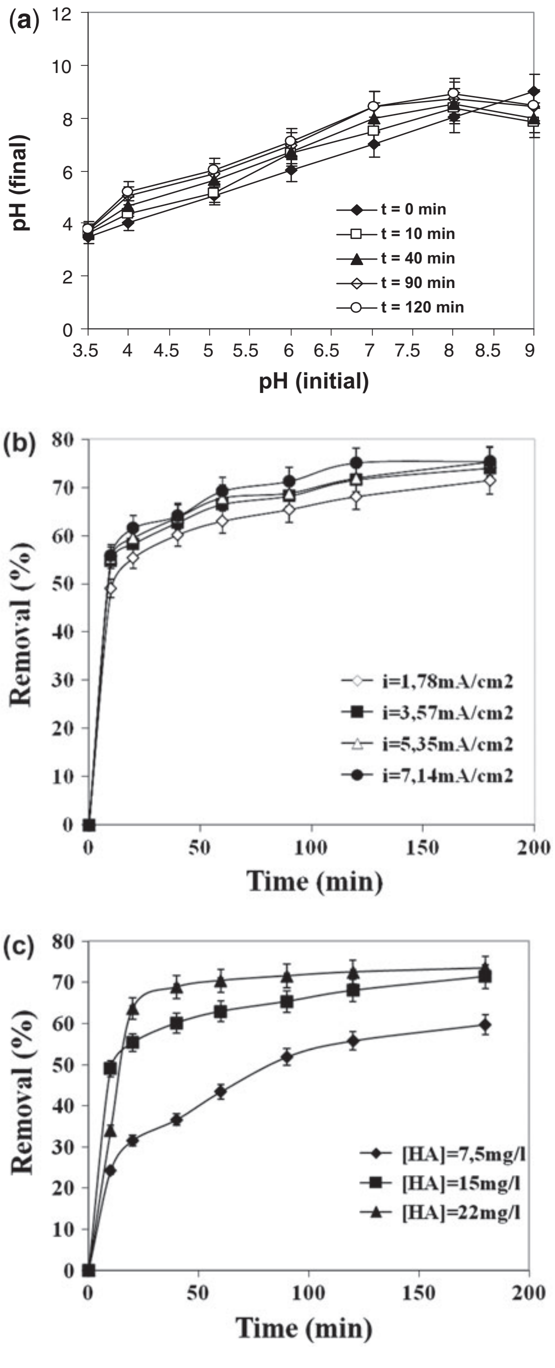

Fig. 4. (a) Variation of pH evolution during EC (Ci = 15 mg/L and i = 1.78 mA/cm^2). (b) Effect of current densities on HA removal (Ci = 15 mg/L and pH 6). (c) Effect of initial HA concentration on the removal rate (pH 6 and i = 1.78 mA/cm^2).

as follows: 3.58, 5.35 and 7.14 mA/cm^2; the corresponding residual concentrations of aluminium were as follows: 0.64, 0.67 and 0.73 mg/L, respectively).

3.5. Effect of initial HA concentration

To examine the effect of HA concentrations on the performance of EC treatment, three experiments were

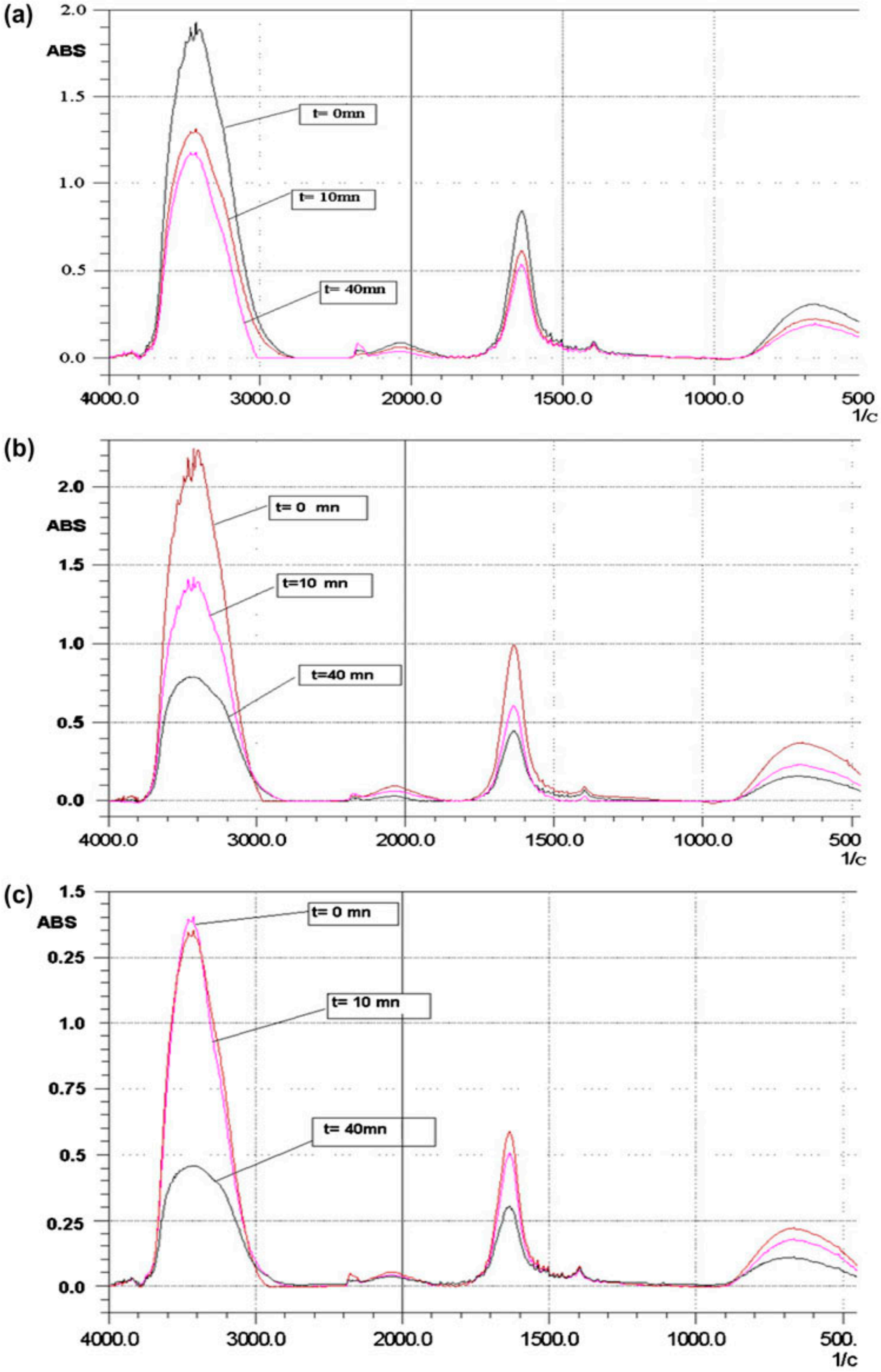

Fig. 5. (a) FTIR spectra of HA molecules treated at three different times at pH 3.5. (b) FTIR spectra of HA molecules treated at three different times at pH 6. (c) FTIR spectra of HA molecules treated at three different times at pH 9.

performed using three different HA concentrations at a fixed current density (equal to 1.78 mA/cm^2) and an optimum initial pH (equal to 6) (Fig. 4(c)). The findings revealed that HA removal increased when the HA concentration increase up to no more than 20 min of electrolysis. Whilst the removal rate was noted to reach 55.8% after 120 min of treatment for a concentration of 7.5 mg/L, it amounted to 72.5% for the same duration of electrolysis and a concentration of 22.5 mg/L. These results can be explained by the increase in the probability of contact between the HA molecules and the aluminium hydroxide through the formation of flocs of important sizes. This facilitates their separation by the attachment of the gas bubbles on those flocs. Accordingly, the richer the solution in suspension is (flocs), the more significant the possibility of particle bubble collision becomes.

3.6. Structural changes in HA molecules

All the results pertaining to the structural changes of the HA molecules submitted to EC treatment are given in Fig. 5. The spectra obtained for the HA used in the present work (time zero) showed peaks that were comparatively typical of humic matter and which, taking into account currently available bibliographical data, allowed the following attributions [49]:

The first principal peak was located at 3,409,9 cm^{-1} (O–H or N–H stretch). The second peak was observed in the spectrum located at 1,635,5 cm^{-1} (C=O stretching of amide I; C=N stretch; asymmetric stretching of COO–; C=O stretching in CHO and quinones or in conjugation with alkenes; aromatic C=C stretch). The third major peak was recorded between 1,458 and 1400.2 cm^{-1}; the absorbance in this area of the spectrum was charged to the presence of the aliphatic structures (deformation of aliphatic C–H; phenolic OH stretch; symmetric stretching of COO–) [50]. Between 2,950 and 2,850 cm^{-1}, the spectrum of AH showed types of vibration that were characteristic of the CH bonds. The latter showed very weak bands of vibration and had the following frequencies: ν_{as} (CH_2) = 2,926 cm^{-1}, ν_s (CH_2) = 2850.6 cm^{-1}.

The data presented in Fig. 5 best corroborate the results previously obtained through UV–vis analyses (Fig. 5(a) and (b)). The IR spectra (Fig. 5(c)) of the various samples observed after EC treatment did not show any disappearance of the new functional groupings, which indicates that the HA molecule did not undergo any changes in terms of structure. A reduction was, however, observed in the intensity of the absorption bands corresponding to the time, which indicates the quantitative removal of the HA present in the treated solution. As the figure shows, a significant reduction in about 67% was recorded in the intensity of most of the peaks after 40 min of treatment with pH 6, whereas a weak reduction was observed with pH 3.5.

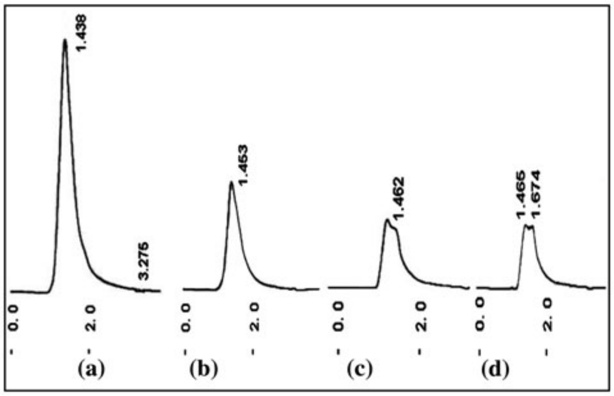

Fig. 6. HPLC analysis of HA solution sampling at different times of treatment by EC. (a) 0 min. (b) 25 min. (c) 35 min. (d) 45 min.

3.7. Products formed during EC treatment

Fig. 6 shows HPLC chromatograms of HA solutions treated by EC with optimal pH (equal 6). The samples were taken at various times, namely 25, 35 and 45 min. The chromatogram obtained during the analysis of the HA solution (15 mg/L) at $t = 0$ min reveals the occurrence of only one peak characterized by a retention time of 1.438 min. Moreover, a reduction in the surface of the same peak which was recorded with $t = 0$ min can be clearly observed after 35 min of treatment. This was characterized by a retention time of 1.453 min without appearance of any new peaks, which shows that HA removal was performed by a physical phenomenon and without any structural changes. It was, therefore, an adsorption on aluminium hydroxides ($Al(OH)_{3(s)}$) formed during electrolysis, thus translating a reduction in the concentration of the HA. However, after 45 min of treatment, a clear, new and very adjacent peak whose retention time was 1.674 min was observed. On the other hand, it appears that this peak existed as a shoulder in all: not very clear at $t = 0$ and slightly obscure at $t = 25$ min. This result can be explained by the mere interpretation of the results obtained with regard to EC treatment where the residual quantity of the HA could form with the aluminium of the soluble organometallic complexes in the water which are presumably behind the appearance of this peak.

4. Conclusion

The results presented in the current study demonstrate that the HA present in surface water can be effectively removed through the application of the EC method equipped with aluminium electrodes. In fact, the best removal rate was obtained at pH 6. Overall, the findings indicated that the removal of HA from water is controlled by several individual and synergistic factors including the following: (i) for lower pH values (3–5), the mechanism of charge neutralization would prevail and for pH values ranging between 5 and 7, the appropriate mechanism would be sweep coagulation and (ii) the cations $(Al^{3+}_{(aq)})$ formed *in situ* would neutralize the humic macromolecules and contribute, together with $Al(OH)^{4-}_{(aq)}$, to the formation of hydroxides $(Al(OH)_{3(s)})$. The obtained improvements of the EC effectiveness are as follows: 8% (from 62 to 69.88% of removal) by increasing the current density from 1.78 to 7.14 mA/cm^2 and 17% (from 55.8 to 72.5% of removal) by increasing the HA concentration from 7.5 to 22.5 mg/L. The data from FTIR spectra and HPCL analyses allowed for the confirmation of the results obtained by UV–vis, namely that the HA molecules did not undergo any structural modifications. Considering the promising new opportunities that EC might open with regard to water treatment and distribution, further studies are needed to investigate the optimum operating conditions for a continuing process and to carry out a detailed comparative study on the energy consumption of the proposed treatment system and the conventional methods so as to come up with a blueprint for constructing a potentially strong treatment system for ultimate large scale industrial application.

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References

[1] A.A. Basfar, K.A. Mohamed, A.J. Al-Abduly, A.A. Al-Shahrani, Radiolytic degradation of atrazine aqueous solution containing humic substances, Ecotoxicol. Environ. Saf. 72 (2009) 948–953.

[2] E. Oguz, A. Tortum, B. Keskinler, Determination of the apparent rate constants of the degradation of humic substances by ozonation and modeling of the removal of humic substances from the aqueous solutions with neural network, J. Hazard. Mater. 157 (2008) 455–463.

[3] M. Soleimani, M.A. Hajabbasi, M. Afyuni, S. Akbar, J.K. Jensen, P.E. Holm, O.K. Borggaard, Comparison of natural humic substances and synthetic ethylenediaminetetraacetic acid and nitrilotriacetic acid as washing agents of a heavy metal-polluted soil, J. Environ. Qual. 39 (2010) 855–862.

[4] M. del Carmen Vargas-García, F. Francisca Suárez-Estrella, M. José López, J. Moreno, Influence of microbial inoculation and co-composting material on the evolution of humic-like substances during composting of horticultural wastes, Process Biochem. 41 (2006) 1438–1443.

[5] J.M. Sieliechi, B.S. Lartiges, G.J. Kayem, S. Hupont, C. Frochot, J. Thieme, J. Ghanbaja, J.B. d'Espinose de la Caillerie, O. Barres, R. Kamga, P. Levitz, L.J. Michot, Changes in humic acid conformation during coagulation with ferric chloride: Implications for drinking water treatment, Water Res. 42 (2008) 2111–2123.

[6] A.J. Simpson, W.L. Kingery, M.H. Hayes, M. Spraul, E. Humpfer, P. Dvortsak, R. Kerssebaum, M. Godejohann, M. Hofmann, Molecular structures and associations of humic substances in the terrestrial environment, Naturwissenschaften 89 (2002) 84–88.

[7] P. MacCarthy, The principles of humic substances, Soil Sci. 166 (2001) 738–751.

[8] M. Klavins, L. Ansone, O. Purmalis, A. Zicmanis, Characterization of interaction between tricyclic structures containing pharmaceuticals, their models and humic substances, Water Sci. Technol. 63 (2011) 845–852.

[9] T. Grinhut, N. Hertkorn, P. Schmitt-Kopplin, Y. Hadar, Y. Chen, Mechanisms of humic acids degradation by white rot fungi explored using 1H NMR spectroscopy and FTICR mass spectrometry, Environ. Sci. Technol. 45 (2011) 2748–2754.

[10] M.Y. Eish, M.J. Wells, Assessing the trihalomethane formation potential of aquatic fulvic and humic acids fractionated using thin-layer chromatography, J. Chromatogr. A 1116 (2006) 272–276.

[11] L. Pinhedo, R. Pelegrini, R. Bertazzoli, A.J. Motheo, Photoelectrochemical degradation of humic acid on a $(TiO2)_{0.7}(RuO2)_{0.3}$ dimensionally stable anode, Appl. Catal. B 57 (2005) 75–81.

[12] A.J. Motheo, L. Pinhedo, Electrochemical degradation of humic acid, Sci. Total Environ. 256 (2000) 67–76.

[13] R. Al-Rasheed, D.J. Cardin, Photocatalytic degradation of humic acid in saline waters. Part 1. Artificial seawater: Influence of TiO2, temperature, pH, and air-flow, Chemosphere 51 (2003) 925–933.

[14] J.W. Feng, Y.B. Sun, Z. Zheng, J.B. Zhang, S. Li, Y.C. Tian, Treatment of tannery wastewater by electrocoagulation, J. Environ. Sci. (China) 19 (2007) 1409–1415.

[15] F. Chemat, P.G. Teunissen, S. Chemat, P.V. Bartels, Sono-oxidation treatment of humic substances in drinking water, Ultrason. Sonochem. 8 (2001) 247–250.

[16] M. Kobya, F. Ulu, U. Gebologlu, E. Demirbas, M.S. Oncel, Treatment of potable water containing low concentration of arsenic with electrocoagulation: Different connection modes and Fe–Al electrodes, Sep. Purif. Technol. 77 (2011) 283–293.

[17] P. Nuñez, H.K. Hansen, S. Aguirre, C. Maureira, Electrocoagulation of arsenic using iron nanoparticles to treat copper mineral processing wastewater, Sep. Purif. Technol. 79 (2011) 285–290.

[18] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci. 100 (2003) 475–502.

[19] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.

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

[21] T.-H. Kim, C. Park, E.-B. Shin, S. Kim, Decolorization of disperse and reactive dyes by continuous electrocoagulation process, Desalination 150 (2002) 165–175.

[22] C. Feng, N. Sugiura, S. Shimada, T. Maekawa, Development of a high performance electrochemical wastewater treatment system, J. Hazard. Mater. 103 (2003) 65–78.

[23] T.H. Kim, C. Park, J. Lee, E.B. Shin, S. Kim, Pilot scale treatment of textile wastewater by combined process (fluidized biofilm process-chemical coagulation-electrochemical oxidation), Water Res. 36 (2002) 3979–3988.

[24] A. Lopez, M. Pagano, A. Volpe, A.C. Di Pinto, Fenton's pretreatment of mature landfill leachate, Chemosphere 54 (2004) 1005–1010.

[25] U.D. Patel, J.P. Ruparelia, M.U. Patel, Electrocoagulation treatment of simulated floor-wash containing Reactive Black 5 using iron sacrificial anode, J. Hazard. Mater. 197 (2011) 128–136.

[26] C.L. Lai, S.H. Lin, Treatment of chemical mechanical polishing wastewater by electrocoagulation: System performances and sludge settling characteristics, Chemosphere 54 (2004) 235–242.

[27] J.Q. Jiang, N. Graham, C. Andre, G.H. Kelsall, N. Brandon, Laboratory study of electro-coagulation-flotation for water treatment, Water Res. 36 (2002) 4064–4078.

[28] Y.M. Award, N.S. Abuzaid, The influence of residence time on the anodic oxidation of phenols, Sep. Purif. Technol. 18 (2000) 2227–2236.

[29] G.A. Ciorba, C. Radovan, I. Vlaicu, L. Pitulice, Correlation between organic component and electrode material: Consequences on removal of surfactants from wastewater, Electrochim. Acta 46 (2000) 297–303.

[30] H. Inan, A. Dimoglo, H. Simsek, M. Karpuzcu, Olive oil mill wastewater treatment by means of electrocoagulation, Sep. Purif. Technol. 36 (2004) 23–31.

[31] P.K. Holt, G.W. Barton, M. Wark, C.A. Mitchell, Electrocoagulation as a wastewater treatment, The Third Annual Australian Environmental Engineering Research Event, 1999, pp. 23–26.

[32] M.Y. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)–science and applications, J. Hazard. Mater. 84 (2001) 29–41.

[33] J. Besson, J. Guitton, Manipulation d'électrochimie [Handling of electrochemistry], Masson, 6th ed., Paris, 1972.

[34] A. Saiba, S. Kourdali, B. Ghernaout, D. Ghernaout, In Desalination, from 1987 to 2009, the birth of a new seawater pretreatment process: Electrocoagulation—An overview, Desalin. Water Treat. 16 (2010) 201–217.

[35] D. Ghernaout, B. Ghernaout, A. Kellil, Natural organic matter removal and enhanced coagulation as a link between coagulation and electrocoagulation, Desalin. Water Treat. 2 (2009) 203–222.

[36] D. Ghernaout, B. Ghernaout, A. Boucherit, M.W. Naceur, A. Khelifa, A. Khellil, Study on mechanism of electrocoagulation with iron electrodes in idealised conditions and electrocoagulation of humic acids solution in batch using aluminium electrodes, Desalin. Water Treat. 8 (2009) 91–99.

[37] V.K. Kovatcheva, M.D. Parlapanski, Sono-electrocoagulation of iron hydroxides, Colloids Surf. A 149 (1999) 603–608.

[38] V.Y. Baklan, I.P. Kolesnikova, Influence of electrode material on the electrocoagulation, J. Aerosol Sci. 27 (1996) 209–210.

[39] A. Savas, S. Yalcın, E. Yildiz, B. Keskinler, D. Nuhi, Effect of initial pH on the removal of humic substances from wastewater by electrocoagulation, Sep. Purif. Technol. 59 (2008) 175–182.

[40] M. Kobya, E. Senturk, M. Bayramoglu, Treatment of poultry slaughterhouse wastewaters by electrocoagulation, J. Hazard. Mater. 133 (2006) 172–176.

[41] M. Bayramoglu, M. Kobya, T.C. Orhan, M. Sozbir, Operating cost analysis of electrocoagulation of textile dye wastewater, Sep. Purif. Technol. 37 (2004) 117–125.

[42] D. Belhout, D. Ghernaout, S. Djezzar-Douakh, A. Kellil, Electrocoagulation of a raw water of Ghrib Dam (Algeria) in batch using aluminium and iron electrodes, Desalin. Water Treat. 16 (2010) 1–9.

[43] A.E. Martell, R.J. Motekaitis, Coordination chemistry and speciation of Al(III) in aqueous solution, in: T.E. Lewis (Ed.), Environmental Chemistry and Toxicology of Aluminium, CRC Press, Chelsea, MI, 1989, pp. 3–18.

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

[45] M. Tir, N. Moulai-Mostefa, Optimization of oil removal from oily wastewater by electrocoagulation using response surface method, J. Hazard. Mater. 158 (2008) 107–115.

[46] Q. Zuo, X. Chen, W. Li, G. Chen, Combined electrocoagulation and electroflotation for removal of fluoride from drinking water, J. Hazard. Mater. 159 (2008) 452–457.

[47] M. Kobya, E. Demirbas, O.T. Can, M. Bayramoglu, Treatment of levafix orange textile dye solution by electrocoagulation, J. Hazard. Mater. 132 (2006) 183–188.

[48] F. Ilhan, U. Kurt, O. Apaydin, M.T. Gonullu, Treatment of leachate by electrocoagulation using aluminum and iron electrodes, J. Hazard. Mater. 154 (2008) 381–389.

[49] J. Ge, J.Q. Lei, H. Liu, New bipolar electrocoagulation-electroflotation process for the treatment of laundry wastewater, Sep. Purif. Technol. 36 (2004) 33–39.

[50] N. Senesia, V. D'Orazioa, G. Riccab, Humic acids in the first generation of eurosoils, Geoderma. 116 (2003) 325–344.