

Comparative study of humic acid removal and floc characteristics by electrocoagulation and chemical coagulation

Lucy Semerjian · Ahmad Damaj · Darine Salam

Received: 17 October 2014 / Accepted: 22 September 2015 / Published online: 5 October 2015
© Springer International Publishing Switzerland 2015

Abstract The current study aims at investigating the efficiency of electrocoagulation for the removal of humic acid from contaminated waters. In parallel, conventional chemical coagulation was conducted to assess humic acid removal patterns. The effect of varying contributing parameters (matrix pH, humic acid concentration, type of electrode (aluminum vs. iron), current density, solution conductivity, and distance between electrodes) was considered to optimize the electrocoagulation process for the best attainable humic acid removal efficiencies. Optimum removals were recorded at pH of 5.0–5.5, an electrical conductivity of 3000 $\mu\text{S}/\text{cm}$ at 25 °C, and an electrode distance of 1 cm for both electrode types. With aluminum electrodes, a current density of 0.05 mA/cm^2 outperformed 0.1 mA/cm^2 yet not higher densities, whereas a current density of 0.8 mA/cm^2 was needed for iron electrodes to exhibit comparable performance. With both electrode types, higher initial humic acid concentrations were removed at a slower rate but ultimately attained almost complete removals. On the other hand, the best humic acid removals (~90 %) by chemical coagulation were achieved at 4 mg/L for both coagulants. Also, higher

removals were attained at elevated initial humic acid concentrations. Humic acid removals of 90 % or higher at an initial HA concentration of 40 mg/L were exhibited, yet alum performed better at the highest experimented concentration. It was evident that iron flocs were larger, denser, and more geometrical in shape compared to aluminum flocs.

Keywords Humic acid · Electrocoagulation · Chemical coagulation · Aluminum electrodes · Iron electrodes · Floc characteristics

Introduction

Humic substances (HS) are complex macromolecules produced from the decomposition and degradation of plant and animal remains. Humic acids (HA) are the fraction of HS that is soluble in water at pH values higher than 2, and the main functional groups they exhibit are carboxylic acids (COOH), phenolic alcohols (OH), and methoxy carbonyls (C = O) (Fig. 1) (Yuan and Zydney 1999).

During chlorination of surface or groundwaters, natural organic matters (NOMs), of which humic substances are a major fraction, cause the formation of disinfection by-products (DBPs). Selected DBPs, such as chloroform and bromo-dichloromethane, have been suspected to be carcinogenic compounds. Furthermore, NOMs contribute to color, taste, and odor in waters and stimulate the growth of microorganisms, hence the importance of removing these products from municipal

L. Semerjian (✉) · A. Damaj · D. Salam
Department of Civil and Environmental Engineering, American University of Beirut, P.O. Box 11-0236, Beirut, Lebanon
e-mail: lsemerjian@sharjah.ac.ae

Present Address:

L. Semerjian
University of Sharjah, P.O. Box 27272, Sharjah, UAE

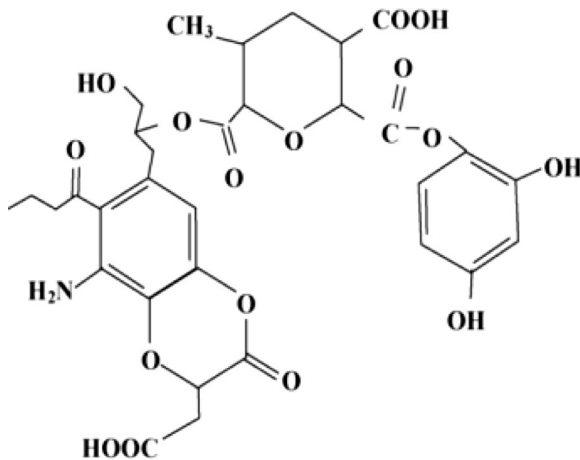


Fig. 1 The chemical structure of humic acid

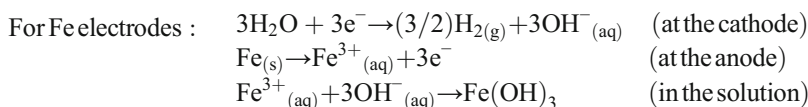
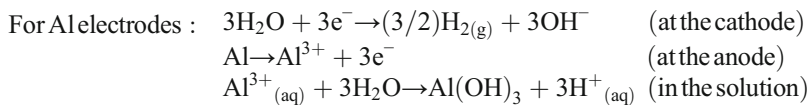
waters. In addition, the presence of humic substances has been known to affect the adsorption of pollutants onto different adsorbents and to cause the deterioration of the adsorbents (Yildiz et al. 2007).

Another important problem caused by HA is fouling of microfiltration and reverse osmosis (RO) membranes when used for filtration of surface or groundwater (Yuan

and Zydney 1999; Nystrom et al. 1996). Nystrom et al. (1996) found that the presence of HA in water will cause a drastic decrease in the flux through the membrane, and they attributed this to the interaction between the negatively charged HA and the positively charged inorganic membranes.

Conventional methods for removing HA from waters and wastewaters include conventional coagulation/flocculation methods (Zouboulis et al. 2004), nanofiltration (Hong and Elimelech 1997), and adsorption onto different media such as chitosan beads (Yan and Bai 2006; Wan Ngha and Musa 1998), fungal media (Zhou and Banks 1993), and activated carbons (Lee et al. 1981; McCreary and Snoeyink 1980).

The electrocoagulation (EC) process is a rather new alternative to the conventional coagulation (CC) process. During this process, variable current is applied between the anode–cathode electrodes to generate coagulant agents in situ through the dissolution of a sacrificial anode. Different electrodes can be employed in EC, typically made of aluminum (Al) and iron (Fe). The chemical reactions that take place at the anodes and cathodes for Al and Fe electrodes proceed as the following equations:



Although both electrocoagulation and chemical coagulation use the same mechanisms of pollutant removal, EC may offer several advantages over CC. These advantages mainly are higher adsorption capacity, absence of manual addition of chemicals, less land requirements for the setup, lower capital cost, and less maintenance. Furthermore, EC requires less coagulant and produces less sludge when removing the same amount of pollutant compared to CC (Mills 2000; Lakshmanan et al. 2010). Also, flocs formed by EC are larger and contain less bound water than those formed by CC, are acid-resistant, and might float at the top of the solution due to the formation of hydrogen bubbles which makes them easier to control and remove. Another important

advantage of EC is that no chemicals are added to the water; therefore, there is no need to neutralize excess chemicals and there is no possibility of secondary pollution (Mollah et al. 2001).

The removal of several types of pollutants by EC has been reported in the literature. EC showed favorable removal (>90 %) of several heavy metals from solution such as arsenic (Balasubramanian et al. 2009; Lakshmanan et al. 2010), chromium and copper (Zaroual et al. 2009), lead and cadmium (Escobar et al. 2006), as well as the metalloid boron (Isa et al. 2014; Zeboudji et al. 2013). Furthermore, Akyol (2012) employed EC to attain successful removals of chemical oxygen demand (COD) and total organic carbon (TOC)

by up to 93 % from paint manufacturing wastewater. EC was also successfully used to remove 90 % of oils from oily and olive mill wastewater (Tir and Moulai-Mostefa 2008; Tezcan Un et al. 2006) and of the pesticides metribuzin (up to 89 %) and malathion (over 90 %) from contaminated groundwater (Behloul et al. 2013; Yahiaoui et al. 2011). On several occasions, EC has been tested for the removal of phosphate and exhibited very good removal potential (Irdemez et al. 2006; Vasudevan et al. 2009). EC was also positively used for removal of color, turbidity, COD, fluoride, and other pollutants found in wastewaters from textile industries, tanneries, and photovoltaic systems (Drouiche et al. 2012; Gilpavas et al. 2011; Kobya et al. 2007; Bayramoglu et al. 2004). Complete decolorization of Disperse Red 167 azo dye was achieved by electrocoagulation in a study by Lemlikchi et al. (2012).

The current study aims at investigating the efficiency of EC for the removal of HA from contaminated waters. The effect of varying contributing parameters will be considered to optimize the EC process for the best attainable removal efficiencies. Investigated parameters include matrix pH, HA concentration, type of electrode (Al vs. Fe), current density, solution conductivity, and distance between electrodes. Moreover, generated flocs will be imaged and characterized for size and stability. The EC process will be compared to optimized CC of HA by aluminum and iron salts, also investigated as part of this study.

Materials and methods

Experimental setup

Electrocoagulation experiments were conducted in $14 \times 9 \times 9$ -cm plexiglass jars containing 1 L of deionized water spiked with varying concentrations of HA. The Al and Fe plates employed as electrodes measured 13×1.8 cm (area = 23.4 cm^2), with an immersed area of 18.9 cm^2 , based upon which the required current to achieve a certain current density was calculated. The current was provided by a triple-output DC power supply (Agilent, model 3631A, USA), and the jars were positioned on an orbital shaker (Lab-Line, Model, USA) at 100 rpm throughout the duration of the experiments to maintain a homogeneous solution in the reactor. The pair of electrodes was positioned at varying distances in accordance to experimental objectives. The

temperature during the experiment was ambient laboratory temperature of 21 ± 2 °C. Figure 2 depicts the components of the experimental system.

Conventional coagulation experiments were conducted using a standard six-paddle jar testing apparatus (Phipps & Bird, USA) with $12 \times 12 \times 19.5$ -cm plexiglass jars, containing 1 L of deionized water spiked with varying concentrations of HA. Flash mixing was initiated at 100 rpm for 1 min, mixing speed was then reduced to 30 rpm and maintained for 20 min to allow flocculation, and last a 30-min quiescent settling was allowed before the collection of samples for analysis.

CC and EC experimental parameters

A 1000-mg/L stock solution of HA was prepared by dissolving 1 g of powdered HA (Acros Organics, USA) in 62.5 mL of 1 M NaOH and then filling to the 1-L mark with deionized water. Dilutions of the stock solution were made depending on the HA concentrations needed in the experiments.

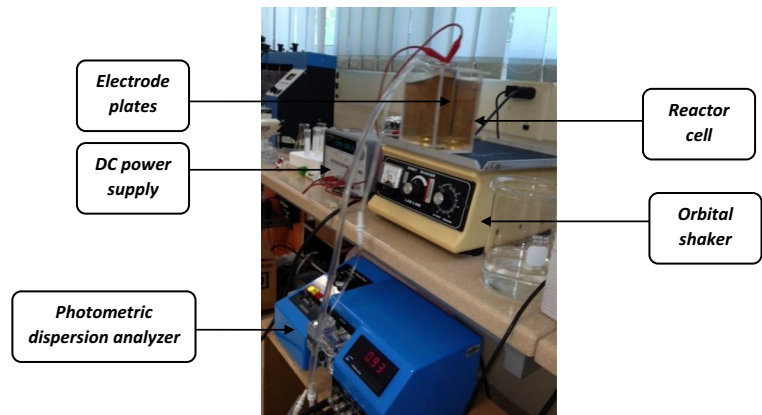
In conventional coagulation experiments, varying doses of Fe and Al ranging from 0.5 to 5 mg/L were experimented on an initial HA concentration of 20 mg/L and a solution pH of 5, as determined from the literature. Furthermore, the removal of different initial HA concentrations ranging from 5 to 80 mg/L was investigated in the presence of optimal doses of coagulant salts.

In electrocoagulation experiments, the effect of solution pH, current density, HA concentration, solution conductivity, and distance between electrodes was investigated when either Al or Fe was used as electrodes. Effluent samples were periodically collected by syringe and filtered through $0.45\text{-}\mu\text{m}$ in-syringe microfiltration membranes for further analysis.

Analytical procedures

Initial and residual HA concentrations were measured using a UV spectrophotometer (HACH, Model 4000U, USA) at a wavelength of 254 nm. It is noted that during the experiments with Fe electrodes, a significant interference was caused by the formation of iron oxides that caused the absorbance readings to increase drastically. Therefore, TOC was mostly used as a surrogate parameter to assess HA concentrations when using Fe electrodes. TOC levels were also measured every 30 min in effluent samples for experiments done with Al electrodes. TOC concentrations were measured using an

Fig. 2 Experimental setup of electrocoagulation process



analytical total organic carbon analyzer (Shimadzu, Model TOC-V_{C_{SH}}, USA). The formation and characteristics of flocs, under varying experimental conditions, were studied using a photometric dispersion analyzer (PDA) (Rank Brothers Ltd., Model PDA2000, UK). High-magnification images of generated flocs were produced by scanning electron microscopy (TESCAN, USA) as well as compound microscopy (Axiostar Plus, Carl Zeiss, Germany). Residual Al and Fe concentrations were measured at the end of experiments using flame atomic absorption spectroscopy (Thermo Electron Corporation, M Series, USA).

Results and discussion

Chemical coagulation experiments

The effect of change in coagulant dose and in initial HA concentrations was investigated through a series of conventional chemical coagulation experiments. The pH at which the experiments were conducted was adjusted to 5, the optimal pH at which both alum and ferric chloride operate as coagulants as specified in previous research (Wang et al. 2011; Huang and Shiu 1996; Zouboulis et al. 2004).

Effect of coagulant dose on HA removal

Varying doses of coagulants (0.5–5 mg/L Al or Fe) were added to 1 L deionized water containing 20 mg of HA. After 1 min of fast mixing at 100 rpm, 20 min of flocculation at 30 rpm, the mixing was stopped to allow

flocs to settle. Residual HA concentrations in sampled aliquots were measured at 254 nm, and recorded results are depicted in Fig. 3.

Figure 3 clearly indicates that, generally, alum contributes to better and faster removals of HA, especially at lower coagulant doses. Whereby 1 mg/L of Al is able to remove 80 % of HA from solution, a dosage of 3 mg/L of Fe will be able to match the removal. Best removals (~ 90 %) are achieved at 4 mg/L for both coagulants.

Effect of initial HA concentration

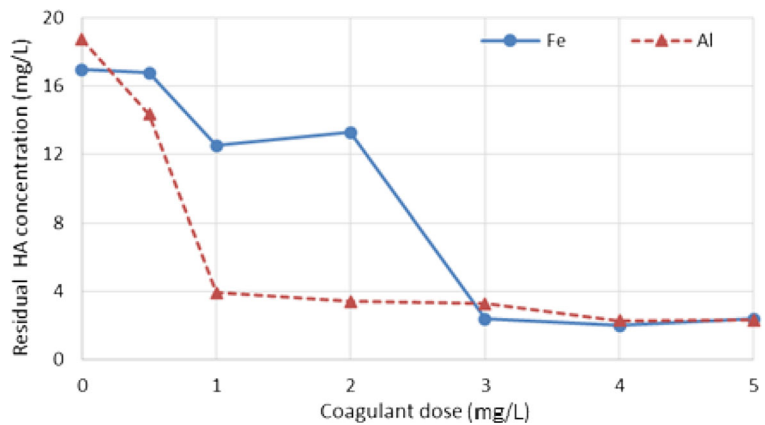
Based on the outcomes in the previous section, a concentration of 4 mg/L for both coagulants was selected, and the initial concentration of HA was varied between 5 and 80 mg/L. Residual HA concentrations in sampled aliquots were measured at 254 nm, and attained HA removals are illustrated in Fig. 4.

It is clear that for both coagulants, higher removals are attained at elevated initial HA concentrations. Both CC processes exhibited HA removals of 90 % or higher at an initial HA concentration of 40 mg/L, yet CC with alum performed better at the highest experimented concentration.

Electrocoagulation experiments

All EC experiments were performed using the setup detailed in previous sections and by varying a single parameter per experiment, depending on the experimental objectives. EC was conducted with both aluminum and iron plates as the

Fig. 3 Effect of coagulant dose on residual HA concentrations



electrodes. Removal of HA was monitored by sampling aliquots at an interval of 10 min, filtering, and measuring the residual HA concentrations.

Effect of solution pH (Al electrodes)

As solution pH was varied from 3 to 9 in intervals of 2 pH units, HA removal was noted to be slower at pH 9 compared to other lower pH levels (Fig. 5). HA removals at pH 3, 5, and 7 were very comparable, yet pH 5 presented a slight advantage and was therefore adopted in the remaining experiments.

Effect of varying current density (CD) (Al electrodes)

After several preliminary assessments, it was found that HA removal will still be possible even at low current densities; thus, experiments were conducted

to investigate the extent to which the current may be lowered while still obtaining successful HA removals. All experiments were conducted in a minimum of duplicates, at two different initial HA concentrations (20 and 40 mg/L), and for durations enough to reach almost 100 % HA removals. Adopted parameter values as well as recorded outcomes are summarized in Table 1 for initial HA concentrations of 20 and 40 mg/L.

The results are as expected; increasing the applied current to the electrodes will cause a decrease in the time needed to reach complete removal as larger amounts of Al will be released into solution. Contradictory to expectations though were the outcomes for experiments conducted at a current density of 0.05 mA/cm² which consistently outperformed outcomes of experiments at 0.1 mA/cm², reaching higher removal in shorter periods.

Fig. 4 HA removals in CC with Al and Fe salts versus initial HA concentration

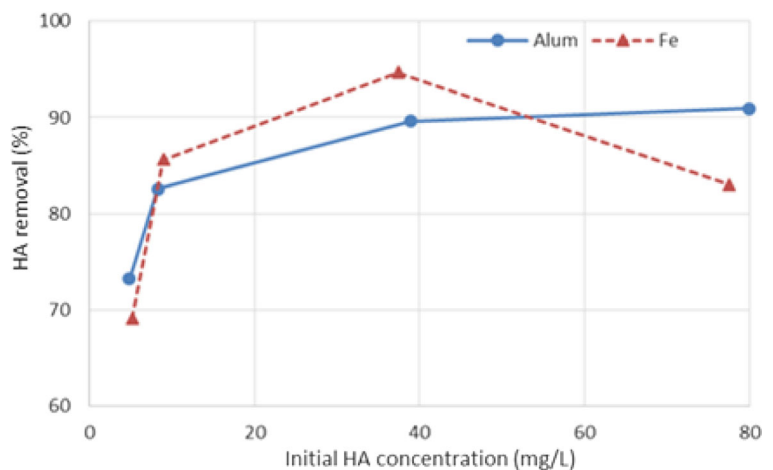
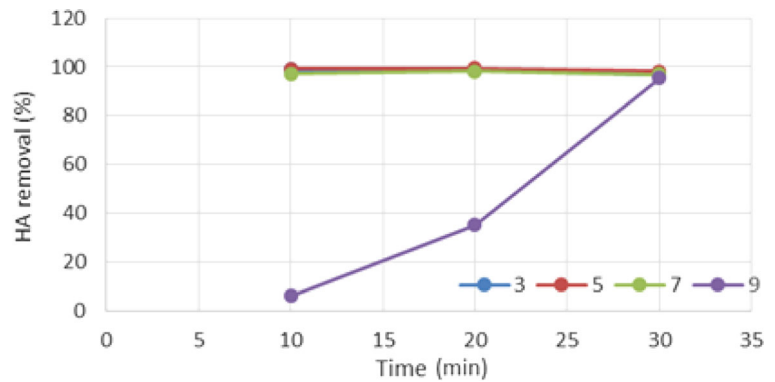


Fig. 5 Effect of pH on HA removal efficiency using Al electrodes (initial HA = 23 mg/L, current density = 1.6 mA/cm², conductivity = 1000 μ S/cm)



Effect of varying HA concentration (Al electrodes)

Varying initial HA concentrations, ranging from 10 to 80 mg/L, were assessed for their effect on HA removal efficiency. Each HA concentration was experimented at two different current densities to ensure reproducibility of results under varying conditions. It is noteworthy to mention that all experiments were conducted at an initial conductivity of 1700 μ S/cm at 25 °C to match that of the solutions containing 80 mg/L HA. Figures 6 and 7

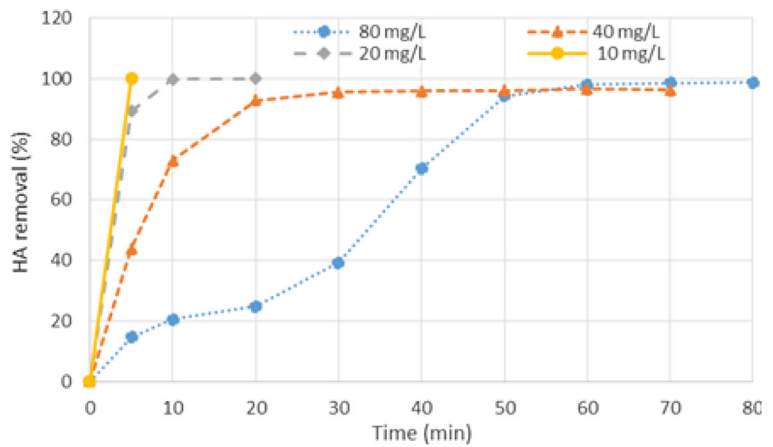
illustrate HA removal efficiencies under varying initial HA concentrations and for current densities 0.2 and 0.42 mA/cm², respectively.

It is evident that higher HA concentrations are removed at a slower rate, but it is noteworthy to observe that as EC progresses, a high HA removal rate will be attained for all initial HA concentrations. It is also important to note that doubling the concentration of HA in solution does not cause the removal rate to decrease proportionally.

Table 1 Effect of varying current density on HA removal efficiency at initial HA of 20 and 40 mg/L

HA = 20 mg/L, pH = 5, EC = 1000 μ S/cm at 25 °C								
Time (min)	CD = 0.05 mA/cm ²		CD = 0.1 mA/cm ²		CD = 0.2 mA/cm ²		CD = 0.42 mA/cm ²	
	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)
0	14.37	0.0	19.51	0.0	14.37	0.0	21.06	0.0
10	1.06	92.7	10.93	44.0	0.07	99.5	0.31	98.5
20					0	100	0	100
30	0.14	99.0	0.36	98.2				
40	0.00	100.0	0.21	98.9				
50								
60			0	100				
HA = 40 mg/L, pH = 5, EC = 1000 μ S/cm at 25 °C								
Time (min)	CD = 0.05 mA/cm ²		CD = 0.1 mA/cm ²		CD = 0.2 mA/cm ²		CD = 0.42 mA/cm ²	
	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)
0	40.64	0.0	41.52	0.0	40.64	0.0		
10	2.81	93.1	14.03	66.2	1.06	97.4		
20	0.96	97.6			0.64	98.4		
30	0.43	99.0	2.40	94.2	0.40	99.0		
40	0.05	99.9	1.13	97.3	0.33	99.2		
50			0.88	97.9				
60	0.14	99.6	1.04	97.5	0.29	99.3		
80			0.51	98.8				
90			0.98	97.6				

Fig. 6 Effect of initial HA concentration on HA removal efficiency (pH 5, CD = 0.2 mA/cm², EC = 1700 μS/cm)



Effect of varying electrode distance (Al electrodes)

For this experimental objective, the distance between the electrodes was varied while maintaining all other parameters in an attempt to assess the effect of distance between the electrode plates on HA removal efficiency. Table 2 summarizes HA removal efficiencies as electrode distance was varied in increments of 1 cm, between 1 and 3 cm.

Increasing the distance between the anode and the cathode will cause a decrease in the current passing

through the cell. In turn, this decrease in current will lead to a decrease in amount of metal released into solution as shown by Faraday’s law (Eq. 1) (Escobar et al. 2006; Harif et al. 2012). Therefore, an increase in the electrode distance will lead to slower or insufficient HA removal from solution. This conforms with what was obtained and summarized in Table 2, whereby when the electrodes were 1 cm apart, the highest and fastest removal was obtained, followed by the distance of 2 cm, and when they are 3 cm apart, the reaction was slower.

$$w = \frac{I \cdot t \cdot M}{Z \cdot F}$$

w	=	metal dissolving (gM/cm ²)
I	=	current intensity (A)
t	=	time (s)
M	=	molecular weight of metal (g/mol)
Z	=	number of electrons involved in the oxidation/reduction reaction
F	=	Faraday’s constant (96,485 C)

(1)

Fig. 7 Effect of initial HA concentration on HA removal efficiency (pH 5, CD = 0.42 mA/cm², EC = 1700 μS/cm)

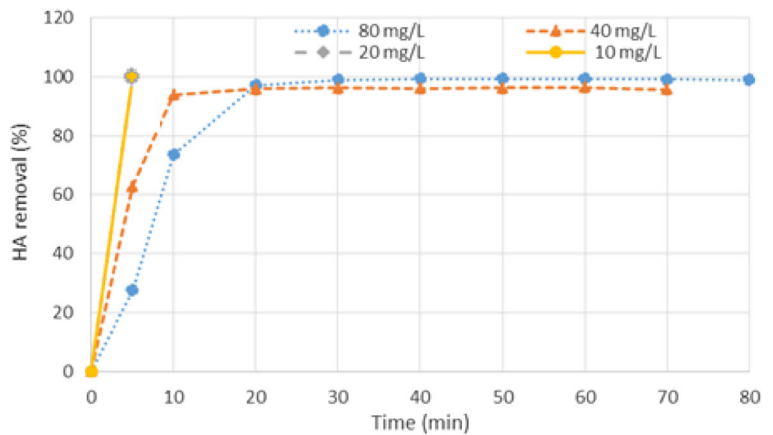


Table 2 Effect of electrode distance on HA removal efficiencyHA = 40 mg/L, CD = 0.2 mA/cm², EC = 1300 μS/cm at 25 °C

Time (min)	1 cm		2 cm		3 cm	
	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)
0	41.06	0.0	41.06	0.0	41.06	0.0
10	1.38	96.6	2.18	94.7	4.70	88.6
20	0.00	100.0	0.00	100.0	0.64	98.4
30					0.00	100.0

Effect of varying solution conductivity (Al electrodes)

Conductivity of the solution was increased by adding the required volume of potassium chloride (KCl) solution. Increasing the conductivity of the solution should render metal solubility easier, therefore making the removal reaction faster and more complete. The experimental parameters and recorded outcomes for different conducted experiments are summarized in Table 3.

It is noted that when using both current densities (0.2 and 0.42 mA/cm²), HA removal is faster in the solution with higher conductivities, although all solutions will eventually reach almost complete removal.

Additionally, a limited set of experiments were conducted using iron plates as electrodes in the EC process because of difficulties in monitoring HA removal efficiencies accurately as iron oxide dissolving into the solution during the EC process was rendering the solution yellow and interfering with the UV absorption at the same wavelength as the HA in solution. Samples taken at the beginning of the experiments were most affected by the interference, probably due to the fact that iron oxide is still present in solution and has not formed any flocs yet; therefore, samples from the first 20 min were not considered in the calculations. The experiment, although not as comprehensive as those conducted with aluminum electrodes, helped in determining the parameters at which HA is best removed with iron electrodes.

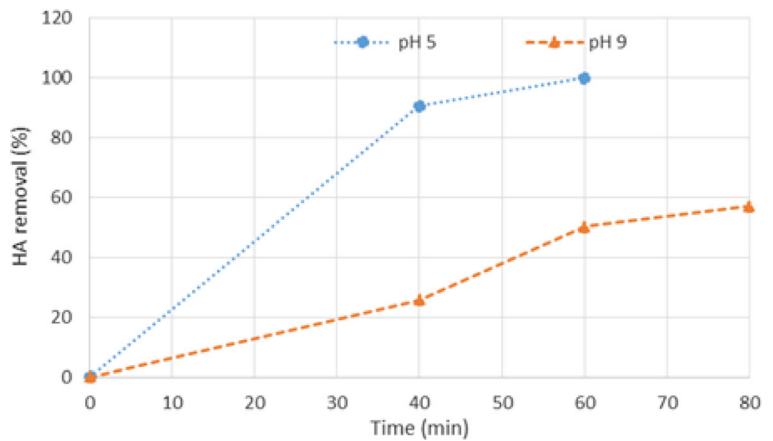
Table 3 Effect of solution conductivity on HA removal efficiency at current densities of 0.2 and 0.42 mA/cm²HA = 40 mg/L, pH 5.5, CD = 0.2 mA/cm²

Time (min)	1000 μS/cm at 25 °C		2000 μS/cm at 25 °C		3000 μS/cm at 25 °C	
	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)
0	43.72	0.0	42.74	0.0	41.06	0.0
10	24.00	45.1	11.66	72.7	13.86	66.2
20	6.24	85.7	3.02	92.9	3.91	90.5
30	2.32	94.7	1.71	96.0	2.08	94.9
40	1.85	95.8	1.62	96.2	1.90	95.4
50	1.80	95.9	1.43	96.6	1.43	96.5

HA = 40 mg/L, pH 5.5, CD = 0.42 mA/cm²

0	43.72	0.0	42.74	0.0	41.06	0.0
10	23.35	46.6	11.43	73.3	6.10	85.1
20	1.62	96.3	1.43	96.6	0.82	98.0
30	0.54	98.8	0.50	98.8	0.12	99.7
40	0.00	100.0	0.21	99.5	0.17	99.6
50			0.36	99.2	0.00	100.0

Fig. 8 Effect of initial pH on HA removal efficiency using Fe electrodes (HA 20 mg/L, CD = 0.6 mA/cm², EC = 1000 μS/cm)



Effect of solution pH (Fe electrodes)

To test the effect of pH on HA removal efficiency, the experiments were initially conducted under two different solution pH values, 5 and 9, and results are illustrated in Fig. 8 for an HA solution with an initial HA concentration of 20 mg/L, a solution conductivity of 1000 μS/cm at 25 °C, and an applied current density of 0.6 mA/cm². It is clear that at pH 5, the iron electrodes are more efficient at removing HA and in shorter periods of time. Note that the experiment performed at pH 9 was stopped at 120 min because it was considered to be unrealistic to go beyond that duration. No further pH values were considered as obtained results agreed with the literature which considers pH 5 to be the optimal pH at which HA is removed by CC and EC using iron electrodes (Koparal et al. 2008; Katal and Pahlavanzadeh 2011; Bazrafshan et al. 2012).

Effect of varying current density (Fe electrodes)

Preliminary experiments showed that although employed iron and aluminum plates have the same dimensions, iron plates apparently required a higher current density to exhibit the ability to remove HA as listed in Table 4.

The molar mass of Fe (55.8 g/mol) is larger than that of Al (26.98 g/mol), and according to Eq. 1, this indicates that at the same conditions, more Fe should be dissolved into solution and will be free to react with the HA. However, at a current density of 0.42 mA/cm² for instance, and although more Fe is being released into solution, removal of HA is much slower when using the Fe electrodes as compared to the Al electrodes. This is an indicator that Fe is effectively less efficient in settling HA from solution.

Further increasing the current density, as shown in Table 5, did not exhibit significant improvements in HA removal efficiencies. It was noted during these experiments that the amounts of flocs formed are more than what was obtained with lower current densities, and this

Table 4 Effect of varying current density on HA removal efficiency when using Fe electrodes

HA = 20 mg/L, pH 5.5, EC = 1000 μS/cm at 25 °C

Time (min)	CD = 0.42 mA/cm ²		CD = 0.6 mA/cm ²		CD = 0.8 mA/cm ²	
	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)
0	22.41	0.0	22.41	0.0	22.41	0.0
30	3.25	85.5	3.30	85.3	0.82	96.3
40	1.10	95.1	0.17	99.2	-	-
50	-	-	0.00	100.0	-	-

Table 5 Effect of higher current density on HA removal efficiency when using Fe electrodes

Time (min)	Initial HA = 20 mg/L				Initial HA = 40 mg/L			
	CD = 1.2 mA/cm ²		CD = 2 mA/cm ²		CD = 1.2 mA/cm ²		CD = 2 mA/cm ²	
	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)	HA conc. (mg/L)	HA removal (%)
0	21.24	0.00	21.24	0.00	37.74	0.00	37.74	0.00
20	4.70	77.87	1.34	93.71	0.79	36.24	3.16	91.63
40	0.45	97.89	0.17	99.21	0.12	4.56	1.48	96.09
60	0.07	99.65			0.04	1.10	1.10	97.08
80					0.02	0.17		

probably caused more interference with UV absorption. However, at a current density of 2 mA/cm², it was noted that formation of flocs started at 20 min, earlier than any other experiment with iron electrodes in this study.

Effect of initial HA concentration on HA removal efficiency (Fe electrodes)

The effect of varying the initial HA concentration on HA removal efficiency was investigated for the lower HA concentrations, as at higher concentrations, removal was very slow and a large amount of flocs were formed with significant interference with analytical procedures. As recorded in Table 6, at higher HA concentrations, the EC process using iron electrodes needs prolonged duration to exhibit successful HA removals.

Table 6 Effect of varying initial HA concentration on HA removal efficiency when using Fe electrodes

Time (min)	20 mg/L		40 mg/L	
	Conc. (mg/L)	% removal	Conc. (mg/L)	% removal
0	20.87	0.0	43.67	0.0
30	1.90	90.7	19.33	55.8
40	0.00	100.0	N/A	N/A
60			1.34	96.9
75			0.78	98.2

N/A not available

Characterization of flocs

Photometric dispersion analysis

Characteristics of flocs, generated under varying experimental conditions, were investigated with a PDA. This technology monitors the state of the flocs by passing illumination through a small volume of the sample, peristaltically pumped from the solution through a clear tubing, at a rate of 25 mL/min, for this study. The data obtained will indicate changes in the state of aggregation suspension (flocculation–aggregation/de-flocculation–disaggregation–dispersion) versus the progression of the experiment, thus assisting in assessing the onset of floc formation, as well as the size and strength of formed flocs by monitoring the ratio of root mean squared (RMS) voltage to direct current (DC) voltage.

Characteristics of flocs during EC with Al electrodes

Characteristics of flocs during the EC process utilizing aluminum electrodes with solution pH adjusted to 3, 5, or 9 are graphed in Fig. 9. The graph clearly shows a difference among process reactions at the three pH values whereby at pH 3, and although complete HA removal was achieved, formed flocs are too small and do not cause a change in the RMS/DC ratio. This was confirmed by visual inspection as contrary to other experiments, almost no visible flocs were formed at pH 3. At pH of 5, it is evident that floc formation starts earlier when compared to that at pH 9 (600 s compared to 1500 s). Furthermore, the lower ratio achieved in the experiment conducted at pH 5 compared to that at pH 9 was caused by

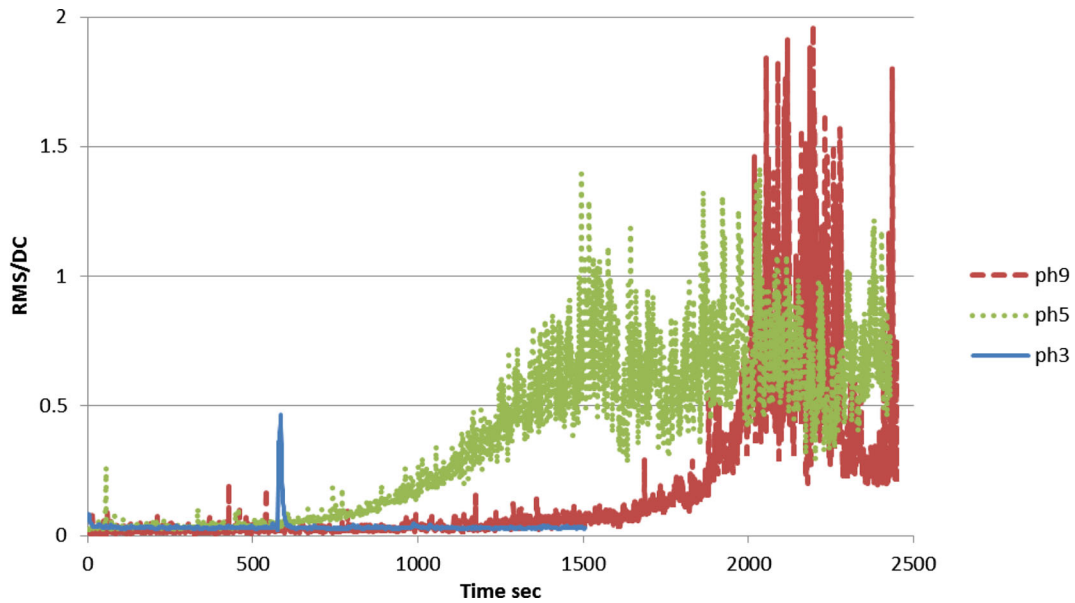


Fig. 9 Floc analysis at different pH values during EC with Al electrodes

lower RMS values, not by higher DC values, which indicates that flocs formed at pH 9 were both larger and stronger than those formed at pH 5.

Furthermore, floc formation was also investigated for EC with aluminum electrodes while

varying initial HA concentrations as illustrated in Fig. 10.

At a concentration of 10 mg/L, HA is removed very rapidly and with the formation of a very small amount of flocs that do not significantly change the PDA readings.

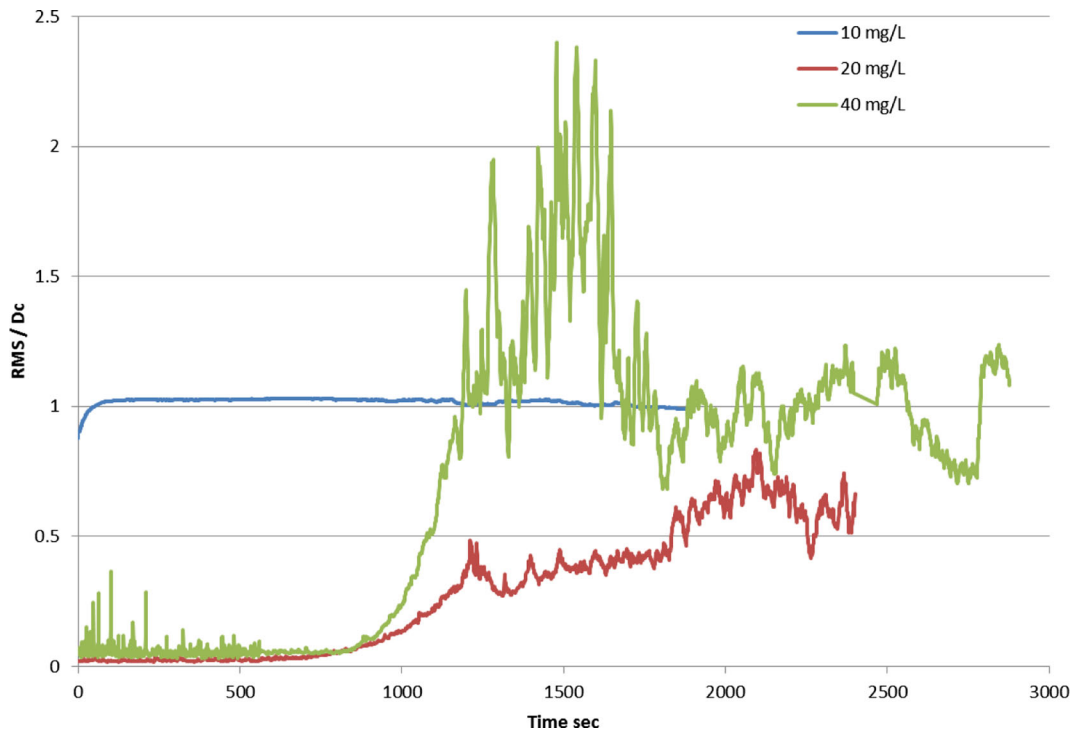


Fig. 10 Floc analysis at different initial HA concentrations during EC with Al electrodes

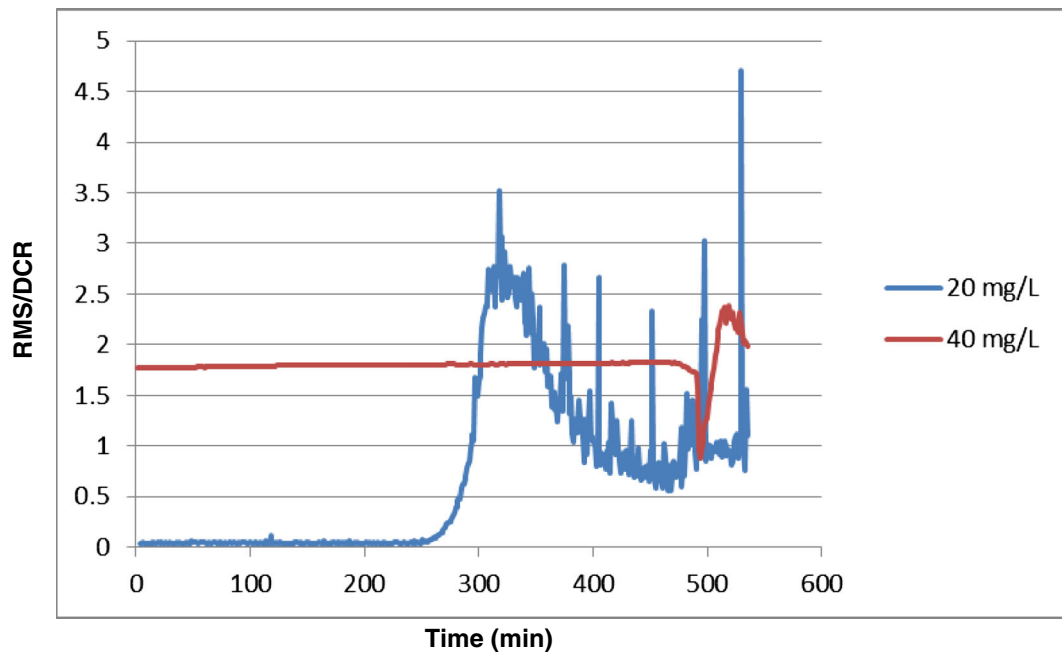


Fig. 11 Floc analysis at different initial HA concentrations during EC with Fe electrodes

It is noticed though that floc formation starts at the same time for 20- and 40-mg/L HA solutions, but as expected at 40 mg/L, more flocs are formed, thus larger aggregation leading to a higher ratio.

Characteristics of flocs during EC with Fe electrodes Floc formation was also investigated for EC with iron electrodes while varying initial HA concentrations as illustrated in Fig. 11. It can be noted that although the onset of flocculation is earlier with the 40-mg/L HA solution, yet flocs formed with the 20-mg/L HA solution are larger and of higher strength

which translated into faster and higher HA removals during the EC process.

Microscopy imaging

Flocs generated from EC processes using both types of electrodes were imaged with a compound microscopy system with imaging capabilities (Carl Zeiss Axiostar Plus, Germany). Images indicate Fe flocs to be larger and denser than flocs generated with aluminum electrodes (Fig. 12), although this does not correlate with HA removal efficiencies.

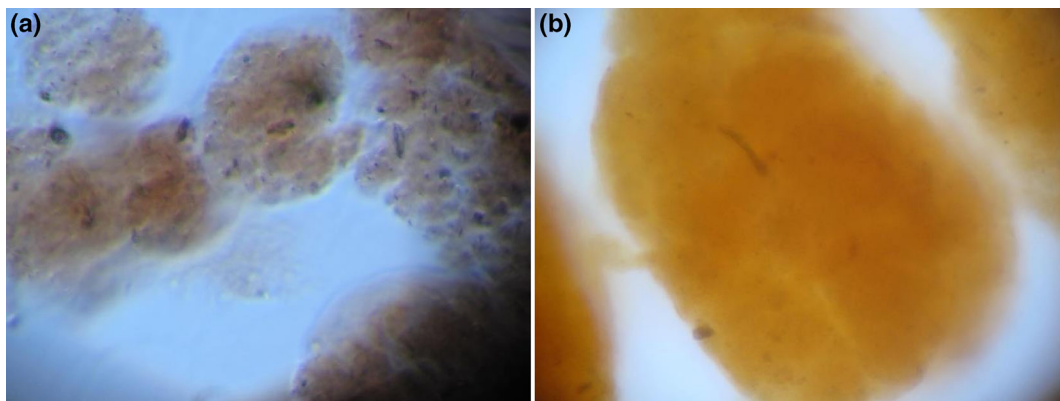


Fig. 12 Flocs formed during EC with Al electrodes (a) and Fe electrodes (b), visualized at $\times 100$ in oil immersion

For further details, flocs were also investigated by scanning electron microscopy at higher magnifications, and produced images (Fig. 13) illustrate a larger size and a denser as well as a more geometric shape of iron flocs.

Conclusions and recommendations

The efficiency of electrocoagulation for the removal of humic acid from contaminated waters and the effect of varying contributing parameters (matrix pH, humic acid concentration, type of electrode, current density,

solution conductivity, and distance between electrodes) on the process were thoroughly investigated in the present study. Outcomes of experiments allow the following conclusions:

- Electrocoagulation of humic acid at a solution pH of 5.0–5.5 was optimum for both electrode types.
- With aluminum electrodes, a current density of 0.05 mA/cm² outperformed 0.1 mA/cm² yet not higher densities, whereas iron electrodes needed higher current densities (0.8 mA/cm²) to exhibit comparable humic acid removal efficiencies.

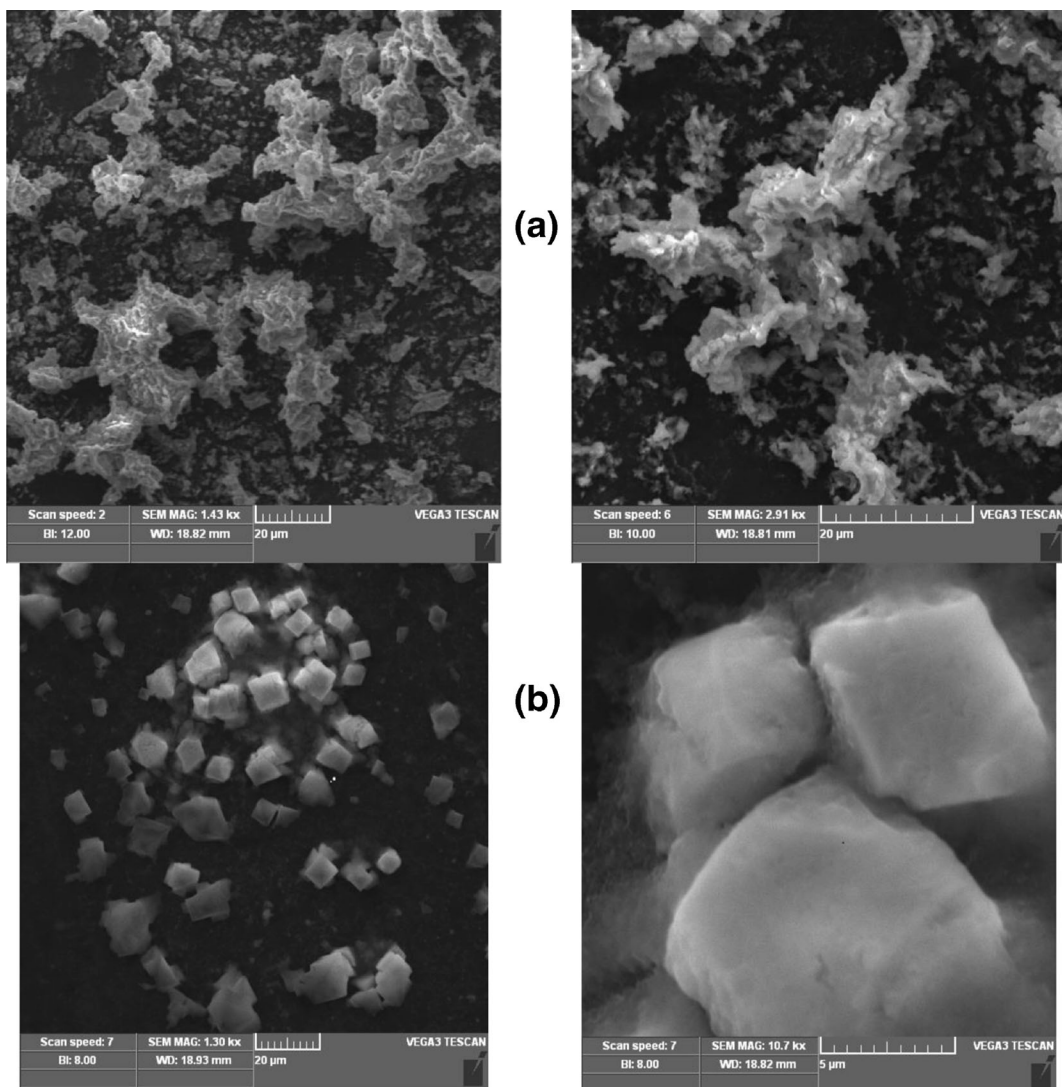


Fig. 13 SEM images of flocs formed during EC with Al electrodes (a) and Fe electrode (b)

- With both electrode types, higher initial humic acid concentrations were removed at a slower rate but ultimately attained almost complete removals.
- Also, removal rates were higher in solutions with higher electrical conductivity (3000 $\mu\text{S}/\text{cm}$ at 25 °C) and an electrode distance of 1 cm.
- It was evident by SEM that iron flocs were larger, denser, and more geometrical in shape compared to aluminum flocs.
- The electrocoagulation process was compared to optimized conventional chemical coagulation of humic acid by aluminum and iron salts whereby it proved to be faster in the removal of humic acid and produced less amounts of sludge.

Based on the above outcomes and as recommendations for more efforts towards further optimizing the process of electrocoagulation, it remains of high significance to study the effect of combination of the parameters and evaluate the most contributing parameter(s) for the best humic acid removals. This entails an experimental design with a representative sample size that allows statistical analysis and leads to bivariate correlations with credible significance levels. Cost implications as well as large-scale applicability of the process ought to also be investigated for the proper selection of the optimum process.

References

- Akyol, A. (2012). Treatment of paint manufacturing wastewater by electrocoagulation. *Desalination*, 285, 91–99.
- Balasubramanian, N., Kojima, T., Basha, A., & Srinivasakannan, C. (2009). Removal of arsenic from aqueous solution using electrocoagulation. *Journal of Hazardous Materials*, 167(1), 966–969.
- Bayramoglu, M., Kobya, M., Taner Can, O., & Sozbir, M. (2004). Operating cost analysis of electrocoagulation of textile dye wastewater. *Separation and Purification Technology*, 37(2), 117–125.
- Bazrafshan, E., Biglari, H., & Hossein Mahvi, A. (2012). Humic acid removal from aqueous environments by electrocoagulation process using iron electrodes. *E-Journal of Chemistry*, 9(4), 2453–2461.
- Behloul, M., Hocine, G., Drouiche, N., Abdi, N., Lounici, H., & Mameri, N. (2013). Removal of malathion pesticide from polluted solutions by electrocoagulation: modeling of experimental results using response surface methodology. *Separation Science and Technology*, 48, 664–672.
- Drouiche, N., Aoudi, S., Lounic, H., Drouiche, M., Ouslimane, T., & Ghaffour, N. (2012). Fluoride removal from pretreated photovoltaic wastewater by electrocoagulation: an investigation of the effect of operational parameters. *Procedia Engineering*, 33, 385–391.
- Escobar, C., Soto-Salazar, C., & Ines Toral, M. (2006). Optimization of the electrocoagulation process for the removal of copper, lead and cadmium in natural waters and simulated wastewater. *Journal of Environmental Management*, 81(4), 384–391.
- GilPavas, E., Dobrosz-Gomez, I., & Gomez-Garcia, M. A. (2011). The removal of the trivalent chromium from the leather tannery wastewater: the optimization of the electrocoagulation process parameters. *Waste Science and Technology*, 63(3), 385–394.
- Harif, T., Khai, M., & Adin, A. (2012). Electrocoagulation versus chemical coagulation: coagulation/flocculation mechanisms and resulting floc characteristics. *Water Research*, 46(10), 3177–3188.
- Hong, S., & Elimelech, M. (1997). Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *Journal of Membrane Science*, 132, 159–181.
- Huang, C., & Shiu, H. (1996). Interactions between alum and organics in coagulation. *Colloids and Surfaces*, 113, 155–163.
- Irdemez, S., Demircioglu, N., Sevki Yildiz, Y., & Bingul, Z. (2006). The effects of current density and phosphate concentration on phosphate removal from wastewater by electrocoagulation using aluminum and iron plate electrodes. *Separation and Purification Technology*, 52, 218–223.
- Isa, M. H., Ezechi, H. E., Ahmed, Z., Magram, S. F., & Kutty, S. R. M. (2014). Boron removal by electrocoagulation and recovery. *Water Research*, 51, 113–123.
- Katal, R., & Pahlavanzadeh, H. (2011). Influence of different combinations of aluminum and iron electrode on electrocoagulation efficiency: application to the treatment of paper mill wastewater. *Desalination*, 265, 199–205.
- Kobya, M., Bayramoglu, M., & Eyvaz, M. (2007). Techno-economical evaluation of electrocoagulation for the textile wastewater using different electrode connections. *Journal of Hazardous Materials*, 148, 311–318.
- Koparal, A. S., Yildiz, Y. S., Keskinler, B., & Demircioglu, N. (2008). Effect of initial pH on the removal of humic substances from wastewater by electrocoagulation. *Separation and Purification Technology*, 59, 175–182.
- Lakshmanan, D., Clifford, D. A., & Samanta, G. (2010). Comparative study of arsenic removal by iron using electrocoagulation and chemical coagulation. *Water Research*, 44, 5641–5652.
- Lee, M., Snoeyink, V., & Crittenden, J. (1981). Activated carbon adsorption of humic substances. *American Water Works Association*, 37(8), 440–446.
- McCreary, J., & Snoeyink, V. (1980). Characterization and activated carbon adsorption of several humic substances. *Water Research*, 14(2), 151–160.
- Mills, D. (2000). A new process for electrocoagulation. *American Water Works Association*, 92, 34–43.
- Mollah, M. Y., Schennach, R., Parga, J., & Cocke, D. (2001). Electrocoagulation (EC)—science and applications. *Journal of Hazardous Materials*, B84, 29–41.
- Nystrom, M., Ruohomoki, K., & Kaipia, L. (1996). Humic acid as a fouling agent in filtration. *Desalination*, 106, 79–87.

- Tezcan Un, U., Ugur, S., Koparal, A. S., & Bakir Ogutveren, U. (2006). Electrocoagulation of olive mill wastewaters. *Separation and Purification Technology*, 52, 136–141.
- Tir, M., & Moulai-Mostefa, N. (2008). Optimization of oil removal from oily wastewater by electrocoagulation using response surface method. *Journal of Hazardous Materials*, 158, 107–115.
- Vasudevan, S., Lakshmi, J., Jayaraj, J., & Sozhan, G. (2009). Remediation of phosphate-contaminated water by electrocoagulation with aluminum, aluminum alloy and mild steel anodes. *Journal of Hazardous Materials*, 164, 1480–1486.
- Lemlikchi, W., W., Khaldi, S., Mecherri, M. O., Lounici, H., & Drouiche, N. (2012). Degradation of disperse red 167 azo dye by bipolar electrocoagulation. *Separation Science and Technology*, 47, 1682–1688.
- Wan Ngah, W. S., & Musa, A. (1998). Adsorption of humic acid onto chitin and chitosan. *Journal of Applied Polymer Science*, 69, 2305–2310.
- Wang, Q., Gao, B., Wang, Y., Yang, Z., Xu, W., & Yue, Q. (2011). Effect of pH on humic acid removal performance in coagulation-ultrafiltration process and the subsequent effects on chlorine decay. *Separation and Purification Technology*, 80(3), 549–555.
- Yahiaoui, O., Aizel, L., Louinici, H., Drouiche, N., Goosen, M. F. A., & Pauss, A. (2011). Evaluating removal of metribuzin pesticide from contaminated groundwater using an electrochemical reactor combined with ultraviolet oxidation. *Desalination*, 270, 84–89.
- Yan, W., & Bai, R. (2006). Adsorption of lead and humic acid on chitosan hydrogel beads. *Water Research*, 38(4), 688–698.
- Yildiz, Y., Koparal, A., Irdemez, S., & Keskinler, B. (2007). Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes. *Journal of Hazardous Materials*, B139, 373–380.
- Yuan, W. L., & Zydney, A. L. (1999). Humic acid fouling during microfiltration. *Journal of Membrane Science*, 157, 1–12.
- Zaroual, Z., Chaair, H., Essadki, A. H., El Ass, K., & Azzi, M. (2009). Optimizing the removal of trivalent chromium by electrocoagulation using experimental design. *Chemical Engineering Journal*, 148(2–3), 488–495.
- Zeboudji, B., Drouiche, N., Lounici, H., Mameri, N., Ghaffour, N., et al. (2013). The influence of parameters affecting boron removal by electrocoagulation process. *Separation Science and Technology*, 48, 1280–1288.
- Zhou, J., & Banks, C. (1993). Mechanism of humic acid color removal from natural waters by fungal biomass biosorption. *Chemosphere*, 27(4), 607–620.
- Zouboulis, A., Chai, X.-L., & Katsoyiannis, I. (2004). The application of bioflocculant for the removal of humic acids from stabilized landfill leachates. *Journal of Environmental Management*, 70, 35–41.