



Humic Acid Removal from Aqueous Environments by Electrocoagulation Process Using Iron Electrodes

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Abstract: At present study the performance of electrocoagulation process using iron electrodes sacrificial anode has been investigated for removal of HA from artificial aqueous solution. The experiments were performed in a bipolar batch reactor with four iron electrode connected in parallel. Several working parameters, such as initial pH (3, 5, 7, and 9), electrical conductivity (50 V) and reaction time were studied in an attempt to achieve the highest removal capacity. Solutions of HA with concentration equal 20 mg L⁻¹ were prepared. To follow the progress of the treatment, samples of 10 ml were taken at 15, 30, 45, 60, and 75 min interval. Finally HA concentration was measured by UV absorbance at 254 nm (UV₂₅₄) and TOC concentration was measured by TOC Analyser. The maximum efficiency of HA removal which was obtained in voltage of 50 V, reaction time of 75 min, initial concentration 20 mg L⁻¹, conductivity 3000 µS/Cm and pH 5, is equal to 92.69%. But for natural water samples at the same optimum condition removal efficiency was low (68.8 %). It can be concluded that the electrocoagulation process has the potential to be utilized for cost-effective removal of HA from aqueous environments.

Keywords: Humic acid, Electrocoagulation, Iron Electrodes, Aqueous environments.

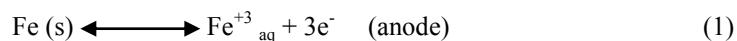
Introduction

Organic matter in the environment can be divided in two main classes of compounds, non-humic material, such as proteins, polysaccharides, nucleic acids, *etc.* and humic substances¹. Humic acids (HA) are one of the major components of humic substances which arise by the microbial degradation of biomolecules. They may account for up to 90% of NOM². The presence of humic substances in surface and ground waters, pose a variety of problems in treatment operations and distribution systems. For example its presence in water introduces taste, odor, and a yellowish to brown color³. Moreover, high affinity of humic substances (Figure 1) for complexation with various pollutants including heavy metals causes

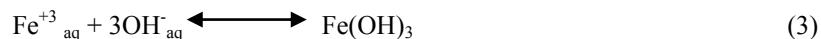
contamination of ground and surface water^{4,5}. In addition, HA will form very toxic disinfection byproducts (DBPs); *i.e.* chlorinated organic compounds, for example, trihalomethanes (THMs), which exhibit mutagenic properties during chlorination step in tap or drinking water production or water treatment^{4,6}. The guideline values for DBPs in drinking water announced by the World Health Organization should not exceed 100 µg L⁻¹⁷. Consequently, removal of HA from surface water or wastewater is important and considered of great health and environmental concern. This is usually accomplished by coagulation and precipitation, *i.e.*, adding salts of hydrolysed metals, such as aluminium sulfate and organic polymers, followed by gravity sedimentation or filtration⁸⁻¹⁰. Other treatment techniques, which have been examined for the removal of HA, are ion exchange¹¹, sorption⁶, membrane processes, such as reverse osmosis and ultrafiltration¹², flotation¹³, bioflocculation¹, and chemical oxidation such as ozonation² and Fenton process³.

Electrocoagulation process is an alternative of the conventional coagulation process in which coagulant agents are generated *in situ* through the dissolution of a sacrificial anode by applying current between the anode–cathode electrodes. The electrocoagulation process has several advantages that make it attractive for treating various contaminated streams. In the past decades electrocoagulation has been applied for the treatment of many kinds of wastewater such as landfill leachate, restaurant wastewater, textile wastewater, petroleum refinery wastewater, tannery wastewater, laundry wastewater, and for removal of fluoride, pesticides and heavy metals from aqueous environments¹⁴⁻²¹.

An examination of the chemical reactions occurring in the electrocoagulation process shows that the main reactions occurring at the iron electrodes are:



In addition, Fe³⁺ and OH⁻ ions generated at electrode surfaces react in the bulk wastewater to form ferric hydroxide:



The iron hydroxide flocs formed remains in the aqueous stream as a gelatinous suspension and act as adsorbents and/or traps for pollutants and so eliminate them from the solution^{22,23}. The main purpose of this work is to study of the electrocoagulation process efficiency for HA removal from aqueous environments with iron electrodes and determination of the effects of pH, electrical conductivity and reaction time on the removal efficiency.

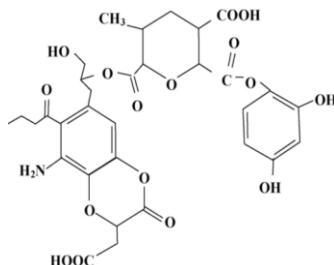


Figure 1. The chemical structure of humic acid.

Experimental

At present study all chemicals were of standard analytical grade and used without further purification unless otherwise noted. A stock solution of HA at 1 g L^{-1} is prepared by dissolving 1 g of HA in 62.5 mL of NaOH (2 N) solution, as HA dissolves well under alkaline conditions, and then completed to 1 L with distilled water (with $10 \mu\text{S cm}^{-1}$ at 25°C as conductivity) in a 1 L vial. This solution is submitted to magnetic agitation during 48 h and then conserved at 4°C in the absence of light. Working solutions (HA solutions, 20 mg L^{-1}) were prepared by dilution of stock solution in de-ionized water.

Set-up and Procedure

Experiments were performed in a bipolar batch reactor, with four iron electrode connected in parallel. The internal size of the cell was $10 \text{ cm} \times 13 \text{ cm} \times 12 \text{ cm}$ (width \times length \times depth) with an effective volume of 1000 Cm^3 . The volume (V) of the solution of each batch reactor was 1 L. The active area of each electrode (plate) was $10 \times 10 \text{ cm}$ with a total area of 400 Cm^2 . The distance between electrodes was 2 cm. A power supply pack having an input of 220V and variable output of 0–60V (50 V for this study) with maximum electrical current of 5 ampere was used as direct current source. The temperature of each system was maintained at $25 \pm 1^\circ\text{C}$.

After the introduction of HA solution to treat in the electrocoagulation reactor (Figure 2), the pH is adjusted at its selected initial value (3, 5, 7, and 9) using HCl and NaOH solutions (0.1 N) and also the electrical conductivity is adjusted at its selected initial value (1000 , 1500 , 2000 and $3000 \mu\text{S cm}^{-1}$) using KCl solution (0.1 N). The chloride salt added to the solution can also prevent the formation of the oxide layer on the anode and therefore reduce the passivation problem of the electrodes. The pH values in influent and reactor unit were measured using a pH meter model E520 (Metrohm Herisau, Switzerland). A Jenway Conductivity Meter (Model 4200) was employed to determine the conductivity of the solution. Samples were taken for analysis every 15 min (up to 75 min) from the solution by pipetting.

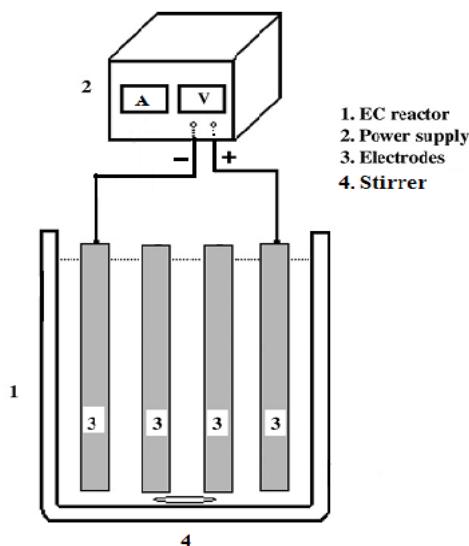


Figure 2. The schematic view of electrochemical reactor.

Ultraviolet (UV) absorption spectroscopy and total organic carbon (TOC) were used for HA measurement. In the UV method, the samples were placed in a 4 mL quartz cuvette and UV absorbance values of the samples were measured at a wavelength of 254 nm. A standard calibration curve of UV_{254} absorbance against HA concentration ($0.1\text{--}30\text{ mg L}^{-1}$) was produced, from which the concentration of unknown sample can be obtained. Also, the total organic carbon of samples was measured using a TOC Analyser (ANATOC Series II). The analyser was first calibrated and a standard curve was produced by varying the concentration of HA. Samples were placed in 40 mL glass vials, placed in a circular holder of the machine. The sample collection and measurements were done automatically. During the runs, the reactor unit was stirred at 70 rpm by a magnetic stirrer to allow the chemical precipitate to grow large enough for removal. During electrocoagulation, an oxide film formed at the anode. In order to overcome electrode passivation at the anode, the electrodes were rinsed in diluted HCl solution (5% v/v) after each experiment and rinsed again with tap water and finally weighted. All analyses were conducted in duplicate for reproducibility of data, and all of the data in the Figures and Tables were the average ones.

Results and Discussion

The electrocoagulation process is quite complex and may be affected by several operating parameters, such as pollutants concentrations, initial pH, applied voltage, electrical conductivity, and reaction time. In the present study, electrocoagulation process has been evaluated as a treatment technology for HA removal from synthetic solutions. HA removal efficiency at different condition (pH, conductivity and reaction time) was evaluated.

Effect of Initial pH

It has been established that the pH has a considerable influence on the performance of electrocoagulation process^{24–27}. Therefore, pH (3, 5, 7 and 9) was examined as one of the main variables affecting electrocoagulation removal of HA from synthetic solutions. The results are shown in Figure 3, from which the variation of removal efficiency of HA with the solution initial pH could be clearly identified. The optimal pH was 5 (removal efficiency ~92.69%), at which higher HA removal efficiency could be reached. The average HA removal for a conductivity value of 5 3000 $\mu\text{S/cm}$ increased from 87.45% to 92.69% when the pH was increased from 3 to 5. Further increasing the pH to 7 and 9 resulted in a reduction of HA removal efficiency to 80.12% and 71.9%, respectively. This result support that electrocoagulation process efficiency is a function of initial pH. On the other hand, the results indicate that the reaction performance is dependent on initial pH values, where the lower pH values lead to faster reactions and better efficiency. This result is in agreement with results obtained by other researchers²⁸.

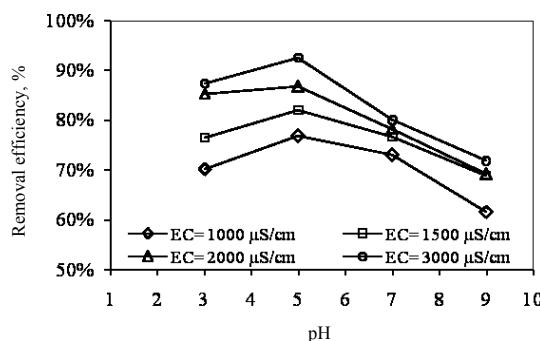


Figure 3. Effect of pH on the removal efficiency of HA (initial concentration of HA: 20 mg L^{-1} , applied voltage: 50 V and reaction time: 75 min).

Theoretically, pH values of the solution affect the appearance of HA directly. An aromatic ring is the basic unit of HA (Figure 1); it is a reticular macromolecule polymer connected by hydrogen bonds between functional retentions. The most active functional retentions are carboxyl and phenolic hydroxyl groups. As a consequence dissociation of H^+ form carboxyl or hydroxyl relates to the pH value of the solution. When the pH value is lower, carboxyl and hydroxyl radicals exist in the chemical form of $-\text{COOH}$ and $-\text{OH}$ respectively. When pH values are higher, they exist in the form of $-\text{COO}^-$ and $-\text{O}^-$. It's clearly that under conditions of a higher pH, HA takes on a more negative charge and more Fe^{3+} is consumed to neutralize the negative charge. Therefore, the removal efficiency will decrease under higher pH values.

Furthermore, as shown in Figure 4, the pH of the solution changes during the process. The pH variation of the solution after electrocoagulation process (Figure 4) showed that the final pH for all of the experiments with iron plate electrodes is higher compared to the initial pH, which is in agreement with results obtained by other researchers^{18,29,30}.

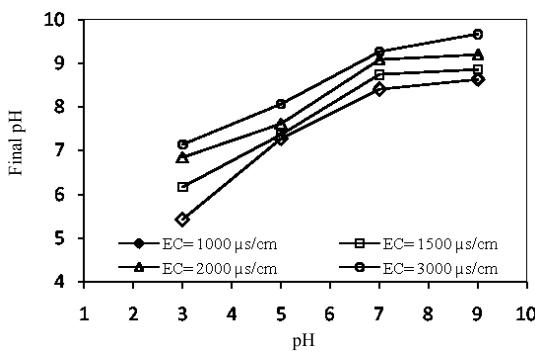


Figure 4. Variation of initial pH during electrocoagulation process (initial concentration of HA: 20 mg L⁻¹, applied voltage: 50 V and reaction time: 75 min).

It has been shown that variation of energy consumption with initial pH of the water as a function of time in Figure 5. When examining Figure 5, it can be seen that energy consumptions have generally minimum values, when initial pH and conductivity equals 5 and 1000 $\mu\text{S}/\text{cm}$, respectively and it is maximum for other initial pH and conductivity values. On the other hand, when the initial pH increased from 3 to 5 (at conductivity: 3000 $\mu\text{S}/\text{cm}$), the HA removal efficiency increased appreciably, from 87.45% to 92.69%, whereas the corresponding specific energy consumption increased only slightly. Therefore, in present study, initial pH 5 is chosen as optimum pH for electrocoagulation process.

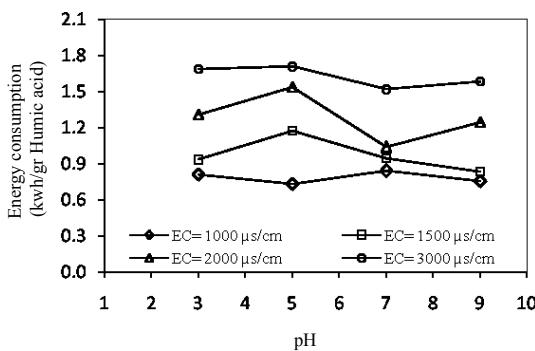


Figure 5. Variation of energy consumption as a function of initial pH and conductivity (initial concentration of HA: 20 mg L⁻¹, applied voltage: 50 V and reaction time: 75 min).

Effect of Reaction Time

In accordance with Faraday Act, the time of electrolysis in electrocoagulation process affects the rate of metal ion released into the system³¹, so, the removal efficiency of HA in the electrocoagulation cell was evaluated as a function of the reaction time.

HA removal efficiencies as a function of electrocoagulation time at constant electrolysis voltage (50 V) are shown in Figure 6. At the beginning of the reaction, the removal efficiency of HA obviously changed with the reaction time. As shown in Figure 6 and 7, HA removal increased with increasing reaction time and most of the reduction in HA was achieved within the first 15 min of the reaction and was approximately 52.1% at conductivity 3000 $\mu\text{S}/\text{cm}$. A further increase in reaction time to 75 min resulted in an improved HA removal of approximately 92.69% (HA concentration $<1.46 \text{ mg L}^{-1}$). The same trend of evolution of removal efficiency with electrocoagulation time was reported by other researchers^{15,16,28,32,33}. The process can be divided into two steps: a primary rapid step and a secondary slow step, resembling the adsorption rate of Pb^{2+} ions onto the microparticles in a previous study by Huang *et al.*³⁴.

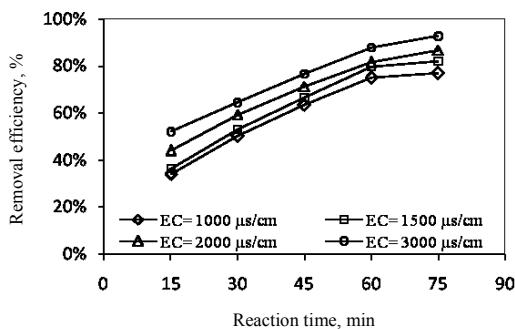


Figure 6. Effect of reaction time on the HA removal efficiency as a function of conductivity (initial concentration of HA: 20 mg L^{-1} , pH: 5, applied voltage: 50 V).

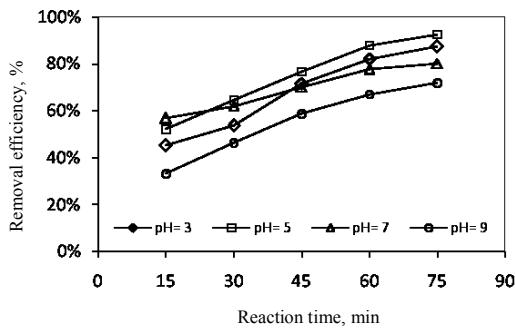


Figure 7. Effect of reaction time on the HA removal efficiency as a function of pH (initial concentration of HA: 20 mg L^{-1} , conductivity: 3000 $\mu\text{S}/\text{cm}$, applied voltage: 50 V).

Effect of Electrical Conductivity

A set of experiments was performed to determine the effect of electrical conductivity of solution on HA removal efficiency as a function of pH and reaction time. These experiments

were performed using KCl as the electrolyte in the range of 1000–3000 $\mu\text{S}/\text{cm}$ at applied voltage of 50 V, initial HA concentration equal 20 mg L^{-1} and pH range 3–9.

The results obtained at different electrical conductivity values (Figure 8 and 9) showed that conductivity of solution has a considerable influence on the performance of electrocoagulation process, which is in agreement with results obtained by Gulsun Kilic and Hosten³⁵. As the solution conductivity increased from 1000 $\mu\text{S}/\text{cm}$ to 3000 $\mu\text{S}/\text{cm}$, the HA removal efficiency increased from 76.95 to 92.69% for the pH 5. The residual HA concentration was 1.46 mg L^{-1} after 75 min of electrocoagulation at conductivity of 3000 $\mu\text{S}/\text{cm}$. When the conductivity of the solution increased, the current flow during electrocoagulation increased; as a result, the efficiency of HA removal was enhanced. Golder *et al.* reported that the availability of metal coagulants increases with increasing conductivity³⁶.

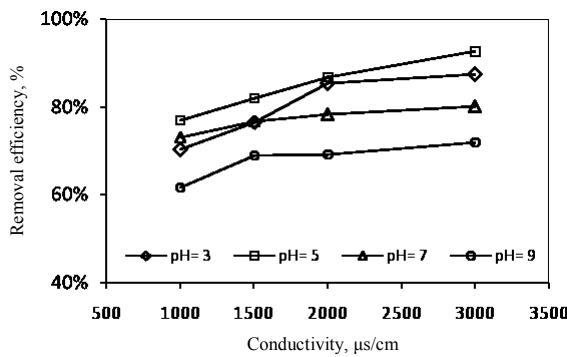


Figure 8. Effect of conductivity on the HA removal efficiency as a function of pH (initial concentration of HA: 20 mg L^{-1} , reaction time: 75min, applied voltage: 50 V).

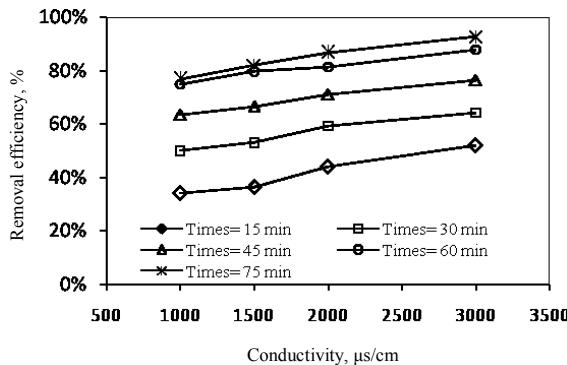


Figure 9. Effect of conductivity on the HA removal efficiency as a function of reaction time (initial concentration of HA: 20 mg L^{-1} , pH: 5, applied voltage: 50 V).

In previous studies, Chen *et al.* found that conductivity had little effect on the separation of pollutants from restaurant wastewater in the investigated range from 443 $\mu\text{S}/\text{cm}$ to 2850 $\mu\text{S}/\text{cm}$ ¹⁷. Kobya *et al.* studied the effect of wastewater conductivity on the performance of the electrocoagulation process using aluminum and iron electrodes¹⁸. They found that the turbidity removal efficiency remained almost unchanged in the conductivity range of 1000–4000 $\mu\text{S}/\text{cm}$ for both electrode materials. But, it was in contrast to that given by Lin and Peng for electrocoagulation of textile wastewater using iron electrodes³⁷.

Increasing solution conductivity resulted in the reduction of cell voltages that caused a decrease in electrical energy consumption³⁸. But our findings showed (Figure 10) that at constant voltage, increasing of solution conductivity resulted in the increase of electrical energy and electrode consumption.

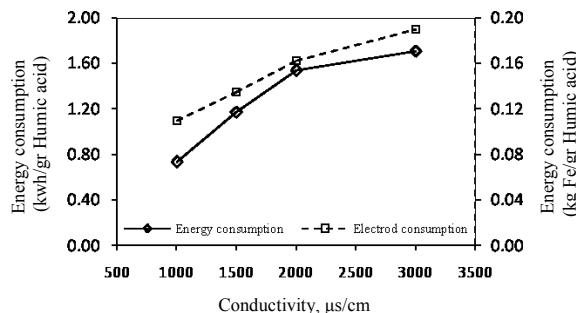


Figure 10. Effect of conductivity on the electrical energy and electrode consumption (initial concentration of HA: 20 mg L⁻¹, pH: 5, applied voltage: 50 V, reaction time: 75 min).

It can be seen from Figure 10 that electrical energy and electrode consumption were found to increase with increasing the conductivity of solution. An increase in conductivity from 1000 to 3000 $\mu\text{S}/\text{cm}$ causes an increase in energy consumption from 0.735 to 1.71 kWh g⁻¹. Also, an increase in conductivity from 1000 to 3000 $\mu\text{S}/\text{cm}$ causes an increase in electrode consumption from 0.11 to 0.19 kg g⁻¹ of HA.

When the conductivity was increased from 1000 to 3000 $\mu\text{S}/\text{cm}$, the HA removal efficiency increased appreciably, from 76.95% to 92.69% for pH 5, whereas the corresponding specific energy and electrode consumption increased only slightly. Therefore, in present study, 3000 $\mu\text{S}/\text{cm}$ is chosen as optimum conductivity for electrocoagulation process.

Conclusion

The present study attempted to investigate the applicability of an electrocoagulation method using Fe electrodes in the removal of HA from aqueous environments. The influence of various variables such as pH, reaction time, and conductivity of solution on the removal of HA was investigated. The results showed that electrocoagulation process with Fe electrode could successfully remove HA from the aqueous environments. The results obtained with synthetic solutions revealed that the most effective removal capacities of HA achieved at pH 5. In addition, the increase of reaction time, in the range of 15-75 min, enhanced the treatment rate. The maximum efficiency of HA removal which was obtained in constant electrolysis voltage of 50 V, reaction time of 75 min, initial concentration 20 mg L⁻¹, conductivity 3000 $\mu\text{S}/\text{Cm}$ and pH 5 is equal to 92.67%. Also the results showed that at constant voltage, increasing of solution conductivity resulted in the increase of electrical energy and electrode consumption. Finally, the results show that electrocoagulation process can effectively reduce HA contaminant to a very low level.

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