The Effect of Different Electrodes on Humic Acid Removal by Electrocoagulation

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Abstract

The present study is about the reduction of humic acids (HA) by electrocoagulation (EC) method. Undesirable color, odor, taste, reacting with chlorine to produce toxic materials in water, and making a complex with heavy metal ions are some unfavorable environmental consequences of HA. Platinum and graphite as anode electrodes and platinum, titanium, and aluminum as cathode electrodes were used for this purpose. Also, solutions consisting of sodium sulfate (Na_2SO_4), as the electrolyte support, and humic acids at a concentration of 30 mg.l^{-1} were used in the reduction tests. We investigated the best condition for pollutant removal at pH values of 3, 5, and 7 and voltages of 5, 10, and 18. The samples were taken during the electrolysis and were analyzed by the pH meter and UV-visible spectrophotometer. Moreover, the oxidation phenomena on anodes surface were studied by cyclic voltammetry tests. The results confirm that the Gr/Al electrodes by coagulation phenomena shows the best performance in the elimination of HA at an electrolyte support concentration of 0.02 molar after approximately 23 min at a pH of 7 and a voltage equal to 10 V.

Keywords: Humic Acid (HA's), Eelectrocoagulation, Absorption

1. Introduction

Organic materials can be divided into non-humic and humic substances. The non-humic group includes substances with defined chemical characteristics such as carbohydrates, proteins, amino acids, and low molecular weight organic acids. On the other hand, the humic substances are composed of aliphatic and aromatic acids, with a dark color (Motheo and Pinhedo, 2000). Their major functional groups are carboxylic acids, phenolic, alcoholic hydroxyls, ketone, and quinone groups (Voelker and Sulzberger, 1996; Weber et al., 2005; Aeschbacher et al., 2012). Humic acids are the most chemically active compounds in the soil (Mema, 2006), and they are soluble in dilute alkaline solution, but precipitate in acidic solution (pH <2) (Camper, 2004). Undesirable color, odor, taste, and blockage of

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eclipse filters used to purify drinking water are some unfavorable environmental consequences of HA (Yuan and Zydney, 2000; Bond et al., 2010). Furthermore, they can react with chlorine to produce toxic materials in water (Schulten and Schnitzer, 1993; Motheo and Pinhedo, 2000), and they can make a complex with heavy metal ions. The formation of this complex makes it even harder to remove HA's (Reuter and Perdue, 1977, Steinmann and Shotyk, 1995, Motheo and Pinhedo, 2000). Moreover, if humic acids are available in water usage in petroleum industries, it causes heat exchange rate to decrease, it can form sludge in eclipse filters, or it may increase corrosion effects. Thus, the presence of humic acids can cause many problems and its removal from water is necessary. Refinery effluent-derived humic substances are important for developing refinery effluent reclamation techniques and studying the environmental chemistry of wastewater effluents. A research in China showed that the concentration of dissolved organic carbon (DOC) in the refinery effluent was 9.9 mg/l, in which humic acids and fulvic acids (FA) accounted for 2.3 and 34.6% respectively. A large number of oil refineries suffer from inadequate water supplies. Wastewater reclamation and reuse provides an effective approach for their sustainable development. It is important to understand organic matter in refinery effluents for developing suitable wastewater recycling techniques and evaluating the potential environmental risk of wastewater effluents (Li et al., 2005). Various authors used different removal methods such as activated carbon adsorption, enhanced coagulation, membrane filter technique, electrocoagulation, sonochemical methods, biological methods, electrochemical oxidation, photocatalytic oxidation, photoelectric chemical method, O_3 oxidation, and Fenton processes (Wu et al., 2014). Motheo and Pinhedo used dimensionally stable anodes (DSA) to degrade humic acid, extracted from a peat area located at Sao Paulo, Brazil. They found that the electro-oxidation method could eliminate humic acid effectively (Motheo and Pinhedo, 2000). Chen and Deng used a combination of electrocoagulation with submerged flat sheet ultrafiltration membranes to coagulate humic acids and the reduction of ultrafiltration (UF) membrane fouling by titanium-based electrocoagulation (Chen and Deng, 2012). Feng Qiyan et al. used electrocoagulation method with aluminum electrodes for the removal of humic acid from groundwater. The results suggest that at a small electrode interval and/or at a high current density, a lower pH value leads to an improved removal rate of humic acid (Feng et al., 2007). Andréia P. Silva et al. used cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to study humic acid adsorbed onto Pt and PtO films at a pH of 7.0 (Silva et al., 2011). Uyguner et al. used suspended Degussa TiO_2/UV as a pre-treatment prior to the coagulation of humic acid and decreased the removal efficiency of coagulation by 15%. On the other hand, by prior air condition (AC) filtration, the advanced oxidation process (AOP) increased the removal by about 45% (Uyguner et al., 2007; Matilainen and Sillanpää, 2010). Zhang et al. used TiO_2 nanotube/low pressure (LP) UV/membrane filtration for removing a synthetic humic acid solution, and nearly complete mineralization (93–98%) of humic acid was observed. Nanotubes were totally separated and recovered with membrane filtration, and reused efficiently (Ghernaout et al., 2009; Matilainen and Sillanpää, 2010).

A literature survey indicates that regarding the cost of process, the time of process, and the disposal energy, electrocoagulation (EC) is an efficient treatment process for different wastes. EC is an effective process for the destabilization of finely dispersed particles by removing hydrocarbons, grease, suspended solids, and heavy metals from different types of wastewater (Ghernaout et al., 2009). In this study, electrocoagulation (EC) was used to remove humic acid from wastewater. The effect of conjugated electrodes with different metals in the anode and cathode was also investigated. By applying these electrodes, we obtained good removal efficiency by using cheaper electrodes at a lower time compared to other electrodes. The effects of pH, voltage, and type of anode and cathode electrode on removal efficiency were also evaluated.

2. Experimental

2.1. Material and method

Humic acid (Sigma-Aldrich, Fluka), sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), and sulfuric acid (H_2SO_4), from Merck were purchased and used without further purification.

0.50 gr. of HA was dissolved in 125 ml NaOH (1 N) and was then diluted by distilled water to 1 l. The prepared solution was agitated for 24 hrs by magnetic stirrer and was then filtered to separate solid particles. The cleared solution was preserved in an incubator at 4 °C in the absence of light. In order to prepare electrolyte support, 2.84 gr of Na_2SO_4 was added to 60 ml of the cleared solution and was then diluted by distilled water to 1 l. The electrochemical tests were performed for 160 ml of the solution. The pH was adjusted to 3, 5, and 7 by adding the appropriate amount of sodium hydroxide and sulfuric acid. The distance between electrodes was adjusted at 1.5 cm, while the immersed surface area was fixed at 8 cm². The electrodes were connected to a direct current power supply at 20 V and 7.5 A as the maximum voltage and intensity respectively. For understanding the effects of anode electrodes on the oxidation of humic acid, cyclic voltammetry test by IVIUMSTAT.XRe was used. In this research, platinum and graphite were used as the anode electrodes, while platinum, titanium, and aluminum were connected as the cathode electrodes. Before performing any test, in order to remove any pollutants on the surface of the platinum electrode, it was immersed in 0.01 M nitric acid, and the other electrodes were first grinded by emery paper and were then rinsed with distilled water. To achieve good mass transfer and mixing in the system, a magnetic stirrer at 120 rpm was used. For each pH, the anode and cathode configurations of the electrodes consist of Pt/Pt, Pt/Ti, graphite/Al, and graphite/Ti respectively. The best state was obtained with the variation of voltage and pH.

2.2. Analytical technique

In order to measure the concentration of humic acid after electrochemical tests, UV-Vis spectrophotometer (UNICO 2800) with a 1 cm quartz cell at 293 nm was used.

The removal of humic acid was calculated using the following relation (Equation 1):

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

where, Ab_i is initial UV absorbance, and Ab_f is the final UV absorbance. For all the tests, the concentration of humic acid was fixed at (30 mg/l), almost with an initial absorbance of 0.712. A calibration curve at a pH of 7 with a linear form is presented in Figure 1, expressing UV absorbance as a function of humic acid concentration; it shows that the UV absorbance is an accurate method to measure humic acid concentration.
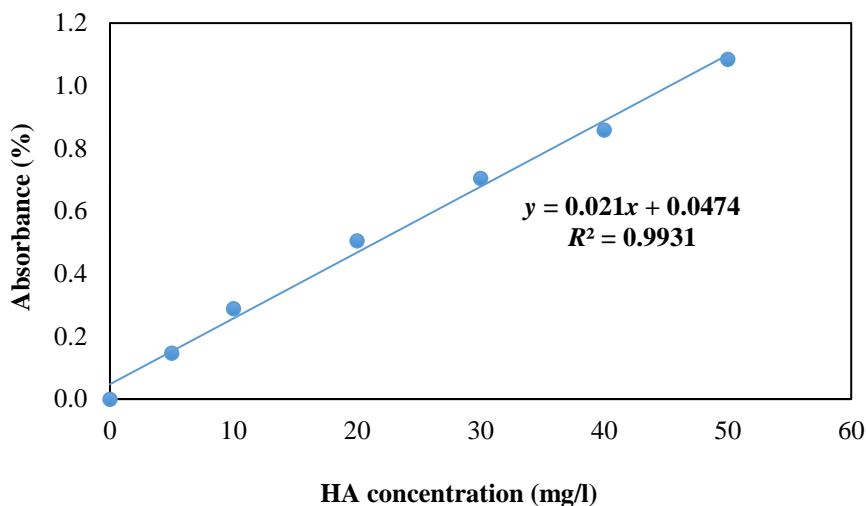
Figure 1
Calibration curve of UV absorbance at λ=293 nm and pH=7.

3. Results and discussion

3.1. Effect of pH

Humic acid is soluble in alkaline solutions and precipitates when pH decreases to less than 2. The first tests were the measurements of pH; it is possible to observe that pH increases by the electrolysis time. This phenomena can be explained by the reactions happened on the surface of the anode and cathode. On the anode surface, two reactions occurred; oxygen is released and H^+ is produced, which decreases pH and causes organic oxidation reactions too. On the cathode surface, hydrogen is released and OH^- is produced, which increases pH. Because of the occurrence of these two reactions on the anode and one reaction on the cathode, released OH^- is more than released H^+, and pH is higher at the end of the test. Figures 2, 3, 4, and 6 show the effect of pH on different combinations of the anode/cathode. For the combination of Pt/Pt, Pt/Ti, Gr/Ti, from Figures 2-4, it is clear that the performance of the electrodes is not so sufficient, and only in an acidic condition humic acid is coagulated. Thus, for the best efficiency GR/Al electrode combination was used. According to Figure 6, it is obvious that the efficiency of humic acid removal is improved for Gr/Al combination at a neutral pH compared to an acidic condition, so Gr/Al electrodes are sufficient for removing humic acid.

3.2. Effect of anode and cathode electrodes

On the surface of the cathode, the following reactions (Equations 2 and 3) occur and hydrogen gas is released:

$$2H_2O_{(l)} + 2e^- \longrightarrow 2OH^-_{(aq)} + H_{2(g)} \tag{2}$$

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} \tag{3}$$

while on the surface of the anode, oxygen is released through the following step:

$$2H_2O_{(l)} \longrightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^- \tag{4}$$

The formation of Pt oxide corresponds to a two-step reaction mechanism which takes place with PtOH as an intermediate, according to the following reactions:

$$Pt + H_2O \rightleftharpoons PtOH + H^+ + e^- \tag{5}$$

$$PtOH \longrightarrow PtO + H^+ + e^- \tag{6}$$

The first step of Pt oxidation occurs reversibly when the surface is almost completely covered with a monolayer of hydroxides (Boudenne et al., 1998). The PtOH formed may also participate in a place-exchange mechanism to form PtO (Hu and Liu, 1999). This oxide formation is believed to cause or enhance the catalytic properties of the inert metals. It has also reported that the reduction of oxides gradually became irreversible. At the first test, the synthetic humic acid solution contained 2.84 gr (0.02 molar) of electrolyte support, and the experiments were started at a voltage of 10 V. At the beginning, Pt/Pt electrode combination at a voltage of 10 V was used. Firstly, it seems that the Pt/Pt must create the best condition because as the anode, Pt is so powerful, and as the cathode it can usefully assist. We applied voltage for 90 min, but the results show that it is not true. The couple of Pt/Pt is not so good for coagulation, and at a pH of 3 and 5, humic acid removal occurred (see Figure 2); the reason is related to the characterization of Pt. On the surface of Pt, the direct oxidation reactions of humic acid happened, and a little coagulate was formed. At a neutral pH no coagulate is formed because Pt is more powerful in intensive acidic or alkaline conditions.
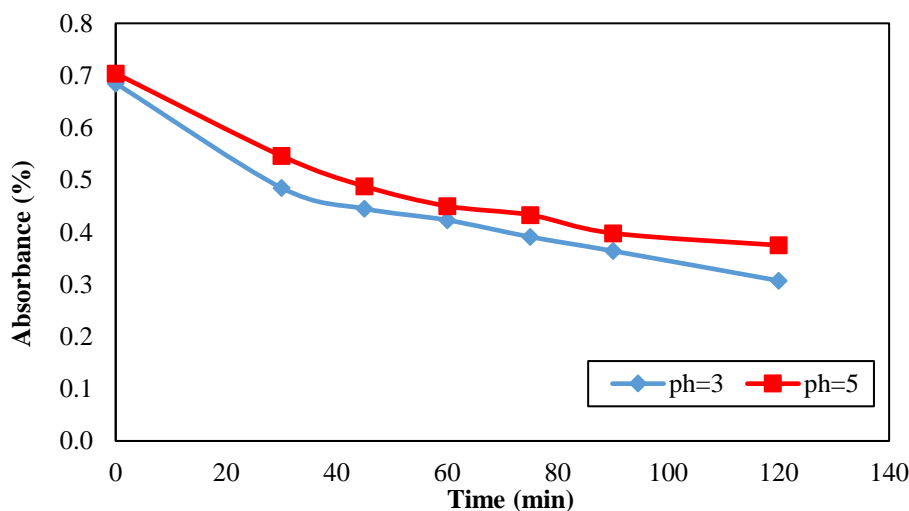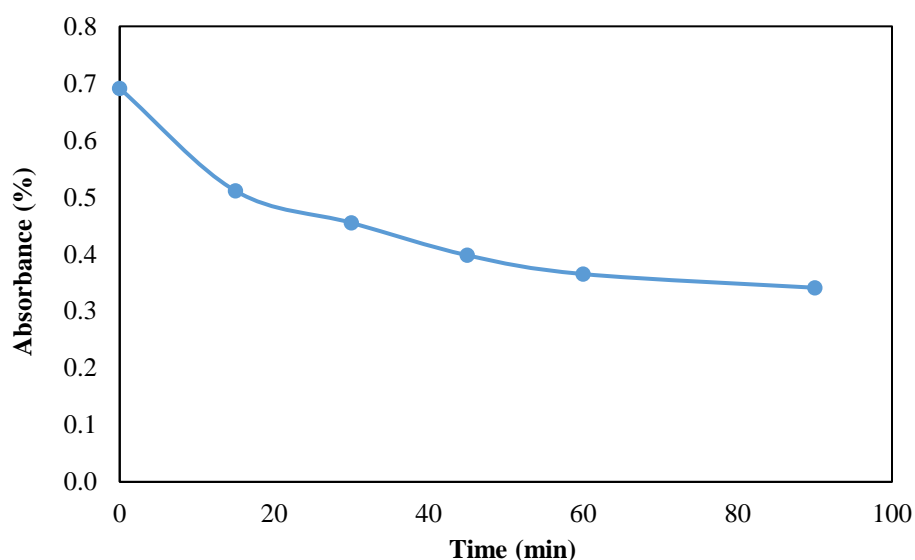

Figure 2
Effect of pH on the removal of humic acid from wastewater by Pt/Pt electrodes at V=10 V.

For the combination Pt/Ti, a voltage of 10 V was applied for 90 min too, and we did not obtain good result again; however, the results are slightly better than Pt/Pt combination. Moreover, for these electrodes a little coagulate is formed at a neutral pH although it is not significant to be shown (see Figure 3). Thus, we can confirm that Ti as a cathode is better than Pt because more coagulate is formed and less oxidation happens. For couples of Pt/Pt and Pt/Ti, Pt performs the main task in oxidation of humic acid as the anode electrode.
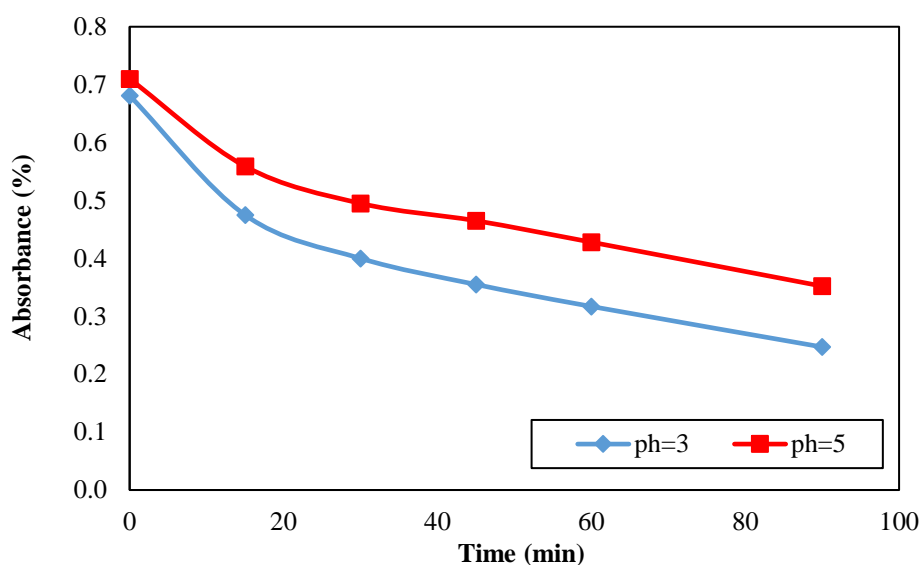
Figure 3
Effect of pH on the removal of humic acid from wastewater by Pt/Ti electrodes at V=10 V.

For Gr/Ti combination at a pH of 3 the test was repeated, and the result is shown in Figure 4; higher pH values do not result in any noticeable progress, so they are not reported. Furthermore, by increasing the time of the experiments, because of voltage exposure, the ingredient of graphite electrode was released to the solution, which darkened the color of the solution after a while; thus, the result of the UV absorbance analysis was not reliable. Hence, in case of using graphite as the electrode, the experiment conditions must be limited to small times and low voltages.

Figure 4
Effect of time on the removal of humic acid from wastewater by Gr/Ti electrodes at pH=3 and V=10 V.

Figure 5 displays the efficiency of humic acid removal by Pt/Pt, Pt/Ti, and Gr/Ti electrodes at 90 min and pH=3. It is obvious that Pt/Ti is more efficient than Pt/Ti and Gr/Ti electrodes as the amount of coagulated humic acid shows. For Pt/Ti combination, more coagulation occur compared to the other combinations; for Pt/Pt combination, the direct oxidation phenomena happen, and a little coagulate is

formed, confirming the low efficiency of the system. According to the results, we conclude that the Pt/Pt, Pt/Ti, and Gr/Ti combinations of the electrodes are not very good, and they can only coagulate humic acid and treat the wastewater in acidic solutions.
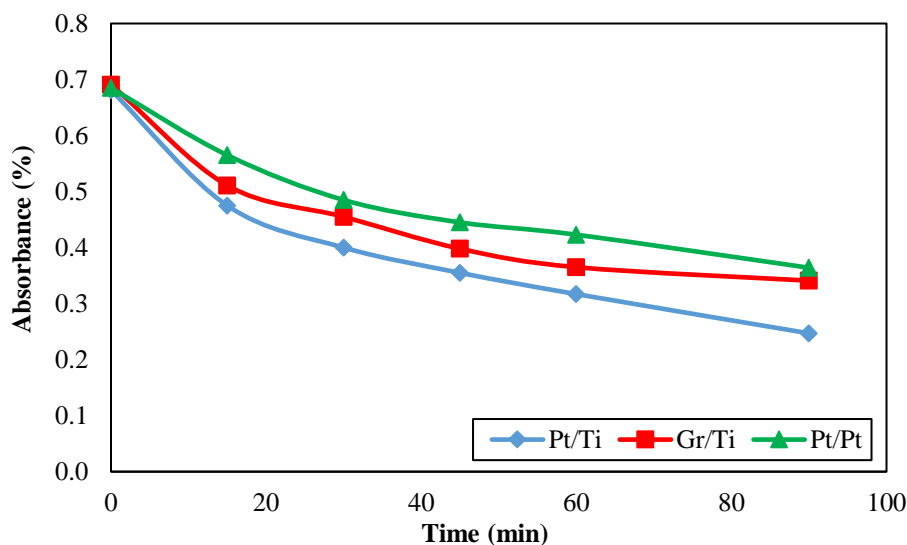
Figure 5

Efficiency removal comparison of Pt/Pt, Pt/Ti, and Gr/Ti electrodes at 90 min and pH=3.

At the next stage, in the same conditions of pH and voltage, Gr/Al electrodes were used and worthy results were obtained (Figure 6). The highest efficiency of 98% was obtained by coagulating humic acid at 23 min and in a neutral condition (pH=7). Thus it was concluded that cathode has an important effect on coagulation phenomena. By instantaneously increasing pH, metal hydroxyl of Al (on cathode surface) was released to solution, which acted like an absorbent medium and reacted with humic acid; this reaction formed higher amounts of humic acid coagulation. Aluminum hydroxyl released at a neutral pH is higher than the one released in an acidic condition. Moreover, because of a low exposure time, a very little amount of graphite was released to the solution in case of Gr/Al combination, which can be ignored.
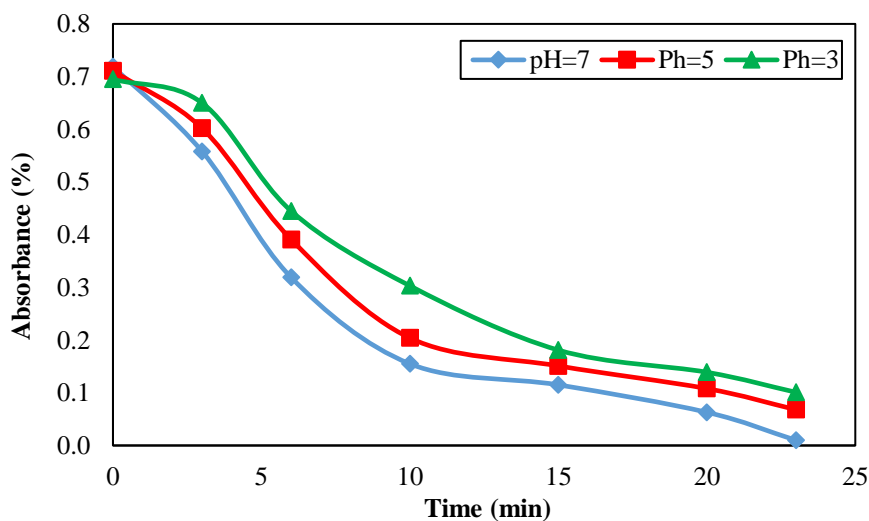
Figure 6

Effect of time and pH on the removal of humic acid from wastewater by GR/Al electrodes at V=10 V.

As it is apparent from the figures, the coagulation rate is greater at initial moments than the end of the experiments; also, the amount of humic acid removal from wastewater is almost equal after a specific time for each pair of electrodes at different pH values; in other words, after long times of exposure, the efficiency of each pair of electrodes is equal, so efficiency was calculated in different interval times. Table 1 shows the efficiency of the degradation of humic acid for different electrodes at different test times. According to this table, the best results are achieved by GR/Al combination. Humic acid removal was reached 98.61% after 23 min at a pH of 7.

Table 1
The summary of the results of the experiments at 0.02 M concentration of Na_2SO_4.

Electrodes	Voltage	pH_i	°C	Initial absorption (%)	Final absorption (%)	Electrochemical time (min)	Removal efficiency (%) R (%) $= \dfrac{Ab_i - Ab_f}{Ab_i} \times 100$	pH_f
Pt/Pt	10	3	23	0.685	0.307	120	55.18%	4.1
		5	23	0.704	0.375	120	46.73%	6.2
		7	23	——	——	——	———	—
Pt/Ti	10	3	23	0.681	0.247	90	63.73%	3.9
		5	23	0.710	0.352	90	50.42%	6.1
		7	23	——	——	——	———	—
Gr/Ti	10	3	23	0.691	0.341	90	50.65%	4.1
		5	23	——	——	——	———	
		7	23	——	——	——	———	
Gr/Al	10	3	23	0.695	0.101	23	85.47%	3.9
		5	23	0.711	0.068	23	90.44%	6.4
		7	23	0.719	0.01	23	98.61%	8.5
Pt/Al	10	3	23	0.687	0.097	15	85.88%	4.5
		5	23	0.702	0.077	15	89.03%	6.3
		7	23	0.718	0.025	15	96.52%	8.7

3.4. Effect of voltage

In this section, the effect of voltage on the removal efficiency of humic acid by the best electrode configuration (Gr/Al) is presented. To investigate the effect of voltage, 0.02 M electrolyte concentration at ambient temperature and in a neutral solution was used. Figure 7 shows that the maximum removal efficiency is obtained at 10 V. This may be explained by the fact that at a low voltage (V=5 V), the power of the electrodes and the produced electrons are low for the oxidation and coagulation; also, at a high voltage (V=18 V), the current transmission generates more bubbles on the electrode surface, which enhances the turbulence in the system and dissolves the coagulated humic acid in the solution; thus efficiency is reduced. Although other methods have reached the same removal efficiency, time, versatility, energy efficiency, amenability to automation, and cost effectiveness are very important in industrial operations; overall, considering these requirements, the EC method outperforms other methods.
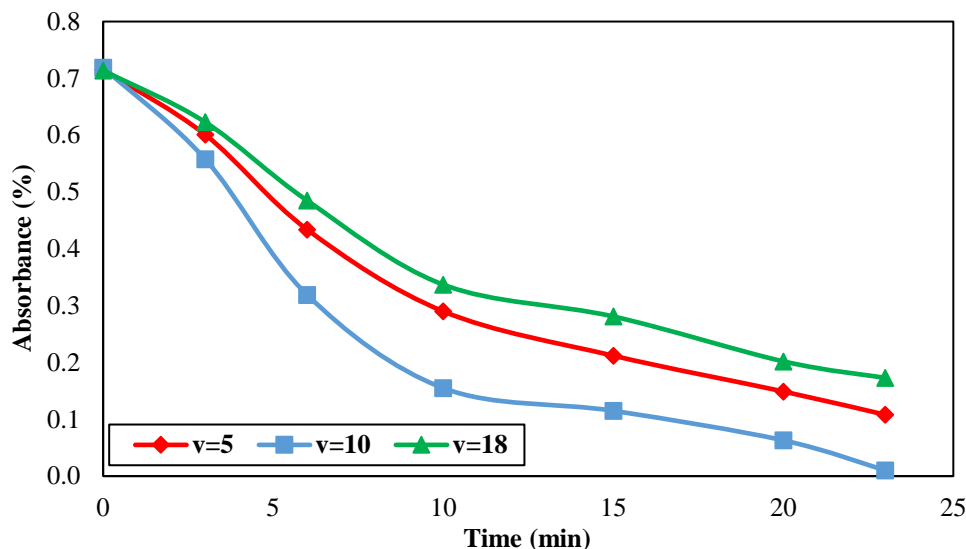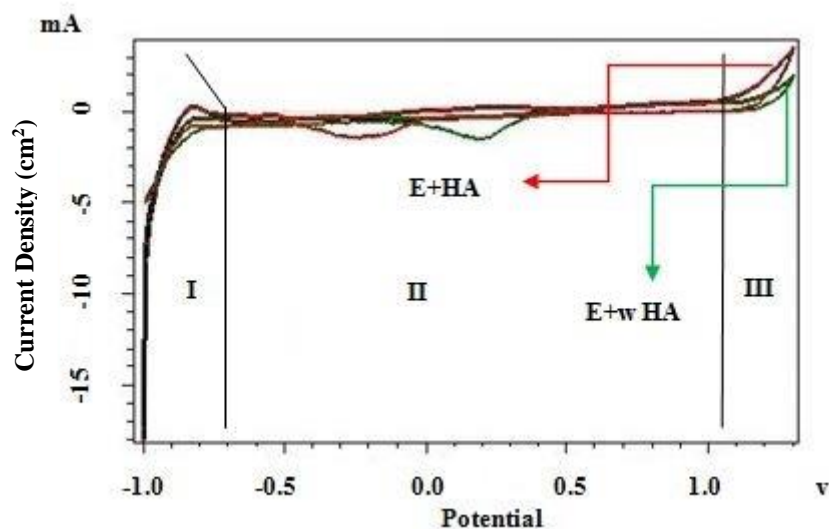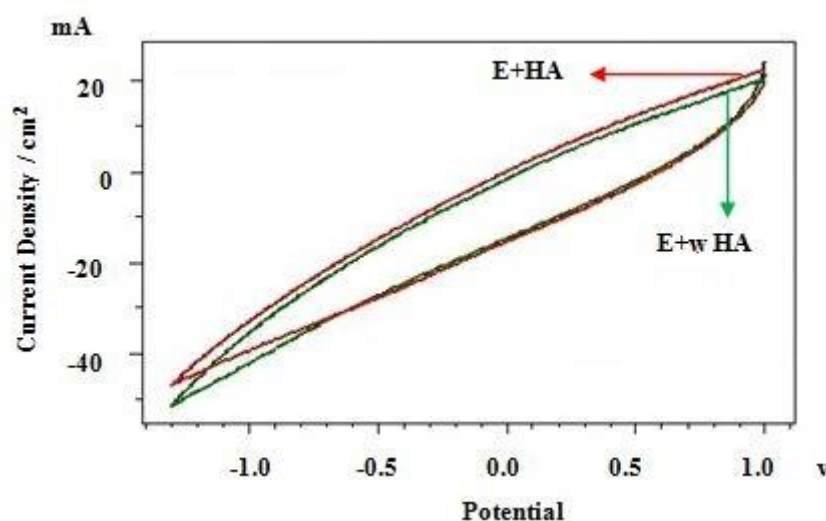
Figure 7
Effect of voltage on the removal of humic acid from wastewater by GR/Al electrodes at 25 °C.

3.5. Cyclic voltammetry

The standard cyclic voltammetry (CV) at a scan rate of 20 mV/s was used to confirm the oxidation on the anode surface. Solutions containing 0.02 M electrolyte support were used in the presence and in the absence of humic acid. According to the graphs, it is quite obvious that there not remarkable differences between the peaks of two solutions at a low concentration of humic acid, but there is an oxidation phenomenon. The results show that there is a little amount of humic acid oxidation on the anode surface. For the Pt anode applied voltage was E start= -1.000 V to 1.300 V as vertex 1 and back to -1.000 V as vertex 2 vs. saturated commercial Calomel electrode (SCE). The CV tests was carried out at a neutral pH; as shown in Figure 8, the green line (lower) is related to the solution containing an electrolyte without humic acid, and the red line (upper) is related to the solution containing an electrolyte and 30 mg/l of humic acid. Briefly, region I is related to hydrogen adsorption/desorption, and region II is about the double layer charging/discharging of the Pt surface; region III shows the oxidation of the Pt surface to form a Pt oxide, and it is possibly related to the oxidation of the adsorbed compounds. For the graphite electrodes, we repeated the tests at different potentials. The Gr anode applied voltage was E start= 1.000 V to -1.300 V as vertex 1 and back to 1.000 V as vertex 2 vs. saturated commercial Calomel electrode SCE (see Figure 9). The result states that there is no oxidation phenomenon on the graphite surface.

Figure 8
E / I vs. SCE for Pt electrode.

Figure 9
E / I vs. SCE for Gr electrode.

In the absence of humic acid, the behavior observed is typical of thermally-prepared oxide layer electrodes. The broadness of the peaks in the CV's, the characteristic of this kind of electrodes, can be understood in terms of a large heterogeneity in the surface sites. On the other hand, in the presence of the organic substance, due to the potential region studied, the behavior is practically the same as the situation in the presence of the supporting electrolyte alone, with slight differences in the positive potential region. A displacement of the surface oxidation potential range to less positive values in the presence of the organic substance can be observed for the oxide electrode.

4. Conclusions

The present study suggests that electrochemical method can serve as an effective and low cost choice for removing pollutants. In order to measure the concentration of humic acid, UV-Vis spectrophotometer at 293 nm was used. The standard cyclic voltammetry was used to monitor

oxidation on the anode surface. It is clear that when Pt is selected as the anode, just a little coagulate is formed and oxidation phenomena occur on the Pt surface. The performance of the Pt/Pt, Pt/Ti, and Gr/Ti combinations of the electrodes are not effective, and only in an acidic condition, humic acid is coagulated or oxidized. The highest removal efficiency (98.61%) is achieved by Gr/Al combination after 23 min at pH=7 and V=10 V. At V=5 V, the power of electrodes for coagulation is decreased, while at a voltage of 18 V, the turbulence in the system is enhanced, so the coagulated humic acid is dissolved in the solution again, thereby reducing the efficiency. Further research can be conducted to evaluate the efficiency of the system in the presence of other metals as the anode and cathode.

Nomenclature

Al	: Aluminum
CV	: Cyclic voltammetry
EC	: Electrocoagulation
Gr	: Graphite
HA	: Humic Acid
Pt	: Platinum
Ti	: Titanium
UV	: Ultra Violet
V	: Voltage

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