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Feasibility evaluation of combined electrocoagulation/adsorption process by optimizing operating parameters removal for textile wastewater treatment

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ABSTRACT

In this study, a combined electrocoagulation (EC)/adsorption process was employed to separate highly concentrated organic pollutants dyes from a raw textile wastewater. The removal of chemical oxygen demand (COD), turbidity, color, conductivity, salinity and TDS from a raw textile effluent was experimentally investigated by EC technique, using aluminum electrodes, followed by adsorption of treated wastewater on granular activated carbon (GAC). The main purpose was to investigate the effects of several working parameters such as current density, electrolysis time, adsorbent dose and contact time, in an attempt to achieve higher removal efficiency. Based on EC experiments, the highest rate constant abatements of COD, turbidity and color under optimal operating conditions, that is, current density of 28.57 mA/cm^2 and electrolysis time of 120 min were achieved respectively at 62.33%, 74.43% and 72.79% using Al electrode. The addition of GAC adsorbent as a second treatment step, under optimal operating conditions, that is, adsorbent dose of 0.75 g/L and contact time of 120 min, reduced pollutants concentrations below admissible legal level. The maximum removal efficiencies of COD, turbidity and color achieved 98.33%, 100% and 98.37%, respectively, by overall combined process. EC/GAC coupling process was not beneficial in terms of conductivity, salt and TDS rejection rates as their percentage removals did not exceed 43.29%, 40.35% and 41.5%, respectively. However, EC followed by GAC adsorption improves efficiently permeate quality of the studied raw textile effluent, and thus this process combination is reported to produce effluent of reuse standard. The results of this investigation provide important data for the development of a hybrid EC/GAC process to remove significant highly concentrated organic pollutants dyes from raw textile wastewater, using moderate activated carbon dose and aluminum consumption, and thereby, lowering the cost of treatment. Consequently, EC/GAC combined processes are inferred to be superior to these processes alone.

Keywords: Electrocoagulation; Adsorption; Combined process; Textile wastewater treatment; Optimization

1. Introduction

Textile industries are well known as water intensive sectors as they generate considerable amount of wastewater, which contains strong color, suspended particles, non-biodegradable materials, high chemical oxygen demand (COD) and biological oxygen demand (BOD$_5$) concentrations, high salinity and hence, causes severe water pollution. Also these effluents have complex and variable characteristics and can contain different auxiliary chemicals (e.g., acid, base, salt, dye, inorganic materials) that are toxic, carcinogenic, and mutagenic to various microbiological or animal species [1].

Therefore, the reuse and the recycling of the consumed effluent water are necessary as it provides an opportunity to achieve environmental and economic benefits [2,3].

Electrochemical oxidation [4], coagulation [5], nanofiltration and reverse osmosis [6], enzymatic decolorization and ozone oxidation [7] have been employed and some of these techniques have been applied by industry [8]. These

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treatments are usually efficient but require high concentration of chemical added substances along with high-cost energy consumption [9].

Among electrochemical treatments, electrocoagulation (EC) is an effective tool for the treatment of industrial wastewater, by virtue of various benefits including environmental compatibility, versatility, energy efficiency, safety and selectivity [3,10,11].

It provides efficient color, COD and turbidity removal and it is a reliable, simple, and economical way to treat dye-containing wastewater without excessive chemical additions and subsequent secondary pollution [8,12,13].

However, the traditional EC process has the serious disadvantages of anodic passivation and cathodic polarization which can impede the electrolytic process in a continuous operation [8,14]. Moreover, it is straight forward to combine EC with other methods for increased color and COD removal [8,15].

Adsorption on activated carbon appears as successful efficient alternative for the removal of organic and inorganic compounds in wastewater [9,16]. Activated carbon remains the most effective adsorbent [16]. The contaminants are generally physically adsorbed or chemically adsorbed onto the adsorbent surface [17].

Nevertheless, as an individual process for treating effluents, adsorption requires overdoses of the adsorbent. Thus, to reduce potentially pollution, the best solution for industrial wastewaters involves a combination of two or more efficient techniques [9].

Besides, it would be of more practical significance to the textile industry to operate the combined process because of the variability of textile wastewater composition and characteristics.

Recently, the possibility to enhance EC systems by means of granular activated carbon (GAC) has been suggested. It was found that hybrid EC/GAC systems are more efficient and faster separation techniques in comparison with the conventional EC.

Although many researches on treatment of synthetic or real wastewaters with EC are available, very few researches have been carried out on the coupling applicability of EC/GAC. Secula et al. [18] studied the performance of GAC-enhanced EC process involved in color removal from dye solutions, using three textile dyes: Acid Blue 74, Basic Red 1, and Reactive Black 5.

The adsorption process using GAC is an efficient treatment to remove the suspended solids produced by the EC process while it helps to remove all soluble pollutants that were not effectively trapped by the flocs.

This combined technology demonstrates a very good efficiency in the removal of many different pollutants (Cardboard paper mill effluents, Cr(VI), Marine Blue Erionyl MR, Reactive Black 5, Marine Blue Erionyl MR, Industrial Wastewater, etc.).

In this study, a novel approach for optimizing EC-based techniques is presented. In this context, the combination of EC and adsorption processes is proposed as an interesting alternative to treat a raw colored textile wastewater.

The aim of the present work is to investigate the performance efficiency of EC process enhanced by GAC adsorption in order to remove pollutants from a raw textile effluent. This efficiency was evaluated in terms of maximum COD, color, turbidity and salinity removal.

As it is important to take into account that the complex mechanisms of EC/GAC system depend on the operating conditions and pollutant characteristics, the effects of operating parameters such as current density, electrolysis time, adsorbent dose and contact time have been evaluated.

2. Material and methods

2.1. Textile wastewater source and wastewater characterization

Sample of colored raw textile wastewater, without receiving any treatment before flow into the treatment plant and before discharge on the local collector, was collected from an equalization tank of an industrial textile factory SITEX, located in ksar Helal, Tunisia.

The predominant activities in this fabric are those related to dyeing, printing and finishing operations, which are also the most polluting stages in the textile chain. These activities are combined in an equalization tank from which the sample was taken. The real textile effluent was generated during the industrial cotton dyeing and showed a dark blue color associated with the complex mixture of several classes of organic dyes (Reactive, Direct, Dispersive, Vat and Acid dyes), as well as other pollutants used in the textile process.

Table 1 shows the physico-chemical characteristics of this effluent. The raw textile effluent was characterized in terms of pH, conductivity, salinity, TDS, COD, color, as well as turbidity and the results are presented in Table 1, from which one can see that both COD and color are still too high to discharge or reuse the effluent. No information on its specific components was provided due to trade secret concerns.

2.2. EC experiments (apparatus and procedure)

The experimental diagram of bench-scale two-electrode EC is schematically shown in Fig. 1.

For conducting of experiments, the EC working volume of reactor was 2 L. A pair of aluminum electrodes was made of plates with the same dimensions (8 cm × 6 cm × 1 mm, purity of 98%) and an immerged area of the electrode 48 cm^2 each (8 cm × 6 cm) were used as the anode and cathode. The electrodes were positioned vertically and parallel to each other with an inner adjustable gap of 2 cm between cathode and anode.

Table 1
Physico-chemical characteristics of the rinsing textile wastewater sample of SITEX[a]

Parameters	Raw textile wastewater
pH	11.51
Conductivity (mS/cm)	6.58
Salinity	3.4
TDS (g/L)	3.6
Color	1.221
Turbidity (NTU)	184
COD (mg/L)	1200

[a] Error limits of parameters are less than ±5%.

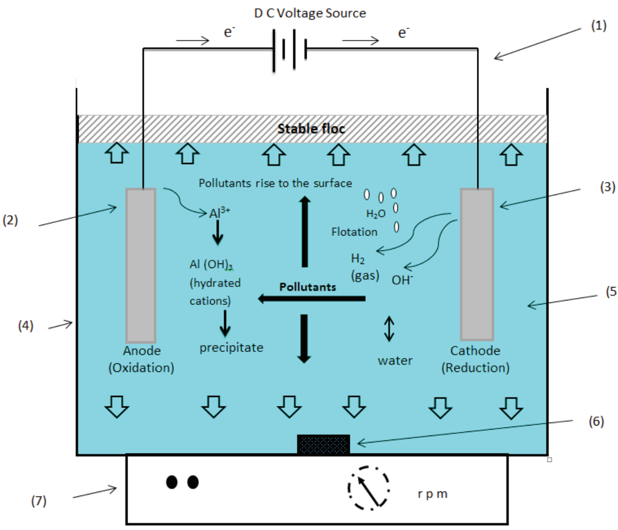

Fig. 1. Diagram of the experimental setup for the EC process: 1 – Digital DC power supply; 2 – Sacrificial anode; 3 – Cathode; 4 – EC reactor; 5 – Textile wastewater solution; 6 – Magnet; 7 – Magnetic stirrer.

Electrodes were connected in monopolar mode to a digital DC power supply (Statron, model 2224.1) characterized by the ranges 0–5 A for current and 0–25 V for voltage.

Before each run, the electrodes were abraded with sand-paper to remove scale and then washed with acetone and cleaned with successive rinses of water to remove any impurities on the aluminum electrode surface. Then, they were stocked for 3 min in a sodium hydroxide solution (5 mol/L) to form $Al(OH)_3$. Just after that, they were washed by pure water and restocked for 5 min in a solution freshly prepared of HCl (3 mol/L) to obtain pure aluminum electrodes. A second wash with pure water was made.

During the runs, the reactor unit was stirred at 150 rpm by a magnetic stirrer. All experimental runs were performed at room temperature of about 25°C. The temperature of the electrolyte was controlled to the desired value, 25°C, by adjusting the rate of flow of thermostatically controlled water through an external glass-cooling spiral.

Two parameters studied in this work were optimized current density (varied from 4.76 mA/cm^2 to 42.86 mA/cm^2) and electrolysis times (varied from 20 min to 180 min). Samples were collected each 20 min for analysis.

At the end of each electrochemical reaction, samples solutions were decanted for 12 h and then the supernatant was collected for the analysis of water properties with care taken to prevent contamination by fine solids. The used anode and cathode plates were interchanged for effective electrode utilization.

Electrodes were weighed before and after EC by means of an Acculab ATL-224-I analytical digital balance (accuracy of 0.1 mg) to estimate the amount of aluminum electrode dissolved.

2.3. GAC adsorption experiments

The batch technique was used for the adsorption studies on the performance of GAC/EC coupling process using commercially available GAC called Charcoal Activated Granular Extrapure procured from LOBA CHEMIE and used as a second step of the textile wastewater treatment. The studied activated carbon was commonly and especially used in liquid phase adsorption due to its porosity and it was interesting to use it in the combined EC/GAC process.

Table 2
Quantification of surface oxygen groups by the method of Boehm

GAC	Charcoal activated granular
Carboxylic groups (meq/g)	2.73
Phenolic groups (meq/g)	0.325
Lactonic groups (meq/g)	0.475
Total acid (meq/g)	2.82
Total basic (meq/g)	3.21
Character (meq/g)	Neutral-slightly basic

Prior to use, commercial GAC was milled and sieved to achieve particles of diameter less than 80 µm. Following sieving, the adsorbent was washed several times with deionized water and then dried in an oven at 120°C for 24 h, to remove any volatile impurities.

First, the chemical properties of the GAC were determined. GAC was characterized for its surface chemistry by pH measurement of the point of zero charge (pH_{PZC}) and semi-quantitative titrations of surface functional groups ("Boehm" method). The method of [19] was used to determine the pH of point of zero charge (pH_{PZC}) [20]. In terms of chemical surface, GAC has a basic surface with a pH_{PZC} value of 7.89.

The surface oxygen groups were determined according to the Boehm method [20,21]. A weight of 0.2 g of activated carbon was introduced into 25 mL of the following 0.1 mol/L solutions: NaOH, Na_2CO_3, $NaHCO_3$ and HCl. The GAC/solution mix was placed in a thermostated multi-agitation apparatus at 25°C under mechanical stirring at 150 rpm for 48 h. The suspension was filtered through a 0.45 µm membrane filter and the excess of base or acid was titrated with 0.1 mol/L solutions of HCl or NaOH, respectively. Following the Boehm method, the carboxyl, phenol, and lactone groups were quantified. The number of surface basic groups was calculated (but not identified) from the amount of HCl, which reacts with the carbon [20].

Table 2 shows the results of quantification of acidic and basic functions of the GAC studied surface. The dosage of Boehm was performed three times for the studied GAC to validate the results.

The studied GAC presents a high surface functions number. It has a surface acidic functional groups (total acid = 2.82 meq/g) and a surface functional group of basic character (total base = 3.21 meq/g). The proportion of acidic groups is 96.81%, 11.52%, and 16.84%, respectively, for carboxylic, phenolic, and lactonic groups.

When the solution pH value is superior to 3, the carboxylic and phenolic groups of the GAC can be deprotoned and are susceptible to release protons.

Secondly, GAC was characterized for its adsorption properties by N_2 adsorption at 77°K. BET surface area of GAC was measured (at 77°K) on a BET (Brunauer–Emmett–Teller method) Specific Surface Area Analyzer (Micromeritics

Gemini 2370C) [22]. The studied Granular Activated Charcoal has an average diameter of 1.5 mm, a BET surface area of 99.5 m^2/g, a bulk particle density of 0.4 g/cm^3, and a pore size < 5 nm (67%).

The investigations were performed at residual solutions collected from EC process under optimal conditions.

GAC adsorption experiments were conducted using different known amounts of GAC (5–300 mg) and pre-set contact time intervals (15–180 min). The weighed quantity of GAC was added to a 300 mL glass-stoppered flask containing 100 mL of sample.

Isothermal studies were conducted by sealing the flasks with parafilm and shaking the reaction mixture in a thermo stated water bath shaker at a rolling speed of 110 rpm at a constant temperature of 25°C ± 2°C. Just after, the adsorbent was separated from the solution by filtration with a 0.45 µm filter membrane through a glass fiber filter under vacuum conditions. The residual COD in the reaction mixture was analyzed after equilibrium contact time.

Suitable experimental conditions were determined and the optimum parameters (adsorbent dose and contact time) found in these tests were applied to adsorption treatment of the studied textile wastewater.

2.4. Chemicals

The chemicals used in the study were purchased from Sigma Aldrich. All the chemicals were used as such without any change in their chemistry or purity. All chemical solutions were prepared in the DI water.

2.5. Analytical methods and measurements

The degradation of the color intensity of feed and permeate samples was analyzed by a UV-Visible Thermospectronic UV1 spectrophotometer. The color was assayed using the integral of the absorbance curve in the whole visible range (400–800 nm) with 1 cm quartz cuvette.

Electric conductivity, TDS, salinity and pH measurements were performed at a constant temperature of 25°C using a conductivity/pH meter Consort C561 (multi-parameter analyzer), that was calibrated routinely with buffer solutions in the range of the values used in the experiments.

The COD values were obtained using a Fisher Bioblock Scientific reactor COD 10119 type COD-meter. The COD is the measure of oxygen consumed during the oxidation of the organic matter by a strong oxidizing agent. COD was estimated by open reflux method. The protocol presents a method derived from the standard AFNOR T90101 [23]. The sample was refluxed in an acidic medium with a known excess of potassium dichromate and the remaining dichromate was titrated with ferrous ammonium sulfate.

Turbidity was measured with a Lutran electronics Model TU-2016 turbidimeter. Data were given in Nephelometric Turbidity Unit (NTU).

The removal efficiency R (%) of different studied parameters as COD, conductivity, total dissolved solids (TDS), salinity, turbidity and color after EC and EC/GAC treatments was determined using the following equation:

$$R(\%) = 100 \times (1 - X_{\text{treated}}/X_{\text{feed}}) \quad (1)$$

where X_{treated} and X_{feed} represent the measured parameters (COD, conductivity, turbidity TDS, salinity and color) respectively, in the treated and the feed streams.

3. Results and discussions

3.1. Optimization of EC treatment process

3.1.1. Effect of current density

The current density is the amount of current per area of the electrode [17]. It has already been reported by several authors that the applied current density has significant influence on the efficiency of the EC process [9,24].

Several preliminary studies were performed in order to establish a favorable value of current density for the EC process. Previous experience achieved on dye removal from aqueous solutions by conventional EC [18,25] helped us to establish the correct ranges for studying operating factors. Taking into account the active electrode surface, inter-electrode distance, and safe-operating limits of power supply, we considered a minimum level of 4.76 mA/cm^2 and a maximum of 42.86 mA/cm^2 for the current density factor. In this study, different values of current density applied were chosen to be applied during simple EC: 4.76, 11.9, 19.05, 28.57, 35.71 and 42.86 mA/cm^2. The current densities were maintained for different times as 20, 40, 60, 80, 100 and 120 min.

Figs. 2–4 depict respectively COD, turbidity and color removal efficiencies as function of electrolysis time, at different current densities.

It can be ascertained from Fig. 2 that the percentage of COD removal increased significantly with increasing current density from 4.76 to 42.86 mA/cm^2.

This can be explained by the fact that the amount of Al^{3+} species formed by dissolution of the anode, increases with the current density according to Faraday's law [25]. Higher amounts of dissolved aluminum allowed higher coagulation efficiency and more significant dye removal. One of the most

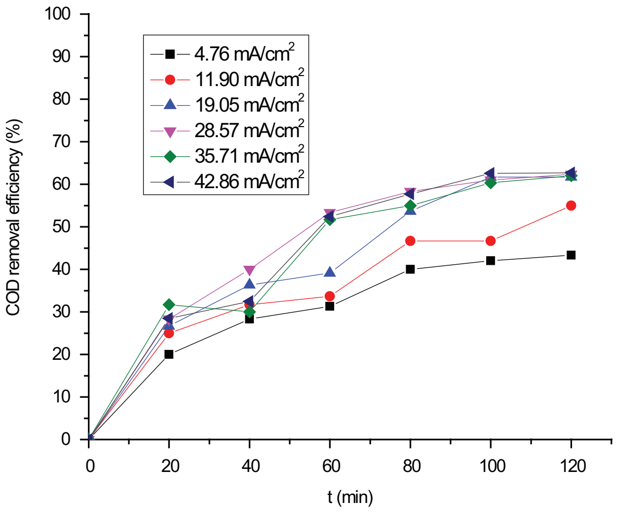

Fig. 2. Evolution of COD removal efficiency (%) from textile wastewater as function of electrolysis time at different values of current densities.

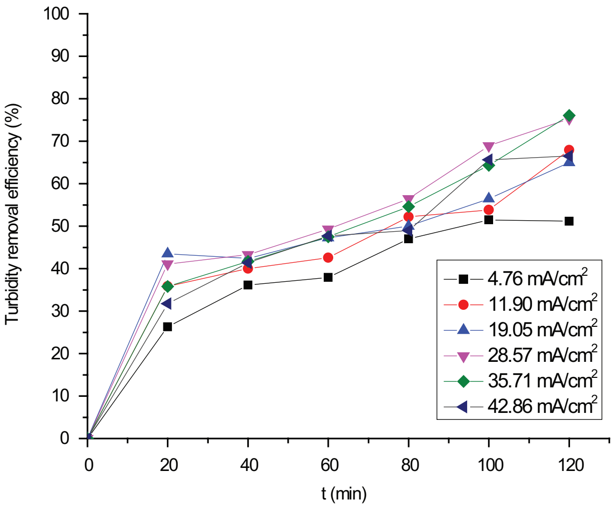

Fig. 3. Evolution of turbidity removal efficiency (%) from textile wastewater as function of electrolysis time at different values of current densities.

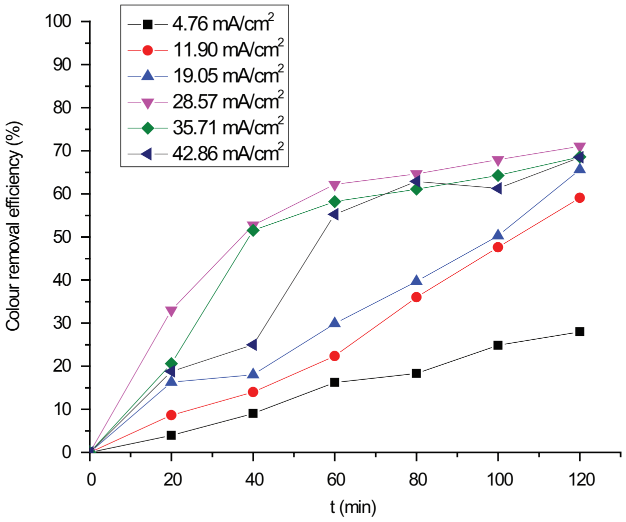

Fig. 4. Evolution of color removal efficiency (%) from textile wastewater as function of electrolysis time at different values of current densities.

important pathways of dye removal by EC is adsorption of dye molecules on metallic hydroxide flocs.

Moreover, higher production rates of hydrogen allowed by higher currents, favors the flotation of the flocculated matter. During electrochemical treatment, an increase in the gas bubbles density with reduction in their size and their growth of the flocs, enhances upwards flux resulting in increased pollutant degradation and sludge flotation [9,26]. Gas bubbles formed on the electrode surfaces play a role in flotation assisting the pollutant removal. Bubble formation and size depends on current density and surface of the electrode material.

However, it can be noticed that increasing the current density beyond 28.57 mA/cm^2 did not show any significant improvement in the percentage of COD removal.

Furthermore, as it can be seen in Fig. 2, the COD efficiencies were about 62.33%, at optimal current density of 28.57 mA/cm^2. This relatively low COD removal may indicate the low decomposition of dye molecules to small organic substance via electro-oxidation. It is probable that the adsorption capacity of metallic hydroxide flocs was not enough for dye adsorption [22].

Another explanation could be due to the presence of other anions which could interfere to the EC process and lower the dye removal efficiency in real colored wastewater.

Similar observation has been recorded for percentage of turbidity removal. In effect, as shown in Fig. 3, using aluminum as sacrificial anode, the removal efficiency of turbidity was effectively reduced to 74.43%, when current density increased from 4.76 mA/cm^2 to 28.57 mA/cm^2, after an operating time of 120 min. This shows that most of the particles that generated turbidity in textile wastewater were removed, forming a floating scum layer.

Han et al. [9,27] compared efficiencies of the EC with conventional chemical coagulation through a set of batch experiments. The authors concluded that the EC is more efficient than chemical coagulation for turbidity removal.

An increase in current density above the optimum current density does not result in an increase in the pollutant turbidity removal efficiency as sufficient number of metal hydroxide flocs is available for the sedimentation of the pollutant.

When too large current is used, cell voltage increases and there is a high chance of wasting electrical energy in heating up the water. More importantly, too large current density would result in a significant decrease in current efficiency [28].

The adsorption capacity of flocs is limited and specific amount of flocs is able to adsorb specific amount of dye molecules [29]. Therefore, with sufficiently high concentration of pollutants, amount of produced flocs is insufficient to adsorb all dye and particles pollutants molecules, therefore turbidity removal do not increase more.

Moreover, it was observed from Fig. 4 that 72.79% of color removal was achieved after 120 min of operation, for best current densities equal to 28.57 mA/cm^2. This was due to the fact that, the total amount of produced flocs was not enough to remove all the colored pollutant molecules in the solution and it required more time to achieve higher color removal efficiency.

Decolorization efficiency mainly depends on the amount of electrodissolution of cations, which is in direct proportion to the electric current through the electrodes and EC time, as the cell voltage is greater than the potential of O_2 evolution. For a hypothetical inter-electrode distance, color removal will be enhanced as the current density increases, resulting in the electrodissolution and formation of more aluminum species. Consequently, effective color removal is obtained by sweep flocculation on to a large dosage of aluminum flocs [3,30]. However, if enough bubbles evolve as the electric current increases (current density greater than 28.57 mA/cm^2) and adhere to the aluminum flocs causing them to float without adsorbing enough dyes, then insufficient color removal effectiveness is observed.

Increasing current density below 28.57 mA/cm^2, leads to increased generation of hydroxyl radicals OH^-, Cl_2, OCl^- and aluminum ions, this may evolve into aluminum polymers, resulting in increasing color removal. However, on increasing current density above 28.57 mA/cm², the rate of bubble generation increases and increased floc flotation occurs resulting in reduced dye adsorption [31].

Thus, it is advisable to limit the current density to avoid excessive oxygen evolution and to eliminate other adverse effects such as heat generation [32].

It is also well known that Cl^- anions can destroy the formed passivation layer on aluminum electrode and therefore enhance anodic dissolution rate of metal which lead to produce more aluminum hydroxide [13,33].

The removal of colored pollutant molecules during EC is due to the combined effect of chemical precipitation, co-precipitation, sweep coagulation and adsorption.

It has been established that the influence pH is an important parameter influencing the performance of the electrochemical process [34]. The effect of pH can be explained as follows.

At low pH, such as 2–3, cationic monomeric species Al^{3+} and $Al(OH)_2^+$ predominate. When pH is between 4 and 9, the Al^{3+} and OH^- ions generated by the electrodes react to form various monomeric species such as $Al(OH)_2^+$, $Al(OH)_2^{2+}$, and polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$ that finally transform into insoluble amorphous $Al(OH)_{3(s)}$ through complex polymerization/precipitation kinetics [34,35].

Two main mechanisms are generally considered: precipitation for pH lower than 4 and adsorption for higher pH. Adsorption may proceed on $Al(OH)_3$ or on the monomeric $Al(OH)_4^-$ anion depending on the pollutant chemical structure. The formation of $Al(OH)_{3(s)}$ is therefore optimal in the 4–9 pH range. When pH is higher than 10, the monomeric $Al(OH)_4^-$ anion concentration increases at the expense of $Al(OH)_{3(s)}$, which corresponds to the pH value of the investigated wastewater solution in this work.

Concerning salinity removal efficiencies, Figs. 5–7 show respectively the evolution of removal efficiencies of conductivity, salinity and TDS at different studied current densities.

As it can be noticed, conductivity, salinity and TDS presented a slight decrease as a function of the applied current density. For the whole range of electrolysis time, efficiencies percentages didn't exceed 33.29%, 33.15% and 33.88% for conductivity, salinity and TDS, respectively.

According to the results, depending on applied current density, conductivity was reduced as a result of electrochemical process. This decline was due to the fact that the electrolysis is accompanied by consumption of protons which are mainly responsible of the conductivity of the solution [36].

In addition, the conductivity decrease appears to result mainly from the salinity removal by EC. The salinity decrease

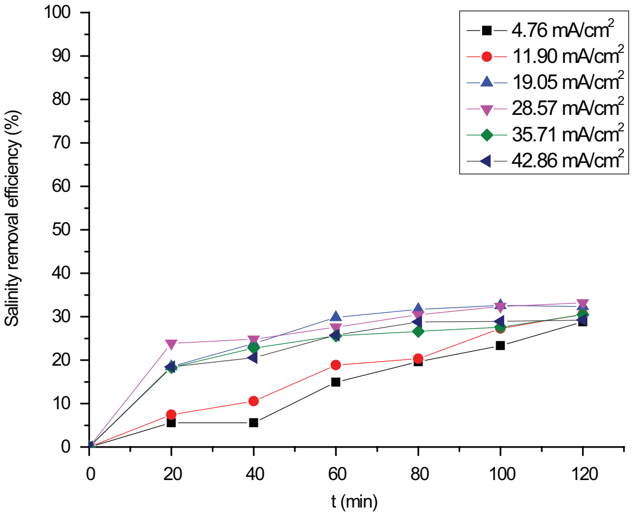

Fig. 6. Evolution of salinity removal efficiency (%) from textile wastewater as function of electrolysis time at different values of current densities.

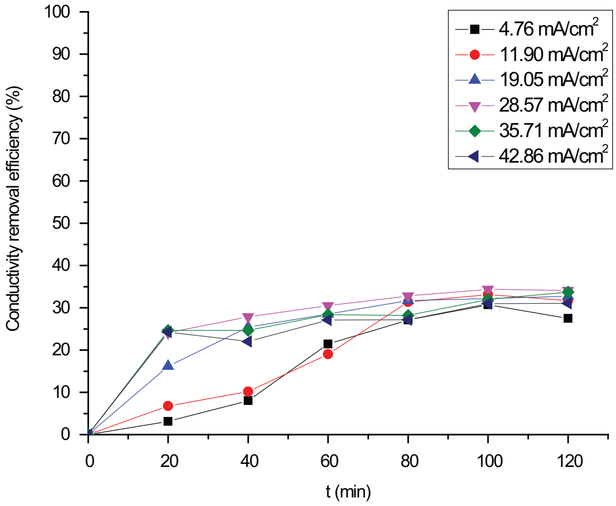

Fig. 5. Evolution of conductivity removal efficiency (%) from textile wastewater as function of electrolysis time at different values of current densities.

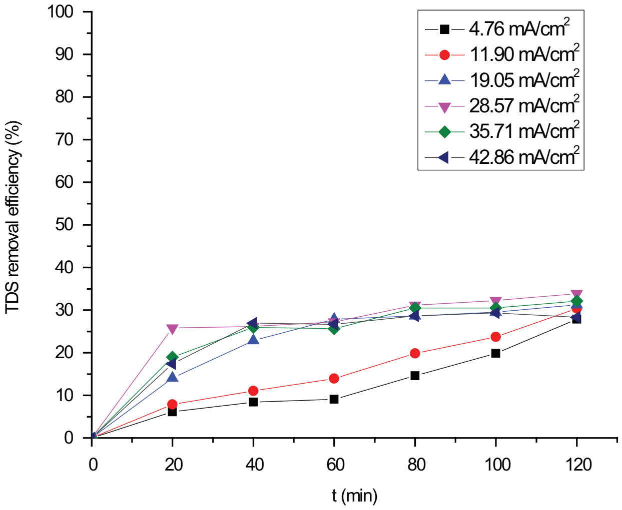

Fig. 7. Evolution of TDS removal efficiency (%) from textile wastewater as function of electrolysis time at different values of current densities.

is explained by the adsorption of anions and cations on the aluminum hydroxides and the precipitation of salts, such as $CaCO_3$, $CaSO_4$, $MgCO_3$ and $MgSO_4$ [37]. In fact, calcium and magnesium carbonate precipitate can then be incorporated in the aluminum hydroxide sludge. It is possible that the $CaCO_3$ and/or $MgCO_3$ precipitation and its probable co-precipitation with the other precipitates are involved in the mechanisms leading to the improvement of salt removal efficiency [38].

The partial removal of salinity was also attributed to more sweep flocculation in high pH conditions. Actually, more $Al(OH)_3$ was formed in alkaline environments, more flocs would be generated and more carbonate and sulfate salts would be trapped. In this way, hardness and consequently salinity were reduced as the precipitation settled down [39].

Therefore, in the following experimental investigations, to maximize removal efficiencies of the studied parameters, and considering the excess of electrical energy consumption for higher densities, the current density 28.57 mA/cm^2 was therefore applied as the optimum and the most appropriate current density.

3.1.2. Effect of electrolysis time

The EC time is an important factor due to its influence on the treatment efficiency of the EC process [13]. Therefore, several experiments in various operating times were carried out. EC time factor was investigated in the range of 20 min up to 180 min. The effect of electrolysis time was studied at optimum current density of 28.57 mA/cm^2. Removal efficiencies of all studied parameters as function of electrolysis time are given in Fig. 8. These efficiencies exhibit an explicit increasing trend with increasing of electrolysis duration till 120 min of operating time.

The pollutant removal efficiencies depend on dosage of aluminum, and dosage of coagulant depends on time of reaction. So, while one of two parameters increases, production of coagulants and flocs increase and pollutants are removed.

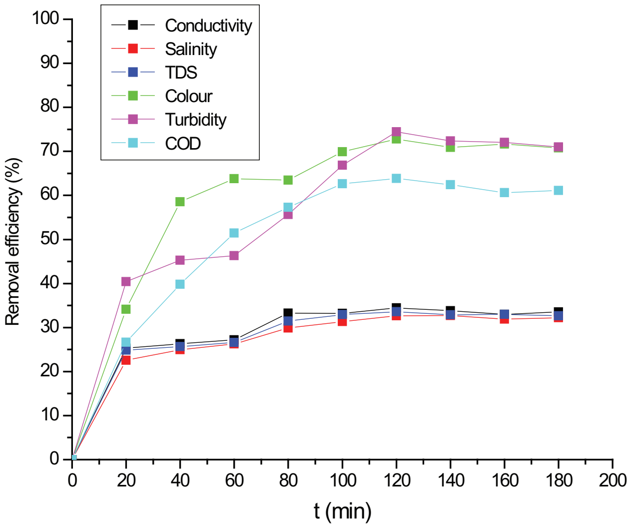

Fig. 8. Effect of electrolysis time on removal efficiency (%) of studied parameters at an optimum current density (J_{opt} = 28.57 mA/cm^2).

The time constants for each process, settling, and flotation are different. The time taken to settle is far greater than the time taken to float. Settling can be increased with larger aggregates which require a greater coagulant dosage. Likewise, flotation can be increased by increasing bubble density requiring an increase in current.

The dye removal efficiency depends directly on the concentration of metal ions produced on the electrodes. When the electrolysis period increases, the concentration of metal ions and their hydroxide flocs increases [13,40].

Above an optimum reaction time of 120 min, removal ratios almost reached maximum values and it stayed nearly constant in higher operation times. In fact, as it can be seen, for a fixed current density, removal efficiencies for all parameters did not increase obviously with a prolongation of the EC time beyond than 120 min. For a longer electrolysis time, there is an increase in the generation of flocs resulting in an increase in the pollutant removal efficiency. It can be said that, increasing the operation time increases the accumulation of dye residue causing passivization on cathode material. Thus, anodic dissolution diminishes and then metal hydroxide formation diminishes too [41]. As a result, the pollutant removal efficiency does not still increase as sufficient numbers of flocs are available for the removal of the pollutant.

With the current density of 28.57 mA/cm^2 and operating time of 120 min, the process needed no longer EC time to reach maximum efficiencies. Consequently, 120 min of operating time was chosen as the most appropriate electrolysis time for EC in this study.

After the completion of the EC process for a particular electrolysis time, the solution is kept for fixed period (retention time) to allow settling of the coagulated species. As the retention time is increased the removal efficiency of pollutant increases.

This is due to the fact that with an increase in retention time, all coagulated species settle down easily to give clear supernatant liquid and the sludge. But providing a retention time more than the optimum retention time results in the reduction of pollutant removal efficiency as the adsorbed pollutant desorbs back into the solution [42].

Based on the above results, a set of design parameters that was effective for treating the real textile wastewater was: current density of 28.57 mA/cm^2, an electrolysis time of 120 min.

3.2. Optimization of combined EC/GAC process

3.2.1. Effect of adsorbent dose

In this work, adsorption process was applied to the solutions treated under optimal conditions by EC.

The results of the EC/GAC coupling experiments were presented in the following graph in Fig. 9 that shows the variation of removal efficiencies of studied effluent at different GAC adsorbent doses to the EC setup, for a contact time of 120 min, demonstrating the influence of the amount of GAC on the removal efficiency. The adsorbent concentration was varied from 0.05 g/L to 3 g/L in steps of 0.25 g/L.

In the kinetic study of GAC-enhanced EC, it can be observed that with increasing adsorbent dose, the percent removal efficiencies of COD, color and turbidity increased substantially. From the very beginning of the EC/GAC

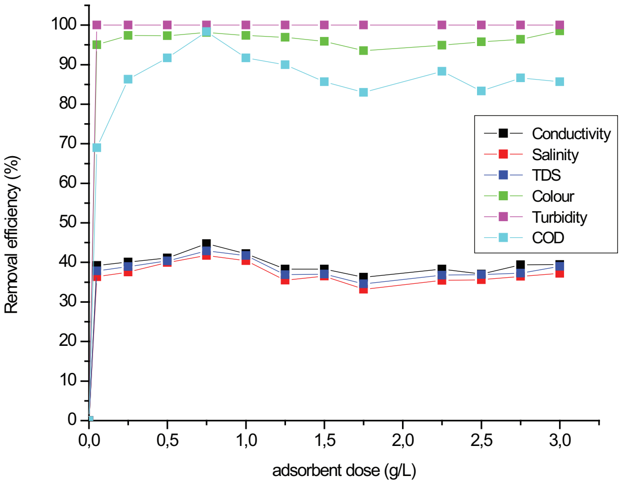

Fig. 9. Evolution of removal efficiency of different studied parameters as function of adsorbent concentration (J_{opt} = 28.57 mA/cm^2, t_{opt} = 120 min, contact time = 120 min).

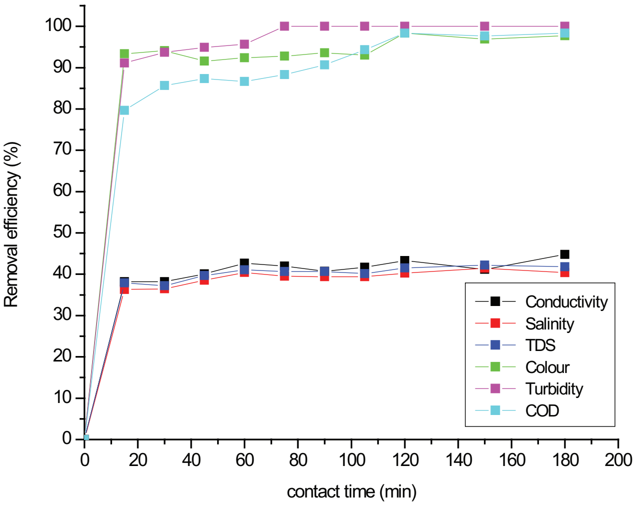

Fig. 10. Evolution of removal efficiency of different studied parameters as function of contact time (J_{opt} = 28.57 mA/cm^2, t_{opt} = 120 min, optimum adsorbent dose = 0.75 g/L).

coupling process, it can be seen that adding low amounts of GAC, for example, 0.05 g/L is the minimum dose where there is a significant improvement of the constant rates values compared to that obtained in the case of conventional EC. In fact, removal rates of 69%, 95% and 100% were obtained respectively in terms of COD, color and turbidity.

At an adsorbent dose of 0.75 g/L, removal efficiencies were found to be maximum. This sufficient dose allowed that GAC adsorbs most organic pollutants molecules and increased significantly COD to 98.33% after 120 min adsorption. This is because GAC can act as catalyst to chemically reduce strong oxidants to nontoxic products.

In case of the response of color removal efficiency, the highest enhancement of decolorization was obtained at 98.12%, for all the range of adsorbent dose. Turbidity of pollutants was completely removed at 100%. Increase in adsorption with adsorbent dose can be attributed to increase in adsorbent surface area and availability of more adsorption sites.

However, an increase in the same dose to 0.75 g/L did not further reduce conductivity, salinity and TDS rates and seems to have only a slight effect on removal efficiencies of these parameters, comparing with those obtained in the case of simple EC process. These percentages achieved only 43.29%, 40.35% and 41.5%, respectively.

This suggests that a slight amount of salts present in the textile effluent solution was not effectively removed by GAC.

However, the addition of a quantity of GAC higher than 0.75 g/L, maintaining the other parameters constant, has a negative influence on all removal efficiencies as it results in a decrease in the constant removal rates values.

The GAC has efficient role in the EC/GAC coupling to improve the removal of COD, color and turbidity. Therefore, its addition of adsorbent enhances the process of EC.

GAC dose is more significant in the case of a high value of pH, which is due to the residual acidity of GAC charcoal vegetal; taking into account that most textile effluents are of an alkaline character [18,43] and that effluent treated by EC result in higher value of pH. From those results, it was found that the optimum value of adsorbent dose is 0.75 g/L.

3.2.2. Effect of contact time

In the EC/GAC process, the variation in percentage removal efficiencies was studied at desired values of contact time varying between 20 min and 180 min, while other optimum parameters were kept unchanged (current density = 28.57 mA/cm^2, electrolysis time = 120 min and adsorbent dose = 0.75 g/L). The experimental results are presented in Fig. 10.

It is illustrated from that figure (Fig. 10) that removal rates increased with increase in shaking or contact time and reached a plateau, so that adsorption equilibrium was attained and established in around 120 min (for residual water after Al-EC). For a given value of 0.75 g/L of adsorbent dose, 120 min was sufficient for maximum removal efficiencies.

As it can be shown, complete and maximum removal of COD, color and turbidity was observed just after 120 min. The same observations were made in the case of conductivity, salinity and TDS removal efficiencies, even the maximum removals obtained did not exceed 43%, 40% and 41%, respectively. This equilibrium can be explained that the available adsorption sites available were sufficient in the beginning. As the process goes on and when contact time was greater than 120 min, the adsorption sites became saturated gradually. These deadlines were sufficient to give the maximum adsorption of the organic matter.

Contact time is very influential parameter on adsorption of organic matter concentrations. Short contact time appears insufficient, because it does not allow the formation of the physicochemical bonds between the organic matter and the adsorption sites of the solid phase. In addition, a longer contact time causes the release of certain fixed organic matter amounts [44].

Based on the experimental results, the optimum contact time to achieve the maximum efficiency is 120 min.

Table 3
Summary of the main characteristics of water treated by EC treatment and by conventional EC/GAC[a]

Parameters	After conventional EC process	After EC/GAC process
Conductivity (mS/cm)	4.31	3.73
Salinity	2.29	2.03
TDS (g/L)	2.39	2.10
Color	0.33	0.02
Turbidity (NTU)	47.05	0.00
COD (mg/L)	433.80	20.04

[a] Error limits of parameters are less than ±10%.

Under the optimal operating conditions: current density = 28.57 mA/cm^2, electrolysis time = 120 min, adsorbent dose = 0.75 g/L and contact time = 120 min, the final characteristics of the treated wastewater are shown in Table 3.

Table 3 compares also the properties of the textile effluent after EC treatment process and after combined EC/GAC treatment process.

Comparing the experimental results after treatment of real textile wastewater by single EC process and by EC/GAC process, it can be seen that hybrid coupling EC/GAC was necessary as it presented better performances than a single EC pretreatment step in terms of color abatment (about 98%), COD reduction (98%), turbidity removal (100%) after hybrid coupling EC/GAC, whereas after single EC pretreatment, these parameters did not exceed 72%, 74% and 62%, respectively, in terms of color, turbidity and COD removals. Concerning salinity rate decrease, combined EC/GAC process showed similar results (40%) comparing with simple EC process (33%).

The great and remarkable reductions of the color, COD and turbidity after EC/GAC combined coupling show that this hybrid process is a technique of choice for the clarification and purification of textile wastewater.

In comparison with conventional techniques, the present method achieves faster removal of pollutants. Hence, coupling of different mechanism to develop hybrid treatment process, may pave way for a new dimension in the field of water treatment.

4. Conclusions

The treating of raw colored textile wastewater by EC/GAC process using aluminum electrodes was strongly and significantly affected by the current density, electrolysis time, adsorbent dose and contact time.

EC/GAC hybrid process operation is completely successful, under the optimal operating conditions, to improve the quality of primary wastewater treatment not only in terms of COD removal efficiency response but also in color and turbidity removal, especially when the treated effluent has proper conductivity that favors the electrophoretic transport.

In terms of conductivity removal, this combined process did not significantly decrease salinity rate and presented limitations in terms of removal efficiencies. However, EC/GAC combined process might prove a judicious choice for treating textile wastewater with mixtures of pollutants and it seems appropriate to assure sufficient water quality required by textile finishing processes.

In accordance with Tunisian standard of treated wastewater for irrigation (NT 106.03), the final treated quality obtained of treated textile wastewater is satisfactory and suitable for reuse/recycle inside the textile factory, discharge to saline surface water and even to dispose it directly into receiving water to the environment. Wastewater is then not considered as waste but as a resource of water, of energy, or of chemicals.

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