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The applicability of combined physico-chemical processes for treatment and reuse of synthetic textile reverse osmosis concentrate

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ABSTRACT

The purpose of this research aims to investigate the feasibility of combined processes by applying electrocoagulation (EC), electrofenton (EF) enhanced by electrodialysis (ED) for treating a synthetic textile reverse osmosis (RO) concentrate stream, using different concentrations of dyes (mixture of reactive red 70% and reactive orange 30%) and monovalent NaCl salt. Firstly, single degradation step was integrated using aluminum and iron electrodes respectively for EC and EF, to reduce COD and color, under operating parameters such as electrolysis time, current density, pH, interelectrode distance and peroxide dosage. Secondly, ED was applied for desalination step. Finally, cost analysis was made according to sludge removal, chemicals, electrodes and energy consumptions, for all systems. Hybrid EF/ED and EC/EF/ED were found as effective and economically feasible for treating RO concentrate, as they presented similar results and the best removal efficiencies (total decolorization, 98 and 99.2% COD, 92 and 94% salinity, respectively). As regards hybrid EC/ED, COD, color and salinity abatement rates did not overpass 58, 86 and 40%, respectively. Moreover, by implementing EF, operating cost (2.41 US$/m^3) was slightly low comparing with EC (3.56 US$/m^3), and therefore cost analysis proves EF was economically more efficient than EC. EF/ED process was suitable in reducing ED membrane fouling and improving deionization efficiency of the treated RO brine, which facilitates its direct discharge or reuse.

Keywords: Electrocoagulation (EC); Electro-Fenton (EF); Electrodialysis (ED); Combined process; Reverse osmosis (RO); Textile RO concentrate

1. Introduction

Reverse osmosis (RO) is a widely used membrane process with its great improvement in water treatment, cost reduction and increased flux and selectivity with reduced fouling. In the textile industry, the diluted exhausted dye baths are treated by RO process. These baths contain high concentrations of dyes, additives and salts. The reuse of RO permeate as a process water for dyeing or rinsing is usually possible [1–3].

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RO concentrate is a highly charged stream which contains high concentrations of organic and inorganic compounds. Generally, it is not possible to discharge directly or recycle dyes or other chemical because of complexity of the concentrate composition and also owing to the components modification [1]. Thus, the treatment of RO concentrate presents one limitation for RO application in textile wastewater treatment. Conventionally, concentrated stream produced from RO treatment is equivalent to 5–25% of feed brine and 4–20 times of feed water in concentration, which leads to an increase in the electrical conductivity and chemical oxygen demand (COD) [4,5]. This will result in reducing the efficiency of RO process due to the risen fouling of RO membranes [6,7]. In addition, due to the high pollutants concentration in the resulting RO concentrate, its direct discharge into surface water will cause serious ecotoxicological risks and environmental impacts [2]. Therefore, a suitable physicochemical process is urgently needed for the efficient abatment of RO concentrate [8–11]. Traditional treatment methods such as biological processes are not suitable and efficient for RO concentrate treatment as the contaminants are not easy to be treated, due to the persistant organic pollutants such as synthetic dyes that are hardly biodegradable and also because of the elevated salinity presented [8,11].

EC is an alternative electrochemical technique for water and wastewater treatment systems and efficient mostly in removing organic and inorganic pollutants and pathogens [11–14]. Compared with conventional chemical coagulation, electrocoagulation presents many advantages such as simple equipment, easy operation and automation, a short electrolysis time, relative acceptable amount of sludge production and no chemical requirement. EC is a process based on destabilization of suspended, emulsified, or dissolved pollutants in an aqueous solution, contacting the field of electric current [14]. Different types of materials can be used for the anodes, such as Pt, TiO_2, Al and Fe which are the most frequently used electrodes in EC process [12]. Moreover, with regard to RO brine, Fenton treatment (H_2O_2/Fe^{2+} system) is an advanced oxidation process and seems to be the most promising technique for degrading non-biodegradable organic compounds, in terms of reduced toxicity of reagents, high mineralization efficiency, and ease of operation [15,16].

A typical Fenton wastewater treatment process has four different stages-oxidation, neutralization, coagulation/flocculation and solid-liquid separation [17]. The ferrous/ferric ions can serve as catalyst and react with hydrogen peroxide to form a strong oxidizing agent (hydroxyl radical) with a determined oxidation potential and thus Fenton reaction can take place in the bulk solution in the presence of ferrous ions [18]. Besides to oxidation mechanism, in Fenton process, similarly to EC process, the ferrous/ferric ions can serve as a coagulant. Fenton's coagulation is mainly simple ferric coagulation to follow the oxidation step [19]. Electrochemical degradation techniques profit from the enhanced salt content of RO brines, which results in a better electrical conductivity compared to conventional wastewater. Minghua et al. [8] applied EF process to degrade organics from steel plants RO concentrate stream and more than 62% COD removal after 3 h of treatment were obtained. Van der Bruggen et al. [1] found that hydrogen peroxide combined with Fe^{2+} ions is an effective proven method for textile wastewaters pressure driven (RO and NF) membrane brines. However, EC and EF processes are not appropriate to remove salt ions in RO concentrate stream. Therefore, additional processes which are efficient in desalination, such as electrodialysis (ED) are required.

Electrodialysis (ED) is a widely applied desalination technology for brakish and saline waters. ED is an electromembrane process in which ions are transported through ion exchange membranes from one aqueous solution to another by medium of an electric field as driving force [20,21]. ED shows technically and economically remarkable advantages, as a reagent-free, environmentally friendly, power saving process, with a high rate of initial water recovery [22]. Recently, electrodialysis (ED) was reported to be a good and effective option to treat RO concentrate stream, to improve RO/ED water recovery above 95% [23] and to reach a "near zero liquid discharge approach" [24].

The purpose of this study was mainly to set up and investigate the degradation performance and efficiencies of different hybrid combined processes (EC/ED, EF/ED, EC/EF/ED) for the abatment of color and COD and also for salts removal from an RO synthetic textile concentrate. Firstly, the feasibility of removing organic pollutants (COD, color) from high-salinity RO concentrate by electrochemical (EC) and electrochemical oxidation (EF) processes to meet the local environmental discharge requirement, was studied. For the treatability evaluation of the coupling processes, optimization of experimental conditions (current density, electrolysis time, pH, interelectrode distance and hydrogen peroxide H_2O_2 concentration) was achieved (by applying single EC and EF processes) to investigate the effects of these operating parameters on color and COD removal percentage. Secondly, electrodialysis was used in this study to remove salts of monovalent NaCl ions from synthetic RO concentrate in an effort to alter the salt composition to bring water quality to agricultural irrigation use or an increase in current flow. Experiments of combined processes were carried out under optimum operating parameters in which processes had their highest efficiencies, to reduce salinity by ED process. Finally, operating cost analysis study including energy consumption of applied processes has been achieved.

2. Materials and methods

2.1. Chemicals

In this study, almost all chemicals, including the model textile reactive red 120 dye, were procured from Merck company (Germany). The commercial available reactive orange 16 dye was provided from Sigma-Aldrich. All chemicals and reagents were used as received without further purification.

2.2. Synthetic model solutions

Commercial reactive red 120 and reactive orange 16 dyes, available in powder form, were used in this study. Reactive orange 16 ($C_{20}H_{17}N_3Na_2O_{11}S_3$), a highly soluble dye, with a molecular weight equal to 617.54 g/mol, has two sulfonate groups which present negative charges in an aqueous solution. Reactive red 120 ($C_{44}H_{24}Cl_2N_{14}Na_6O_{20}S_6$), with a molecular weight of 1,469.98 g/mol and a water solubility of 70 g/L, has six sulfonate groups. These groups present negative charges even in highly acidic solutions as their pKa values are lower than zero [25]. Both reactive dyes have a maximum wavelength λ_{max} equal to 494 nm.

The main characteristic structural features of a typical reactive dye molecule are [26]:

- the reactive system, making the dye able to form covalent bonds with the cotton fiber; the chromophoric group, responsible of the color and much of its for cellulose.
- a bridging group that joins the reactive system to the chromophore; solubilizing groups that facilitate the solubility of dye in water.

In this study, pollutants of synthetic RO concentrate were found in the dye/salt mixture. As it is known in textile industry, without the addition of salt, the adsorption of dye to fiber will not occur.

Firstly, to simulate dye-salt bath effluents from dyeing processes with azo reactive dyes and NaCl salt, the dye and salt concentrations were assumed as 500 mg/L and 600 mg/L, respectively. Then, nine different synthetic solutions of dye-salt RO concentrates were prepared with a mixture of reactive red 120 (30%), reactive orange 16 (70%) dyes and sodium chloride (NaCl) salt. The concentrations of dyes (1,600 ppm, 2,500 ppm, 5,000 ppm) and salts (1,500 ppm, 2,000 ppm, 3,800 ppm) were chosen for preliminary studies as these correspond approximately to the real concentrations of a real textile wastewater RO concentrate (synthetic RO stream concentration was chosen as equivalent to 4–5 times of the feed brine concentration, which is assumed as 500 mg/L and 600 mg/L, respectively for dye and salt concentrations).

These concentrations of synthetic RO concentrate solutions were obtained using this formula:

$$[Y]_c = \frac{[Y]f - \frac{pr}{100} x [Y]_p}{1 - \frac{pr}{100}} \quad (1)$$

where $[Y]_c$, $[Y]_f$, and $[Y]_p$ means respectively salt or dye concentration of concentrate stream, feed stream (which was assumed as 500 mg/L and 600 mg/L, respectively) and permeate stream; Pr represents specific permeation rate and was selected as 70%, 80% and 90%.

The physicochemical characteristics of the prepared nine solutions are shown in Table 1.

A desired amount of reactive dyes and salts was accurately weighed and working solutions were obtained by diluting successively with deionized water, at room temperature, of the dye stock solution to the required concentrations. The dye was easy to dissolve in water and only a simple mixing was sufficient to achieve its complete dissolution in water. The stock solution was kept in a cool dark room to avoid possible decolorization by light until use. Natural pH of solutions was kept and no adjustment has been required.

2.3. EC and EF processes

EC and EF experimental studies were carried out with RO synthetic concentrate samples and pretreated EC samples (for EF treatment), which were placed into the electrochemical cell, in a 0.5 L glass-made batch reactor, equipped with a cathode and anode as working electrodes, both of which, made of aluminum (during EC experiments) and iron (during EF experiments) and installed in parallel.

Electrodes dimensions were 7.2 cm × 6 cm × 0.1 cm, with a total effective electrode area of 43.2 cm^2. The electrodes placed in monopolar connection mode were supplied from a digital DC power source (GW INSTEK GPD 330S; 0–30 V, 0–3 A).

Before each run, aluminum electrodes were washed with acetone and the impurities on the aluminum electrode surfaces were removed by dipping for 3 min in a sodium hydroxide solution (5 mol/L) to form $Al(OH)_3$. Just after, they were washed by pure water and redipped for 5 min in a freshly prepared solution of HCl (3 mol/L) to obtain pure aluminum electrodes. A second wash with pure water was made. For the maintenance of iron electrodes, only hydroxide sodium washing step was not applied.

Table 1
Physicochemical parameters of different nine synthetic textile RO concentrate solutions[a]

Solutions	[Dye] (mg/L)	[NaCl] (mg/L)	pH	Conductivity (mS/cm)	COD (mg O_2/L)	Color (Pt-Co) (mg/L)
1	1,600	1,500	5.86	3.7	1,336	4,763
2	1,600	2,000	5.86	4.5	1,312	4,752
3	1,600	3,800	6.92	7.42	1,328	4,645
4	2,500	1,500	6.41	4.16	2,080	8,2225
5	2,500	2,000	5.27	4.84	2,078	7,645.66
6	2,500	3,800	5.3	7.9	1,810	8,050
7	5,000	1,500	5.26	5.47	3,850	16,200
8	5,000	2,000	6.22	6.25	3,700	15,450
9	5,000	3,800	5.9	9.25	3,976	14,505

Sol*: Solution, [Dye]*: Dye concentration, [NaCl]*: NaCl concentration. [a] Error limits of parameters are less than ± 10%.

Experiments were performed using a constant magnetic stirring (250 rpm, Heidolph MR Hei-Mix D model). All runs were performed at room temperature and the sample temperature was controlled to the ambiant value of 25°C by adjusting the rate of water flow through an external glass-cooling spiral.

In both EC and EF processes, firstly, an optimization step of operating parameters was run. Applied current density and interelectrode distance were varied from 11.6 mA/cm^2 to 69.5 mA/cm^2 and from 0.5 cm to 3 cm, respectively.

Regarding electrolysis time and pH, during EC experiments, these parameters were modified from 15 min to 120 min and from 3.5 to 9.5, respectively. For EF experiments, the variation ranges was from 20 min to 120 min and 1.55 to 5, respectively.

Concerning EF experiments, hydrogen peroxide H_2O_2 concentrations were varied from 998 to 4,994 mg/L.

In Fenton's reagent, the H_2O_2 dosage was referred to as the stoichiometric weight ratio between the hydrogen peroxide and COD, $R = H_2O_2/COD = 2.125$.

Thus, the working range of hydrogen peroxide concentrations was chosen taking in consideration the mentioned stoichiometric weight ratio.

In the first step of fenton's oxidation process, pH of the RO synthetic textile wastewater was adjusted to the desired value 2.8 prior to the experiment, by adding H_2SO_4 (0.1 M). Then, before electrical current was turned on, an appropriate amount of H_2O_2 was added to the sample reactor. The current density was adjusted to a desired value, and then electrolysis was started and kept on until all H_2O_2 was consumed.

After the oxidation and flocculation processes, in order to prevent interferences in analytical measurements, the pH of collected supernatant sample was increased to about 8.0 by adding NaOH gradually to precipitate Fe^{2+} ions in the form of $Fe(OH)_3$.

After each EC and EF trial, samples were withdrawn at predetermined and appropriate intervals, and then left settling for 12 h. Then, the collected liquid phase or supernatant of the beaker was taken out and filtered using a 35 µm filter paper. Just after, to determine the efficiency of EC and EF processes, COD and color were analyzed.

At the end of the experiment, the electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried and reweighed.

2.4. ED process

The electrodialysis based desalination process was carried out for RO synthetic textile wastewater solutions, pretreated by EC, EF and EC/EF using a labscale electrodialysis apparatus. The electrodialysis cell used was the PCCell B-ED 1–3 Cell unit obtained from the PCCell GmbH, Germany.

During desalination process, the ED system was operated in a batch configuration mode. The process was stopped when conductivity in the feed stack was not high sufficiently to keep constant the desired voltage.

The laboratory scale ED set up consisted of a membrane stack, three separated circuits having the flow for three compartments (feed, concentrate, and electrode rinse) and the electrical power. Separate centrifugal gear electrodialysis pumps were used to circulate each of the three process streams. The flow rate through each stream was monitored continuously. The flow was controlled using Stübbe digital liquid flowmeter. The brine flow rate through the ED stack was 60 $L\cdot h^{-1}$ in the concentrated and diluted compartments and the electrolyte rinsing chamber ran 0.257 M (3 mS/cm) NaCl solution. During all experiments, a temperature control system maintained the solution temperature at ±25°C. The volume of the feed stream container was 1.5 L and the volume of the concentrate stream tank was 1 L. A variable power source (0–25 V; 0–5 A) model 2224.1, Statron, supplied a desired fixed voltage in the stack. The ED desalination experiments were performed at a constant voltage of 10 V.

During the ED experiments, one cell pair in the stack (1 standard PCA cation exchange membrane and 2 PCA anion exchange membranes, supplied by the PCA-Polymerchemie Altmeier GmbH und PCCell GmbH, Germany) were used. The effective surface area was 64 cm^2 for each membrane. The membrane stack was connected to the DC electrical potential through TiO_2-coated titanium electrodes.

2.5. Operating cost analysis

One of the most important parameters that affect the application of any method of wastewater treatment greatly is the cost. In this preliminary economic study, sacrificial electrodes, produced sludge, chemicals and energy costs are taken into account in the calculation of the operating cost, as US$ per m^3 of wastewater treated or US$ per kg of COD removed [27].

Aluminum and iron electrodes and produced sludge costs are relative to EC and EF processes, chemicals concern EF process and energy costs concerns EC, EF and ED processes. Other cost items such as power supply device, maintenance, sludge dewatering and disposal are assumed fixed and are not included in the calculations.

$$\begin{aligned} \text{Operating cost} = {} & a\,C_{energy} + b\,C_{electrode} + c\,C_{chemicals} \\ & + d\,C_{produced\ sludge} \end{aligned} \tag{2}$$

where C_{energy} (kWh/m^3 of wastewater treated or kWh/kg of COD removed) is energy consumption; $C_{electrode}$, $C_{chemicals}$ and $C_{produced\ sludge}$ are consumed electrodes, chemicals and produced sludge consumptions (kg/m^3 of wastewater treated or kg/kg of COD removed) [28].

Unit prices, *a*, *b*, *c* and *d* are obtained from Turkish market, October 2017, as follows; (a) electrical energy price (0.057 US$/kWh), (b) electrode material price (0.3 US$/kg for iron and 1.3 US$/kg for aluminum) (c) cost of chemicals (0.045 US$/kg for H_2O_2, 0.2 US$/kg for NaOH and 0.186 US$/kg for HCl), (d) cost of produced sludge (0.067 US$/kg). The operating costs were calculated on the basis of US$/$m^3$.

For both EC and EF processes, to estimate the amount of aluminum and iron electrodes dissolved, experimental anode consumption was calculated from the differences between initial anode and final anode masses following the next equation (3):

$$W_{exp} = W_{initial} - W_{final} \quad (3)$$

where W_{exp}, $W_{initial}$ and W_{final} represent experimental anode weight or the amount of dissolved anode material, initial anode weight before EC or EF electrolysis process and final anode weight after EC or EF electrolysis process, respectively.

In addition, samples were filtered after EC and EF treatment, by predried 35 µm coarse filter paper (during one hour at 105°C). After filtration, filters were dried again and weighed. From the differences between the last and first weight values, the formed quantity of produced sludge was determined with relation (4):

$$W_S\,(\mathrm{g/L}) = (W_{F+R} - W_F)/V_{sample} \quad (4)$$

where W_S is the weight of produced sludge, W_{F+R} is the weight (g) of both filter and residue, W_F is the weight (g) of filter and V_{sample} is a volume of filtered sample (L).

The electrical energy consumption were determined according to equation (5) [27]:

$$E = (U\,I\,t)\,/\,V \quad (5)$$

where E, U, I and V are electrical energy consumption (kWh/m^3), voltage (V), current (A), time of reaction (h), and the volume of solution (L), respectively.

Operation cost during wastewater treatment processes includes cost of electricity, chemical reagents, cost of sludge disposal, labors, maintenance, and equipments. In electrochemical process the most important parameters that affect operating cost are cost of electrode material and consumed electrical energy. Thus these items are calculated in this research to determine operating cost:

2.6. Analytical methods

In this study, pH was measured by WTV 3110 pH meter and salt concentration in diluate and concentrate was indirectly and proportionally determined by measuring the solution conductivity using HQ40D conductivity meter, respectively.

COD was analyzed using the closed reflux titrimetric method given in standard methods 5220 C [29]. Chemical oxygen demand (COD) was determined by the dichromate method. The desired amount of sample was introduced into a commercially available digestion solution containing potassium dichromate, mercuric sulfate and sulfuric acid. The mixture was then refluxed and incubated during 120 min at 150°C in a COD reactor (Model DRB 200 45600-Hach Company, USA). After refluxing, the remaining dichromate was titrated with ferrous ammonium sulfate, using titroline easy titrator, in presence of ferroin indicator.

The color intensity (Pt-Co) of feed and permeate samples was analyzed by a Hach Lange DR 5000 UV-Visible spectrophotometer to measure reactive red 120 and reactive orange 16 dyes mixture absorbance. The concentration of organic mixed dyes in both diluate and concentrate was determined spectrophotometrically at maximum absorbance wavelength (λ_{max} = 494 nm), from a calibration curve of absorbance versus concentration and concentration values were used for calculations of decolorization efficiency.

Duplicate experiments were carried out and all used data were mean values of two replicate determinations.

The general abatement rate for the synthetic RO treatment was calculated using the following equation:

$$A\,(\%) = 100 \times (1 - X_{treated}/X_{feed}) \quad (4)$$

where A (%) represents the abatement rate, $X_{treated}$ and X_{feed} represent the measured operating parameters (COD, color, dye concentration, conductivity and salt concentration) respectively, in the treated and the feed streams.

3. Results and discussions

3.1. Optimization of EC, EF and ED operating parameters

3.1.1. Optimization of EC and EF

The study was performed to determine the effects of operating parameters on COD and color removal in order to achieve the best removal efficiencies.

During EC and EF optimization processes, intermediate concentrations of dye and salt were chosen as 2,500 mg/L and 2,000 mg/L, respectively.

Time optimization experiments for EC and EF were carried out for different series of six electrolysis times, i.e., (15, 30, 45, 60, 75, 90 and 120 min) and (20, 40, 60, 75, 90 and 120 min), respectively.

During EC treatment, the time effect was studied under the following experimental conditions: current density J = 46.3 mA/cm^2, pH = 6.7, interelectrode distance = 1 cm. Meanwhile, during EF experiments, time effect was studied at the following constant operational conditions: current density J = 46.3 mA/cm^2, pH = 2.8, interelectrode distance = 1 cm, hydrogen peroxide concentration = 3,996 mg/L.

The evolution of COD and color removal efficiencies (%) during the operational period of electrolysis, for EC and EF processes was studied.

Experimental results related to EC process showed that COD decreased with increasing operation time. During EC treatment, COD removal rate increased gradually from 47% to a maximum percentage of 65% for an applied current density of 46.3 mA/cm^2, when the time increased from 15 min to 90 min. This increase in COD removal with increasing electrolysis time is caused by the adsorption of organic matter (dye mixture) on the $Al(OH)_3$ flocs formed in solution. From 90 min to 120 min of EC treatment, COD removal takes place, but it did not exceed 65% and decreased to 47%, due to desorption or oxidative degradation of organic matter particles.

As regards EF process, this process was more efficient in terms of COD removal than EC. In fact, COD removal occurred in the first 20 min when the rate of dye removal was very fast, as COD removal reached already 61%. This result demonstrated that organic materials were rapidly degraded by EF method [30]. After 40 min, the decrease of residual COD slowed down to reach maximum rate of 85% when the reaction was nearly completed at 60 min. Over one hour of EF treatment, COD removal decreased to 79%.

During electrolysis, the positive electrode is the area of anodic reactions while cathodic reactions occur on the negative electrode. The particle charges are neutralized by the released ions and thereby initiation of coagulation occurs. The dissolution of the anode enhances the formation of the metal hydroxides. For a fixed current density and upon increasing the treatment time, there is an increase in the ions concentration and the generation of their hydroxide flocs, resulting in an increase of the pollutant removal efficiency. Consequently, with an increase in the electrolysis time, the removal of dye efficiency increases [31]. But beyond the optimum electrolysis time, the pollutant removal efficiency does not increase with an increase in the electrolysis time.

The color removal efficiency depends directly on the concentration of ions produced by the electrodes. Accordingly, an increase from 15 to 90 min yields an increase in the color removal from 45% to 97%, during EC treatment. After 120 min, color removal efficiency decreased to 88%. Besides, after only 20 min of EF treatment, color reduction reached around 85%. A maximum color removal rate (100% decolorization efficiency) was attained at the current density of 46.3 mA/cm^2 at treatment time of 40 min, by EF electrolysis process. Beyond 120 min of treatment, color removal rate is kept constant. The experimental results showed that the color removal efficiency was significantly affected by electrolysis time. This behavior can be explained by the fact that the treatment efficiency was mainly affected by charge loading [12,32]. By using aluminum electrodes, highly charged poly-nuclear hydroxy aluminum and iron complexes were formed and could make coagulation of colloidal solids, which enhances the removal of color in the treated solution [33,34]. The removal of color may involve physically adsorption by these hydroxyl aluminum complexes and thus alter some of substituents, which determine the color [12,35].

According to Faraday's law, electrolysis time also affects the treatment efficiency of the electrochemical process as it may increase or decrease with current density [36].

Based on previous results, for further experiments, the electrolysis time for the EC and EF treatment processes was determined to be 90 min and 60 min, respectively. Then, optimizing electrolysis time became an important operating parameter for avoiding higher energy consumption and high process costs.

3.1.2. Current density

During EC treatment, the effect of current density was studied under the following experimental conditions: optimum electrolysis time = 90 min, pH = 6.7, interelectrode distance = 1 cm. As regards EF experiments, the current density effect was studied at the constant operational conditions: optimum electrolysis time = 60 min, pH = 2.8, interelectrode distance = 1 cm, and hydrogen peroxide concentration = 3,996 mg/L.

The effect of the current density on color and COD removal efficiencies for the treatment of RO synthetic concentrate, in EC and EF processes was studied. Current density was varied in range of 11.6–69.5 mA/cm^2.

Experimental results indicated that in both EC and EF processes, significant improvements in COD removal efficiencies (55% in EC and 64% in EF) were observed at 11.6 mA/cm^2. Then, COD removal efficiencies were slightly improved from 55% to 65% during EC treatment and were increased gradually from 64% to 80% during EF process at 90 min and 60 min when the current density was varied from 11.6 to 46.3 mA/cm^2 and from 11.6 to 23.15 mA/cm^2, respectively. More COD was removed when current increased, indicating an enhancement of the degradation power.

From 46.3 to 69.5 mA/cm^2, no noticeable changes in terms of COD removal were observed in EF process. From 23.15 to 69.5 mA/cm^2, a decline of COD reduction from 65% to 53% was observed in EC process. The current density played a significant role on the COD removal. Thus, current density is an important operating parameter for controlling the reaction rate in most electrochemical processes such as EC and EF processes. Current density determines the amount of coagulant and bubble generation, its flocs size and distribution, and hence affects the development of flocs ($Al(OH)_{3(s)}$ coagulating particles) in the EC process. In EC and EF processes, OH^- formation rate is controlled by the applied current density during the electrolysis. In addition, when anode potential is sufficiently high, secondary reactions may occur also, such as direct oxidation of organic compounds and Cl^- ions present in RO dye-salt concentrate. The produced chlorine is a strong oxidant that may oxidize organic compounds and increase electrode reactions [32,37].

During the initial stage of electrolysis, EF has a very good efficiency as oxidizable products were rapidly destroyed by hydroxyl radicals [30]. The applied current is the driving force for oxygen reduction, implying the generation of hydrogen peroxide at the cathode. Higher current increases the amount of produced hydrogen peroxide, therefore, it increases the number of hydroxyl radicals in the electrolyte, which are responsible for the degradation. Higher applied current density means higher applied voltage in the electrochemical reaction [38]. Also with increasing current, higher electro-regeneration of ferrous ion from ferric ion increases the efficiency of Fenton chain reactions [39].

The decolorization efficiency was also studied. The color abatement rate was faster in EF process, the solution becoming colorless at a low current density. The color almost disappeared 96% at an initial current density of 11.6 mA/cm^2, which represents a high removal rate. The synergistic action of coagulation by $Fe(OH)_n$ and oxidation mediated by active chlorine, which may be formed by anodic discharge of chloride anions, yielded 100% color abatement at 23.15 mA/cm^2, thereby it remained constant at higher current densities.

In EC process, only 70% decolorization was achieved with Al instead of 96% reached with EF at the same current density value. At a higher value of current density 46.3 mA/cm^2, color abatement reached 97%, due to the higher electro-regeneration of ferrous ion from ferric ion and of aluminum anion from solid aluminum, with increasing the current density. Then, color reduction decreased again to 90% at a current density of 57.87 mA/cm^2 and remained almost constant at 69.5 mA/cm^2.

In the case of EC process using Al electrode, however, the presence of chloride reduces the anode passivation, which is a typical phenomenon for Al in other media due to the formation of an isolating and compact oxide interlayer [40]. However, the progress of the color removal was significantly slower than that obtained with the Fe anode.

In conclusion, plots against current density reveal that the highest current efficiencies are obtained at 46.3 and 23.15 mA/cm^2, respectively for EC and EF processes. Therefore, these optimum current densities were selected for this study.

3.1.3. pH

pH effect experiments were carried on in EC and EF processes, at optimum electrolysis time of 90 and 60 min, and current density of 46.3 and 23.15 mA/cm^2, respectively. The working interelectrode distance for both processes was of 1 cm and the hydrogen peroxide concentration during EF process was 3,996 mg/L.

During EC process, pH was changed following the values of 3.5, 5, 6.7 (natural), 8 and 9.5. As regards to EF process, pH was varied as following: 1.55, 2.2, 2.8, 3.5, 4.2 and 5.

The influence of initial pH values on COD and color removal efficiencies was studied during EC and EF processes.

Experimental results indicated that for EC process, 58 to 65 % of COD removal was obtained, for pH varying between 3.5 to 6.7. A further increase of pH from 6.7 to 9.5 decayed COD removal from 65% to 39%. A slower and poorer COD abatement was achieved at more alkaline pH, which can be accounted mainly when the less favorable formation of $Fe(OH)_3$ coagulant occurred, according to the iron specification diagrams.

With regard to color removal, 81 to 97% were obtained for a range of acidic pH varying from 3.5 to 6.7. At a weak basic pH 9.5, color removal decreased to 81%.

Besides, during EF process, the decontamination was achieved at acidic pH values from 1.55 to 2.8, due to the combination of coagulation with electrochlorination that yielded 83% COD removal. At pH equal to 4.2, COD removal decreased to 65% and than increased again to 73% at pH 5. During the whole acidic range of pH, no obvious change on COD removal was detected and a total color disappearance 100% of treated solution was observed.

The increase in pH during EF process implies electrocoagulation and consequently pollutants are removed by electrostatic attraction and complexation of reactions due to the transformation of $Fe^{2+}$and Fe^{3+} to $Fe(OH)_n$ type structures [39].

These facts indicated that the degradation of COD and color performed well in wide ranges of pH. In addition, the maximum removal efficiency in COD and color removal were achieved at original acidic pH 6.7 and 2.8, respectively for EC and EF processes, rendering the pH adjustment as unrequired and thus reduced the treatment cost in practical applications.

It is known that EC and EF processes depend largely on pH due to the large range equilibria. pH is an important operating parameter affecting dye removal efficiency in both processes [41].

During EC process, using aluminum as sacrificial anode, at low initial pH, cationic monomers such as $A1^{3+}$ and $Al(OH)_2^+$ are the dominant species. Double-layer compression is the basic mechanism for the dyes coagulation. Therefore, the coagulation efficiency to remove dyes at pH 3.5 was low. When the pH was varying between 4 and 9, the formation of polymeric species (such as $Al_{13}O_4(OH)_{24}^{7+}$) and precipitate $AI(OH)_{3(s)}$ occurred. The polymeric species were efficient in dyes coagulation and dyes precipitation was favored by the adsorption mechanism, charge neutralization and enmeshment. Therefore, COD reduction at the initial pH 3.5 was lower than that when the initial pH was greater than 3 in acidic solution [42].

For the EF process, most studies have indicated that the most appropriate optimal pH varies from 2 to 4 and more precisely, it is about 3 [39]. This is due to the high production of H_2O_2. At pH equal to 3.5, the solubility equilibrium is controlled by Fe^{3+} and $Fe(OH)_3$. For a solution pH greater than 3.5, this equilibrium is dominated only by $Fe(OH)_3$.

In this case, pollutant removal is basically due to the coagulation process. At pH < 3.5, the equilibrium is controlled by Fe^{3+} and removal of pollutants is dominated by EF process. During dye degradation, organic acids are formed which implies a decrease in the pH [43].

At a low pH equal to 2, the reaction occurring between hydrogen peroxide and Fe^{2+} could be slowed due to the stability of H_2O_2 resulted by a proton solvatation to form an oxonium ion (H_3O^+) [44].

At a pH higher than 3, the oxidation effectiveness is rapidly reduced because of the decomposition of H_2O_2 into molecular oxygen, with the absence of sufficient amounts of hydroxyl radicals [44]. In addition, at high pH, $^{\bullet}OH$ will be decreased due to the presence of ferric hydroxide complexes. This was confirmed at pH 5–6 during the EF process [45].

During EC and EF processes, COD and color removal on Al and Fe electrodes, were improved as these electrodes were capable of efficient generation of chlorine as a direct oxidation, for the abatement of RO concentrate. Evidently, active chlorine present in the solution was affected by the pH value. At a pH between 1 and 3, chlorine is the predominant chlorine species, meanwhile at pH varying between 5 and 7, it is HClO, while above 8 it is ClO^- [46]. Thus, in the present work, at original pH 2.8 for EF process, the secondary anodic oxidation product was chlorine, but at original pH 6.7 for EC process, the main product should be HClO, and at the original pH of 8.3, it was ClO^- [46].

Therefore, since the natural pH of RO synthetic solutions 6.7 and 2.8 showed the best removal efficiencies, all the subsequent EC and EF experiments were carried out at these pH values, which increases the economic viability of the treatment.

3.1.4. Interelectrode distance

The effect of interelectrode distance was investigated under optimum conditions (electrolysis time = 90 min, current density = 46.3 mA/cm^2, pH = 6.7, in EC process and electrolysis time = 60 min, current density = 23.15 mA/cm^2, pH = 2.8, hydrogen peroxide concentration = 3,996 mg/L, in EF process). The interelectrode distance effect was studied in the range between 0.5 and 3 cm, meaning values of 0.5, 1, 2 and 3 cm.

The evolution of COD and color removal efficiencies as function of interelectrode distance was studied. In both EC and EF processes, for a distance of 0.5 cm, COD removal efficiency was 57 and 61%, respectively. For an interelectrode distance of 1 cm, COD removal efficiency of 65% was achieved within 90 min of EC treatment and COD reduction of more than 82% was achieved after 60 min of EF treatment. The shorter or longer distance beyond this interelectrode distance of 1 cm would only achieve lower COD removal efficiency, i.e., 55% of COD removal for 2 cm of distance and 58% of COD removal for 3 cm of distance, during EF process. At the same electrodes gaps of 2 and 3 cm, COD reduction (%) in EF process was around 78 and 80 %, respectively.

Further increase in the distance between electrodes resulted in a lower removal efficiencies. These findings are consistent with those observed in the study of Modirshahla et al. [47]. When the space between anode and cathode rises, attraction applied by electrodes on generated aluminum polymers diminishes. Thus, these formed polymers would react with a slower movement to aggregate easily in flocs, and therefore they enhance the adsorption of dye molecules. When the distance is more than 1 cm, dye molecules and flocs interactions are lower, which leads to the decrease of the removal efficiency [48].

Similarly, color removal increases slightly from 85 and 93% with increasing electrode gap from 0.5 to 1 cm, to achieve a maximum removal efficiencies of 97 and 100%, respectively in EC and EF processes. When the interelectrode distance increased to 2 and 3 cm, color removal decreased slightly and ranged around 91% during EC process, and it was nearly the same (total decolorization 100%) in the case of EF process.

The interelectrode distance plays also a significant role in EC process as the electrostatic field depends on the distance between the anode and the cathode. The pollutant removal efficiency increases by raising the interelectrode distance from the minimum until the optimum. This is due to the fact that by further rising of the distance between the electrodes, a decrease in the electrostatic effects will occur, resulting in a weaker movement of the generated ions. It requires more time for the generated metal hydroxides to agglomerate and to form the flocs needed to coagulate the pollutant, resulting in an increase in the removal efficiency of the pollutants by sedimentation, as they get degraded by collision with each other due to high electrostatic attraction [31,36]. Aouni et al. [49] and also Parsa et al. [50] found that using EC process, the most suitable interelectrode distances to apply are respectively 2 cm and 1 cm.

In EF process, distance between electrodes is also an important factor that affects the pollutants removal. The decrease of the distance between the electrodes provokes the decrease of the ohmic drop through the electrolyte and then an equivalent decrease of the cell voltage and energy consumption. Also when the electrodes are placed closer to each other, oxidation of electro-regenerated Fe^{2+} to ferric ion Fe^{3+} at the anode could easily occur.

Longer distance causes the limiting mass transfer of ferric ion Fe^{3+} to the cathode surface that governs ferrous ion regeneration [30]. Therefore, the reaction that produce $^{\bullet}OH$ radical could not be propagated efficiently from Fe^{2+} ion regeneration [39].

Atmaca [51] found that the use of long electrode distance in EF reactor affects significantly the energy consumption making it higher [39,51].

In conclusion, the best color and COD efficiencies during interelectrode effect study were obtained with a weak distance of 1 cm in both EC and EF processes. Thus optimal electrode distance was observed as 1 cm.

3.1.5. Hydrogen peroxide concentration

Differently from other effects that were studied during both EC and EF processes, the influence of H_2O_2 concentration on COD and color removal efficiencies was evaluated obviously during only EF process.

The experiments were carried out in the following optimum conditions: electrolysis time = 60 min, current density = 23.15 mA/cm^2, pH = 2.8, interelectrode distance = 1 cm.

The variation of COD and color removal as function of six different H_2O_2 concentrations in range of 998–4,994 mg/L was studied.

Experimental results showed that at only 998 mg/L of H_2O_2, COD and color reduction achieved already 68 and 85%, respectively. As the dosage of H_2O_2 increased from 998 to 2,996 mg/L, COD removal increased from 68% to 83% and color removal efficiency was considerably enhanced as a total decolorization was reached (>99%). Increasing the concentration of H_2O_2 from 2,996 mg/L up to higher doses as 4,994 mg/L did not improve COD removal more. In turn, it varied slightly between 82–86% for a peroxide dosage varying from 3,996 and 4,994 mg/L, while the color removal remained constant in maximum efficiency (>99%).

This shows that the oxidation reactions end-products are basically constituted by short chain organic acids that are hard to oxidize [30,52].

In general, the removal rate of color increases with increasing the dose of hydrogen peroxide until an optimum peroxide concentration. This is due to the fact that at higher H_2O_2 concentration, enough formed hydroxyl radicals lead to almost complete decolorization [53].

Above optimum dose of peroxide, the removal may decrease or become constant [54]. This is in agreement with the fact that an excess amount of hydrogen peroxide will slightly retard the destruction and removal of dyes [54].

This behavior is consistent with the fact agrees that an excessive amount of hydrogen peroxide in the solution slightly delay the destruction and elimination of dyes [54]. This behavior may be due to self-decomposition of H_2O_2 to oxygen and water and recombination of $^{\bullet}OH$ radicals. Since $^{\bullet}OH$ radicals react with H_2O_2 itself and contribute to $^{\bullet}OH$ scavenging capacity, so that H_2O_2 should be added at an optimal concentration to achieve the best degradation.

Similar to other studied operating parameters efficiency using EF process, the efficiency of hydrogen peroxide could also achieve 100% in color removal. This could be also explained by the fact that in EF process, COD was removed by both oxidation and coagulation [30,55].

Although the COD removal increased up to 86% by increasing H_2O_2 concentration up to maximum H_2O_2 dosage 4,994 mg/L, optimum H_2O_2 concentration was chosen as 2,996 mg/L yielding 83% COD and > 99% color removal, as it entails lower energy consumption.

Taking in consideration energy consumption, peroxide dosage of 1,498 mg/L was considered as optimum for further EC experiments.

3.2. Performance evaluation of EC and EF processes

During optimization of operating parameters in EC and EF processes, solution 5 ([Dye] = 2,500 mg/L, [NaCl] = 1,500 mg/L) was used for these experiments. This solution was chosen because it has intermediate values of dye and salt concentrations range chosen.

After optimization of operating parameters in EC and EF processes, single EC and single EF processes were applied for the treatment of synthetic RO concentrate of different dye mixture and salt concentrations. Each solution was treated by single EC and single EF processes, in determined optimum parameters. Dye and salt concentrations of these nine solutions are shown in Table 1, in materials and methods section.

As it can be illustrated in Figs. 1 and 2, dye and salt concentrations were plotted against respectively related COD and color abatement (%) in single EC and EF processes, using the optimum conditions obtained previously for electrolysis time, current density, pH, interelectrode distance and peroxide dosage.

It is clearly obvious that dye and NaCl concentrations had a slightly higher effect on COD removal, especially for EC process during the whole range of dye and salt concentrations, and particularly, for EF process at high dye concentrations of 5,000 mg/L, for both EC and EF processes.

As shown in Fig. 1, related to EC process, at a dye concentration equal to 1,600 mg/L, with increasing salt concentration from 1,500 up to 3,800 mg/L, COD rate improved from 48% to achieve a maximum removal of 65%, and then progressively decreased to around 50% and did not overpass 54%, as the dye content was raised up to 5,000 mg/L.

This means that once a threshold amount of active chlorine already has a low chloride content, the additional benefits that might result from a higher chloride content of more oxidative degradation are neutralized by the lower coagulation efficiency, because of (i) the formation of by-products which are more difficult to coagulate and (ii) increased ionic strength which affects the equilibria of reactions between the charged and /or colloidal species in EC.

Meanwhile, in EF process, for example, at NaCl concentration equal to 3,800 mg/L, COD reduction slightly decreased from 89 to around 81–85%, and then was reduced sharply to 56% respectively for dye concentrations equal to 1,600; 2,500 and 5,000 mg/L, probably because the dye content becomes too high in comparison to the amount of coagulant formed into the solution. It could be also due to the insufficient hydroxyl and metal ions produced on the electrodes in the high dye concentrations and at constant current density.

It seems therefore that there is an optimum ratio between dye and coagulant concentrations that promotes sweep coagulation.

As can be seen in Fig. 2, a higher NaCl and dye concentration did not bring any significant acceleration of the color removal, in both EC and EF processes. In fact, all solutions were completely decolorized in EF process, and color abatement reached around 83–88% during EC treatment, for all ranges used of dye and salt concentrations. Therefore, the effect of dye and salt remained negligible, as the plateau region was reached, up to the concentration of 100 mg L^{-1}, the removal percentage was relatively constant. This means that low chloride contents are capable of providing enough chlorine to promote maximum oxidation of the dye at an optimal time of electrolysis.

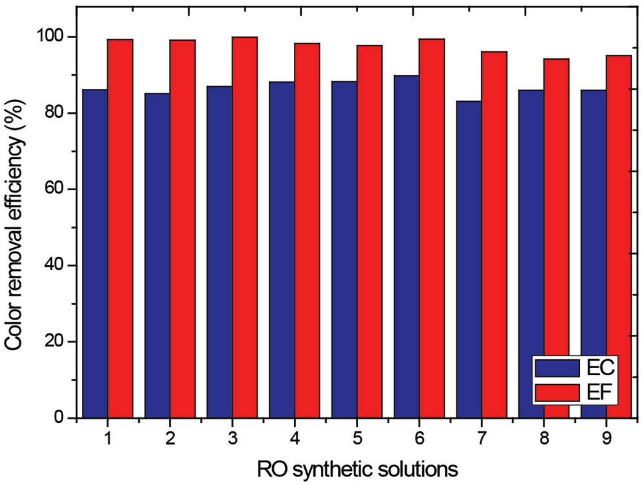

Fig. 1. Color removal efficiency (%) of different synthetic RO concentrate solutions treated by single EC and EF processes under the optimum experimental conditions.

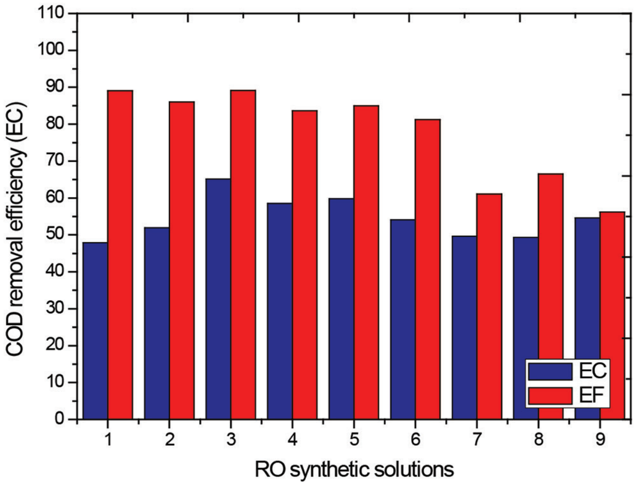

Fig. 2. COD removal efficiency (%) of different synthetic RO concentrate solutions treated by single EC and EF processes under the optimum experimental conditions.

Similarly to COD removal efficiency, the trends of color removal (%) show that the decolorization efficiency, during the used range of dye and salt concentrations revealed a better performance of EF in comparison to EC. However, from the results of this investigation, it can be clearly seen that dye and salt concentration has the greatest effect on COD removal efficiency.

After single EC and EF step, as solution 5 presented high removal efficiencies in terms of COD and color removal (COD 60%, color 88% in EC process, COD 85%, color 98% in EF process, a preliminary study was carried out by collecting the solution 5 pretreated by single EC and EF processes to treat it by ED process in order to check the salinity and conductivity removal efficiencies and also to verify the influence of these dye and salt concentrations on ED membrane fouling. However, during combined processes EC/ED and EF/ED, low efficiency in terms of salinity removal was obtained, and the current across the stack after 120 min (results not shown) was insufficient between the cathode and anode, to continue the desalination process, during ED process.

Taking these findings into account, solution 1 ([dye] = 1,600 mg/L, [NaCl] = 1,500 mg/L) was chosen for the treatment of RO concentrate by combined processes EC/ED, EF/ED and EC/EF/ED, under optimum conditions. This solution presented also high removal efficiencies (COD 48%, color 86% in EC process, COD 89%, color 100% in EF process) at optimum operating conditions and especially it entails weak energy consumption as it presents the lowest dye and salt concentrations.

3.3. Evaluation of treatment performances for combined processes applied for synthetic RO concentrate

During combined processes experiments, pretreated solutions by EC, EF and EC/EF were collected and further treated by ED process, to remove salinity.

Figs. 3–5 graphs show the performance of ED process for salt removal from the pretreated residual solutions as function of time.

It can be clearly seen that conductivity and applied current vary conversely with concentrate evolution, during deionization time.

As can be ascertained in Fig. 3, during EC/ED hybrid process, conductivity and NaCl concentration in the diluate slightly decrease within the initial 15 minutes. After this point, the decrease in conductivity and salt concentration slowed down to around 40% (equivalent to 2.78 mS/cm and 1,365 mg/L respectively) and was kept constant until around 56 min of treatment. Moreover, an accompanying incremental decrease from 3 to 0.38 A in the current between the two electrodes within the stack was noted during time. This can be explained with both concentration polarization in the membrane boundary layer as well as depletion of electron carriers in the diluate.

After EF pretreatment step, the results from the tests conducted during ED final process, and, with an initial salinity solution of NaCl, equivalent to 4.53 mS/cm conductivity, are presented in Fig. 4.

As the ions were continuously separated from the diluate and transported to the concentrate, a significant decrease in conductivity of diluate was achieved during desalination time and about 86.5% of salinity removal was obtained; this decrease is faster during the first 3 min of treatment. The maximum conductivity in the feed stack could be reduced down to 92.01% after 16 min of desalination treatment. Meanwhile, the conductivity of the concentrate increased sharply from initial value of 3.22 to 17.57 mS/cm. The applied current decreased from 4.13 to 1.78 A, due to the lower conductivity [56,57].

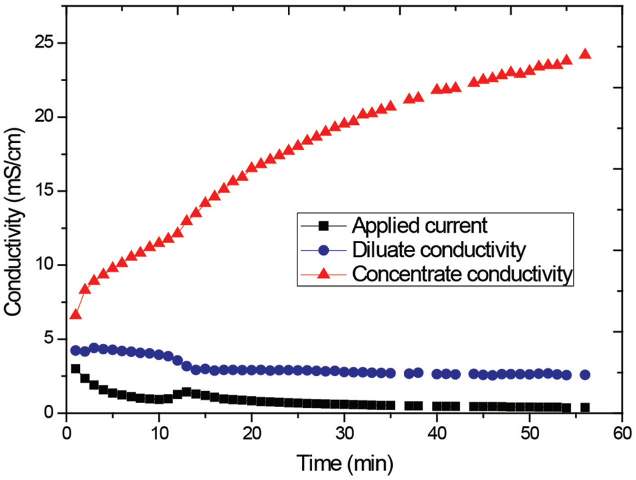

Fig. 3. Evolution of conductivities of the diluate and the concentrate as function of time during ED deionization in combined process EC/ED.

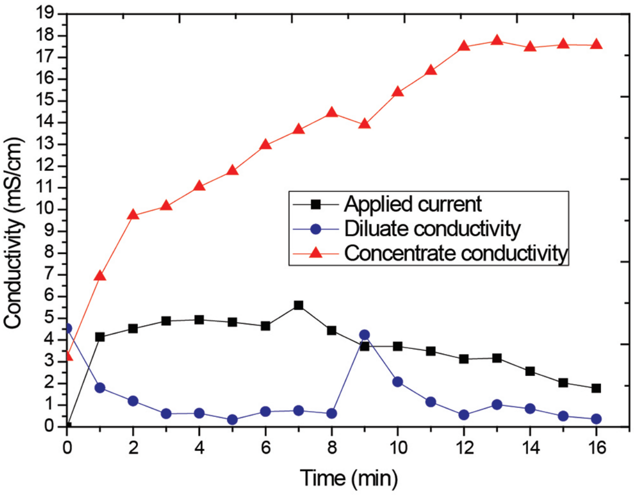

Fig. 4. Evolution of conductivities of the diluate and the concentrate as function of time during ED deionization in combined process EF/ED.

Similar results were obtained during ED process after pretreatment step EC/EF. Fig. 5 shows that the RO synthetic concentrate that was pretreated by hybrid process EC/EF, was desalinated by ED to reduce initial water conductivity from 5.41 to 0.345 mS/cm (94% of salinity removal) after a time of 3 min. The conductivity increased during one minute and then decreased again to become constant until 26 min.

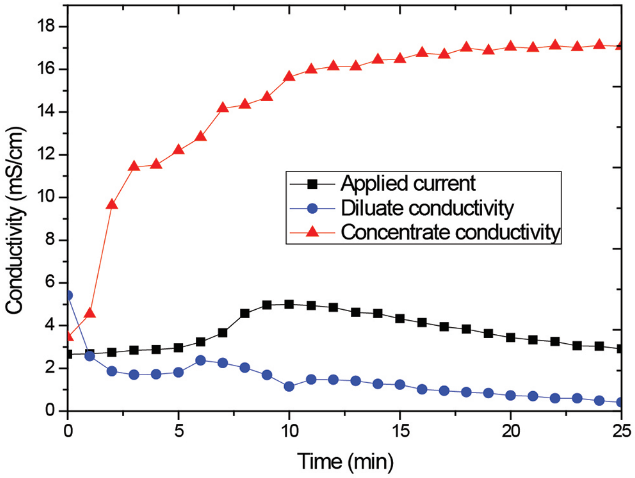

Fig. 5. Evolution of conductivities of the diluate and the concentrate as function of time during ED deionization in combined process EC/EF/ED.

As conclusion from ED desalination experiments, the best efficiency of salt removal was obtained after pretreatment process EF and EC/EF (92 and 94% respectively) during a short time of 3 min. However, after pretreatment using EC process, salt removal did not exceed 40% and the desalination time was longer (15 min).

As shown in Fig. 6, ED anionic exchange membrane showed clearly a high sensitivity to fouling after EC/ED combined process, comparing to membranes used during EF/ED and EC/EF/ED processes.

This is due to high concentrations of dyestuffs, which essentially arise from the precipitation of organic dyes on the surface of the membrane or inside the membrane and a fouling problem reduces the transport of ions. Fouling problems result in an increased membrane strength, a loss of membrane selectivity, and a negative effect on membrane performance, resulting in high energy consumption and low separation efficiency [58].

In addition, the ED anionic exchange membrane used during EC/EF/ED presented less sensitivity to fouling, comparing with the one used during EF/ED process, even similar results in terms of salinity removal were obtained for both EF/ED and EC/EF/ED processes.

Fig. 7 shows the final results of combined processes EC/ED, EF/ED and EC/EF/ED in terms of the highest maximum efficiencies of COD, color and salinity removal, at optimum operating conditions.

It can be clearly seen that the best COD, color and salinity reduction rates were obtained after hybrid processes EF/ED and EC/EF/ED as they presented almost equal results (total decolorization for both combined processes, 98 and 99.2% as COD removal, 92 and 94% as salinity removal, respectively). However, after EC/ED process, only 58% and 86% of COD and color removal were obtained respectively.

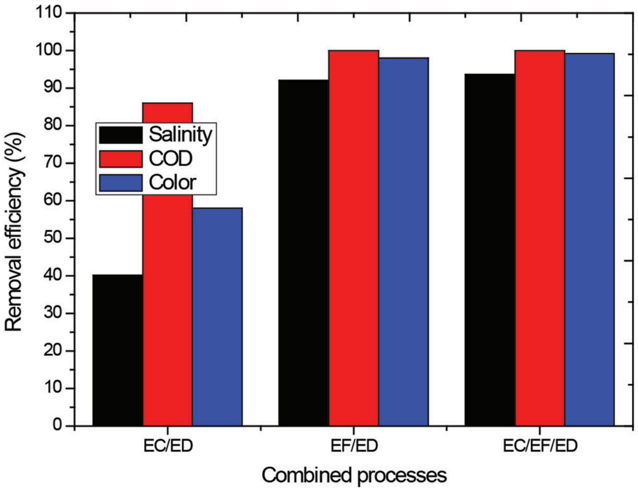

Fig. 7. Salinity, COD and color removal efficiencies of combined processes EC/ED, EF/ED and EC/EF/ED under optimum conditions for RO concentrate treatment using [dye] = 1,600 ppm and [NaCl] = 1,500 ppm.

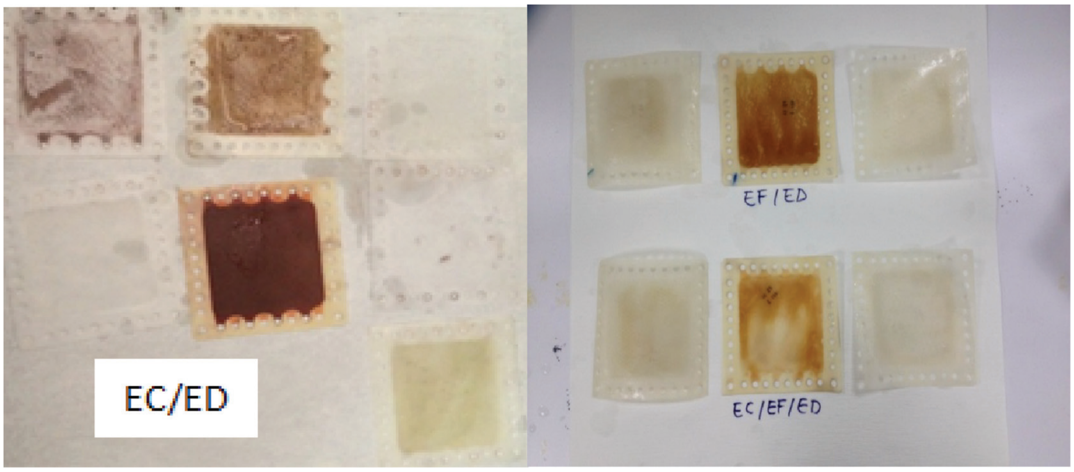

Fig. 6. Photo illustrating surfaces of ED exchange membranes behaviors after EC/ED, EF/ED and EC/EF/ED processes.

3.4. Cost evaluation

Results presented in Table 2 show operating costs of the studied processes EC and EF, for concentrate treatment, at optimum operational conditions.

As it can be seen in Table 2, cost calculations show that total operating costs for EC and EF processes are 3.56 US$/m^3 and 1.86 US$/m^3. The operating cost for EF process was found to be 2 times lower than that of EC process, even EC process is not affected by chemicals consumption. The electrode consumption cost is higher with aluminum during EC process (1.35 US$/m^3) than that of the EF process (0.684 US$/m^3), also the produced sludge (0.335 US$/m^3) and energy consumption (0.011 US$/m^3) costs are lower with iron, using EF process, comparing with those of EC process (0.556 US$/m^3 and 1.66 US$/m^3).

Electrode consumption cost accounts nearly 36% and 38% of the operating cost of EF and EC processes, respectively. Produced sludge consumption presented 18.01% and 15.59% of the operating cost of EF and EC processes. Concerning energy consumption, it accounts the highest percentage 46.55% of the total cost for aluminum and the lowest one 0.59% of the operating cost of EF process.

From the obtained results, EF process was found to be more effective than EC process with respect to operating cost, as it was less expensive.

Akyol et al. [60] found that operating costs for the EC and the EF processes were calculated as 0.74 €/m^3 and 1.23 €/m^3, for treating a liquid organic fertilizer manufacturing wastewater (LFW). EF process was found to be more effective than EC process with respect to the removal efficiencies of TOC (total organic carbon) and color. However, EF process was more expensive than EC process.

Table 3 shows calculations of energy consumptions and costs related to EC, EF and ED processes. It is clearly seen that EC process showed slightly higher energy consumption cost (1.66 US$/m^3) than ED process (1.29 US$/m^3). On the other hand, energy consumption cost of EF process was very low (0.011 US$/m^3).

Table 3
Energy costs of studied processes[a]

Process	Energy consumption (kWh/m^3)	Cost[b] (US$/m^3)
EC	29.106	1.66
EF	0.208	0.01
ED	22.56	1.29
Total		2.961

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

[b] 1 kWh costs 0.057 US$.

It is clear that by calculating the energy cost (%) of each process, EC process is the most costly, as it presented 56.06% of the total cost of energy consumptions. Meanwhile, ED and EF processes showed energy consumptions costs of about 43.56% and 0.37%. Therefore, cost analysis study shows that EF is a feasible and a cost effective choice to treat RO concentrate.

Zhang et al. [61] found that for treating RO concentrate by ED process, energy consumption of ED process is ranging between 0.01 and 1.023 kWh/m^3, and the energy cost varies between 0.06 and 0.107 €/m^3.

It is important to mention that unit prices of consumables for EC, EF and ED processes are changeable from one market to another, for this reason it is hard to make a real comparison between different studies related to cost analysis.

4. Conclusions

As the selection of the most suitable treatment is based on the concentrate composition, EC, EF and ED processes were proposed for the treatment of textile synthetic RO concentrate stream. It was found that optimum parameters (electrolysis time, current density, pH, interelectrode distance and peroxide dosage) strongly influence the

Table 2
Operating costs for the studied processes EC and EF processes [a]

Consumables for EC process	Unit prices of consumables	Consumption of treated concentrate	Cost (US$/m^3)
Aluminium electrode	1.3 (US$/kg)	1.042 (kg/m^3)	1.35
Produced sludge	0.067 (US$/kg)	8.3 (kg/m^3)	0.556
Energy	0.057 (US$/kWh)	29.106 (kWh/m^3)	1.66
Total			3.566
Consumables for EF process		Consumption of treated concentrate	Cost (US$/m^3)
H_2O_2 (30%)	0.045 (US$/kg)	13.32 (kg/m^3)	0.59
HCl (37%)	0.186 (US$/kg)	0.43 (kg/m^3)	0.08
NaOH	0.2 (US$/kg)	0.8 (kg/m^3)	0.16
Iron electrode	0.3 (US$/kg)	2.28 (kg/m^3)	0.684
Produced sludge	0.067 (US$/kg)	5 (kg/m^3)	0.335
Energy	0.057 (US$/kWh)	0.208 (kWh/m^3)	0.011
Total			1.86

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

performance of EC and EF processes. After optimization of both EC and EF, these two processes were implemented as a single degradation step at optimum conditions, before ED process and then as combined processes with ED. Based on color and COD removal, it was proved that for treating a synthetic RO solution with a dye and NaCl concentrations of 2,500 and 2,000 mg/L, EF process showed the best removal efficiencies in terms of COD and color (COD 60%, color 88% in EC process, related to COD 85%, color 98% in EF process) under optimum conditions.

Experimental results showed that after ED process, using a dye and NaCl concentrations of 1,600 and 1,500 mg/L, combined processes EF/ED and EC/EF/ED showed the highest efficiencies and the best performances and presented similar results in terms of COD, color and salinity removal (total decolorization for both combined processes, 98 and 99.2% as COD removal, 92 and 94% as salinity reduction, respectively) during a short desalination time. On the other hand, EC/ED process presented limitations as COD, color and salinity rates did not exceed 58 %, 86 % and 40%, respectively. In addition, the cost analysis study showed that operating cost (1.86 US$/m^3) using EF process was lower than that using EC process (3.56 US$/m^3). In terms of energy consumption, EC presented also the highest energy consumption cost (1.66 US$/m^3) meanwhile ED and EF processes showed an energy cost of 1.29 US$/m^3 and 0.01 US$/m^3. Not only EF process showed a satisfactory COD and color removal performance, but also economically, it was more viable choice for treating RO concentrate.

It was found also that, even the combined processes increase the cost of operating system, pretreatment steps of EC and EF were necessary before ED desalination step. Actually, EF pretreatment step raised life time of ED membranes, which is a key parameter for ED process cost. It reduced sharply membrane fouling by reducing COD and color, as well as it improved the quality of final permeate as it enhanced to lower water salinity. Combined processes EF/ED and EC/EF/ED were efficient for treating synthetic textile RO concentrate, as the obtained permeate quality reduces the environmental impact of the original hypersaline brine discharge, thus facilitating its direct discharge.

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