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Treatment of pharmaceutical effluent by electrocoagulation coupled to nanofiltration

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ABSTRACT

Electrocoagulation (EC) is an efficient technique for the treatment of various industrial effluents. EC using aluminum electrodes was applied to a pharmaceutical effluent which contained Metoclopramide hydrochloride. The influence of the electrolysis parameters was investigated with the decrease of the chemical oxygen demand (COD). EC was found to be effective for the COD decrease. The main mechanisms of COD removal by EC seemed to be the coagulation and the adsorption. The best COD removal efficiency in EC was recorded for the synthetical solutions 9.5 g L^{-1}, 15 g L^{-1} and the sample of pharmaceutical waste diluted to 4/5 at 95, 96 and 70%, respectively. Experiments were carried out by coupling EC with nanofiltration (NF) processes. Organic compound retention was obtained for two synthetic solutions (% COD from 60.5 to 85.0%) and effluent solution (from 76.0 to 78.0%). The minimal energy consumed during the electrolysis of the solutions (9.5, 15 g L^{-1} and pharmaceutical waste) was 0.074 kWh/m^3 for pH associated 7.43, 8.01 and 7.87, respectively. In NF, the optimal energies observed for obtaining a better rate of elimination of COD for the three selected model solutions (9.5, 15 g L^{-1}, and pharmaceutical waste) were recorded to be equal to 3.49, 3.08 and 3.46 kWh/m^3 for percentages of elimination respectively equal to 64.46, 84.95 and 78%. The treatment by coupling of EC and NF requires a consumption of electrical energy equivalent to 1,711 kWh/m^3.

Keywords: Electrocoagulation; Nanofiltration; Pharmaceutical waste; COD decrease; Metoclopramide hydrochloride

1. Introduction

The problems related to the environment, in particular those concerning the rejection of industrial wastewater, are a major concern for the population and a priority for the public authorities.

The pharmaceutical industry is among the leading sources of water pollution in Algeria. The Algerian pharmaceutical market is classified third in Africa in

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matter of drugs production. These investments related to 912 types of drugs on the 5.683 marketed in Algeria and include 56 production plants, and covers one third of the national needs [1]. Indeed, in a highly competitive environment, all industries reject large amounts of effluents with an increasing number of pollutants [2–4]. Even some of the effluents were not very hazardous, they constitute a large potential of pollution due to their great polluting loads. We can also quote the case of washing waters from the pharmaceutical units amounts which are mixtures of various compounds whose complete removals would be very expensive if not very difficult to realise. The legislation on the rejection requires the use of practical treatment techniques and proposes the recycling as a possibility for certain products as well as the reuse of purified water as a sub-product in the process for other specific uses.

The pharmaceutical waste treatment by conventional methods, e.g. a simple chemical treatment, using addition of coagulants and flocculating reagents and by unconventional processes do not lead to a better effectiveness seen given the complexity and the specificity of the water components. Indeed, the "refractory" pollutants caused by pharmaceutical industries cannot easily be degraded by traditional biological processes and remain in the effluent, e.g. activated sludge, toxic chemicals may greatly inhibit the microorganisms activities [2–4].

Enhancing the treatment of complex effluents need the research of new hybrid processes which associate sequential operations, like electrolytic purification followed by a membrane filtration [5,6] or complexation–ultrafiltration [7,8]. The objective of this contribution is to investigate the use of a hybrid process to the pollution treatment of industrial effluents. This paper examines the interest of electrocoagulation (EC) hyphenateded to nanofiltration (NF) which was applied to an effluent arising from a pharmaceutical plant. Particular attention was devoted to the treatment of the liquid wastes from the production line of a pharmaceutical unit.

Various products are produced and commercialized by Biotic Pharmaceutical Factory of Algeria (BPFA), particulary: tablets, syrups and ointments. The purpose of this treatment is to highlight the aptitude of these two processes to eliminate the majority of organic and mineral pollutants as well as the suspended matter.

The origin of the pharmaceutical wastes result from the processes of extraction or transformation from the raw materials in order to manufacture medical products. The steps involved in the compounding of drugs may include extraction, processing, purification and packaging. Pharmaceutical industry is among the major contributors to industrial wastes [9–11]. Its effluents when carelessly handled and disposed endanger health both (human and environment) [12]. Waste waters arising from pharmaceutical industries are extremely heterogeneous and present large varieties of chemical pollutants, such as solids or dissolved forms, inorganic or organic compounds, metals, hydrocarbons, solvents, polymers, oils, greases and salts with various levels of toxicity [13,14]. These complex compositions require a specific approach of treatment for each type of effluents. The environmental impacts of the wastes and the consumed products are a major stake for any industrial actor in terms of health hazard but also of the market access. The pharmaceutical products are specifically designed to have biological persistent and lipophilic effects, which aggravate their polluting potential. Furthermore, they are mixed with large quantities of pollutants agents like plasticizers, detergents, cosmetic products, hydrocarbons and other heavy metals rejected into the rivers and increase their toxicity through some parameters (chemical oxygen demand (COD), BOD, Turbidity and SM) [15–18].

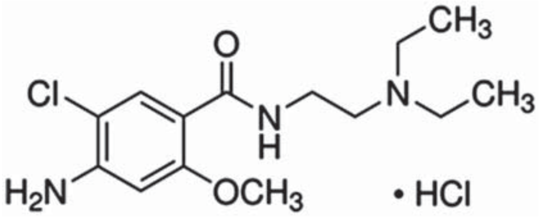
Indeed, with the increase in cancer cases observed, the fall of the fertility and congenital malformations, the suspicions are made every day [19]. Scientific research gathered over the last few decades shows that endocrine disrupting chemicals can decrease immune defenses and prevent consequently the organism from fighting against the appearance of cancer cells [18,19].

Furthermore, recent observations have revealed that a wide range of pharmaceuticals has been found in fresh and marine waters at physiological active concentrations, and it has been shown that even in reduced quantities, some of these compounds are potentially capable of causing harm to both aquatic and terrestrial organisms [19,20].

2. Materials and methods

2.1. Reagents

MTC was supplied by Sigma–Aldrich, and a $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ stock solution was prepared in deionised water, and then stored in a brown flask at 4°C. Standard solutions of MTC were prepared by dilution of the stock solution with redistilled water. MTC tablets (each tablet containing 10 mg MTC and weighs 119.4 mg) which were produced by BPFA, were purchased from a local market. Non-medicinal ingredients include: corn starch, mannitol (E421), microcrystalline cellulose, gelatin, magnesium stearat and purified water. The chemical name for metoclopramide hydrochloride is 4-amino-5-chloro-2-methoxy-*N*-[2-(diethylamino)ethyl] benzamide hydrochloride.



CAS number: 54143-57-6

Empirical formula (Hill Notation) $C_{14}H_{22}ClN_3O_2 \cdot HCl$

Molecular weight: 336.26 g.mol^{-1}

Very soluble in water (200 g L^{-1} at 25°C), freely soluble in alcohol, sparingly soluble in methylene chloride

Fig. 1. Chemical structure and physico-chemical characteristics of MTC.

The chemical structure and physico-chemical characteristics of MTC are shown in Fig. 1.

MTC is a benzamide derivative and has two ionisable groups. The aromatic primary amine has a pKa of 0.48 [21]. The tertiary amine has a pKa of 9.36 and is ionised at neutral pH [22]. Hydrochloric acid (0.1 mol L^{-1}) and sodium hydroxide solutions (0.1 mol L^{-1}) were used for the adjustment of water pH-value.

2.2. Pharmaceutical wastewater characteristics

The study was undertaken with a sample of waste water resulting from the first washing of the production tank of tablets provided by the pharmaceutical plant in Algiers. This division produces enormous quantities of wastewater (representing a significant proportion of the consumption in the area), which is currently rejected without treatment in the El-Harrach river, located 15 km east of Algiers, pouring into the sea.

It can lead to the contamination of the seaside and of the river near the polluting production facilities. The volume of waste water rejected daily into the sea is estimated to more than 37,000 m^3. The principal characteristics of the liquid wastewater used in this study are given in Table 1.

2.3. Principle and experimental procedure of EC

2.3.1. Description of the EC process

EC involves the generation of coagulants (Fe^{2+} and Fe^{3+} or Al^{3+}) by electrolytic oxidation of an appropriate sacrificial anode (e.g. iron or aluminum) by the application of a direct electric current. Accompanying electrolytic reactions evolves a gas (usually as hydrogen bubbles) at the cathode.

Table 1
Chemical characteristics of the effluent as received from the factory

Parameters	Results
Temperature (°C)	20
pH	5
DCO (mg L^{-1})	6,535
DBO_5 (mg L^{-1})	27
Turbidity (NTU)	884
Conductivity (μS cm^{-1})	1,020

The dissolution of the metal cathode lead to the formation of the metal hydroxides, metal oxy-hydroxides and polymeric hydroxides. These compounds generally have a better effectiveness of coagulation than that from the chemicals used in the conventional techniques.

They can destabilize colloids in suspension, while adsorbing, neutralizing or precipitating the dissolved polluting species in the liquid, and finally transform into flocs easily extractable by precipitation, filtration or flotation [23].

Insoluble flocs are generated at a pH range comprised between 6.0 and 7.0 as can be seen from pH-solubility diagrams for aluminum hydroxide Al $(OH)_3$ showing how the solubility varies with pH values [24]. The main reactions occurring at the electrodes when aluminum is used as electrode are as follows [25]:

At the anode, aluminum oxidation:

$$Al_{(s)} \rightarrow Al^3 + 3e^- \tag{1}$$

In the solution, the aluminum ions can react with the water according the following reaction:

$$Al^{3+} + 3H_2O \rightarrow +Al(OH)_{3(s)} + 3H^+ \tag{2}$$

At the cathode, water reduction:

$$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^- \tag{3}$$

The electrolytic oxidation at the anode results in formation of Al^{3+}, which is hydrolyzed to form hydroxides depending on the value of the pH. The magnitude of the pH decrease depends on the Al concentrations in the solution [26]. The theoretical amount of aluminum dissolved m_{th} during EC was calculated using the Faraday's law [24] of Eq. (4) where i is the applied current (A), t is the electrolysis time (s), z is the valence number of the *in situ* metal ions ($z = 3$ for Al), F is the Faraday's constant (96,485 C mol^{-1}), M_w is the molecular weight of Al (26.982 g mol^{-1}).

$$\mathrm{m_{th}} = \frac{i \times t \times M_\mathrm{w}}{z \times F} \tag{4}$$

2.3.2. Experimental apparatus and procedure

In order to observe the pollution factors evolution during the experimental treatment, we used in addition to the sample of the effluent resulting from the third washing, two other solutions prepared synthetically in the laboratory. The concentrations of the synthetic effluents were respectively 9.5 and 15 $\mathrm{g\,L^{-1}}$ of tablets.

The solvent which was used for dilution was drinking water. APHA standard methods of examination of water and wastewater were followed in the analysis of samples during the experimental study [27].

The one-step EC process was carried out in an EC reactor as illustrated in Fig. 2, in order to remove various pollutants from pharmaceutical wastewater at ambient temperature using the laboratory scale experimental set-up.

Each aluminum electrodes had the dimensions of 8 cm × 4 cm × 4 cm and 22 $\mathrm{cm^2}$ of the surface was immersed. These were placed 2 cm apart and dipped up to 5.5 cm deep into the magnetically-stirred solution. The electrodes were spaced by a slotted support at the side of the reactor. They were connected to a direct current power supply (Matrix, model MPS-3003D) characterized by the ranges 0–5 A for current (I) and 0–32 V for voltage. The EC reactor had a volume of 1.7 L. A constant stirring speed of 480 rpm was applied during all experiments. Before each run, electrodes were washed by pure water and restocked for 5–10 min in a freshly prepared solution of NaOH (3 $\mathrm{mol\,L^{-1}}$) and then they were rinsed with distilled water.

All experiments were conducted at around 25°C. The electrical conductivity k of wastewater was adjusted using the addition of sodium chloride in the range 1.5–5 mg/L. Knowing, NaCl is a salt exhibiting low toxicity at moderated level, reasonable cost, high conductivity and high solubility, but it played also the role of supporting electrolyte [28].

To be able to follow the evolution of the pollution parameters during the wastewater treatment, an optimization step of the time (t) and of the density of current (J) was made.

The range of dilution factor was selected for the obtaining the representative conditions of concentration under industrial practice. The optimal time for solution electrolysis was fixed to 20 min by studying the evolution of pH function electrolysis time. The results show that after 20 min of EC the pH of solutions was constant and the Fig. 3 below shows clearly the phenomena.

$$J = \frac{I}{s}\,(\mathrm{A\,m^{-2}}) \tag{5}$$

where I is current (A) and s represents the effective surface area of the electrodes ($\mathrm{m^2}$).

The removal efficiency of the membrane is generally expressed by rejection (%R) of COD, conductivity, turbidity and MES, defined by Eq. (6).

$$R(\%) = 1 - \frac{C_\mathrm{f}}{C_\mathrm{o}} \tag{6}$$

where C_f and C_0 respectively represent the constituents measured before and after the EC run.

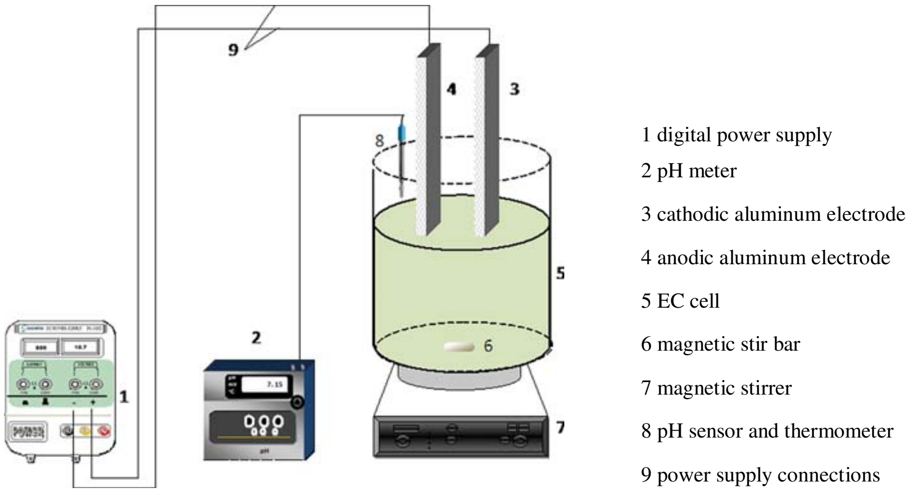


Fig. 2. Experimental apparatus of the batch EC reactor system.

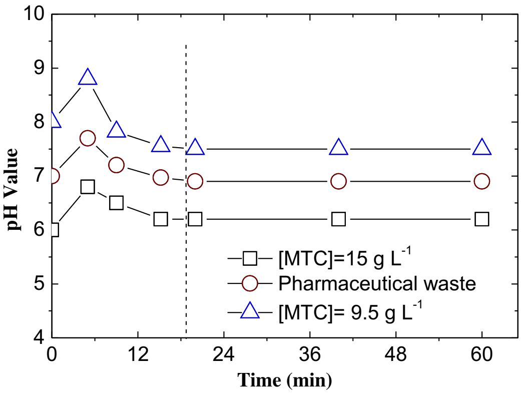


Fig. 3. Variation of the pH values as function of time during electrolysis at 6.5 mA cm^{-2} of synthetic solutions and sample of effluent. The current density was calculated according to Eq. (5).

2.4. Principle and experimental procedure of NF

Filtration experiments were performed with a tangential filtration system (Millipore Proscale pilot) operating in the batch circulation mode [29,30]. The NF module was equipped with Nanomax 50 membrane (Millipore USA) which is a composite polyamide negatively charged membrane in the spiral form with a 0.37 m^2 area and with pure water permeability of 0.58×10^{-11} m s^{-1} Pa^{-1} at a feed flow rate of 90 L h^{-1}. Membrane surface chemical characteristics are determined by a very thin polyamide layer, which makes up the active layer of the NF membrane used in this investigation [30]. This polyamide layer contains both carboxylic and amine functional groups [30] that can be ionised in an aqueous solution. The Nanomax50 membrane has an isoelectric point (IP) at pH 4.5. At $pH < IP$, the membranes have a slightly positive charge. At $pH > IP$, the membrane is negatively charged and it becomes more negative when the pH increases. The separation of ionic species by NF membranes is governed by both size (steric effect) exclusion and electrostatic interaction [31].

The EC process was followed by NF technique in the treatment of the pharmaceutical effluent sample. Fig. 4 shows the experimental setup of the hybrid EC/NF process.

A sample of 1.7 L of pharmaceutical waste (effluent) was electrolyzed for 20 min under conditions as those described above. After treatment by EC, the sample obtained from the EC unit was put into 2 L capacity beaker for decantation. The sample was then left to rest for 45 min, and as soon as separation was achieved, the COD, and turbidity parameters were determined in the supernatant. The supernatant obtained from the EC and decantation process (90% Vol) were then performed in the NF unit wherein the "retentate" is recycled.

3. Results and discussion

3.1. EC treatment

The current density strongly influences the EC process as it determines the rate of coagulant addition,

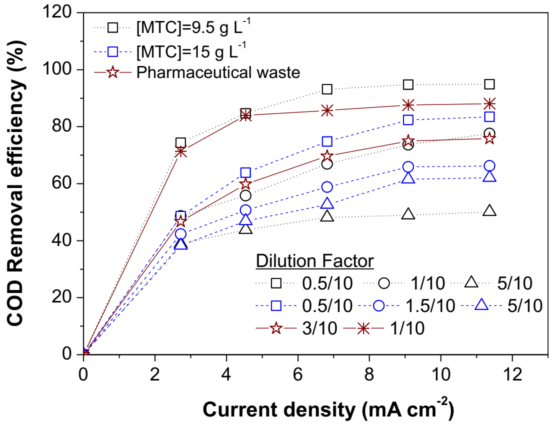


Fig. 5. Removal rate of COD as a function of current density.

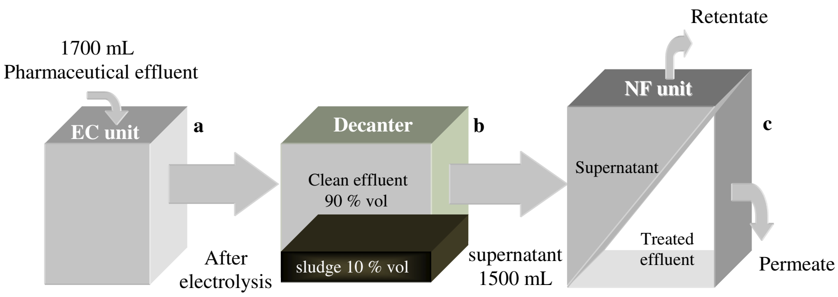


Fig. 4. Scheme of the sequential treatment of pharmaceutical effluent. (a) Electrocoagulation of 1.7 L of effluent in the EC cell (capacity 2 L). (b) Decantation and separation between clear effluent and sludge. (c) 6 L of the supernatant designed for treatment in NF membrane module.

gas evolution, bubble formation and size of floc growth [32]. Fig. 5 shows COD removal efficiency upon current density.

Experimental results show that after 20 min of electrolysis, the effectiveness of treatment increases significantly with the increase of the intensity of the electric current. The higher voltage (>32 V corresponds to 2 A) increases the process of the COD, the turbidity (caused by various particle or colloid matters and of organic or inorganic compounds) and of the electrolytic conductivity with a reduction of 75–95%, 36–96% and 3.5–19.5%, respectively for the different analyzed solutions. Due to the fact that an increase in current results in an quick reduction and a faster anode dissolution resulting in a bigger amount of precipitates and the generation of increased bubble that causes coagulation and flocculation hence leading to a higher amount of pollutant removal. This effect was also observed by other researchers during a single EC process [33–35]. Moreover COD decrease is also related to the appearance of the collecting phenomenon by the presence of the organic compounds or colloids negatively charged in the solution, which bind with Al^{3+} (Lewis Acid) and thus preventing any reaction between aluminum and the hydroxide, according to Eq. (7).

$$Al^{3+} + n\mathrm{MO} \rightarrow [\mathrm{Al(MO)}_n]^{3+} \tag{7}$$

The treatment by EC of the samples of effluent enabled us to obtain a COD reduction (starting solutions: 6,500 mg L^{-1}) from (40%, 4,500 mg L^{-1}) to (70%, 2,500 mg L^{-1}) for dilutions which are respectively for 4/5 and 1/10. A total bleaching of the pharmaceutical wastewater is obtained when the applied voltage has exceeded 17 V.

The effect of the current density on the turbidity is shown in Fig. 6. It can be clearly seen that turbidity removal increased with increasing current density. Furthermore, the results revealed that the maximum turbidity removal reaches 84%, 51% and 48% for synthetic solutions at 9.5 g L^{-1}, 15 g L^{-1} and pharmaceutical waste diluted to 3/10, respectively.

As electrolysis progressed, the rate of turbidity reduction decreases and the turbidity levels out during the stabilizing stage. Beyond this optimum, an increase in turbidity has been observed, this is mainly related to the presence of the Al^{3+} ions excess in the solution. This surplus of Al^{3+} ions causes the neutralization of the residual charge in the solution and formation of the aluminum hydroxides such as: $Al(OH)_3$, $Al(OH)_2^{+4}$, $Al(OH)^{+2}$, $A1(OH)^{-4}$. The solution pH was stabilized to about 8.5 after 17 min of electrolysis.

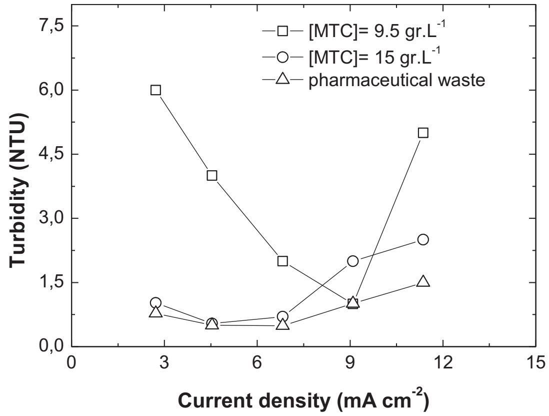


Fig. 6. Turbidity of the EC solutions as a function of current density under different dilutions. For synthetic solutions (9.5 and 15 g L^{-1}) used in this section, the dilution factor was 1/2. The sample of effluent was diluted to 3/10.

Turbidity removal occurs as the result of destabilization of colloids due to the effect of the electric field generated between the electrodes and the reactions with coagulating compounds formed *in situ* during anode oxidation, followed by a subsequent flotation of agglomerates of the particles [36]. Stephenson and Duff [37] confirmed the efficacy of chemical coagulation and precipitation for the removal of organic compounds that contribute to color and turbidity.

Fig. 7 shows the effect of wastewater conductivity on the performance of the EC process. Solution conductivity affects the current efficiency, cell voltage and consumption of electrical energy in electrolytic cells. As a result, increasing solution conductivity resulted in the reduction of cell voltages that caused a decrease in electrical energy consumption. Similar results were previously reported in literature [38–41]. Moreover, the electrical conductivity (i.e. the ionic strength) of

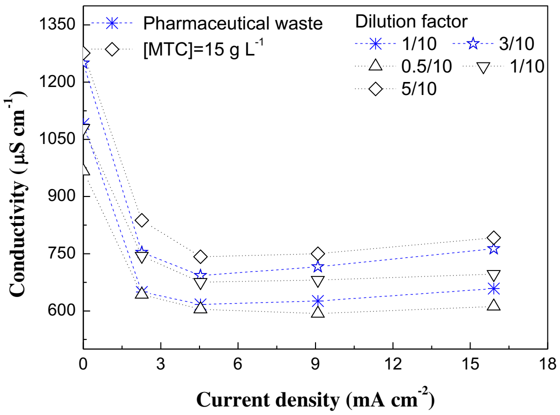


Fig. 7. Effect of the current density on the values of pharmaceutical wastewater conductivity.

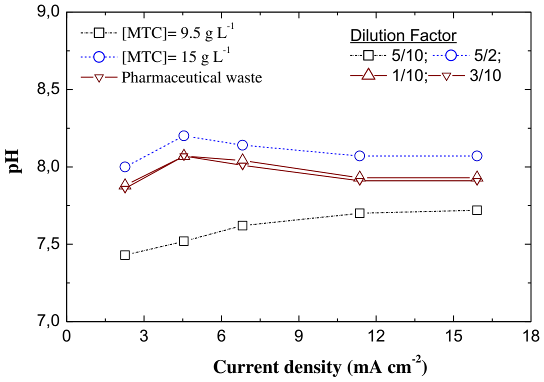


Fig. 8. Influence of current density on pH during the electrolysis of solution for 20 min of electrolysis.

pharmaceutical waste water was adjusted by sodium chloride addition in the range 800–1,200 µS cm^{-1}.

The solution pH is an important parameter in EC process where it has a significant effect on the formation of metal hydroxide species and removal mechanism of ions and pollutants. In order to investigate the pH effect, EC experiments were conducted in the pH range of 5–8.

Fig. 8 illustrates the pH change of the solution during electrolysis. As shown, as the initial pH of solution is slightly acidic (pH 5), pH values rise during electrolysis. An optimal pH seems to exist for a given pollutant, with optimal pH values ranging from 6.5 to 7.5.

The pH variation of the solution after EC process under various voltages shows that the final pH for all of experiments is higher than the initial pH. This observation was in agreement with results of Chen et al. [42]. The final pH at 7.2 allows a possible effluent reject directly in the river receiving mediums without adjusting the pH (after verification of all other neutral parameters).

3.2. NF treatment

The study of the EC/NF combination performances is realized which represent the evolution of COD and solution conductivity in relation to the volume flux.

Fig. 9 shows the effect of the trans-membrane pressure (TMP) ΔP on the permeate flux (J_V) at different concentrations of synthetic solutions of MTC of effluent solution as reported. Experiments were carried out at 25°C and pH 7.0.

The permeate flux at steady-state increased, as expected, with the applied pressure for all the MTC concentrations. For the synthetic solutions and the solutions of effluent, an increase in pressure causes an increase in volume flow that is in agreement with the theory described by the equation of Kedem and Katchalsky [43,44]. Darcy's law was checked from the filtration of distilled water. Figs. 10 and 11 show the retention values for conductivity and COD. It was observed that the retention rate (COD and conductivity) increased with flow up to an optimal value then it decreased with increasing pressure. Indeed, the accumulation of the organic species at the boundary layer at the level of membrane surface gave rise to a diffusion flow which decreased the total transfer flow which diminishes the performance of the process.

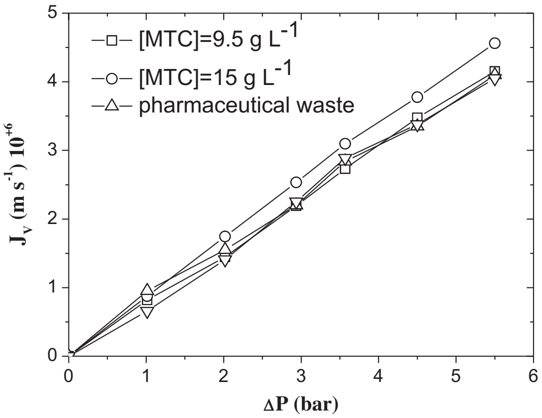


Fig. 9. Effect of TMP on permeate flux at different MTC concentrations at optimized conditions.

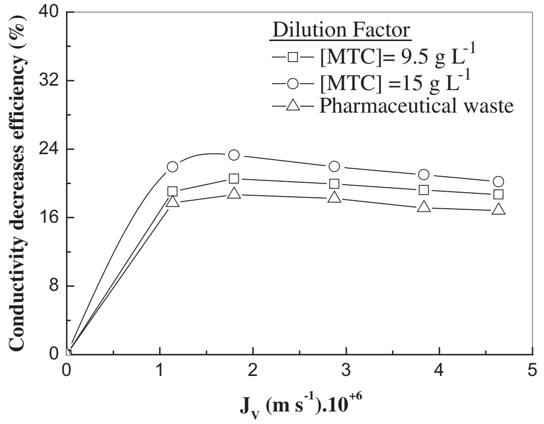


Fig. 10. Evolution of the retention rate of conductivity vs. volume flux following a pharmaceutical effluent NF treatment at optimized conditions.

This phenomenon is called concentration polarization and is described by film theory [45].

Organic compounds retentions were obtained for two synthetic solutions (% COD from 60.5 to 85.0%) and MTC effluent (from 76.0 to 78.0%).

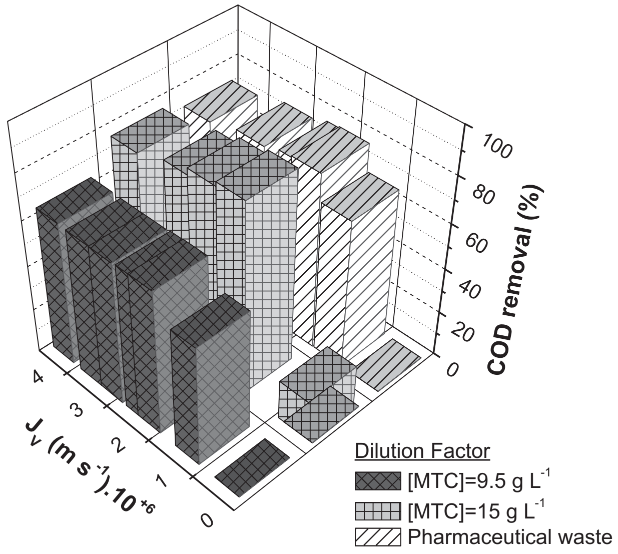


Fig. 11. Evolution of the retention rate of COD with volume flux following an EC/NF pharmaceutical effluent treatment at optimized conditions.

The electrical conductivity removal efficiency of the filtered solutions varies between 19.0 and 26.6%.

This is probably due to the nature of the treated solution which contains organic compounds, and also due to the operating conditions such as the basic-medium close pH, thus preventing the maximum retention.

4. The specific energy consumption

4.1. EC processes

Electrical energy consumption is itself a very significant economic parameter in the EC process, and so the effect of two operational parameters (applied voltage and supporting electrolyte) on the specific energy consumption (SEC) under the optimum conditions was also evaluated in this study. SEC was calculated using the Eq. (8):

$$E_{\mathrm{EC}} = \frac{VIt}{v} \tag{8}$$

where E_{EC} is the electrical energy consumption (kWh/m^3), V is voltage (V), I the applied electrical current (A), t is the time of EC in per hour (h) and v is the volume of the treated solution (m^3).

The study of the influence of current density on the energy consumption represented by Fig. 12 revealed the existence of a linear dependence and there is a direct relationship between current density and E_{EC}. The minimal energy consumed during the electrolysis of the solutions (9.5 g L^{-1}, 15 g L^{-1} and pharmaceutical waste) were observed to be equal to 0.074 kWh/m^3 for pH associated 7.43, 8.01 and 7.87, respectively.

4.2. NF processes

The SEC for NF (E_{NF}, kWh/m^3) depends on several factors, such as plant size, raw water salinity, plant configuration, type of NF membrane and module, and the raw water temperature. The E_{NF} required in a useful NF process is defined as the energy needed to produce a cubic meter of "permeate" of a desired species concentration. Since only one pump is used in our plant design (Fig. 13), the E_{NF} can be expressed in terms of several parameters [46]:

$$E_{\mathrm{NF}} = \frac{\omega_{\mathrm{pump}}}{Q_{\mathrm{P}} \times \eta_{\mathrm{P}} \times A} \tag{9}$$

where η_{P} (0.85) is the pump efficiency, Q_{P} is the permeate flow rate (m/h), A is the membrane surface (0.37 m^2) and ω_{pump} is the rate of pump work, given by:

$$\omega_{\mathrm{pump}} = \Delta P \times Q_{\mathrm{f}} \tag{10}$$

in which ΔP is the pressure applied to the raw feed solution, given by:

$$\Delta P = P_{\mathrm{f}} - P_0 \tag{11}$$

where P_{f} and P_0 are the solution pressures at the entrance of the membrane module and raw feed solution at the source, respectively, and Q_{cir} is the volumetric feed flow rate (m^3/s).

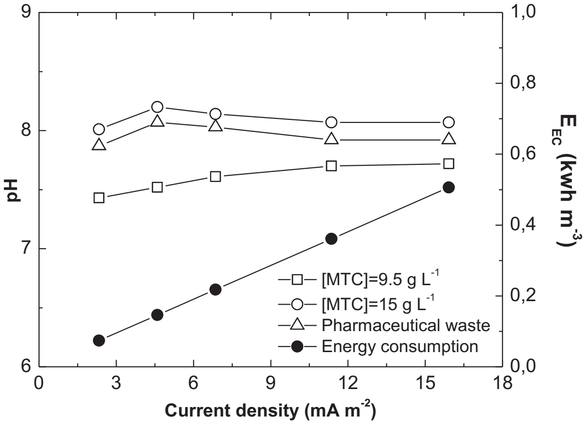


Fig. 12. Effect of current density and pH on energy consumption after 20 min of electrolysis with Al/Al electrode system pair, 13 V applied voltage, 22 cm^2 surface electrodes emerged.

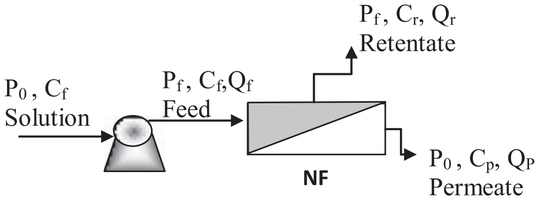


Fig. 13. Schematic of a simplified for single pump NF process.

After substitution of all the terms, the energy consumption E_{NF} becomes Eq. (12).

$$E_{\mathrm{NF}} = \frac{\Delta P \times Q_{\mathrm{f}}}{Q_{\mathrm{P}} \times \eta_{\mathrm{P}} \times A} \tag{12}$$

Fig. 14 illustrates the evolution of the SEC with pressure drop and COD removal efficiency.

The (Nanomax50) membrane was able to produce better quality water with COD removal efficiency for synthetic solutions (9.5, 15 g L^{-1}) and samples of effluent by registering a rate of elimination equals respectively to 64.5, 84.9 and 78.0%. The power, consumed by the pump for the three treated solutions, was estimated to respectively 3.49, 3.1 and 3.46 kWh/m^3. The optimal energies observed for obtaining a better rate of elimination of COD for the three selected model solutions (9.5 g L^{-1}, 15 g L^{-1}, and pharmaceutical waste) were recorded to be equal to 3.49, 3.08 and 3.46 kWh/m^3 for percentages of elimination respectively equal to 64.5, 85 and 78%.

The treatment by coupling of EC–NF requires a consumption of electrical energy equivalent to (0.074 kwh/m^3 in EC + 1.637 kWh/m^3 ($\eta_P = 0.$ 80) in NF, and the total is 1,711 kWh/m^3).

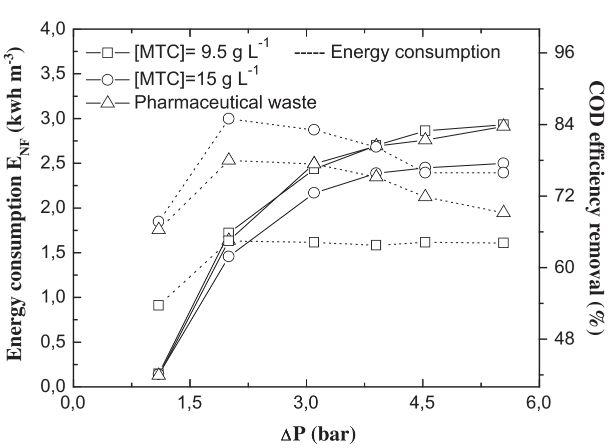


Fig. 14. Effect of TMP on the E_{NF} and COD removal efficiency by Nanomax50 membrane.

It should be noted that the system of filtration conceived in this study uses a module of filtration which has a very small surface of transfer what has due increasing energy consumption.

5. Conclusions

In this contribution, performance of EC using aluminum electrodes and NF processes were investigated for the increases of COD removal from pharmaceutical wastewater originated from the BPFA. The effect of various parameters like pH, current density, concentration (dilution factor) and transmembrane pressure and time electrolysis were studied.

The EC processing of 20 min at a current density of 11 mA cm^{-2} was considered as the most favorable (optimum) conditions for COD removal with an elimination of 98% (from 9,357 to 197 mg L^{-1}). The NF process can decrease this value from 197 up to 20 mg L^{-1} crossing the threshold rate of 90%. The higher voltage (>32 V corresponds to 2 A) increases the process of the COD, the turbidity and of the electrolytic conductivity with a reduction of 75–95%, 36–96% and 3.5–19.5%, respectively for the different analyzed solutions.

The treatment by EC of the samples of effluent enabled us to obtain a COD reduction (starting solutions: 6,500 mg L^{-1}) from (40%, 4,500 mg L) to (70%, 2,500 mg L^{-1}) for dilutions which are respectively of 4/5 and 1/10. Results showed that the maximum turbidity removal reaches 84, 51 and 48% for 9.5 g L^{-1}, 15 g L^{-1} for the pharmaceutical waste diluted to 3/10, respectively. The pH variation of the solution after EC process under various voltages shows that the final pH for the total of the experiments is higher than the initial pH.

The NF process employed in this modest research was determined as efficient for the removal of pollution parameters for pharmaceutical waste. NF also rejects uncharged, dissolved materials and ions according to the size and shape of the molecules in question. In NF filtration, it was observed that the retention rate (COD and conductivity) increased with flow up to an optimal value then it decreased with increasing pressure which can be explained by the apparition of a concentration polarization phenomenon.

Organic compounds retentions were obtained for two synthetic solutions (% COD from 60.5 to 85.0%) and MTC effluent (from 76.0 to 78.0%).

The coupling of processes (EC and NF) for the pharmaceutical waste processing enabled us to have a high rate of elimination of COD. Indeed the optimum conditions from our experiments were: dilution factor of 4/15; electrolysis time of 20 min, current density of 11 mA cm^{-2}. After EC: we onteain elimination of 91% (from 6,535 to 540 mg L^{-1}). Finally, the rejection of COD with NF varies from 0 to 71% depending on the feed concentration and pH. It was found that the influent pH value could affect MTC removal significantly. Data reported here suggest that the hybrid EC/NF process is superior over the conventional process with respect to both COD and turbidity removal.

The minimal energy consumed during the electrolysis of the solutions (9.5, 15 g L^{-1} and pharmaceutical waste) was 0.074 kWh/m^3 for pH associated 7.43, 8.01 and 7.87, respectively. In NF, the optimal energies observed for obtaining a better rate of elimination of COD for the three selected model solutions (9.5, 15 g L^{-1}, and pharmaceutical waste) were enregistred to be equal to 3.49, 3.08 and 3.46 kWh/m^3 for percentages of elimination respectively equal to 64.46, 84.95 and 78%. According to the obtained results, the treatment by coupling of EC and NF requires a consumption of electrical energy equivalent to 1,711 kWh/m^3. EC coupled NF is an energy efficient process to decrease COD and turbidity from pharmaceutical waste.

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