Pharmaceutical Industry Wastewater Treatment by Electrocoagulation and Micellar Ultrafiltration

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The objective of this paper consists in pursuit the efficiency of electrocoagulation and micellar ultrafiltration in terms of color removing, respectively, organic load, found in the final quality of the effluent, which must be within the limits imposed by the regulations NTPA 001 or NTPA 002, considering the company's options regarding recycling or reuse of water. In this work paper were determined: the electrocoagulation and micellar ultrafiltration performance evaluation was analyzed in terms of the main operational parameters influence: pH, current density, working pressure, surfactant nature and concentration, the anode nature and composite membrane nature ; the best results for electrocoagulation were obtained in the following experimental conditions: pH = 5, i = 13.94 mA/cm^2, anode material: iron. In this combination was possible to obtain color/organic matter efficiencies of about 99%. The best performances for micellar ultrafiltration were obtained with: membranes based on 12% polysulfone and 2% polyaniline in dimethylformamide, surfactant:SPAN 80 at 10^{-4} M at a pressure of at least 4 atm and pH = 9.2

Keywords: waste water treatment,electrocoagulation, micelar ultrafiltration, membranes, composite membranes

Industrial activities are the one generating a severe impact on the environment, being the largest water consumer, due to the variety, volume and toxicity of pollutants they contain, but mostly due to unsatisfactory level of treatment before the discharge into the receiver [1].

In recent years, decontamination and disinfection of waters using electrochemical processes applied directly or integrated was considered as a very interesting alternative to conventional processes, due to the significant improvements made to the electrode materials and by switching to renewable "low -cost" energy sources [2].

Also, ideally, water can be treated without using chemical reagents by means of membrane filtration processes [3-5].

Membrane filtration extended its applications to separation chemical species dissolved by system segregation using: surfactants, polyelectrolytes, colloidal particles, nanoparticles [6,7]

These types of separation are generally known as methods of improved colloidal ultrafiltration; techniques that have been investigated until now include: improved micellar ultrafiltration (MEUF); ultrafiltration by polyelectrical intensification (PEUF), ultrafiltration by ion expulsion (IEUF) and colloidal ultrafiltration of micro- and nano- particles (UFC) [8-11].

The activities in the pharmaceutical industry are classified as large producers of wastewater with high and varied refractory organic compounds content [1].

For these waters, one of the biggest environmental problems is reducing the amount of chemical oxygen demand and colour removal.

These wastewater resulting from drug plants are toxic, have intense color and unpleasant odor. High COD concentration and low BOD_5 concentration of these waters, represents a challenge for biological treatment, because the presence of refractory organic compounds has an inhibitory impact on the microorganism's activity [2].

In this context, the electrocoagulation has aroused a great interest, imposing in the last two decades as a major importance treatment method with high efficiency and multiple effects.

On the other hand, micellar enhanced ultrafiltration (MEUF) is the separation technique that most clearly illustrates colloidal ultrafiltration [8].

This technique involves adding a surfactant to a contaminated aqueous solution subjected to ultrafiltration (fig.1) [8-11].

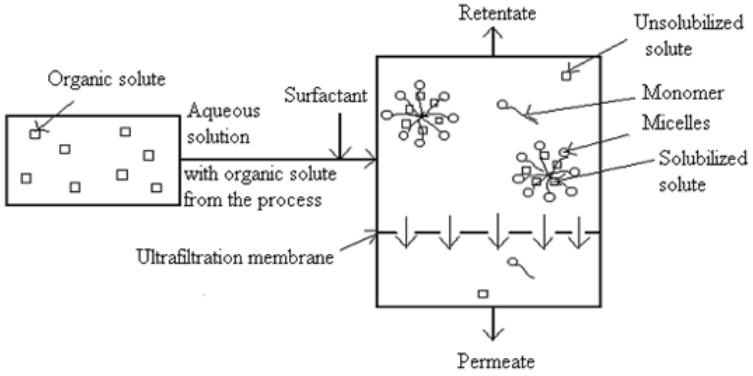

Fig. 1. Schematic diagram of micellar ultrafiltration

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Parameter	Value
Color	Dark blue
pH	6.36
Initial CCOCr (mgO_2/L)	<5000
Conductivity(mS/cm)	<15

Table 1
INITIAL CHARACTERISTICS OF THE PHARMACEUTICAL INDUSTRY WASTEWATER SUBJECTED TO ELECTROCOAGULATION

The surfactant forms spherical aggregates called micelles, containing between 50 and 100 molecules [9].

The micelles interior contains hydrocarbon chain of the surfactant, which thus forms a hydrophobic medium [9,10].

Organic pollutants, in our case, dyes from water, are dissolved or solubilized in micelles primarily by hydrophobic interactions with the surfactant combination [8].

Through this experimental study was taken into account to improve the electrocoagulation efficiency in treatment the waste effluent produced in the pharmaceutical industry by identifying the optimal conditions and the influence of the main operational parameters (current density, *p*H initial value, electrocoagulation time, stirring rate, anodic material type) on the process [12-15].

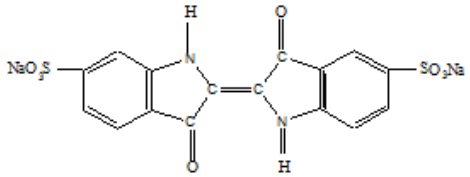
The objective of this paper consists in pursuit the efficiency of electrocoagulation and micellar ultrafiltration in terms of color removing, respectively, organic load, found in the final quality of the effluent, which must be within the limits imposed by the regulations NTPA 001 or NTPA 002, considering the company's options regarding recycling or reuse of water.

Experimental part

Characterization of the waste waters used for the study

In table 1 are given the initial characteristics of the pharmaceutical industry wastewater subject to electrocoagulation.

In addition to the large amount of chemical oxygen demand, these wastewaters were characterized also by a deep blue colouration due to the technological use Indigo carmine dye. Indigo Carmine, or the disodium salt of 3,3 '-dioxo-2, 2'-*bis*-indolyden 5,5'-disulfonic acid that is a blue dye which belongs to the indigoid class of dyes. The chemical structure of indigo carmine is shown in scheme I [15].



Scheme 1. Indigo carmine chemical structure [15]

Indigo carmine is considered a very toxic dye, as it causes skin, gastrointestinal tract irritations causing nausea and respiratory tract irritations by triggering a suffocation sensation [14].

Electrocoagulation

Cathode/anode material type

Anode materials have a major influence on the electrochemical processes efficiency and, therefore, the choice must be made in a more accurate and adapted to the purpose mode. The chosen material must be safe for human health and environment friendly.

The aluminium and iron were selected as anode materials because are readily available, and stainless steel was used as cathode material because is chemically inert. In order to ensure a bubble production which is able to facilitate the achievement of high pollutants removal efficiencies is required to use an inert cathode, from the electrochemical point of view [14-16].

Reagents

In order to adjust the initial *p*H of the real wastewater sample to an acid *p*H, a 6% sulfuric acid solution prepared using 95-97% p.a. Merck, Germany H_2SO_4 was used.

In order to adjust the initial *p*H value of the original wastewater sample, a 0.1N sodium hydroxide solution was used.

Experimental procedure description

The experimental set-up was composed of the following components: heat-resistant glass vessel with 100 mm x 180 mm dimensions, 1.000 mL capacity, four electrodes (two anodes and two cathodes) with identical 81 x 46 x 100 mm dimensions connected in parallel at a 25mm interelectrode constant distance, Mastech HY3005D DC stabilized power supply with operating options under galvanostatic or potentiostatic regime, magnetic stirrer [17].

At the beginning of each electrocoagulation experiment, 800 mL of wastewater were introduced into the electrocoagulation cell, and then the electrodes were immersed and connected to a Mastech HY3005D stabilized power source. The initial *p*H value was adjusted to the desired value using H2 SO4 6% solution respectively, NaOH 0.1N solution.

Due to the low conductivity of the water sample at the beginning of each experiment were added 2 g of NaCl.

In order to evaluate the electrocoagulation process performance, expressed in terms of colour removal, namely organic matter content reduction, the samples were taken after 15, respectively 20 min and analised. The *p*H variation during the process was determined using a Consort C380 pH meter (resolution 0.01 *p*H sensor Pt 1000).

Prior to analysis, the samples were filtered using blue band filter paper and then were analyzed in terms of colour removal using a Cintra 5 double beam UV-Vis spectrophotometer (UV-Vis spectral range 190-1100 nm) at the 610 nm wavelength.

The electrocoagulation process efficiency was calculated using the following formula [14,15]:

- the organic matter content reduction was calculated as follows::

$$R(\%) = \frac{CCO_{Cr_0} - CCO_{Crsample}}{CCO_{Cr_0}} \cdot 100 \quad (1)$$

where: CCOCr0 and CCOCrsample reprtesents the initial organic matter concentration, respectively the organic matter concentration at time t.

- the solution colour removal was determined as follows:

$$R(\%) = \frac{A_0 - A_{sample}}{A_0} \cdot 100 \quad (2)$$

where: A_0 and A_{sample} represents the initial absorbance, respectively the absorbance at time t for Indigo carmine containing sample.

Micellar ultrafiltration

The method

Ultrafiltration was studied using 40 mL stirring cell unit and experiments were conducted at 25° C and 414 kPa (about 4 atm). Polysulfone based membranes were used [8,11]. Working solution volume was 300 mL .

The solution is treated in an ultrafiltration device (fig. 2) with a membrane having the pores sufficiently small in order to prevent the passage of charged micelles [8,11].

Fig. 2. Micellar ultrafiltration device (view)

The conclusion of the experiment is carried out at by passing 200 mL of permeate solution through the membrane [11].

Indigo carmine separation was determined by molecular absorption ion concentration in the permeate - the experimental data being reported to the time in which 100 mL of solution were passed through the membrane.

Materials and procedures

The membranes used for experiments represents polysulfone composite with polyaniline (1-3%) insertions as was shown in a previous paper prepared from a polysulfone solution of 10, 12 and 14% in dimethyl-formamide containing also dispersed polyaniline [18-23].

Indigo carmine concentrations in solution 10^{-8} - 10^{-6} M, were measured using a molecular adsorption spectrophotometer CAMSPEC.

Solute retention (R) is calculated based on balance equations, taking into account the initial concentrations or the ones determined in the permeate according to the equations *(1)* and *(2)*.

For Indigo carmine micellar ultrafiltration was chosen a 4 atm pressure, variable *p*H and an initial dye concentration which falls in the upper limit of 5000 CCOCr (mgO_2/L).

Surfactants (Fluka) chosen for retention study through polyaniline-polysulfone composite membrane [24] are in the scale of the ones previously presented:

-anionic surfactant: sodium dodecyl benzensulfonate (DBSNa),

-cationic surfactant: octadecyl pyridinium chloride (CODP) and

-non ionic surfactant: sorbitan monooleate (SPAN 80)

Surfactant concentration is in the range 10^{-7} M -10^{-4} M, and the feed *p*H is variable.

Results and disscusions

The increased interest manifested in the last twodecades for the electrochemical methods is explained by their versatility and compatibility with environmental standards imposed by law.

The principle underlying the electrocoagulation as treatment method is the use of electrons considered *clean reagents*, which enables the anodic oxidation of iron, respectively aluminum electrodes, followed by *in situ* generation of a number of coagulant character species and metal hydroxides with destabilizing and suspension particles aggregation role, respectively precipitation and adsorption of dissolved contaminants.

At the same time, hydrogen evolution takes place at the cathode, the bubbles being involved in the capture and pollutant's floating, thus making possible the contaminants removal.

Current membrane technology developed in two main directions:

- increase membrane selectivity by promoting new membrane materials;

- improved performance of membrane processes by separation system segregation.

The first dirrection, promoted for almost fifty years, was based on polymeric materials increasingly more evolved (polymer based membranes) or compounds with selectivity becoming more and more pronounced (liquid membranes) [25, 26].

The second direction, studied in this work is based on introduction of some surface-active substances or colloidal particle in the separation system so that the sizes of target chemical species to be enlarged to the size of the ultra - or even micro-filtration pore membranes [8-11]

Further, the results obtained for the study of each selected operational parameter influence on the electrocoagulation and micellar ultrafiltration processes efficiency are presented.

The process efficiency was evaluated in terms of colour and organic matter removal expressed as COD [6,9].

The pH value influence on the electrocoagulation process efficiency

A key parameter of the electrocoagulation process is the waste water initial *p*H. From the researches realised until now, it has been proved that the pH influences the Fe^{2+} to Fe^{3+} conversion kinetics, the solution conductivity, the electrodes dissolution efficiency, the formed hydroxy metal speciation and zeta potential of the colloidal particles [14].

In general, as highlighted, at low, respectively high *p*H values, the generated species are in soluble form, the iron solubility greatly increasing [15].

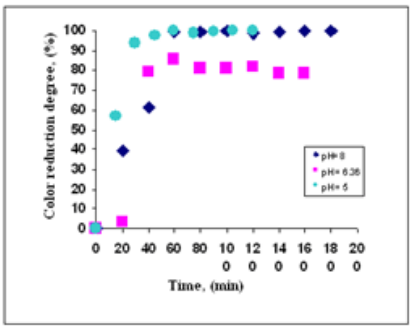
Many metal hydroxides species with coagulating agent role are formed in the acid, alkaline and neutral solution. In the alkaline environment monomeric anions such as $Fe(OH)_4^-$, with lower coagulation efficiency are formed [16]. The formation of $Fe(OH)_4^-$, monomeric anion with no decoloration capacity, leads to a decoloration efficiency decrease at *p*H values higher than 9.

The formation of this complex as a result of the sacrificial anode dissolution leads to a slight decrease in pH value (due to HO^- ions consumption) [17].

The study of the *p*H influence on colour, respectively chemical oxygen demand reduction degree, aimed to determine the optimal *p*H for the electro-co-agulation process.

In order to achieve this goal, prior to the begining of the experiments, the pH samples were adjusted to the desired value using 6% H_2SO_4 and 1N NaOH solution.

In figure 3 are shown the results obtained, standing out that in the process debut stage at *p*H 5 and respectively 8, colour removal degrees obtainde ranged between 39 and



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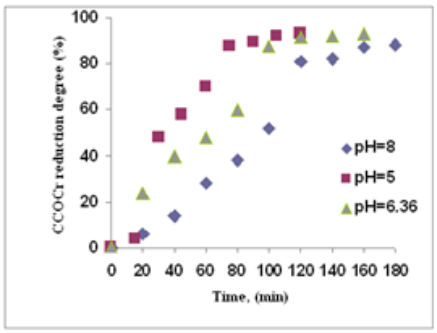
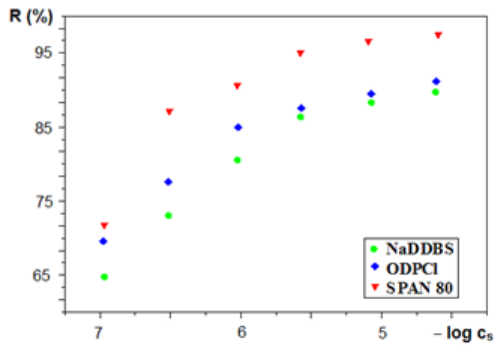


(b)

Fig. 3. The solution *p*H influence on the process efficiency, i = 20.9 mA/cm^2, $CCOCr_i$ = 5000mgO_2/L, stirring rate = 200 rpm, t =50°C



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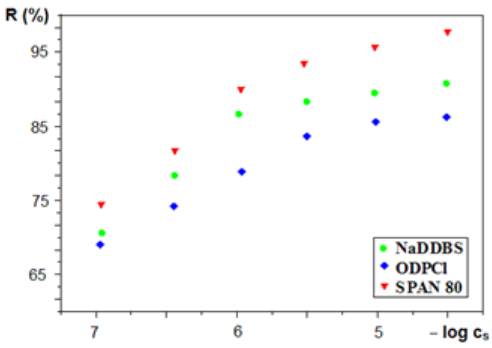


(b)

Fig.4. Retention dependence in the case of Indigo carmine ultrafiltration depending on *p*H [(a) *p*H=4.8 and (b) *p*H=9.2], surfactant nature and concentration

56%, while at *p*H = 6.36 (unadjusted *p*H value of the wastewater) colour removal efficiency was only 3%.

With regard to the system behavior in terms of organic matter content reduction, the results show similiar behavior of the system in the beginning stage of the process (first 40 min), the best results being obtained after 120 min at *p*H = 5, corresponding to a COD reduction degree of 93.2%.

Thus, at *p*H = 8, the maximum COD reduction degree was 88.4% being obtained after 180 min. The low organic matter removal efficiency is due to the formation of $Fe(OH)^{4-}$, in strongly alkaline environment, which is in the dissolved state and has a very low coagulation capacity [28].

During the experiments, the used water color changed in the first 20 min from blue to green, which means that Fe^{2+} has been generated at the anode.

At *p*H = 6.36, very good results have been obtained for the COD reduction degree, the maximum value being 93.4%, value which coincides with the one obtained at *p*H 5.

The high process efficiencies obtained could be due to the high current density of 20.9 mA/cm^2, which caused a metal ion mass generation. Iron hydroxides contribute to the colloidal particles destabilization [29].

The mechanism underlying the electrochemical color, respectively organic matter elimination is very complex and difficult to decipher. It assumes that the removal of organic matter is due to precipitation and adsorption processes, depending on the working *p*H range. Thus, at low pH values, Fe^{2+} metal species generated at the anode, binds to the colloidal anionic particles present in the waste water, leading to their charge neutralization and the solubility reducing. This removing pollutants process is called precipitation [28]. At *p*H values greater than 7, the mechanism involved in the removal of organic pollutants is the adsorption of the organic matter on the amorphous metal hydroxide precipitates. The good results obtained at *p*H <7 are assigned to the charge neutralizing mechanism through cationic monomer [15].

The efficiency of processes that use surfactants are often influenced by feed solution *p*H, nature and concentration of the surfactant [8-10]. In this case, the micellar ultrafiltration results, with a polysulfone-polyaniline composite membrane obtained from a 12% polysulfone solution in dimethylformamide, at 4 atm, under vigorous stirring, shows that retention is dependent on the pH of the feed solution, nature and concentration of the surfactant (fig. 4 and b). Sodium dodecyl bezensufonate (NaDBS), octadecyl pyridinium chloride (CODP) and SPAN 80 were used for this study, at concentrations between 10^{-7} M and 10^{-4} M, and *p*H was specific to acetate -acetic acid buffer (4.8 - fig. 4 a) and the ammonia-ammonium chloride (9.2 - fig. 4 b).Experiments show that Indigo carmine retention is continously increasing with increasing the concentrations of surfactants in feed solution (fig. 4). Although all surfactants have a positive influence on target substance ultrafiltration results are growing in the following order:

DBSNa < CODO <SPAN 80 for *p*H=4.8 and
CODO <DBSNa < SPAN 80 for *p*H=9.2

The occurrence of a retention cap behind 10^{-5} M concentration indicates the achievement of the critical micellization concentration (cmc).

Indigo carmine retention reaches a maximum of about 97% for non ionic surfactant and about 87% for ionic surfactant.

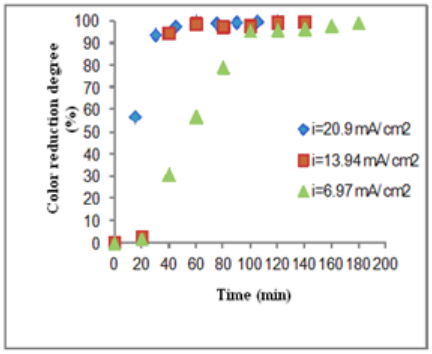
Ionic surfactant behaviour is determined by the acid character of dodecyl pyridinium ion and alkaline character dodecyl benzene sulfonate ion.

The optimum concentration and *p*H is difficult to establish in this case because Indigo carmine dye has acid-base character being a disodium salt of an aromatic disulfonic acid.

In the predetermined operating conditions: 12% polysulfone - polyaniline membrane, pressure: 4 atm, turbulent flow regime, regardless of working *p*H is recommended to use SPAN 80 in concentration over 10^{-4} M.

Current density influence on the electrocoagulation and micellar ultrafiltration process efficiency

The current density is the most important operational parameter in the electrochemical processes because it is



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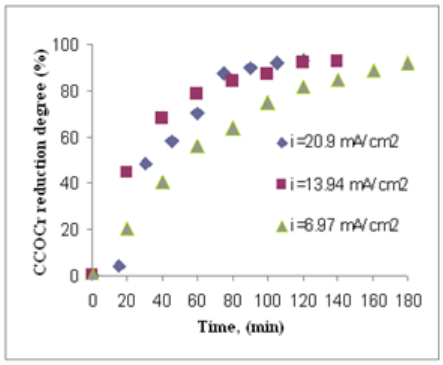


(b)

Fig. 5. The color, respectively organic matter reduction degree variation in time, iron anodes, $CCOCr_i$ = 5000 mgO_2/L , stirring rate 200 rot/min, pH_i = 5, T = 50°C

directly proportional with the reaction rate taking place on the electrodes surface, also having influence on the electrode potential, which defines the type of reaction that takes place at the electrode surface.

In the case of iron and aluminum made anodes, the primary reaction that occurs is dissolution, which is predominant compared with other reactions whose influence is insignificant.

The amount of coagulation agent is proportional to the current density applied to the electrocoagulation cell, also, the sacrificial anode dissolution efficiency and the rate of OH^- radicals generation at the cathode is directly influenced by the density value [14].

In this context, studies have been conducted to identify the optimal current density value and to establish the effect of this parameter on the electrocoagulation efficiency. In figure 5 (a) are presented the results obtained in the range of current density 6.97-20.94 mA/cm^2 for the color reduction degree variation in time, in the system iron anode / stainless steel cathode.

From data analysis, it can be said that in the first 20 min at current denisties of 6.97 and 13.94 mA/cm^2 the behavior was similar, corresponding to color removal degree of about 10%, while at 20.90 mA/cm^2, the yield achieved was 58%.

Doubling the current density from 6.97 to 13.94 resulted in an increase of the color removal effciency from 30% to nearly 94% in only 20 min.

This behaviour of the system is explained by the fact that at high current density, the dissolution rate of the anode increases, resulting in an increase of the amount of iron hydroxides, respectively of the flocs number, intensifying the effectiveness of coagulation process.

Most often, the bubbles generated improve the efficiency of mixing iron hydroxides with dye molecules and hence the color removal efficiency [15].

Also, it can be seen that in the range 40-160 min, the color reduction degree significantly increased finally achieving a 99.40% yield. From data analysis it can be stated that the optimum current density is 13.94 mA/cm^2 becase allowed us to obtain a satisfactory yield with acceptable costs.

In figure 5 (b) the results obtained in the field of 6.97-20.90 mA/cm^2 current density for wastewater organic matter reduction degree variation in time, in the system iron anode / stainless steel cathode are presented.

The current density was determined from the ratio between the current intensity applied to the cell and the electrode surface.

According to Faraday's law, the Fe^{2+} dose generated in the system by anode dissolution depends on the electrocoagulation time and current intensity applied to the electrocoagulation cell. Therefore, increasing the intensity, respectively current density, favors process efficiency improvement [14-16].

The organic matter removal efficiency increased from 20% at 6.97 mA/cm^2 to 44% by modification of current density to 13.94 mA/cm^2.

The increase of density up to a value of 20.90 mA/cm^2 did not lead to a significant improvement of the organic matter reduction degree.

At high current density values the extent to which the anode dissolution happens, is accompanied by the generation of large amounts of Fe^{2+} ions and Fe(OH)n hydroxides.

In addition, the bubbles generation rate increases, and the bubbles size decreases with the current density increase, these trends favor achieving pollutants high removal efficiency by electro flotation with H_2 bubble [17].

On the basis of data analysis it can be concluded that the best results have been obtained at a density of 13.94 mA/cm^2, the efficiency achieved being 92.8%.

In addition, these results indicate that the reactor operation at high current density, does not cause the achievement of the most satisfactory pollutants removal efficiency. Depending on the needs, the optimal density choice is the result of a combination between operational costs and efficient use of the generated coagulant.

Thus, it can be concluded that the current density is a key operational parameter for the electrocoagulation process, which directly affects the response time of the system and the predominant mechanism involved in the removal of pollutants.

In micellar ultrafiltration, after choosing the suitable surfactant, membrane characteristics are the second decisive parameter.

In this study we tried to use polyaniline - polysulfone composite membranes obtained from a solution of 10-14% polysulfone in dimethylformamide [22, 23].

Working pressure was maintained at 4 atm, the flow regime was turbulent and SPAN 80 concentration was 10^{-3} M.

It was aimed the optimization of flow - retention ratio being known antagonistic dependence of these two parameters [7, 8].

Composite membranes based on 10-14% PSf / DMF and 1% polyaniline have a specific behaviour for micro- and ultrafiltration.

Thus, with operating time increase (fig. 6 a nd b) flow decreases, and retention increases. The flow decline is the steepest for PSf 10% membranes and retention increase is maximum for 14% PSf membrane.

After about 8 h of operation retention becomes optimum for membranes 12 and 14%, more than 93%, and the flow stabilizes at about 95 L/m^2·h for all membranes.

It can be concluded that composite membranes based on 12% PSf are best suited as an alternative for Indigo carmine micellar ultrafiltration, under the experimental conditions, in terms of cost-effectiveness, knowing the fact

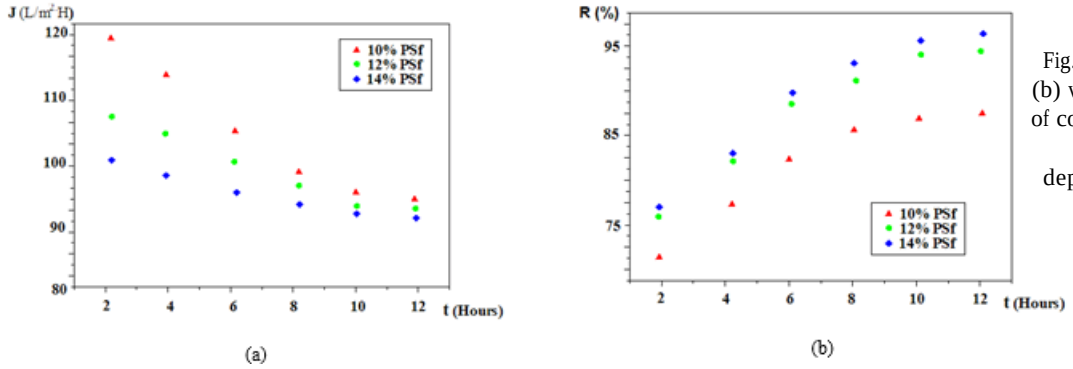


Fig. 6. Flow (a) and retention (b) variation for the three types of composite membranes (10%, 12% and 14% PSf/DMF) depending on operation time

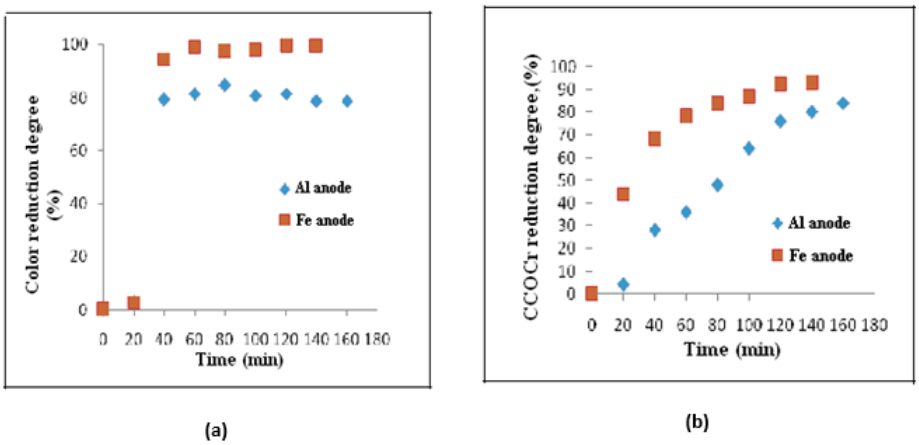


Fig.7. The influence of anode material on the electrocoagulation process efficiency, $CCOCr_i$ = 5000 mgO_2/L, stirring rate 200 rot/min, pH_i = 6.36, T = 50°C

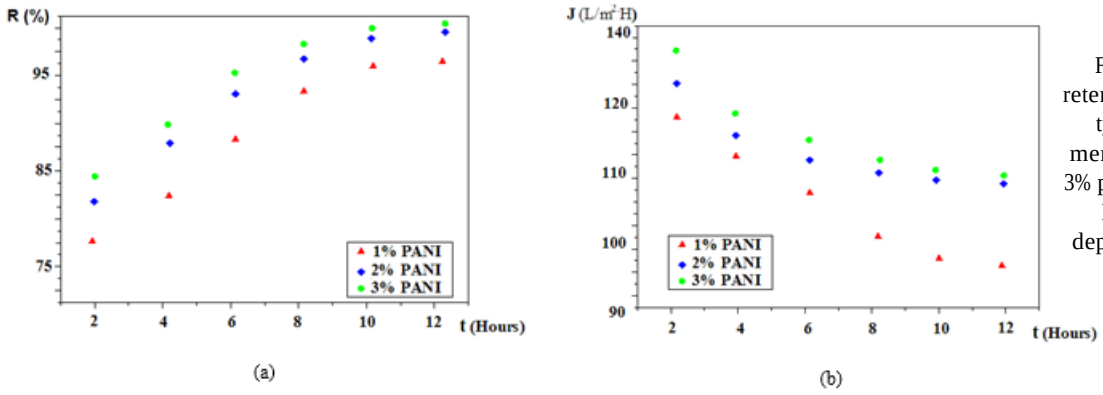


Fig. 8. Flow (a) and retention (b) for the three types of composite membranes (1%, 2% and 3% polyaniline in 12% PSf/ DMF membranes) depending on operation time

that increasing the concentration of the polymer makes more expensive membrane and process [22,23].

The inffluence of anode material on the electrcoagulation process efficiency and polyaniline concentration in the composite membrane for micellar ultrafiltration

In any electrochemical process, the electrode made material plays a very important role, so, the choice should be as accurate and suitable to the purpose.

Aluminum and iron were selected as anode material because are economically affordable, readily available and not at least because they facilitate the generation of a series of amorphous metal oxyhydroxides / hydroxides/ oxides in the system with excellent adsorption properties of species soluble [15,17].

In figure 7 (a) and (b) are presented the experimental results that we have obtained for determining the influence of anode material on the electrocoagulation process efficiency.

The experimental data revealed that the best color, respectively organic matter removal efficiencies, expressed as COD, were obtained for iron sacrificial anodes.

With the regard to the aluminum electrodes, the results were lower the color removal degree achieved was 78.57%, compared to 99% in the case of iron anodes.

Indigo carmine micellar ultrafiltration in the optimal conditions previously determined, at 4 atm, can still behave a variable related to the selective nature of the material: composite membranes.

So, after we have established a favorable concentration of the polymer from which 12% PSf / DMF membrane is obtained, the influence of polyaniline concentration from the polymeric solution composition is tested by varying it in the range 1 - 3%.

Polyaniline concentration increase in the composite membrane leads to both permeate flow and retention increase (fig. 8 a and b).

However, the positive effect of this increase is more prominent in the passage from 1 to 2% than at 2 to 3% polyaniline composite membrane.

From the tehnico-economical point of view is preferable to use 12% polysulfone composite membrane and 2% polyaniline, because the positive effects of the process are acceptable, and the cost is similar to integral polysulfone membranes.

The influence of curent density on the pH variation during the electrocoagulation process and of pressure on micellar ultrafiltration

During the electrocoagulation process, the solution *p*H varies the final value being influenced by the anode

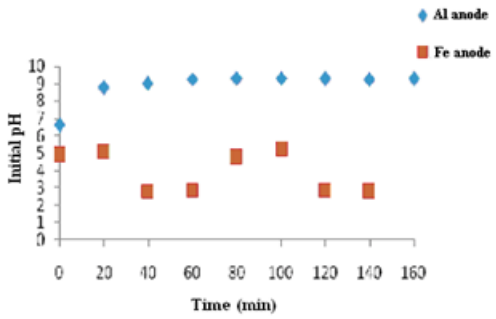
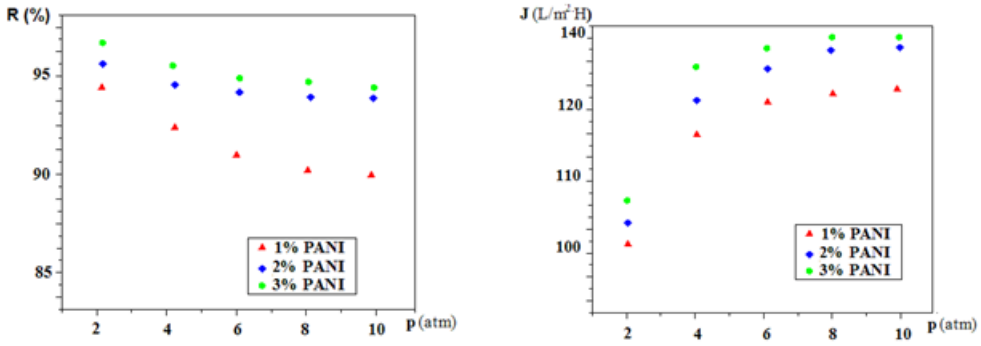


Fig. 9. The *p*H variation during the process, at three current densities studied, iron anodes, $CCOCr_i$ = 5000 mgO_2/L , stirring rate 200 rot/min, pH_i = 5, T = 50°C



(a) (b)

Fig.10. Flow (a) and retention (b) for the three types of composite membranes (1%, 2% and 3% polyaniline in 12% PSf/DMF membranes) depending on transmembranar pressure

material, and also by the initial pH value of the solution. In this regard, during the experiments realised for studying the current density influence on the process efficiency, the pH variation was also monitored and the results are presented in figure 9. From the data analysis it can be observed a non-linear variation of *p*H during the electrocoagulation process, behaviour valid for all three current density values.

At a density of 13.94 mA/cm^2, the *p*H value increase in the first 20 min corresponds to a low efficiency of the electrocoagulation process, which can be explained by the low combination speed of the ions Fe^{2+}/Fe^{3+} with OH^- radicals.

Between 40-60 min , the *p*H value decrease corresponds to process efficiency increase fact that is explained by the decrease of OH^- radical quantity left uncombined. Regarding the system behavior at the other two density values, the *p*H variation is similar with the one described for i = 13.94 mA/cm^2.

Micellar ultrafiltration assumes the operation in an interval from 2 to 10 atm [8,11].

In these experiments we tried to determine the working pressure that lead to optimal flow and retention (fig. 10).

Increasing pressure leads to flow decrease and retention increase.The most drastic decrease in membrane retention is recorded for 12% PSf and 1% PANI.

Retention and flow tests variation depending on the transmembranar pressure performed on 1, 2 and 3% polyaniline membranes in 12% PSf / DMF (fig. 10 a and b) membranes confirms the superior performance of composite membranes when the polyaniline concentration grows.

And this time it is observed that the transition from 1 to 2% polyaniline in membrane, enhance process performances more pronounced than switching from 2 to 3%.

At working pressures over 4 atm membranes performances are maintained quasi constant.

In conclusion, we prefer to operate at working pressures of at least 4 atm and with membranes with minimum 2% Pani in 12% PSf / DMF.

Conclusions

Given the fact that worldwide, the industry generates about 3 million tons of waste with toxic and hazardous potential of which 200,000 tons of sludge from the pharmaceutical industry, it tis justified to try the treatment by electro coagulation and micellar ultrafiltration of this kind of wastewaters.

In this paper were determined:

- the electrocoagulation and micellar ultrafiltration performance evaluation was analyzed in terms of the main operational parameters influence: *p*H, current density, working pressure, surfactant nature and concentration, the anode nature and composite membrane nature ;

- the best results for electrocoagulation were obtained in the following experimental conditions: *p*H = 5, i = 13.94 mA/cm^2, anode material: iron. In this combination was possible to obtain color/organic matter efficiencies of about 99%.

- the best performances for micellar ultrafiltration were obtained with: membranes based on 12% polysulfone and 2% polyaniline in dimethylformamide, surfactant:SPAN 80 at 10^{-4} M at a pressure of at least 4 atm and *p*H = 9.2

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