Pharmaceutical Industry Wastewater Treatment through Electrocoagulation

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The activities in the pharmaceutical industry are classified as large producers of wastewater with high and varied refractory organic compounds content. Wastewater resulting from drug plants are toxic, have intense color and unpleasant odor. In this work we aimed to establish the electrocoagulation process performances in the treatment of a pharmaceutical industry real wastewaters having a high content of organic matter and strongly colored (Indigo Carmine), and also to establish the optimal conditions in order to ensure the highest degree of purification with acceptable costs.

Keywords: wastewater, electrocoagulation, pharmaceutical industry, treatment.

The industrial activities are those that generate a severe impact on the environment, being the largest water consumer, due to the variety, volume and toxicity of the pollutants which they contain, but mostly because of the unsatisfactory treatment level achieved before the discharge into the environment [27].

In the recent years, water decontamination and disinfection using directly or integrated electrochemical processes was regarded as a very interesting alternative to the conventional processes, due to the significant improvements brought to the electrodes materials and by coupling to "low cost "renewable energy sources. 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.

Wastewater resulting from drug plants are toxic, have intense colour and unpleasant odor. High COD concentration and low BOD_5 concentration of these waters, is a challenge for biological treatment, because the presence of refractory organic compounds has an inhibitory impact on the microorganism's activity [20].

In the industrial process of obtaining the capsules for antibiotics packaging are generated wastewaters with a high content of organic matter, coloured compounds, gelatine, reason for which it is imperative to remove these compounds as an obvious need in the environmental protection strategy, but especially aquatic ecosystems [3].

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.

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, pH initial value, electrocoagulation time, stirring rate, anodic material type) on the process.

Thus, the electrocoagulation efficiency regarding colour and organic load removal, found in the final effluent quality must be within the limits imposed by NTPA 001 and NTPA 002 regulations, taking into account the recycling or water reuse company options [2,4].

Experimental part

Characterization of the waste waters used for the study

In figure 1 is shown the technological flow for the waters generated from the antibiotics capsules manufacture and

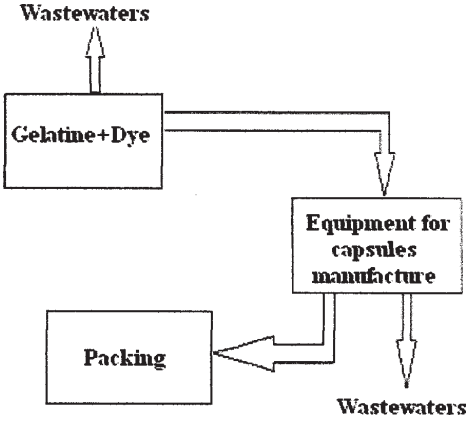

Fig. 1. Technological flow for the wastewaters generated from the antibiotics capsules manufacture

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

Table1

INITIAL CHARACTERISTICS OF THE PHARMACEUTICAL INDUSTRY WASTEWATER SUBJECT TO ELECTROCOAGULATION

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

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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 figure 2 [5].

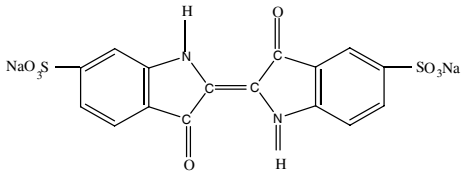

Fig 2. Indigo carmine chemical structure [5]

In the indigo carmine molecule are two nitrogen atoms linked each to one labile hydrogen atom which ingrains to the molecule a vulnerability shown particularly to the hydroxyl radicals attack.

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 [5].

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 [6].

Reagents

H_2SO_4 solution

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.

NaOH solution

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. In figure 3 is shown the electrocoagulation set-up. [7]

At the beginning of each electrocoagulation experiment, a 800 mL volume of water sample was 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 H_2SO_4 6% solution respectively, NaOH 0.1N solution. Due to the low conductivity of the water

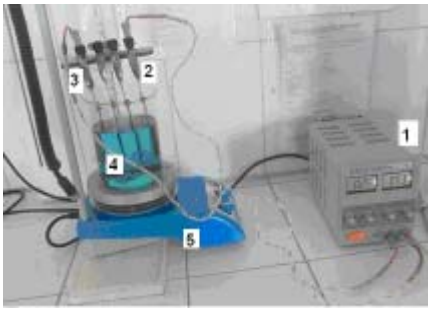

Fig. 3. Experimental set-up: 1 = stabilized power supply; 2 = cathode (stainless steel); 3 = sacrificial anode (iron/ aluminum); 4 = electrolytic cell; 5 = magnetic stirrer.[7]

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 [4,5]:

- the organic matter content reduction was calculated as follows:

$$R(\%) = \frac{CCO_{Cr0} - CCO_{Crproba}}{CCO_{Cr0}} \cdot 100 \quad (1)$$

where CCO_{Cr0} and $CCO_{Crsample}$ reprtesents the initial organic matter concentration, respectively the organic matter concentration at time t.

- the solution colour removal was determined as follows:

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

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

Results and disscusions

The increased interest manifested in the last two decades 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.

Further, the results obtained for the study of each selected operational parameter influence on the electrocoagulation process efficiency will be presented. The process efficiency was evaluated in terms of colour and organic matter removal expressed as COD [6,9].

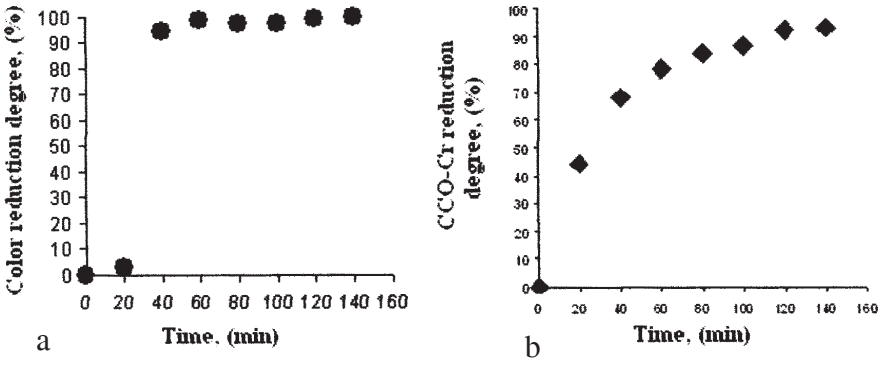

Fig. 4. The electrocoagulation time influence on the process efficiency, i = 13.94 mA/cm^2, CCOCr$_i$ = 5000mgO$_2$/L, *p*H = 5, stirring rate = 200 rpm

The electrocoagulation time influence on the process efficiency

The electrocoagulation time is an operational parameter that directly affects the electrochemical method efficiency.

The speed of Fe^{2+}, respectively Fe^{3+} ions generation, due to the sacrificial anode dissolution is determined by the electrocoagulation time [8].

From the analysis of data obtained for wastewater discoloration (fig. 4 (a)) it can be said that in the first 20 min of the process, the changes were not significant, which corresponded to a colour degree reduction of only 2.77%.

Regarding the evolution of organic matter content reduction degree the process efficiency has been satisfactory since the beginning of the process, allowing us to obtain a 44% yield after only 20 min . In the range 40-140 min the evolution of process efficiency has been the same, beeing characterized by the attainment of a plateau, both in terms of discoloration but also in terms of reducing the content of organic matter expressed as COD, at the end of process yield was over 90%.

The organic matter removal efficiency can be attributed to the precipitation of organic compounds dissolved by electrocoagulation, electroflotation, direct and indirect anodic oxidation due to chloride ions. Most often, the COD removal is mainly due to the electrooxidation, respectively due to adsorption by electrostatic attraction and physical embedding. At the begining of the process, the electrochemical iron dosing in the solution had a limited effect on the colour decrease rate.

The formation mainly of Fe $(OH)_2$ evidenced by the appearance of green flocs led to the solution colour change from dark blue to dark green. After 120 min, the Fe $(OH)_3$concentration has enough increasesd to determine relatively rapid solution colour change from dark green to nearly colorless.

This phenomenon has been attributed by the researchers to Fe $(OH)_3$ floc formation with browning colouration due to spontaneous combination between ferric ions and hydroxyl radicals [10].

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 *p*H 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.

In general, as highlighted in figure 5, at low, respectively high *p*H values, the generated species are in soluble form, the iron solubility greatly increasing.

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. The

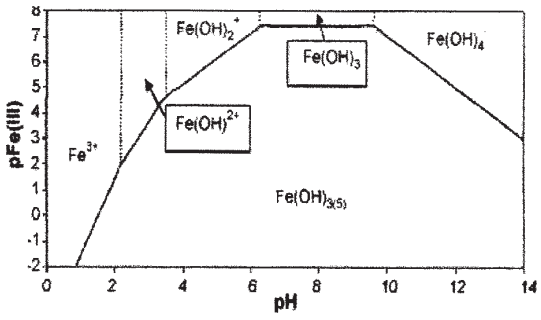

Fig. 5. Distribution of Fe^{3+} species in aqueous solution depending on the *p*H [11]

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 *p*H value (due to HO^- ions consumption) [11].

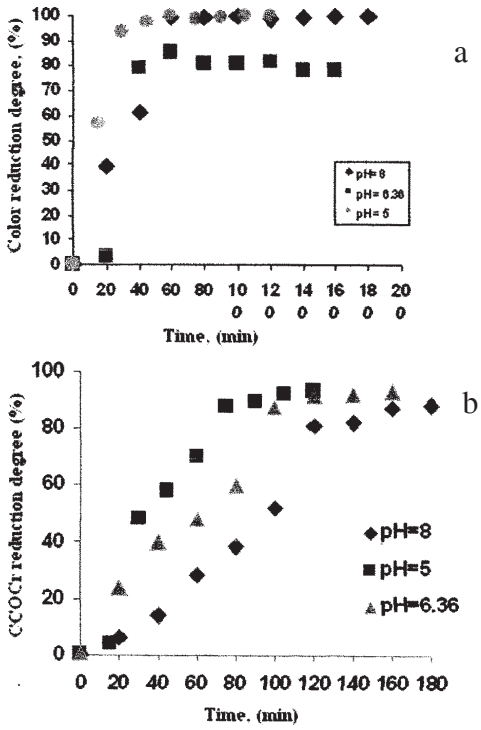

Fig. 6. Solution pH influence on the process efficiency, i = 20.9 mA/cm^2, CCOCr$_i$ = 5000mgO$_2$/L, stirring rate = 200 rpm, T =50°C

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 *p*H samples were adjusted to the desired value using 6% H_2SO_4 and 0.1N NaOH solution.

Figure 6 shows 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 56%,

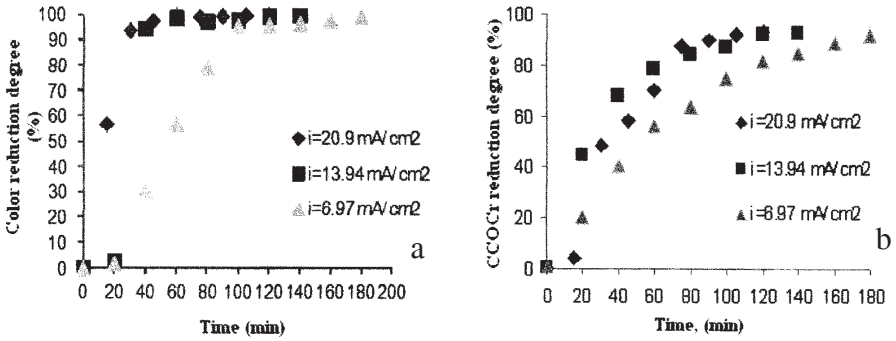

Fig. 7. Colour, respectively organic matter reduction degree variation in time, iron anodes, $CCOCr_i$ = 5000 mgO_2/L , stirring rate 200 rot/min, pH_i = 5, T = 50°C

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

With regard to the system behaviour 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 minutes.

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 [15].

During the experiments, the used water colour 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 ions mass generation . Iron hydroxides contribute to the colloidal particles destabilization [13].

The mechanism underlying the electrochemical colour, 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 *p*H 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 [14].

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.[16]

Current density influence on the electrocoagulation process efficiency

The current density is the most important operational parameter in the electrochemical processes because it is 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. 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 [18,19].

In figure 7 (a) are presented the results obtained in the range of current density 6.97-20.94 mA/cm^2 for the colour 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 minutes at current denisties of 6.97 and 13.94 mA/cm^2 the behaviour was similar, corresponding to colour 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 colour removal effciency from 30% to nearly 94%.in only 20 min.

This behavior 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 colour removal efficiency. [17]

Also, it can be seen that in the range 40-160 min , the colour 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 7 (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, favours process efficiency improvement. [20] 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

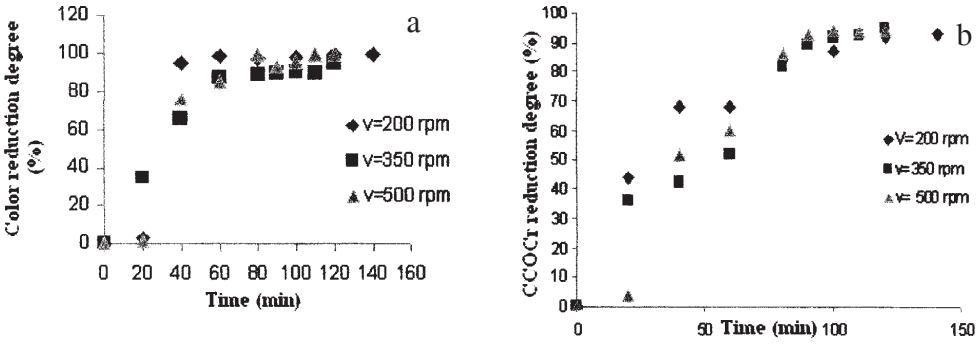

Fig. 8. Influence of stirring rate on the electrocoagulation process efficiency, iron anodes, $CCOCr_i$ = 5000 mgO_2/L , pH_i = 5, i = 13.94 mA/cm^2, T = 50°C

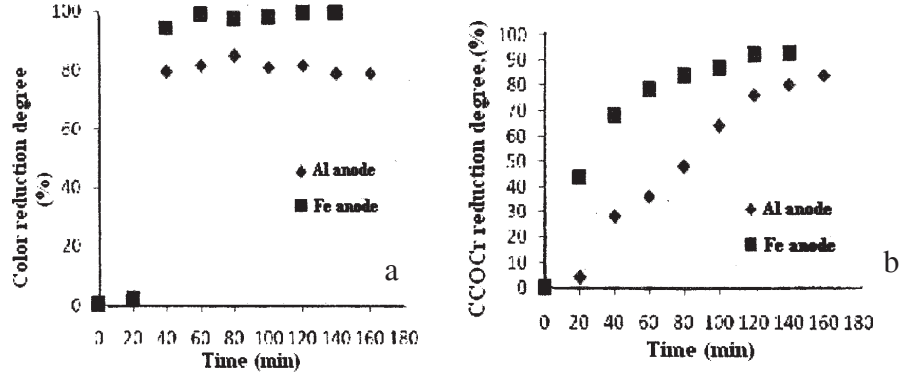

Fig. 9. Influence of anode material on the electrocoagulation process efficiency, $CCOCr_i$ = 5000 mgO_2/L , stirring rate 200 rot/min, pH_i = 6.36, T = 50°C

increase, these trends favour achieving pollutants high removal efficiency by electro flotation with H_2 bubble [21].

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.

The stirring rate influence on the electrocoagulation process efficiency

The influence of stirring rate on the electrocoagulation process efficiency was studied at three different values namely: 200, 350 and 500 rpm.

Based on the analysis of data presented in figure 8 (a) and (b) it may be noted that increasing the stirring speed of the reaction medium does not entail a significant increase in process efficiency. The data obtained show an effectiveness of 93% for colour removal degree, respectively 99.63% for the organic matter reduction degree, for a stirring rate of 200 rpm.

An increase of the stirring rate at 350 rpm resulted in a 1.6% improvement in the efficiency of organic matter removal compared with the value obtained at 200 rpm, while in the case of colour removal degree the value decreased by approximately 5% .

The inffluence of anode material on the electrcoagulation process efficiency

In any electrochemical process, the electrode 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 [22].

In figure 9 (a) and (b) are presented the experimental results obtained for determining the influence of anode material on the electrocoagulation process efficiency. The experimental data revealed that the best colour, 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.

The influence of curent density and anode nature on the pH variation during the electrocoagulation process

Current density influence

During the electrocoagulation process, the solution *p*H varies, the final value is influenced by the anode material, and also by the initial *p*H value of the solution. In this regard, during the experiments realised for studying the current density influence on the process efficiency, the *p*H variation was also monitored and the results are presented in figure 10.

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

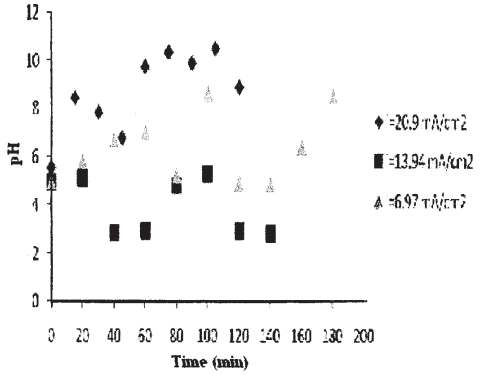

Fig. 10. *p*H variation during the process, at three current densities studied, iron anodes, $CCOCr_i$ = 5000 mgO_2/L , stirring rate 200 rot/min, pH_i = 5, T = 50°C

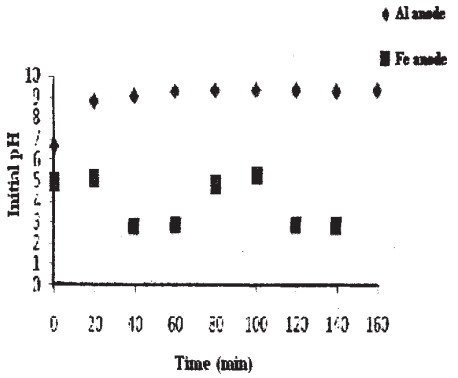

Fig. 11. Variation of *p*H during the electrocoagulation process , i = 13.94 mA/cm^2, CCOCr= 5000 mgO$_2$/L, stirring rate = 200 rpm, T=50°C

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 behaviour at the other two density values, the *p*H variation is similar with the one described for i = 13.94 mA/cm^2.

The anode nature

The results obtained for the study of *p*H variation during the electrocoagulation process when are used iron, respectively aluminium anodes are presented in figure 11.

The evaluation of technical and economical electrocoagulation process aspects

Calculation of current efficiency and specific energy consumption

In order to treat the waste water resulting from the packaging antibiotics capsules production plant electrocoagulation process was used in the presence of sacrificial anodes made from aluminum and iron, pH_i = 5, COD = 5000 mgO$_2$ / L, T = 50 ° C, stirring rate 200 rpm.

As shown previously, almost complete removal of organic matter and colour was obtained after 140 minutes at an initial *p*H of 5 using sacrificial anodes made from iron. The experimental study aimed to establish the optimal operating conditions for the electrocoagulation system and thus calculating the costs of this treatment method.

In order to consider the method effective is necessay to evaluate the technical and economical performances which provides a satisfacatory treatment efficiency (water presents the characteristics required by law for discharge into receptors) at an acceptable cost. The current yield was calculated based on the cations amount generated from the anode, due to metal oxidation, using the formula[13,15]:

$$\eta_j = \frac{m_j}{m_t} \times 100 \quad (3)$$

where: theoretical mass was calculated using Faraday's law.

Considering the initial and final organic matter concentration in the pharmaceutical wastewater at different operation times, the specific energy consumption for the removal of one kg of organic matter was calculated using the formula [18, 20, 23]:

$$E = \frac{U \cdot I \cdot t}{60 \cdot v \cdot (C_i - C)} \quad (4)$$

where:
E = the energy consumed to remove 1 kg of each pollutant (kWh / kg);
U = the applied voltage (V);
I = the current density (A); t = electrolysis time;
C_i = initial pollutants concentration;
C = pollutant concentration after the electrochemical treatment;
v = solution volume (L). Regarding the evolution of current efficiency, this parameter calculation was done according to the amount of dissolved anode at the three values of current density studied: 6.97, 13.94 and 20.9 mA/cm^2.

In table 2 are showed the calculations based on the following operational parameters: current intensity, iron anode mass, iron molecular weight, the number of electrons (z), the practice mass of the two iron anodes.

The electrochemical equivalent (Ke) was calculated using the following relationship [16, 18, 24]:

$$K_e = \frac{M_{Fe}}{z \cdot F}, \quad (5)$$

where:
F is Faraday constant and it is equal to 96500 C/Eg
total mp = (mFe-mpFe$_1$)+(mFe-mpFe$_2$) (g)

The theoretical mass was calculated according to Faraday's law [13, 15, 24]:

$$m_t = K_e \cdot I \cdot t \Rightarrow \eta(\%) = \frac{m_p}{m_t} \times 100 \quad (6)$$

From table 2 it can be seen that the largest anode amount was dissolved of applying an intensity of 1.5A, but the lower current efficiency value compared to the one obtained at an intensity of 1 A was due to the current intensity increase.

In figure 12 is graphically represented the current efficiency evolution for the three values of the current intensity applied to the electrocoagulation system. From the graph, it can be seen that the highest current efficiency value of 69.34% was recorded at an intensity of 1A, which corresponds to the colour, respectively organic matter removal efficiency, higher than 90%.

Therefore, we must identify the optimal treatment conditions that ensure the generation of sufficient cations and hydroxyl radicals quantities, which do not involve high energy consumption.

In the case of an intensity of 0.5, it was determined that in the electrocoagulation process has been dissolved 1.53 g, which corresponds to a current efficiency of 49%.

This result is very clearly correlated with the low applied intensity value, but also with the extension at 180 min of the electrocoagulation time in order to obtain good results in terms of reducing the chemical oxygen demand in the

Time (min)	I(A)	mFe(g)	M_{Fe} (g/mol)	z_{Fe}^+	Ke (C/mol)	mp Fe_1 (g)	mpFe_2 (g)	mp total (g)	n(%)
120	1.5	65	56	2	0.00029	62.90	63.4	3.7	59.046
140	1	65	56	2	0.00029	63.10	63.52	3.38	69.34
180	0.5	65	56	2	0.00029	62.89	62.2	1.53	48.82

Tabel 2
CURRENT EFFICIENCY CALCULATION AT THE THREE CURENT DENSITIES, CCOCr$_i$ = 5000 mgO$_2$/L pH_i = 5, STIRRING RATE 200 rpm, T= 50 °C

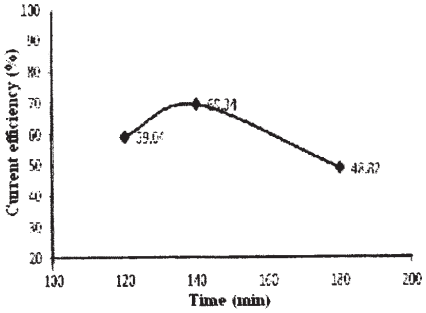

Fig. 12. Current efficiency evolution during the electrocoagulation process

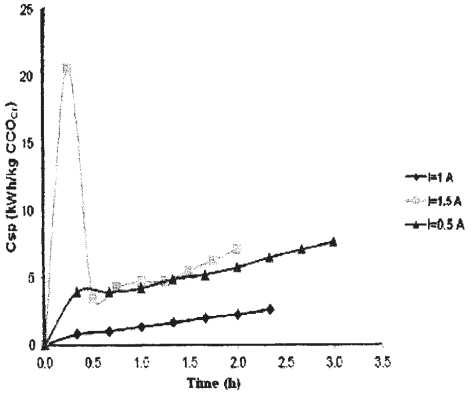

Fig.13. Specific energy consumption for different values of the current intensity applied, iron anodes, $CCOCr_i$ = 5000 mgO_2/L , stirring rate 200 rpm, pH_i = 5, T = 50°C

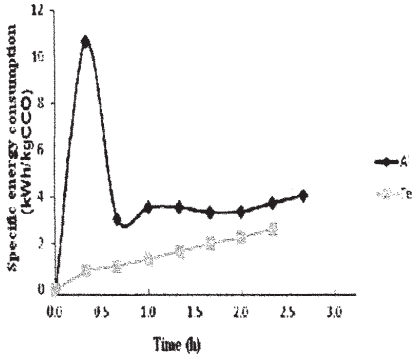

Fig. 14. Specific energy consumption for the two anode materiales used, I = 1A, $CCOCr_i$ = 5000 mgO_2/L , stirring rate 200 rpm, pH_i = 5, T = 50°C

wastewater analyzed. It is obvious that the process is considered effective if it is technically and economically feasible.

The specific energy consumption was calculated using the formula presented above, for the three values of the current intensity applied, and also for the two anodes types used in this study.

From figure 13 it can be observed a large deviation of the specific energy consumption recorded for I = 1.5 A, at the sample taken at 15 min , followed by a sudden drop from 20 kWh / kg to 3.44 kWh / kg. This behaviour of the system may be also due to the high value of the current applied, respectively voltage, and due to low COD removal efficiency (4%). A plausible explanation is that the electrodes immersed in the test sample were new, and therefore at the beginning of the experiment, the electrolytic system was forced to apply a high voltage, in order to facilitate the anodes dissolution [14, 25].

In the case of 1A and 0.5A intensities, the energy consumption variation was approximately linear. The lowest consumption energy values were obtained at I = 1 A, where the maximum value did not exceed 3 kWh / kgCCOCr. Both in terms of colour and organic matter reducing content and specific energy consumption, a current intensity of 1A was considered optimal for the electrocoagulation process use at treatment of pharmaceutical wastewaters.

From the analysis of data presented in figure 14 it is obvious that from economical, but also based on the above observations regarding the influence of anode material on the electrocoagulation process efficiency, the best technical and economic results were obtained using iron made electrodes [14,25].

The jump of the specific energy consumption in the first half of hour at more than 10 kWh / kgCCOCr is due to the fact that the aluminum electrodes were new, after this episode the value droped to 3.5 kWh / which remained almost constant throughout the experiment.

The poorer results obtained in the case of aluminium anodes, are due to $Al(OH)^{4-}$ soluble complex generation at $pH>9$, which obstructs the increase of treatment efficiency. This system anomaly is reflected also in calculation of specific energy consumption [3,26]

Conclusions

Water is the most important element for humans and creatures, being a fundamental natural resource, without which there would be no existence on Earth.

The evolution of pharmaceutical industry from its humble origins to traditional medicine, passing through 100 years of chemistry influence in industry and synthesis of many drugs caused an increase of the production and thus the wastewater volumes generated.

Worldwide, the industry generates about 3 million tons of potentially toxic and dangerous waste from which 200.000 tons of sludge from the pharmaceutical industry.

The electrocoagulation performance evaluation was analyzed in terms of the main operational parameters influence: *p*H, current density, electrocoagulation time, stirring rate, the anode nature.

The optimum *p*H was 5, because allowed us to obtain color, respectively organic matter reduction degrees of about 99% in a relatively short time.

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

In terms of anode material, experimental data have shown that the best efficiency in the removal of colour, namely the organic matter expressed as COD, were obtained using sacrificial anode made of iron. With regard to the aluminum electrodes, results were low, the colour removal degree achieved was 78.57%, compared to 99% obtained in the case of iron anodes.With regard to the aluminum electrodes, results were lower, the colour reduction degree being 78.57%, compared to 99% obtained for iron anodes.

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References

1.SIRÉS, I., BRILLAS, E., Envir. Internat., **40** 2012, p.212–229
2.SECULA, M.S., CREŢESCU, I., PETRESCU, S., Desal., **277,** 2011, p.227–235
3.LINARES-HERNÁNDEZ I., BARRERA-DÍAZ C., ROA-MORALES G., BILYEU B., URENA-NÚNEZ F., Chem. Engin. J., **148**, 2009, p.97–105
4.YETILMEZSOY K., ILHAN F., SAPCI-ZENGIN Z., SAKAR S., GONULLU M.T., J. Haz. Mat., **162**, 2009 ,120–132
5.YOUSUF M., MOLLAH A., SCHENNACH R., PARGA J.R., COCKE D.L., J.Haz. Mat. **B84** 2001, p.29–41
6.O'NEILL, C, HAWKES, F.R., HAWKES, D.L., LOURENCO, N.D., PINHEIRO, H.M., DELÉE, W., J. Chem. Techn. Biotechn., **74,** 1999, p. 1009-1018
7.MIRON,A.R., ORBULEŢ, O., MODROGAN, C.,Rev. Chim. (Bucharest), **62**, no. 2, 2011, p. 163
8.MIRON A. R., MODROGAN C., ORBULEŢ O. D. Rev. Chim.(Bucharest), **61**, no. 7, 2010, p.646

9.HOLT P., BARTON G ., MITCHELL C., In 6th World Congress of Chemical Engineering Conference, Melbourne Australia, **2001**
10.SENGIL A, OZACAR M., J. Haz. Mat., **161** 2009, p.1369–1376
11.POSAVAC S., DRAGIČEVIĆ T.L., HREN M.Z, Mljekarstvo, **60**, 2010, p.198-206
12.KOBYA M., BAYRAMOGLU M, EYVAZ M, J.Haz.Mat, **148**, 2007, p.311-318
13.HOLT, P., BARTON, G., MITCHELL, C., 2001, in 6th World Congress of Chemical Engineering Conference Media CD, Melbourne
14.EMAMJOMEH, M., MUTTUCUMAR, M., SIVAKUMAR, M., J. Environ. Manage., **90,** 2009, p.1663–1679
15.GOLDER A.K., SAMANTA A.N., RAY S., Separ.Purif.Technol., **53**, 2007, p.33-41
16.MOLLAH, M.Y.A., MORKOVSKY, P., GOMES, J.A.G, KESMEZ, M., PARGA, J., COCKE, D.L., J.Haz.Mat., **114**, 2004, p.199-210
17.TEZCAN UN, U., AYTAC E., 2nd International Conference on Chemical Engineering and Application, **23,** 2011
18.DERMENTZIS, K., CHRISTOFORDIS, A., VALSAMIDOU, E., LAZARIDOUN, A., KOKKINOS, N., J.Global Nest., **13**, 2011, p. 412-418
19.UGURLU, M., GURSES, A., DOGAR, C., YALCÝN, M., J. Environ. Manage., **87**, 2008, p.420–428
20.LAFI, W.K., Recent Researches in Energy, Environment, Devices, Systems, Communications and Computers, 2009, p. 61-69
21.EL-NAAS, M. H., AL-MUHTASEB, S.A., MAKHLOUF, S., J. Haz. Mat., **164**, 2009, p.720–725
22.BOROSKI, M., RODRIGUES, A.C, GARCIA, J.C, SAMPAIO, L.C, NOZAKI, J., HIOKA, N., J Haz. Mat., **162**, 2009, p.,448–454
23.FARHADI, S., AMINZADEH, B., TORABIAN, A., KHATIBIKAMAL, V., ALIZADEH, FARD, M., J. Haz. Mat., **219-220,** 2012, p.35– 42
24.RAVIKUMAR,Y.V.L., SRIDHAR, S., SATYANARAYANA, S.V., Separ. Purif. Technol., **110,** 2013, p.20-30
25.STASINAKIS, A.S., J. Global Nest, **10**, 2008, p 376-385
26.PRONK, W, KONÉ, D., Desalination, **8**, 2009, p.248-360
27.HAO, O. J., KIM, H., CHIANG, P.C., Environ. Sci. Technol., **30**, 2000**,** p. 449–505

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