



Original scientific paper

Phenolic compounds removal from mimosa tannin model water and olive mill wastewater by energy-efficient electrocoagulation process

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Abstract

The objective of this work was to study the influence of NaCl concentration, time, and current density on the removal efficiency of phenolic compounds by electrocoagulation process, as well as to compare the specific energy consumption (SEC) of these processes under different experimental conditions. Electrocoagulation was carried out on two different samples of water: model water of mimosa tannin and olive mill wastewater (OMW). Low carbon steel electrodes were used in the experiments. The properties of the treated effluent were determined using UV/Vis spectroscopy and by measuring total organic carbon (TOC). Percentage of removal increased with time, current density, and NaCl concentration. SEC value increased with increased time and current density but it was decreased significantly by NaCl additions (0-29 g L⁻¹). It was found that electrocoagulation treatment of effluents containing phenolic compounds involves complex formation between ferrous/ferric and phenolic compounds present in treated effluent, which has significant impact on the efficiency of the process.

Keywords

Complexation; NaCl; low carbon steel, UV/Vis spectroscopy, total organic carbon (TOC).

Introduction

High amounts of waste water are generated in the Mediterranean area each year during the short periods of the olive oil production process, from October to December. Its direct disposal in nature is not acceptable since it contains dark colour, organic materials, and emulsion oils. Additionally, such waters contain phenolic compounds that have a negative impact on vegetation

and microorganisms, and therefore must be treated in order to remove organic and toxic pollutants. The amount of these compounds is usually in the range of 5-25 g L⁻¹ depending on climate, variety of olive fruit, cultivation, ripeness at harvest, as well as on extraction process [1,2].

Different methods have been developed for olive mill wastewater (OMW) treatment such as biological treatment [3-5], physico-chemical treatments [6], photocatalytic oxidation [7,8], electrooxidation [9], electrocoagulation [10-13], and a number of combined treatments [14,15]. Phenolic compounds extracted from OMWs could possibly be utilized in the cosmetic, pharmaceutical, or food industries [16], or even as potential source of natural dyes [17]. However, none of treatments used were completely satisfying.

Electrocoagulation is a well-known remediation technique that can be used alone [10-18] or in combination with other techniques [19]. It is a simple, effective, and low cost process, easily adaptable to other systems. Furthermore, in remote areas without electricity, it could be directly powered by a photovoltaic system in order to achieve a self-sustainable unit [20-22].

The goal of this work was to study the influence of NaCl concentration, current density and time on the removal efficiency of phenolic compounds by the electrocoagulation process, as well as to compare specific energy consumption (SEC) of the processes under different experimental conditions. Electrocoagulation was carried out for two different samples of water: model water of mimosa tannin and olive mill wastewater (OMW). Mimosa tannin is a phenolic compound similar to those phenolic compounds present in OMW but it is somewhat more complex. In this work it was used in order to examine the influence of pure phenolic compounds on the removal efficiency of the electrocoagulation process. After detailed analysis of the results obtained in model water, experiments were also carried out in OMW. Electrocoagulation processes are usually carried out without or with only small amounts of NaCl to avoid its presence in discharge water. However, since most olive oil production plants are situated on the Mediterranean coastline, additions of NaCl and the disposal of the treated effluent containing NaCl into the sea is acceptable. Additionally, it is well known that the amount of salt is the crucial parameter for energy consumption in the electrolysis process, and for the feasibility of this technique.

Experimental

All the chemicals used in this research were of analytical grade. Mimosa tannin (Mimosa Central Co-operative Ltd., South Africa) solutions were prepared using bi-distilled water with the addition of an appropriate amount of NaCl.

The olive mill wastewater (OMW) used in this study was obtained from a local olive oil manufacturer (Croatia). It was stored in an open puddle for two months before the sampling. Prior to the experiments the OMW was filtrated to remove suspended solids.

Conductivities and pH values were measured using a conductivity meter (Oakton PCD650) and a pH meter (Radiometer, PHM 220).

At the end of the electrocoagulation process of the mimosa tannin model water, the formed colloids were left during the night to settle and afterwards the sludge was separated from the effluent on a Buchner funnel using a water aspirator. The sludge was dried in open air for three days and then the mass of the sludge was determined. Treated effluents were analysed by different techniques (pH meter, conductivity meter, UV/Vis spectroscopy, and TOC). Before the UV/Vis spectroscopy and TOC analysis were carried out, the solutions was centrifuged using 9000 rpm (Hettich Universal, Mikro 12-24 centrifuge).

At the end of electrocoagulation process of the OMW, the water was immediately filtrated in a Buchner funnel and analysed using the same techniques as in the case of mimosa tannin solution.

The phenolic compounds concentration was measured at the wavelength corresponding to the maximum absorbance using a spectrophotometer (Ocean Optics 200, UV light source Analytical Instrument Systems Inc., Model D 1000 CE) connected to a computer, in 1 cm path-length cells. The equation used to calculate the phenol removal efficiency in the experiments was:

$$R / \% = \frac{\gamma_0 - \gamma}{\gamma_0} 100 \quad (1)$$

where γ_0 and γ are defined as the concentration before and after electrocoagulation process. A similar equation was used to calculate total organic carbon (TOC) removal efficiency ($R_{\text{TOC}} / \%$).

The TOC measurements were done on a Shimadzu Analyser TOC V-CSN using the NPOC method.

The electrocoagulation experiments were carried out in a glassy electrolytic cell with dimensions of 7 x 7 x 6 cm. Parallel plate electrodes were immersed in the cell with a working electrode situated between two counter electrodes in order to achieve a good current and potential distribution, and a uniform electrode dissolution. Low carbon steel (composition: 0.06 % C, 0.015 % P, 0.008 % S, 0.007 % Si and 0.35 % Mn) was used for all electrodes. Before the experiment the electrodes were polished using 600 grit emery paper, they were washed with bi-distilled water, and finally, with ethanol. The working electrode had a total immersed area of 10 cm², and the counter electrodes had a total immersed area of 20 cm². The distance between the electrodes was 1 cm. Before the experiment, the appropriate amount of NaCl was dissolved in the treated solutions. During the experiment constant stirring speeds of 600 rpm and DC Power Supply (Iskra, MA 4165; 1.5 A; 25 V) were used.

All the experiments were carried out at room temperature (23±1 °C).

RESULTS AND DISCUSSIONS

Treatment of the model water containing mimosa tannin

The mimosa tannin ($\gamma = 1 \text{ g L}^{-1}$) solution prepared in 0.5 mol dm^{-3} NaCl has pH 5.1 and $\kappa = 38.3 \text{ mS cm}^{-1}$. In order to find out the removal efficiency of mimosa tannin over different durations, the process was carried out for 5, 15, and 35 minutes using current densities of 10 mA cm^{-2} . The characteristic voltage of this process was 1.25 V. The influence of the duration of the experiment on the electrocoagulation efficiency is presented in Table 1.

Within the 5 min removal period removal efficiency reached 92.2 %, while further treatment resulted only in its slight increase (35 min, 96.7 %). Energy consumption during the experiment increased proportionally with time since the current density and voltage were constant throughout the experiments.

To explain the mechanism of the electrocoagulation process one must consider the reactions occurring on both electrodes. During the anodic process iron is oxidized and dissolved as Fe^{2+} . Under the experimental conditions used in this work (pH = 5.1) it does not undergo hydrolysis. However, in aerated conditions it is further oxidized by dissolved oxygen to Fe^{3+} , which is susceptible to hydrolysis, resulting in different aqua and hydroxyl complexes, such as $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})^+$, $\text{Fe}(\text{OH})_3$ under acid conditions, or $\text{Fe}(\text{OH})_6^{3-}$ and $\text{Fe}(\text{OH})_4^-$ under alkaline conditions [23]. Since the pH values registered before and after electrocoagulation process varied from 5-7,

positively charged or neutral particles were expected under the given experimental conditions. Furthermore, negative ions present in water (in the case of NaCl addition it is Cl^-) will surround a positive charge, forming a diffuse layer which makes the particle neutrally charged. These surface properties make the particles unstable and agglomeration takes place. As a result of agglomeration, particles form flocks precipitating or floating by the bubbles of hydrogen (Figure 1.). The stability of the particles and their agglomeration depends on the type and concentration of ions in the solution. The formed flocks can effectively remove pollutants by adsorption or enmeshment in a precipitate.

The aim of this work was to remove mimosa tannin from model water. It is well known from the literature that dissolved iron in the presence of tannin forms ferrous/ferric tannates. These reactions are pretty complex since both ions, ferrous and ferric, can participate in the reaction, and in addition there is also a possibility of Fe^{3+} reduction by mimosa tannins. According to the author's knowledge, the formation of the complex during phenolic compounds removal by electrocoagulation technique was not considered before, although it might be of a great importance for its progress. It can influence the amount of ferrous/ferric ions required for the coagulation, since $\text{Fe}^{2+}/\text{Fe}^{3+}$ are consumed by the complex formation. Additionally, it can also impact the mechanism of the reaction because generated complex will be involved in the adsorption or enmeshment by formed flocks instead of mimosa tannin. It could also be important for the electrode reaction kinetics since tannin inhibits dissolution of iron [24,25]. Therefore it can be concluded that complex formation should not be ignored when considering the electrocoagulation process.

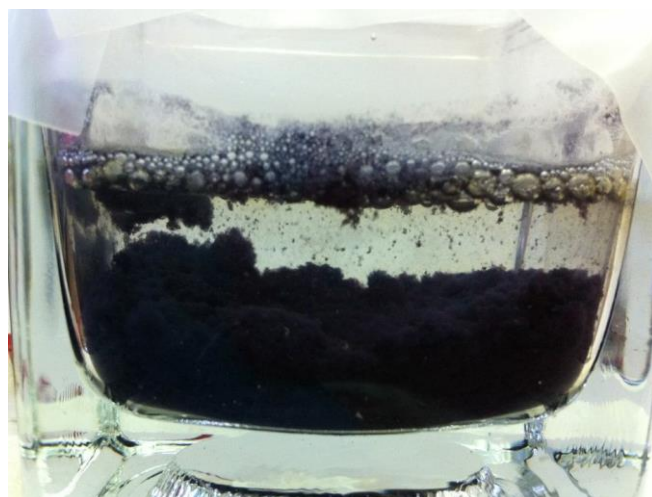


Figure 1. Illustration of flocks precipitating due to gravity, and floating due to the bubbles of gas

An important parameter of the electrocoagulation process is the effluent pH value at the end of the process. In these experiments pH values decreased for processes conducted over 5 min, while they increased for prolonged treatments (15 and 35 min) (Table 1). The increase of pH values were caused due to the intensive hydrogen evolution at the cathode and the generation of OH^- ions. The generated OH^- ions were consumed during the hydrolysis of Fe^{3+} , but the overall reaction obviously resulted in the excess of OH^- ions. The final pH value depended on the equilibrium of each reaction in the process. Additionally, the increase of pH value can be explained by mimosa tannin removal due to its acidic behaviour.

Table 1. Results of treatments at different times ($j = 10 \text{ mA cm}^{-2}$, $U = 1.25 \text{ V}$, $\gamma (\text{NaCl}) = 29.22 \text{ mol g L}^{-1}$, $\kappa = 38.3 \text{ mS cm}^{-1}$, $\text{pH} = 5.1$, $\gamma_0(\text{tannin})=1 \text{ g L}^{-1}$, $V = 0.1 \text{ L}$).

T / min	$R / \%$	$\text{SEC} / \text{kW h kg}^{-1}$	$m(\text{precipitate}) / \text{g}$	$\text{pH}(\text{after EC})$
5	92.21	0.113	0.143	4.81
15	95.54	0.327	0.197	5.74
35	96.68	0.754	0.263	6.31

Since the concentration of ferrous/ferric ions is dependent on current density, the efficiency of the process is dependent on current density as well. In this work the electrocoagulation process was conducted for 15 min using different current values (Figures 2 and 3). When the current increased from 1 to 10 mA cm^{-2} , removal efficiency increased from 10 to 20 % in $0.58 \text{ g L}^{-1} \text{ NaCl}$, from 47 to 93 % in $5.84 \text{ g L}^{-1} \text{ NaCl}$, and from 58 to 96 % in $29.22 \text{ mol dm}^{-3} \text{ NaCl}$ (Figure 2). However, specific energy consumption per mass of mimosa tannin increased more significantly from 0.302 to $7.311 \text{ kW h kg}^{-1}$ in $0.58 \text{ g L}^{-1} \text{ NaCl}$, from 0.034 to $0.469 \text{ kW h kg}^{-1}$ in $5.84 \text{ g L}^{-1} \text{ NaCl}$, and from 0.021 to $0.327 \text{ kW h kg}^{-1}$ in $29.22 \text{ g L}^{-1} \text{ NaCl}$ (Table 2). As evident, the highest removal efficiency was obtained at high current density. The obtained results also show that the highest removal efficiency was registered in the presence of high NaCl concentrations, where the lowest specific energy consumption is required. It is supported by Figure 4, where the colour of the solution suggests more difficult precipitation of flocks for small additions of NaCl causing reduced removal efficiency. This is in accordance with theory that coagulation process depends on type and concentration of ions present in solution. It is obvious that optimal process conditions were obtained in the presence of high amounts of NaCl. These results pointed out the importance of the NaCl concentration as a key parameter for an efficient and low cost process.

NaCl's presence is important because of the two effects: (a) it decreased the applied voltage and energy power demand [26] and (b) it changed the ionic strength that affected the coagulation process as evident from Figures 2 and 4. The influence of ionic concentration and zeta potential on the electrocoagulation process was reported previously [27, 28].

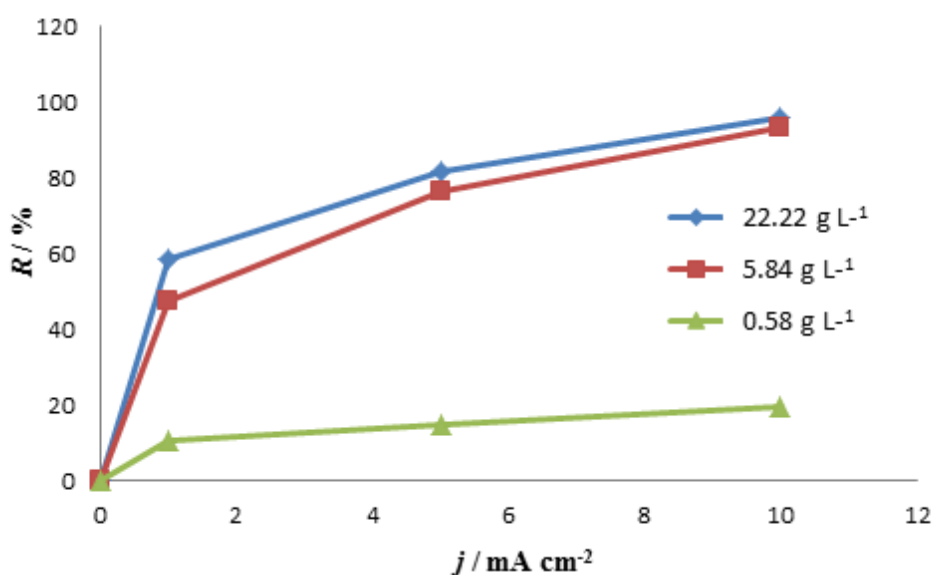


Figure 2. Influence of NaCl concentration and current density on removal efficiency.

The main factor influencing energy consumption is applied voltage. The overall voltage is dependent on equilibrium potential difference ($E_{r,k}-E_{r,a}$), anode and cathode over-potentials (η_a, η_k), and ohmic potential drop in the solution (η_{IR}) according to the equation (2):

$$|U_{er}| = |(E_{r,k} - E_{r,a})| + \eta_a + |\eta_k| + \eta_{IR} \tag{2}$$

Ohmic potential drop in the solution is dependent on cell configuration, electrode area (A / m^2), and the distance between electrodes (d / m), as well on the conductivity of solution ($\kappa / S cm^{-1}$):

$$\eta_{IR} = I \left(\frac{d}{A\kappa} \right) \tag{3}$$

Table 2. Results of treatments at different NaCl concentration and current density ($t = 15 \text{ min}$, $pH = 5.1$, $\gamma(\text{tannin}) = 1 \text{ g L}^{-1}$, $V = 0.1 \text{ L}$).

$\gamma (\text{NaCl}) / \text{g L}^{-1}$	$J / \text{mA cm}^{-2}$	U / V	$\text{SEC} / \text{kW h kg}^{-1}$	$m(\text{precipitate}) / \text{g}$
29.22 ($\kappa = 38.3 \text{ mS cm}^{-1}$)	10	1.25	0.327	0.197
	5	0.95	0.146	0.134
	1	0.50	0.021	0.103
5.84 ($\kappa = 10.11 \text{ mS cm}^{-1}$)	10	1.75	0.469	0.140
	5	1.15	0.188	0.128
	1	0.65	0.034	0.094
0.58 ($\kappa = 0.98 \text{ mS cm}^{-1}$)	10	5.75	7.311	0.080
	5	3.65	3.061	0.044
	1	1.25	0.302	0.038

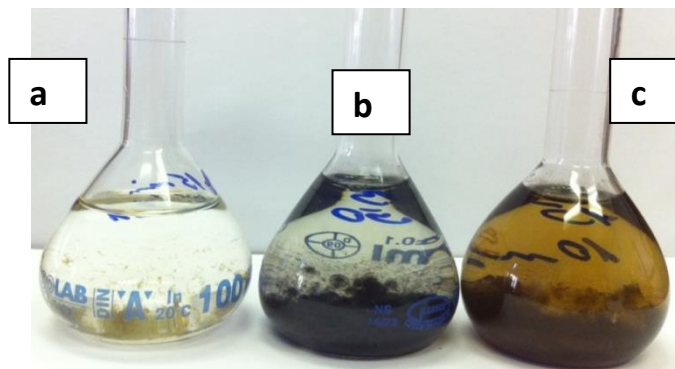


Figure 3. Results of treatments at different current densities in the case of mimosa tannin: (a) 10 mA cm^{-2} ; (b) 5 mA cm^{-2} ; (c) 1 mA cm^{-2} ($t = 15 \text{ min}$; $29.22 \text{ g L}^{-1} \text{ NaCl}$).

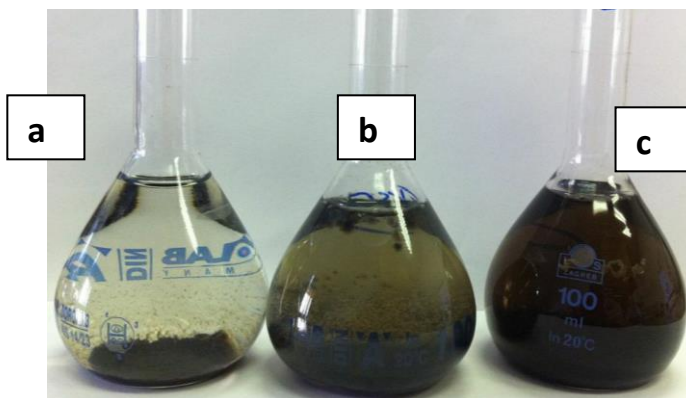


Figure 4. Results of treatments at different NaCl concentrations in the case of mimosa tannin: (a) $29.22 \text{ g L}^{-1} \text{ NaCl}$; (b) $5.84 \text{ g L}^{-1} \text{ NaCl}$; (c) $0.58 \text{ g L}^{-1} \text{ NaCl}$ ($j = 10 \text{ mA cm}^{-2}$; $t = 15$).

SEC is dependent on current value (I), applied voltage (U) and time (t) and it is expressed as energy consumption per mass of removed tannin:

$$\text{SEC} = \frac{IUt}{(\gamma(\text{tannin})_0 - \gamma(\text{tannin}))V} \quad (4)$$

where γ is the mass concentration of tannin or phenolic compound, V is volume of treated solution.

Another important parameter for SEC is the distance between the electrodes, which in most of the previous reports ranged from 0.3-3.0 cm, while the distance in this work was 1 cm. A small distance is preferable to decrease potential drop, but the electrodes should be adequately separated in order to enable unhindered movement of flocks between them.

Conductivity of the solution i.e. salt concentration also plays important role for SEC value and according to our knowledge its value was quite different in different reports.

Kobaya *et al.* [29] treated textile wastewater by electrocoagulation process and it was shown that an addition of NaCl ($\kappa = 1000\text{-}4000 \mu\text{S cm}^{-1}$) did not influence process efficiency but energy consumption decreased with increased wastewater conductivity (2.2-0.75 kW h kg⁻¹ (COD)). Sengil *et al.* [30] have used electrocoagulation for decolourization of Reactive red and it was found that small additions (0.5-2.0 g L⁻¹) of NaCl increase efficiency while further addition did not have any impact. The optimal conditions were found to be 2.3 g L⁻¹ NaCl and 4.54 kW h kg⁻¹ (dye). B. K. Nandi *et al.* [31] varied NaCl concentration from 0.1-1.0 g L⁻¹ and it was found that efficiency had increased from 97-100 % and energy consumption had decreased from 17-3 kW h kg⁻¹ (Fe). X. Chen *et al.* [32] separated pollutants from restaurant wastewater by electrocoagulation process without the addition of NaCl when energy consumption was in the range of 0.2-1.4 kW h m⁻³ depending on the solution conductivity that varied from 770-227 $\mu\text{S cm}^{-1}$. The additions of NaCl changed conductivity from 443-2850 $\mu\text{S cm}^{-1}$ and energy consumption as well, from 0.32-0.29 kW h m⁻³; however, it did not change the efficiency of the process.

From the previous results it follows that NaCl concentration can influence specific energy consumption drastically, which will have an impact on operating cost. However, the dependence of removal efficiency on NaCl concentration is not completely clear and it depends on the type of pollutant and its concentration.

The results of this paper confirm that NaCl addition decreases specific energy consumption in accordance with the previous results. Furthermore, it was shown that efficiency of the phenolic compound removal can also be improved considerably by the addition of NaCl in the range from 0.58 g L⁻¹ to 29.22 g L⁻¹.

Treatment of OMW

The starting OMW solution had the following characteristics: pH 5.37, concentration of phenolic compounds, $\gamma_0 = 0.613 \text{ g L}^{-1}$ (mimosa tannin equivalent), and the TOC value was 1376 mg L⁻¹. These values were somewhat lower in comparison to the values frequently found in the literature [10-12]. This can be explained by the fact that the OMW was kept in an open puddle for 2 months.

During OMW treatment by electrocoagulation process in previous investigations the solution as received was used or it was diluted with water. The conductivity of the pure OMW sample was 11 mS cm⁻¹ [10-12] and for diluted OMW (1:5) conductivity was 3.6 S cm⁻¹ [13]. The SEC value obtained during the OMW treatment was found to be 4 kW h kg⁻¹ (COD) [13] or 20-300 kW h m⁻³ (volume of treated solution) [12], which were quite similar considering the characteristic COD

value for OMW. Also, it was shown that small additions of NaCl improve removal efficiency while additions higher than 2 g L^{-1} decrease removal efficiency. Energy consumption has decreased upon NaCl addition.

From the results of the treatment of mimosa tannin, the current density of 10 mA cm^{-2} was chosen for the OMW treatment. The process was carried out with different additions of NaCl from $0\text{-}20 \text{ g L}^{-1}$ during 35 or 60 min. Depending on NaCl addition conductivity of the solutions was changed from the value similar to the previously reported values (2.3 S cm^{-1}) to the value higher than previously reported (23.7 S cm^{-1}). The SEC value was changed from $8.5\text{-}1.6 \text{ kW h kg}^{-1}$ (mass of phenolic compounds) during 35 min or it was changed from $8.2\text{-}2.6 \text{ kW h kg}^{-1}$ (mass of phenolic compounds) during 60 min.

Similarly as in the case of model water, addition of NaCl had positive impact on removal efficiency (Figures 5 and 6) and energy consumption (Table 3). Furthermore, better efficiency was obtained by prolonged process time while SEC was not increased significantly. At the end of the electrocoagulation process pH value was close to 7, which was acceptable for discharge, while conductivity increased only slightly.

Table 3. Results of treatments at different NaCl concentration and process times ($j = 10 \text{ mA cm}^{-2}$. $\text{pH} = 5.37$. $V = 0.1 \text{ L}$, $\gamma_0 = 0.613 \text{ g L}^{-1}$).

t / min	$\gamma(\text{NaCl}) / \text{g L}^{-1}$	U / V	$\text{SEC} / \text{kW h kg}^{-1}$	$\text{pH}_{\text{after EC}}$	$\kappa(\text{OMW})_{\text{before EC}} / \text{mS cm}^{-1}$	$\kappa(\text{OMW})_{\text{after EC}} / \text{mS cm}^{-1}$
35	0	3.8	8.492	6.65	2.32	3.43
	5	1.9	2.677	6.85	8.23	9.48
	10	1.5	1.998	6.88	13.77	14.75
	20	1.4	1.604	6.9	23.72	24.79
60	0	3.9	8.226	6.7	2.32	3.26
	5	2.1	4.26	6.81	5.99	6.55
	10	1.6	2.941	6.94	10.12	10.98
	20	1.5	2.562	6.98	20.44	21.75

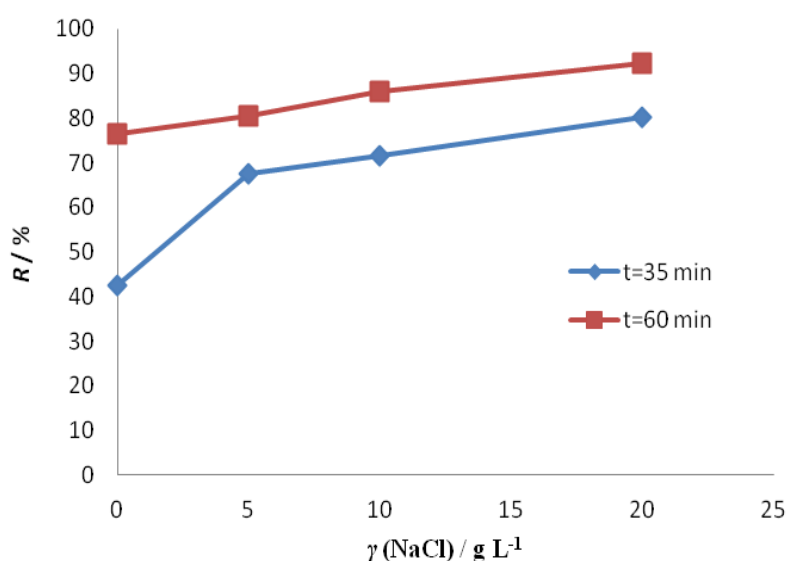


Figure 5. Dependence of removal efficiency of phenolic compound in OMW treated effluent on NaCl concentration and process time.

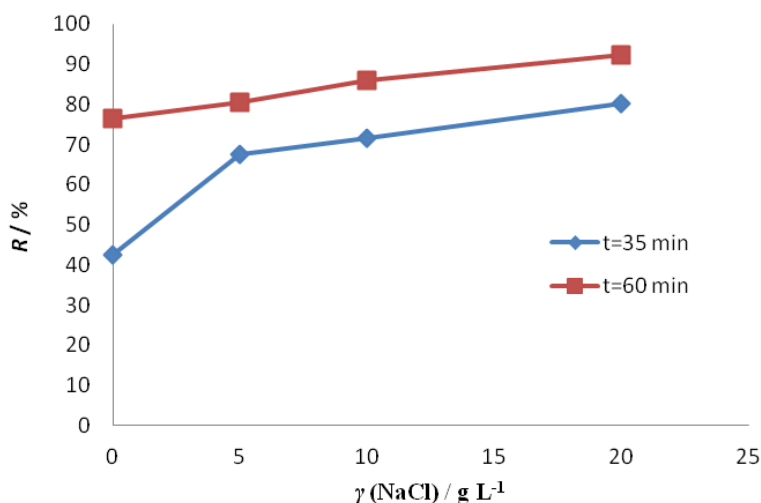


Figure 6. Dependence of removal efficiency of TOC in OMW treated effluent on NaCl concentration and process time.

From Figures 5 and 6 it is evident that the removal of overall organic loading (TOC) is lower (30 - 70 %) in comparison to phenolic compounds (40 - 90 %). Better efficiency in the case of phenolic compounds could be the consequence of complex formation between ferrous/ferric and phenolic compounds present in the OMW. It is also evident that removal efficiency of phenolic compounds in OMW was lower compared to the removal efficiency of mimosa tannin, although longer times were used (Figures 2 and 5). It is not surprising since this solution, apart from the phenolic compounds, contains some other constituents such as oil, sugar, and pulp suspension [2]. Therefore, the capacity of produced sludge for phenolic compounds removal is reduced in the case of OMW compared to the model water.

Conclusions

The results obtained in this paper show that it is possible to obtain high removal efficiency of mimosa tannin and phenolic compounds from OMW by electrocoagulation process. In the case of mimosa tannin, electrocoagulation was able to reduce the phenolic content up to 96 %, while in the case of OMW electrocoagulation was able to reduce the phenolic content up to 92 %. The percentage of removal was increased with increased time, current density, and NaCl concentration. Apart from the increasing removal efficiency of the process, an improvement in energy demand was also obtained with the addition of NaCl. Therefore, it can be concluded that an addition of NaCl can significantly improve the electrocoagulation process. Furthermore, additions of NaCl and the disposal of treated effluent containing NaCl are acceptable for the production plants located close to the coast. At the end of process pH value was close to 7, which is acceptable for discharging.

It was shown that complex formation between ferrous/ferric and phenolic compounds present in treated effluent could change the efficiency of the process. Thus, due to the complexation, removal of phenolic compounds was higher in comparison to removal of overall organic loading (TOC). It was also observed that the removal efficiency of mimosa tannin is higher compared to the removal efficiency of phenolic compounds from OMW although longer times were used. It is explained by the decreased capacity of produced flocks for phenolic compounds removal, in the case of OMW, due to the presence of other organic constituents.

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