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Removal of organic compounds from industrial wastewater using physico-chemical methods

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Abstract

The focus of this study is purifying the wastewater from the lacquers and paint industry in Western Romania, containing different organic compounds.

The organic load in wastewater is found in the form of various organic compounds. Nonpolar organic substances lighter than water form a layer that blocks the flow of oxygen necessary, while polar substances are soluble in water and can be toxic to the fauna or create the effect of eutrophication causing disequilibrium in the biotope.

In this paper we aimed at eliminating these organic compounds from wastewater by physical-electrocoagulation and chemical-oxidation methods to ensure a high degree of removal of these compounds to discharge into the sewage. The wastewater was characterized before and after the treatment following a series of quality indicators (chemical oxygen demand COD, total organic carbon TOC, lead Pb(II), cadmium Cd(II), chrome total Cr_{tot}, copper Cu(II), nickel Ni(II), zinc Zn(II), manganese Mn(II)). The total organic carbon analysis (TOC) was performed before and after the treatment to determine the total content of organic compounds.

The resulting sludge from the wastewater contaminated with organic compounds treatment was subjected to thermal analysis.

Keywords: purge, paints, organic load, total organic carbon (TOC), wastewater.

1 Introduction

It is known from the literature that within resins lacquers and paints industry, basic materials used are higher order alcohols, aldehydes, ketones, some miscible and immiscible organic substances, many of them toxic for the environment [1, 2].

The wastewaters of this industry have a high organic load with complex composition, this makes their treatment difficult. In general, the treatment of these waters requires several steps such as: oxidation, coagulation-flocculation, decantation, biological treatment followed by another decantation [3, 4].

High organic load causes oxidation to be inefficient as a method of removing pollutants, being used only to neutralize dangerous pollutants and transforming organic substances with low biodegradability in readily biodegradable substances.

Recent research has shown that oxidation transforms insoluble or immiscible with water organic substances in soluble compounds miscible with water [2, 4, 5]. A biological treatment is efficient only if chemical oxidation transformed organic substances with low biodegradability in readily biodegradable substances.

Physical methods like ion exchange, reverse osmosis and electro dialysis methods are more expensive being rarely used, chemical methods may be used, but have the disadvantage of high costs related to storage and neutralizing effluents and the resulting sludge [6].

Other research has shown that electrocoagulation process provides an attractive alternative to traditional methods for wastewater treatment mentioned above [6–8].

Electrocoagulation (EC) is a simple and efficient method used in many cases as an alternative in treating different wastewaters, such as wastewater from electro galvanic coatings [3, 9], from restaurant wastewater [3, 10] and poultry slaughterhouse wastewater [3, 11].

Electrocoagulation with soluble anode can successfully replace the following steps after oxidation process because of the way it acts, floating the organic substances with less or equal to water density by the H_2 molecules generated at the cathode, and also removing by flocculation-coagulation processes generated by the iron anode, which produces Fe^{2+}, followed by a decantation process. This process has several advantages such as high removal efficiency of pollutants from wastewater, a compact treatment facility and the possibility of complete automation of the process.

Electrochemical processes are based on the use of electricity in the electrolysis process management, process in which substances are decomposed or new products are formed at the electrode by electrical energy [12–14].

The goal of this paper is the possibility of removing organic pollutants present in wastewaters from the resins, lacquers and paints industry using the physico-chemical methods: oxidation and electrocoagulation processes, separate or combined. Thus, we studied the influence during electrocoagulation process, the NaCl concentration influence and the sequence of stages of treatment (EC process followed by oxidation process, oxidation process followed by EC process, respectively) on optimizing the removal process of organic pollutants with high efficiency.

2 Experimental

In this paper it used an electrocoagulation installation with an anode soluble made from iron. When electric current passes through the cell the following processes occur at the electrodes [3]:

- Anode: - anodic dissolution: $Fe \rightarrow Fe^{2+}_{(aq)} + 2e^-$

$Fe \rightarrow Fe^{3+}_{(aq)} + 3e^-$

- form of hydroxide: $Fe^{2+}_{(aq)} + 2OH^- \rightarrow Fe(OH)_{2(s)}$

$Fe^{3+}_{(aq)} + 3OH^- \rightarrow Fe(OH)_{3(s)}$

- Cathode: $2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-$

Experimental setup is shown in Figure 1. The studies were made by using an electrocoagulation cell with a volume of 1.2 dm^3. Eight plates were installed vertically with a spacer to ensure fixed distance and immersed to a 1 cm depth, were used as electrodes monopolar mode in the experiments. The total immersed area of both anode and cathode electrodes were 115 cm^2. The inter-electrode distance was 1 cm. A Regulated DC Power supply Axio MET-3005DBL AX-3 was used to apply a current density 37 A/m^2. Electrolysis was conducted at a constant current of 3A maintained by a Regulated DC Power supply. Electrolysis cell has a wastewater supply pipe at the bottom, on the opposite wall at a suitable height, a pipeline for evacuation of treated water and an outlet pipe for sludge discharge.

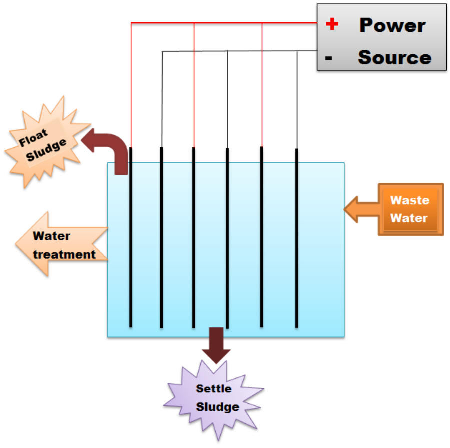


Figure 1: Experimental setup used in the studies.

Ozone has been produced by the laboratory ozone generator Fisher 500 M, the amount of ozone generated is determined using the titration method. The method consists of ozone enriched air barbotage in a KI solution and titrating this solution with $Na_2S_2O_3$ in the presence of starch [13].

For the oxidation process, the ozone enriched air, obtained at a rate of 60 Ndm^3/h at 20°C, has a concentration of 0.47% (v/v). It is necessary to treat a volume of 1.2 dm^3 of wastewater. They were performed in the UV-VIS spectra, following the change of absorbance.

Efficiency of the processes used in removing organic compounds from the wastewater was established by correlating the concentration and absorbance based on the Lambert Beer law:

$$A = \epsilon \cdot l \cdot c$$

A – Absorbance;
ε –molar absorptivity, (L/mol·cm);
l – Absorber layer thickness (cm);
c – Concentration of absorbing species, mol/L.

Absorption spectra in the UV-VIS, in the domain 180–400 nm have been realized using Cintra Spectrophotometer 5 with a 5 mm quartz cuvette. To establish the organic compounds amount existing in the wastewater the chemical oxygen demand (COD-Cr) was determined using volumetric method and the total organic carbon (TOC) was determined using a TOC analyzer device Schimadzu, Japan. Content of heavy metals from wastewater was determined by atomic absorption spectrometry using a Varian SpectrAAS 280FS. Content of organic compounds in the sludge resulted from the wastewater treatment process was established by thermal analysis using a NETZCH STA 449C thermal balance.

3 Results and discussion

3.1 Wastewater analysis

Wastewater from the resins, lacquers and paints industry was analysed to determine the content of toxic compounds. Assay values are shown in Table 1 and it can be noted that in the studied wastewater, the content of organic compounds is very high, requiring the establishment some processes for reducing this content.

Table 1: Wastewater composition.

Parameter	Experimental value
Oxygen chemical demand, CCO-Cr, mg O_2/L	2665
Total organic carbon, TOC, mg C/L	835
Plumb, Pb(II), mg/L	0.07
Cadmium, Cd(II), mg/L	0.02
Chrome total, Cr_{tot}, mg/L	<0.01
Copper, Cu(II), mg/L	<0.01
Nickel, Ni(II), mg/L	0.06
Zinc, Zn(II), mg/L	0.03
Manganese, Mn(II), mg/L	0.02

3.2 Removal processes of organic compounds

3.2.1 Oxidation

UV-VIS spectra for wastewater treatment by oxidation process are shown in Figure 2.

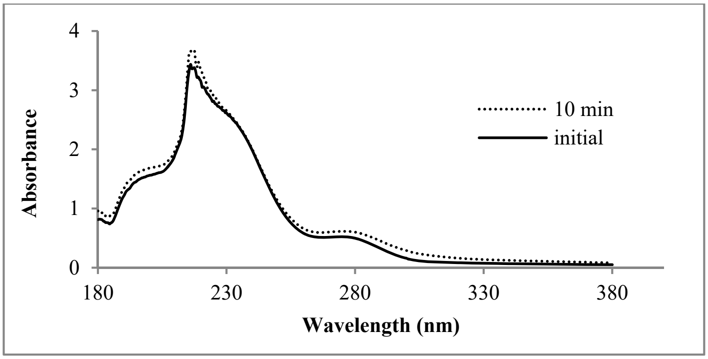


Figure 2: UV-VIS spectra for wastewater treatment by oxidation process.

It is observed that the absorbance increase with increasing time. This is mainly due to the disposal of chemical bonds from organic compounds existing in wastewater, with forming of new organic compounds with lower molecular weight. These results confirm that in these conditions, oxidation process is not a method which can be used as such in the organic compounds removal from wastewater studied.

3.2.2 Electrocoagulation

UV-VIS spectra for wastewater treatment by electrocoagulation process (EC) with and without the addition of NaCl are shown in Figure 3. To increase the efficiency of the electrocoagulation process and to slow passivation process of the anode, NaCl with a concentration of 1 g/L was introduced in the wastewater.

Thus, from the experimental data obtain, it observed that the removing organic compounds from wastewater by EC process, in the presence of NaCl is more efficient than in its absence. It was also found that in the NaCl absence, the wastewater electrolysis voltage was 5.8 V for 3A current intensity, after adding NaCl at a concentration of 1g/L, the necessary voltage decreased to 2.4 V for the same current intensity, causing the reduction of energy consumption by half.

Studies were performed using higher concentrations of NaCl. In this case is not observed significant increase in the efficiency of EC for removing organic compounds.

Based on the results obtained, and literature studies [15], the organic compounds removal from wastewater by combining the two previously studied processes (oxidation and EC) was studied next.

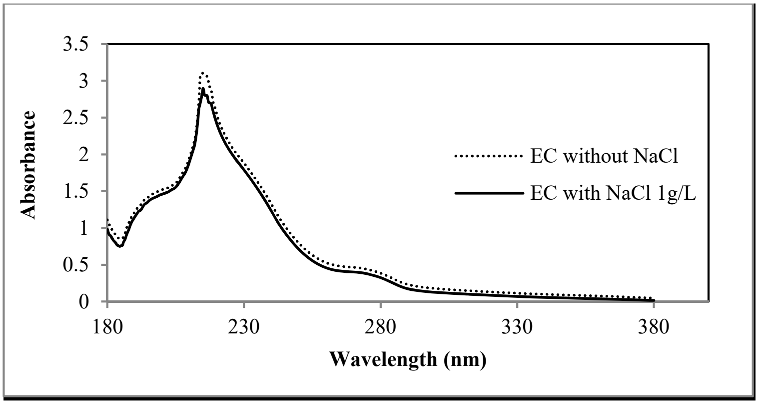


Figure 3: UV-VIS spectra for wastewater treatment by electrocoagulation process (EC).

3.2.3 Oxidation and electrocoagulation processes combined

UV-VIS spectra for wastewater treatment by combining the two methods: oxidation and electrocoagulation (EC) processes with addition of NaCl are shown in Figure 4.

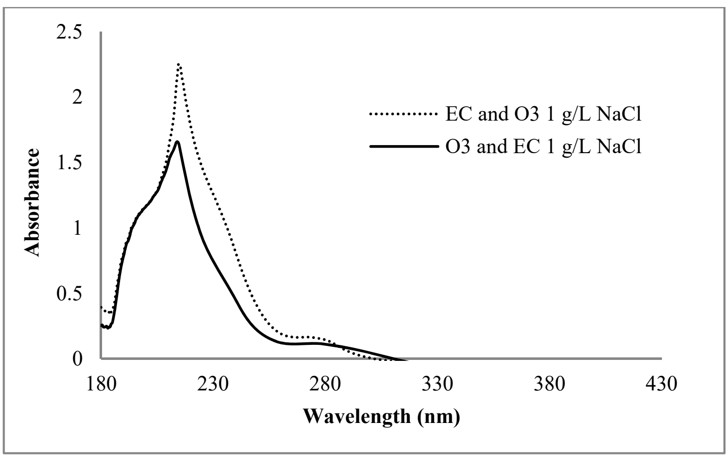


Figure 4: UV-VIS spectra for combining treatment oxidation and electrocoagulation processes.

From Figure 4 it can be observed that in the conditions established (the concentration of NaCl 1 g/L, the current intensity 3A), when the oxidation process is before the electrocoagulation process, the organic compounds removal from the wastewater presents a greater efficiency than if the electrocoagulation process is applied before oxidation process.

3.3 Analysis of treated wastewater

Water treatment after applying the treatment process was analysed. The experimental data is presented in Table 2 and Figure 5.

Table 2: Treated wastewater composition.

Method of treatment / Parameter	Experimental values				
	Oxidation process	Electrocoagulation process		Oxidation following by electro-coagulation	Electro-coagulation following by oxidation
		without addition of NaCl	with addition of NaCl		
Oxygen chemical demand, CCO-Cr, mg O_2/L	2693	1450	1352	1000	1097
Total organic carbon, TOC, mg C/L	835	450	448	427	430
Plumb, Pb(II), mg/L	0.07	<0.01	<0.01	<0.01	<0.01
Cadmium, Cd(II), mg/L	0.02	<0.01	<0.01	<0.01	<0.01
Chrome total, Cr_{tot}, mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Copper, Cu(II), mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Nickel, Ni(II), mg/L	0.06	<0.01	<0.01	<0.01	<0.01
Zinc, Zn(II), mg/L	0.03	<0.01	<0.01	<0.01	<0.01
Manganese, Mn(II), mg/L	0.02	<0.01	<0.01	<0.01	<0.01

From the experimental data it can be observed that the lowest content of organic compounds from wastewater are obtained when using both treatment processes combined. This phenomenon can be explained by the fact that the application of oxidation process leads to neutralization and/or oxidation of alcoholic groups, facilitating their removal by electrocoagulation process, which involves flotation or settling them with the sludge produced during the electrolysis process.

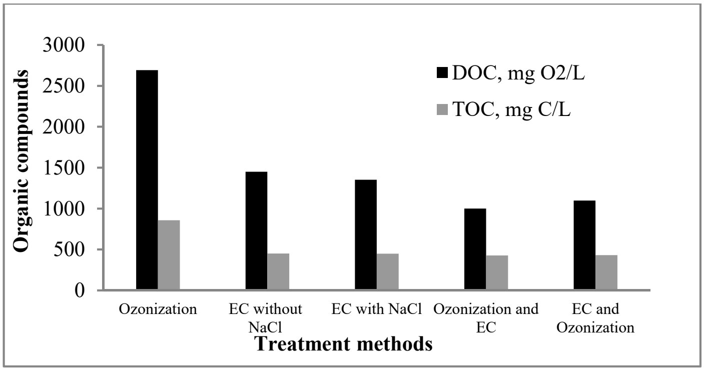


Figure 5: Organic compounds content from water treatment depending on applied process.

3.4 Sludge analysis

The resulting sludge from the wastewater contaminated with organic compounds treatment was air dried for 24 h at 24°C and was subjected to thermal analysis.

Thermo analytical curves recorded for settle sludge and float sludge are presented in figure 6.

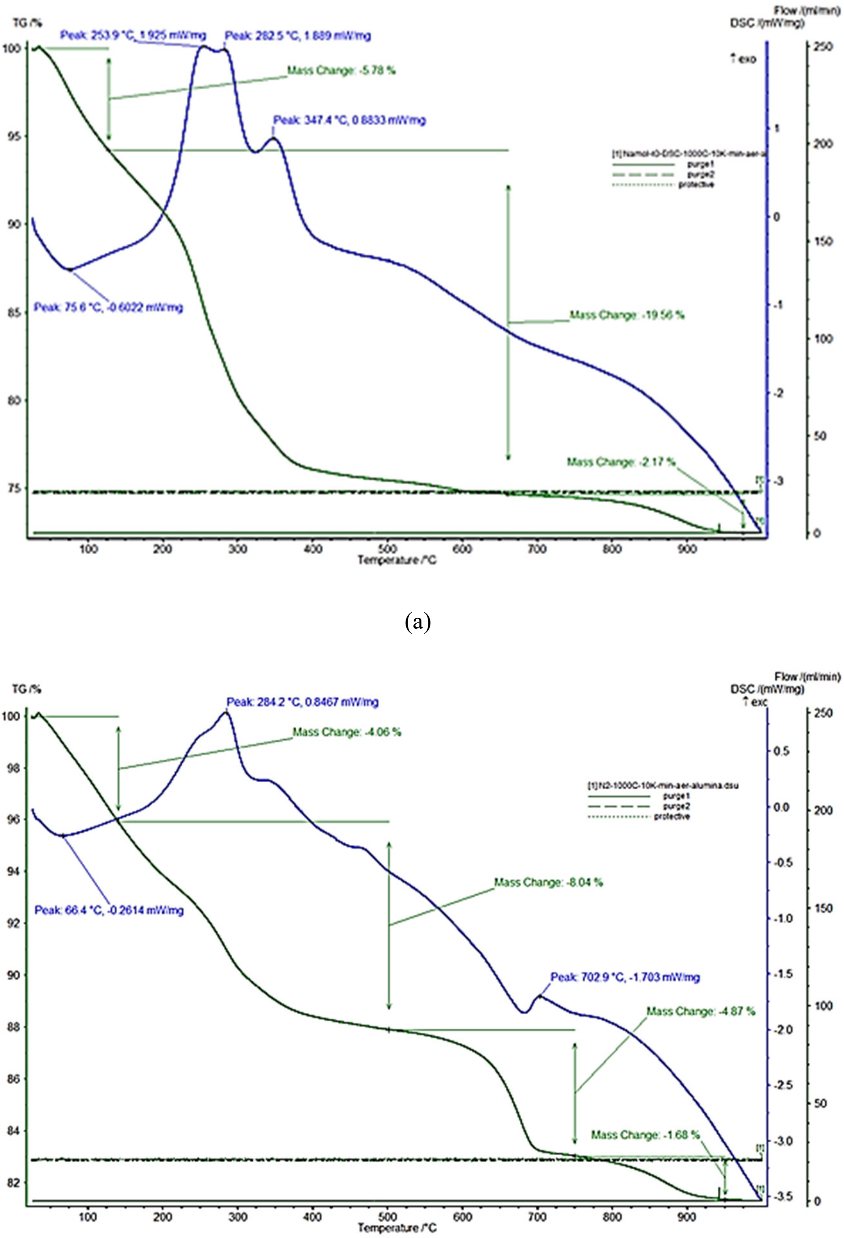
The curves show a similar thermal behaviour of the samples. TG curve of settle sludge indicates a total mass loss of ~17% up to 1000°C (residue 83%), in several steps. In the temperature range 25-130°C the loss of moisture takes place (~4 %) with endothermic effect visible on DTA curve (peak at ~66°C). This is followed between 130 and 400°C by a process with mass loss of ~8% and several exothermic effects with peaks at 260, 284, and 350°C. In this temperature range the burning of organic constituents of the sample occurs (strong exothermic process) overlapped by the dehydration of FeO(OH) (endothermic process) according to

$$2FeO(OH) \rightarrow Fe_2O_3 + H_2O.$$

Up to 1000°C, other processes are visible on the curves: between 600 and 750°C (mass loss ~5%, exothermic peak at 703°C) and between 800 and 940°C (mass loss ~1.7%).

The float sludge sample also loses moisture (~5.8%) in the temperature range 25–130°C, with endothermic effect at 75°C. Between 130 and 400°C the same processes as for settle sludge occur: the burning of organic constituents and the dehydration of FeO(OH). The mass loss is bigger (~19.6%) and the exothermal effects (DTA peaks at 254, 282, and 347°C) are more pronounced. This might indicate that float sludge contains a bigger proportion of organic constituents than settle sludge.

The TG curve of float sludge shows another process with a mass loss of 2.2% between 750 and 930°C. At 1000°C, the residue was of 73%.



(a)

(b)

Figure 6: Thermal analysis of sludge: (a) settled sludge, (b) floated sludge.

4 Conclusions

In this paper, the treatment of resins, lacquers and paints industry wastewater with a high content of organic compounds by physico-chemical processes, was investigated. Thus, it studied the influence during electrocoagulation process, the NaCl concentration influence and the sequence of stages of treatment (EC process followed by oxidation process, oxidation process followed by EC process respectively) on optimizing the process of eliminating organic pollutants with high efficiency.

If used separately, the two processes, oxidation and electrocoagulation, fail to remove the organic load. Electrocoagulation process removes part of the organic pollutants but is not effective enough to be proposed as an independent method in this case.

Combining the oxidation processes with electrocoagulation processes increases efficiency in removing organic pollutants from wastewaters. The comparative study on the results of combining these two processes has shown that oxidation process followed by electrocoagulation process increases the efficiency of the removal of organic compounds from wastewater. The results obtained was indicate that oxidation process followed by electrocoagulation process can be a viable technique on an industrial scale to use in advanced wastewaters purification containing complex organic compounds.

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