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COMBINED OXIDATION AND ULTRAFILTRATION PROCESSES FOR THE REMOVAL OF PRIORITY ORGANIC POLLUTANTS FROM WASTEWATERS

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Abstract

This paper presents a study on the integration of two advanced treatment processes for the removal of priority organic processes from wastewaters: catalytic oxidation (Fenton homogenous process) followed by ultrafiltration. The aim of this study was to assess the removal efficiency for 4-chlorophenol (used as model pollutant), as well as the decrease in effluent toxicity in various processes conditions. The experiments have mainly focused on studying the effect of the oxidant dose of the catalytic oxidation process on the performance of the ultrafiltration process and on the toxicity of the final effluents. Furthermore, the mechanisms of the Fenton homogenous oxidation processes and the removal of heavy molecular weight compounds in ultrafiltration were studied. The results have shown that the toxicity of the effluents decreases significantly through catalytic oxidation, while the ultrafiltration process mainly contributes in removing the oxidation intermediates, especially the high molecular weight compounds.

Key words: advanced wastewater treatment, Fenton catalytic oxidation, 4-chlorophenol, ultrafiltration, toxicity tests

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1. Introduction

Water is one of the most valuable resources, but also one of the most fragile, because of the present climate changes, natural and human-related pollution and the constant population growth. In the context of the increase of the world population, together with the anticipated water shortage over the next years, the solutions emerging are focused on sustainable water management. Nowadays, wastewater management and technology are closely linked to the principles of reduction, recycling and reuse. The reduction of the large volumes of wastewaters produced worldwide can be achieved by the optimal design of plants or water technology, by integrating heat systems, mass streams and pollution prevention measures (Koltuniewicz and Drioli, 2008).

The recycling necessity is correlated with the increased costs of wastewater disposal, the main ideas being the separation of valuable materials from wastewater streams and the reuse of wastewater. Legal enforcements and economics pressures encouraged companies to re-consider their position towards pollution prevention and clean technologies implementation so as to diminish the environmental impacts and risks of the wastewater produced, in terms of quality and quantity. Another positive outcome of this concept implementation is the reduced raw materials requirements which represent an additional cost benefit. The ultimate objective is to obtain a closed water cycle where the majority or the

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entire waste streams are recycled and only output coming from the process is the final valuable product (Cailean, 2011). The idea of water reuse is based on the assumption that various consumers need different quality and quantity of water and each consumer should contribute to reducing water wastage (Asano, 2007). The so-called "sustainable solutions" include the mitigation of groundwater degradation, increasing availability of drinking water and finding suitable usage for industrial/municipal wastewaters once they respect all the necessary quality requirements (Teodosiu et al., 2007).

In order to meet the quality requirements necessary for wastewater recycling and reuse purposes, many technologies have been developed, most of them based on 2 principles: pollutants separations from the main wastewater stream (e.g. membrane processes, activated carbon, etc.) and/or pollutants destruction by using chemical reactions that produce the transformations of the initial toxic pollutants into reaction products less toxic or dangerous for the human health or the environment (e.g. oxidation processes, chemical precipitation etc.). A special attention is drawn by the presence of priority pollutants in the wastewaters, which according to the USEPA classification (EC Decision, 2001) are a class of substances that have been selected based on the following criteria: they are frequently found by monitoring programmes, are toxic at low concentrations, are persistent, carcinogens and able to bioaccumulate (Crathorne et al., 1996). These types of pollutants refer to: refractory organic compounds, inorganic toxic compounds, colloids, nutrients, etc. (Gavrilescu et al., 2008).

Priority organic pollutants are refractory to biological degradation or even toxic to the microorganisms, if the processes proceed at low rates. Among organic pollutants, phenol and phenol derivates, used as raw materials in chemical, petrochemical, and pharmaceutical industries have received increased attention in the last years due their toxicity (Guo and Al-Dahlan, 2003; Liotta et al., 2009). These compounds represent common organic pollutants in water discharged by several industries, and have particularities that make them valuable as a model pollutants, such as: toxicity even at low concentrations, formation of substituted compounds during disinfection and oxidation processes (such as those used currently for the treatment of natural surface water for drinking purposes), phytotoxicity and ability to bioaccumulate in organisms, that have similarities with persistent organic pollutants (POPs) (Busca et al., 2008; Catrinescu and Teodosiu, 2007). Through associated regulations (emission limits) and an integrated approach, the management for industrial activities (with the highest impacts on pollution loads and their effects on human and aquatic ecosystems) has to consider new processes and technologies capable to eliminate priority pollutants, by reducing the effluent volumes, closing water circuits, or by

reusing and recycling the wastewaters (Teodosiu, 2002).

The objectives of this research refer to the study of a combined chemical oxidation and membrane process for the removal of priority organic pollutants from wastewaters. 4-chlorophenol was selected as model pollutant, and the efficiency of combined process was considered in terms of removal efficiencies and decrease of effluent toxicity.

2. Integration of advanced treatment processes for the removal of priority organic pollutants from wastewater

Advanced wastewater treatment technologies, are considered to efficiently eliminate priority pollutants such as non-biodegradable organics (including persistent organic pollutants, POPs), or inorganic toxic compounds to a level that allows water recycling, closing of the water circuits or the discharge into natural water bodies. Such advanced wastewater treatment technologies include pollutant destruction or separation processes such as: advanced oxidation processes (AOPs) (catalytic and photocatalytic oxidation, catalytic wet air oxidation, ultrasound, plasma processes, etc.), chemical precipitation, adsorption on different media, membrane processes, etc. (Zhou and Smith, 2002). Advanced oxidation processes have been reported to be effective for the near ambient degradation of organic pollutants from wastewater (Esplugas et al., 2002). AOPs are characterized by a common chemical feature: the capability of exploiting the high reactivity of HO• radicals in driving oxidation processes which are suitable for achieving the degradation and mineralization of the initial pollutants (Liotta et al., 2009). These processes include catalytic wet air oxidation, methods based on ultrasound, plasma and electrohydraulic discharge along with processes based on hydrogen peroxide, photolysis, photocatalysis and processes based on ozone.

Among the multitude of AOPs, Fenton and Fenton-like processes have been frequently chosen to partially oxidize effluents polluted with organic compounds (Esplugas et al., 2002; Pera-Titus et al., 2004). Fenton process is a liquid phase catalytic oxidation with hydrogen peroxide, which does not form any harmful by-products, and it is a non-toxic and ecological reactant. In the homogeneous process, Fenton's reagent ($Fe^{2+}/Fe^{3+}/H_2O_2$) is used to generate highly reactive hydroxyl radicals from hydrogen peroxide, in mild reaction. To enhance the decomposition of hydrogen peroxide to hydroxyl radicals, the use of a catalytic system is very important (Arsene et al., 2010). The system containing hydrogen peroxide and Fe(II) salts in water solution form hydroxyl radicals following the reaction:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO$$
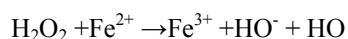
These processes display high efficiencies in abating organic refractory pollutants, the formation of organic intermediates, which can be even more refractory to biological oxidation than the initial pollutant, being also possible. The Fenton process presents many operation advantages such as its operation at room temperature and atmospheric pressure. In addition, required reagents are readily available, easy to store and handle, safe and they do not cause environmental damages (Pignatello et al., 2006). However, two main homogeneous Fenton process drawbacks can be identified. The first is related to the waste of oxidant due to the radical scavenger effect of hydrogen peroxide ($\bullet OH + H_2O_2 \rightarrow \bullet O_2H + H_2O$) and its self-decomposition ($2H_2O_2 \rightarrow O_2 + 2H_2O$). The second refers to the continuous loss of iron ions dissolved in the treated effluent ending, once required effluent neutralization is performed, in form of solid sludge.

The use of hydrogen peroxide as source of hydroxyl radicals in the Fenton chemistry implies an increase of the treatment costs because of its proven radical scavenging character. In addition, hydrogen peroxide can also be self-decomposed at high concentrations. As result, the economic impact of the waste of the bulk oxidant is evident. Hence, designed methods allowing the decrease of the oxidant waste would reduce treatment costs. Hydrogen peroxide may also detrimentally affect the operation of the coupled membrane processes because of its chemical reactivity. Thus, there is a necessity of decreasing the concentration of hydrogen peroxide used in the Fenton oxidation to reduce its wastage and its negative effect on the membranes.

Ultrafiltration represents a feasible option in the advanced wastewater treatment of industrial effluents for recycling purposes (Barjoveanu and Teodosiu, 2009; Musteret et al., 2010). Designing and use of industrial scale membrane processes for effluent treatment is difficult because of the complexity of the phenomena consisting in wastewater matrix - membrane characteristics trelationships, with many phenomena incompletely characterized. Therefore, a laboratory scale approach is the first step to better observe these interactions. In this study, ultrafiltration is considered to have the role of a polishing step for the effluent discharged by the oxidation process.

Membrane separation processes have significant advantages, as compared with other separation techniques, i.e.: no need in changing the effluent phases, which means at the same time less energy consumption; no additions of substances because there is no chemical reaction, easy installation and maintenance operations with the possibility of complete automation of the membrane separation systems (Barjoveanu and Teodosiu, 2009; Cheryan, 1998; Zhou and Smith, 2002).

Pressure-driven membrane processes could decrease the concentration of refractory organic intermediates to a quality level enough for allowing reuse of treated water for different purpose.

Therefore, the installation of the membrane process as next step after Fenton oxidation process would guarantee the correct operation of the process units, the possibility to remove the oxidation intermediates, and/or to recover the iron generated as secondary pollution. In this sequence, oxidation (Fenton type, homogeneous) – ultrafiltration, the oxidation realizes the breakdown of 4-chlorophenol molecules to several intermediates which are further removed by ultrafiltration, enhancing thus the biodegradability of the effluent.

2. Materials and methods

2.1. Materials

The experiments were realized using synthetic wastewaters containing 4-chlorophenol as model for priority organic pollutants. 4-chlorophenol (4-CP) was supplied by Sigma-Aldrich. The oxidation tests were performed at a concentration 500 mg/L of 4-chlorophenol. As catalyst for the Fenton homogeneous oxidation was used $(NH_4)_2Fe(SO_4)_2*6H_2O$, and H_2O_2 as oxidant.

2.2. Analytical methods

The concentration of the phenolic compounds was determined by 4-aminoantypirine standard method (Ettinger, 1951). The catalyst concentration (Fe ions) at the end of the processes was determined with an Atomic Absorption Spectroscopy (GBC Avanta with system 3000 Graphite Furnace). The total organic carbon (TOC) values were analyzed using a Total carbon analyzer (Shimadzu Model TOC-VCSN TNM1). The chemical oxygen demand (COD) concentration was determined according to EPA method 5220, using a Hanna COD reactor and a Jasco UV-VIS 530 series spectrophotometer.

In order to identify the main reaction intermediates, a 10 mL sample was extracted twice with 2.5 mL portions of ethylic ether. The combined extracts were dried over anhydrous sodium sulfate, evaporated under vacuum and concentrated under a nitrogen stream. The derivatization of the hydroxyl groups of the phenolic compounds, N-Methyl-N (trimethylsilyl) trifluoroacetamide MSTFA (0.1 ml) was added to the concentrated solution, followed by heating at 70 °C for 60 min. An Agilent 6890N/MSD GC-MS system, equipped with electron impact (EI) ionization source and a capillary column (30 m HP 5ms), working with He as carrier gas (1 mL/min) was used. The injection was performed in the splitless mode and the data acquisition was carried out in full scan mode. The column was held at 80 °C for 3 min and then heated with 15 °C/min. up to 300 °C and maintained at this value for 7 min.

For the toxicity studies, the Microtox® test, based on the measure of the bioluminescence of *Vibrio Fischeri* marine bacteria, was used. The principle of this test consisted to first measure the bioluminescence of the current bacteria population.

Then, the bacteria population was exposed to the effluent, and the bioluminescence was again measured. At the same time, the blank bioluminescence was also determined. The measurements were carried out by means of the system Microtox®, according to an international standard procedure (ISO DIS 11348). The inhibation effect of water samples that can be expressed quantitatively as Lower Ineffective Dilution (LID) on the series of samples prepared by diluting the original sample. LID define the dilution level to which water sample produce a negligible inhibition, i.e. <20 % in bioluminescence test.

2.3. Experimental set-ups

In order to evaluate 4-chlorophenol removal by combined oxidation and ultrafiltration process, two experimental set-ups were used, as described below. The **oxidation** was carried out in a reaction system of 1500 mL equipped with a magnetic stirrer and a pH electrode, as presented in Fig. 1(a). The catalyst, $(NH_4)_2Fe(SO_4)_2*6H_2O$, was introduced into 1000 mL of an aqueous solution (500 mg/L), at room temperature and the correction of pH at 3.5, the solution was stirred for 60 min and then a solution of

3 % H_2O_2 was added to achieve the selected H_2O_2 ratio, these being the basic conditions for the Fenton oxidation process.

The laboratory scale ultrafiltration set-up is presented in Fig. 1(b) and it consists of a feed tank (2), a demineralized water tank (1), a peristaltic pump (3), which is able to feed the ultrafiltration module (6) with a flow of up to 3.7 L/min. Because the peristaltic pump creates a pulse flow, the laboratory set-up is fitted with a pulsation dampener (4). Pressure in the system is measured with the help of two manometers (5 and 7) and it is regulated with metering valves (V-3, V-4 and V-5).

The ultrafiltration module comprises two tubular membranes made of cellulose acetate connected in series. The ultrafiltration membranes are supplied by PCI Membranes (UK) and have a molecular weight cut-off of 2000 Da.

The ultrafiltration experiments were performed in dead-end mode for 60 minutes, at every 10 minutes samples from the feed, concentrate and permeate were collected. After the UF test itself, the membrane was cleaned by using an optimum cleaning sequence.

Experimental conditions for the combined advanced process are presented in Table 1.
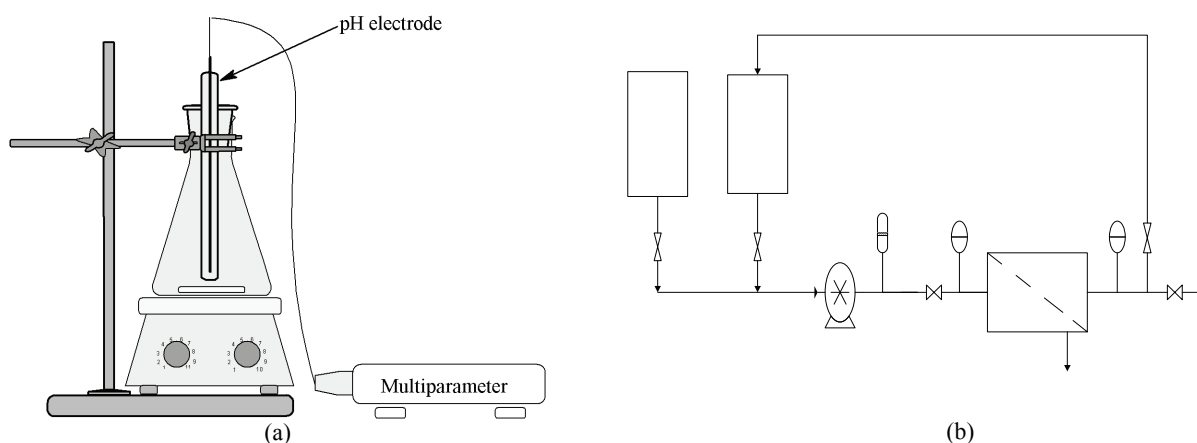

Fig. 1. Laboratory scale (a) Fenton oxidation and (b) ultrafiltration system

Table 1. Experimental conditions for the combined advanced processes

Catalytic oxidation		*Ultrafiltration*	
Type of catalyst	*$(NH_4)_2Fe(SO_4)_2*6H_2O$*	*Type of membrane*	*CA202 (cellulose acetate), MWCO 2000 Da*
Initial concentration of 4-CP	500 mg/L	Pressure	2.5 bar
Reaction time	90 min	Ultrafiltration time	60 minutes
pH	3.5	pH	3.93 – 2.20
Temperature	ambient	Operating mode	Dead-end
Catalyst dose	5 mg/L	Cellulose acetate membrane cleaning conditions after each ultrafiltration test	Chemical cleaning with HNO_3 pH=2; V=500 mL; T=30 ^{0}C; p=3 bar; t=5 min; Washing with demineralized water V_{AD}=1000 mL p=3 bar; T=20 ^{0}C; t=10 min.
Molar ratios (4-CP: H_2O_2)	R_1=1:2.7 (20% H_2O_2) R_2=1:5.4 (40% H_2O_2) R_3=1:8.1 (60% H_2O_2) R_4=1: 12.15 (90% H_2O_2)		

The removal efficiency is calculated using the following equation (Eq. 1):

$$RE = \frac{C_i - C_f}{C_i} \times 100, \, [\%] \qquad (1)$$

where: RE is the removal efficiency, [%]; C_i and C_f – the pollutant concentration, [mg·L^{-1}] in the influent and effluent.

The removal efficiencies were expressed as chemical oxygen demand (COD), total organic carbon (TOC) and 4-chlorophenol concentration (4-CP).

3. Results and discussion

3.1. The influence of hydrogen peroxide concentration on the Fenton oxidation process efficiency

Hydrogen peroxide concentration is an important parameter in the catalytic oxidation. The influence of hydrogen peroxide concentration for 4-chlorophenol removal was evaluated by determining the removal efficiency, expressed in terms of chlorophenol concentration, chemical oxygen demand, total organic carbon and absorbance at 455 nm (color). This wavelength was selected because it was observed that oxidized effluents showed a maximum in the UV-Vis absorption spectrum at this value.

The use of H_2O_2 in excess should be avoided from both economical and technical reasons. The choice of the oxidant dose should be made with precautions because: (i) H_2O_2 is an expensive reagent, (ii) H_2O_2 is dangerous for microorganisms and could affect the overall efficiency of the process, when Fenton oxidation process is used as a pretreatment for biologic oxidation. Consequently, four different H_2O_2 doses of 20%, 40%, 60% and respectively 90% of the stoichiometric necessary molar ratios (4-CP: H_2O_2) were used. Then, in order to enhance the biodegradability of the effluent, the oxidation process was followed by an ultrafiltration process. Fig. 2 presents the influence of the hydrogen peroxide concentration on the removal efficiencies, expressed as chemical oxygen demand, total organic carbon and 4-chlorophenol concentration.

It can be observed that a higher H_2O_2 dose leads to a higher removal efficiency, expressed in terms of chlorophenols, total organic carbon and chemical oxygen demand concentrations (Fig. 2). In addition, it can be observed that Fenton oxidation process produces a decrease of the effluent pH. This behavior can be explained by the generation of higher concentrations of carboxylic acids. As shown in Fig. 3, the H_2O_2 dose has a significant impact on the effluent color, expressed by the value of absorbance at 455 nm. If the effluent obtained by using a H_2O_2 dose of 20% of the stoichiometry is highly colored in dark red and opaque, at higher doses (60 and 90%),

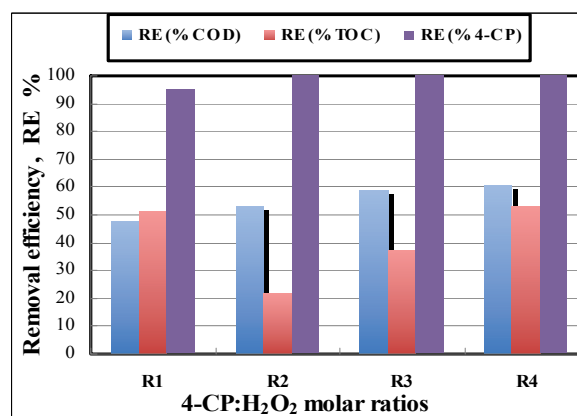the effluents have an orange or light yellow and transparent color.

Fig. 2. The influence of the hydrogen peroxide concentration on the oxidation process. Conditions: 500 mg 4-CP/L, 5 g Fe^{2+}/L, pH 3.5, room temperature

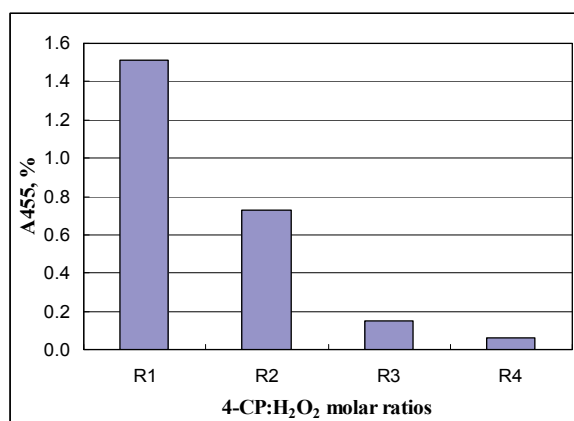**Fig. 3.** The influence of hydrogen peroxide concentration on color effluent. Conditions: 500 mg 4-CP/L, 5 g Fe^{2+}/L, pH 3.5, room temperature

To understand the origin of color due to the oxidation process intermediates it is necessary to know the chemical composition of the effluent or the reaction scheme of the oxidation process. The intermediates identification was performed by gas chromatography-mass spectrometry (GC-MS) analysis after solvent extraction and derivatization.

Fig. 4 shows a typical total ion chromatogram obtained from the oxidation of 500 mg 4-CP/L, followed by extraction and TMS derivatization. Some compounds, such as 4-chlorophenols, 4-chlorocatechol (4-CC), hydroquinone (HQ), 4-chlorohydroquinone (4-CHQ) and chlorinated benzentriols were identified by comparing retention times and mass spectra with those of the authentic standards.

Besides the main degradation products of 4-CP, the appearance of condensation products with high molecular weight probably formed by oxidative coupling reactions is noticed. Some of these products were previously identified (Catrinescu et al., 2011).

The authors proposed a mechanism by which initially a series of intermediates without color (4-CC, HQ, 4-CHQ) are formed and they can be further oxidized to benzoquinone. In addition, dihydroxilated intermediates may react with their quinones to form condensation compounds, intensively colored. This is the case of hydroquinone and p-benzoquinone, which react forming quinhydrone (brown, with intense color).
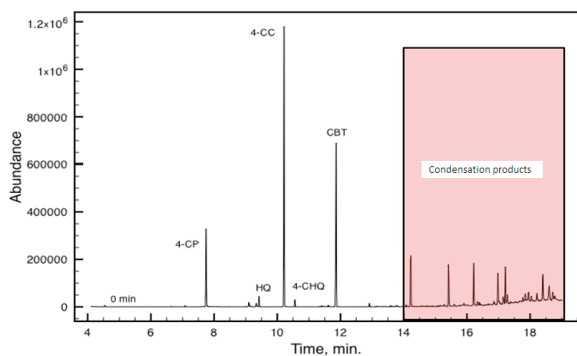

Fig. 4. Typical total ion chromatogram and trimethylsilyl TMS derivatization. Conditions: 500 mg 4-CP/L, 4-CP: H_2O_2=1: 2.7, 5 g Fe^{2+}/L, pH 3.5, room temperature

On the other hand, ferric ion, generated during the Fenton process, could react with dihydroxilated ring compounds, forming green metal-aromatic complexes (Mijangos et al., 2006). It should be noted that these colored compounds are gradually eliminated when the dose of H_2O_2 from the system increases.

The aromatic reaction intermediates are usually non-biodegradable and they can be even more refractory to biological degradation than the initial contaminant. In order to evaluate the toxicity of the effluent, some tests based on luminescent bacteria inhibition produced by *Vibrio bioluminescence fisheri* were performed. These tests are commonly used to assess toxicity of various effluents. The results of these tests are expressed as percentage inhibition of luminescence in the test solutions or LID (Lower Ineffective Dilution) value. A LID value is defined by EN ISO 11348-2/2003, as the dilution of the water sample so as to obtain an inhibition of the luminescence of smaller than 20% in the bacteria test. The influence of the 4-CP: H_2O_2 molar ratios over the luminescence and LID are presented in Figs. 5 and 6.

The toxicity decreases significantly by increasing the oxidant dose, the same trend as for removal efficiency expressed by 4-CP, COD and TOC. It should be noted that for the toxicity tests it was necessary to correct the effluent pH at 7, and in these conditions Fe^{3+} ions from the solution precipitates. To avoid this precipitation, which can affect the determination accuracy, iron ions were eliminated before analysis, by correcting the solution pH at 10-12. Thus, the registered toxicity was derived exclusively from the presence of dissolved organic compounds.

In Fig. 6, it can be observed that the toxicity decreases with the increasing dose of hydrogen peroxide. In conclusion, the resulted effluents require additional treatment (such ultrafiltration) to eliminate toxicity to acceptable values for biomass.
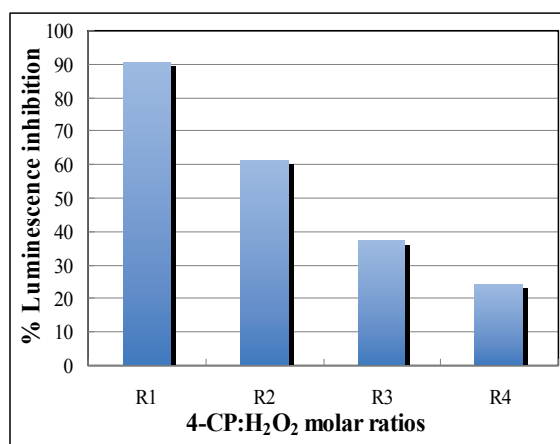

Fig. 5. The influence of hydrogen peroxide concentration on the effluent toxicity expressed as % luminescence inhibition
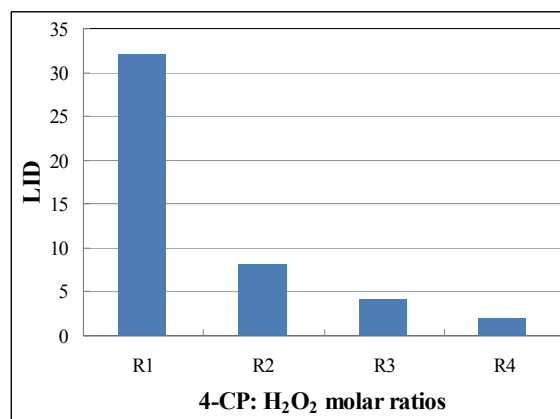

Fig. 6. The influence of hydrogen peroxide dose on the effluent toxicity expressed as LID

3.2. The influence of hydrogen peroxide concentration on the ultrafiltration process efficiency

In order to study the influence of the oxidant concentration on the ultrafiltration process efficiency, the effluents resulted from the Fenton catalytic oxidation were fed to the ultrafiltration (UF) process. The operating conditions are presented in Table 1. The membrane material was cellulose acetate, and the dead-end mode operation was used.

The high molecular-weight compounds resulted from oxidation (condensation products, oligomers, polymers) and other colored compounds, including iron complexes can be theoretically retained by ultrafiltration membranes. The main characteristics of the effluent resulted from the catalytic oxidation are summarized in Table 2.

Table 2. Effluent characteristics resulted from catalytic oxidation

Stoichiometric ratios / Effluents characteristics	*Initial solution (0% R)*	*20% R*	*40% R*	*60% R*	*90% R*
COD, mg/L	1003	528	473	417	401
TOC, mg/L	255	215	200	161	121
4-CP, mg/L	500	24	0	0	0
A455	0	1.510	0.729	0.146	0.065

Fig. 7 displays the evolution of the removal efficiency expressed in terms of COD, TOC, 4-CP, color and Fe^{3+} concentrations, for the ultrafiltration of the effluent resulted from the oxidation with the molar ratio R1 (4-CP: H_2O_2 =1: 2.7).
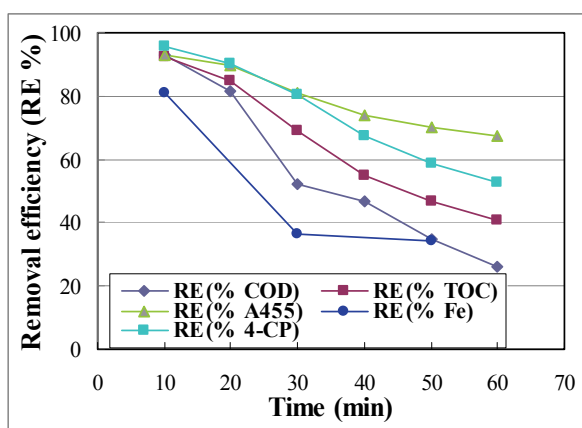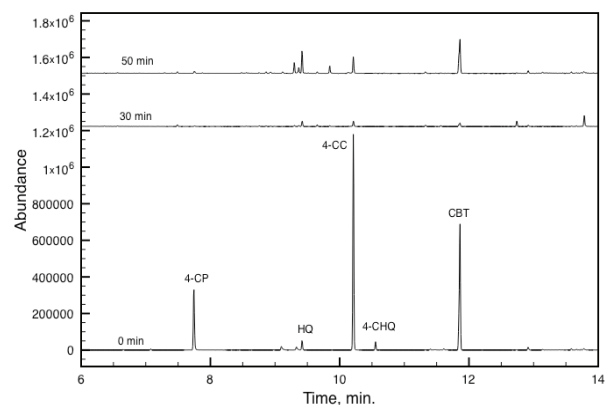

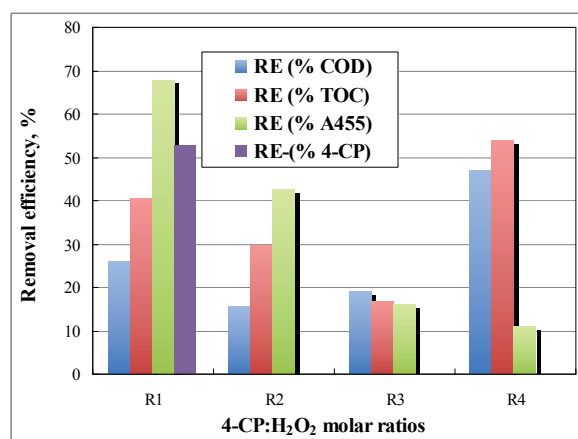**Fig. 7.** Removal efficiency after ultrafiltration process. R=20% H_2O_2

In the first minutes, the removal efficiency for the organic pollutants and Fe^{3+} ions is very high, but it decreases during the ultrafiltration process. It can be observed a more pronounced decrease of the removal efficiency for Fe^{3+}, COD, TOC, while the effluent color is relatively efficiently eliminated during ultrafiltration. For example, after 60 minutes of ultrafiltration, the removal efficiency (expressed as COD) decreases from 93% to 26% while for the A455 it remains at 67%. This behavior confirms the fact that the membranes retain particularly high molecular weight compounds that are responsible for effluent color.

In Fig. 8 three representative chromatograms are presented, corresponding to solution before the ultrafiltration process (effluent resulted from oxidation process with 20% H_2O_2) and permeate after 30 and 50 minutes of ultrafiltration.

At the beginning of the ultrafiltration process (after 30 minutes) the permeate contains small concentrations of phenolic compounds (4-CP and aromatic intermediates), but after 50 minutes they reappear in the effluent, aspect that shows the fact that the ultrafiltration membrane is fouled and thus unable to retain the oxidation products. In Fig. 9 are presented the removal efficiencies obtained after ultrafiltration of effluents resulted from catalytic oxidation.

Fig. 8. GC-MS chromatogram of the effluent before ultrafiltration and permeate after 30 and 50 min

Fig. 9. Removal efficiency of the effluents resulting from the ultrafiltration process

By analyzing the results presented in Fig. 9 it can be observed that the ultrafiltration process has a high efficiency in removing, especially, high molecular weight compounds that are responsible for the color of the effluent resulted from the catalytic oxidation, the removal efficiency (calculated only for the ultrafiltration stage) was 67% (% A455) for oxidation-ultrafiltration effluent obtained by using a stoichiometric ratio value of 20% oxidant. Also, for the same effluent, the following values of the removal efficiencies were obtained: 52% for 4-chlorophenol, 26% for COD and 40% for TOC.

The variation of the permeate fluxes during the ultrafiltration tests are presented in Fig. 10. Regarding the values of permeate flow, it can be observed that they present a slight decrease in time for the

ultrafiltration test using the effluent resulted from the catalytic oxidation with stoechiometric ratio value of 20% R.
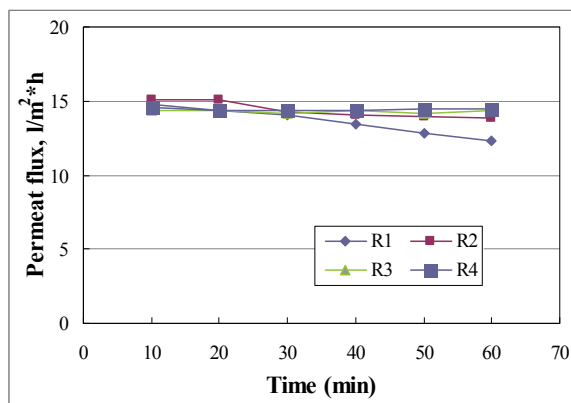

Fig. 10. Variation of permeate fluxes during the ultrafiltration tests

This behavior can occur due to the fact that in these effluents existed high molecular weight compounds, such as 4-chlorocatechol (4-CC), hydroquinone (HQ), 4-chlorohydroquinone (4-CHQ), benzentriols chloride (CBT) and condensation products, which tend to accumulate in the cellulose acetate membrane and thus decrease the permeate flux in time.

4.3. Efficiency of the combined oxidation-ultrafiltration process and influence on the final effluent toxicity

The previous tests showed that the removal efficiencies, for all the measured indicators significantly decreased in the first minutes of ultrafiltration, after more than 20 minutes the ultrafiltration membrane being not capable to remove the pollutants. The evolution of the toxicity during the same ultrafiltration test is presented in Fig. 11. The percentages of luminescence inhibition increase during the ultrafiltration process. Although after the first 10 minutes the percentage of inhibition is below 20% (negligible toxicity), after 50 minutes it reaches values greater than 80%.
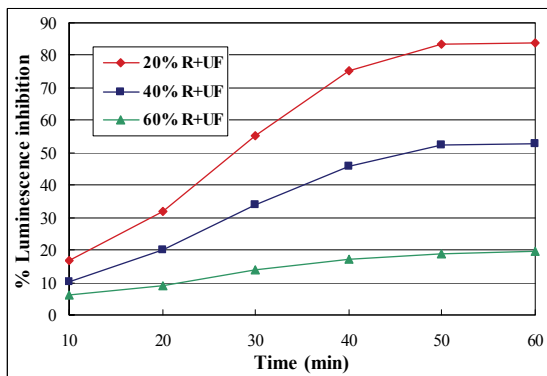

Fig. 11. The evolution of toxicity during the combined process oxidation-ultrafiltration

The toxicity increases with the initial organic concentration of the effluent. This behavior suggests that the retention of pollutants on the membrane is similar to a sorption process. Therefore, once the amount of pollutant retained by the membrane reaches saturation, the membrane is no longer able to retain additional pollutant quantities. The sigmoidal profile of these curves, similar with the breakdown characteristic curves of adsorption process curves, is an additional argument in favor of this sorption mechanism.

Since the initial effluents have different organic concentrations, it is interesting to follow the evolution of the toxicity removal for each effluent (Fig. 12). It can be noticed that the reduction of toxicity is rapidly decreasing after the first 10 minutes of ultrafiltration. In the case of the lower effluent organic molar ratio (60% R) the toxicity removal drops to approx. 50%, a value which is still compatible with a subsequent treatment by a biological process. For the other two effluents containing high initial pollutant concentrations, the toxicity removal decrease sharply at 10-15%. These final effluents are too toxic and cannot be introduced into a consecutive biological process. The evolution of the inhibition percentage depending on the dilution factor for effluent reaction R3, after 60 min of ultrafiltration, is presented in Fig. 13.
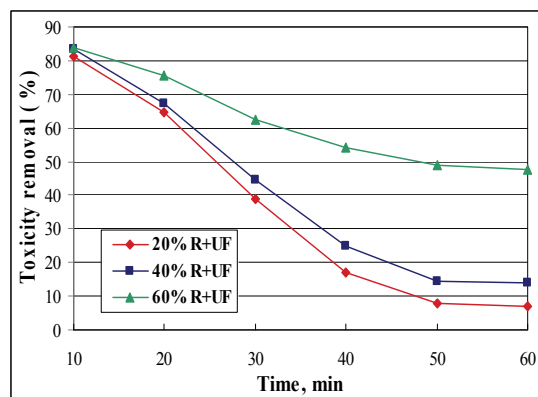

Fig. 12. Toxicity removal efficiency for combined oxidation-ultrafiltration proces
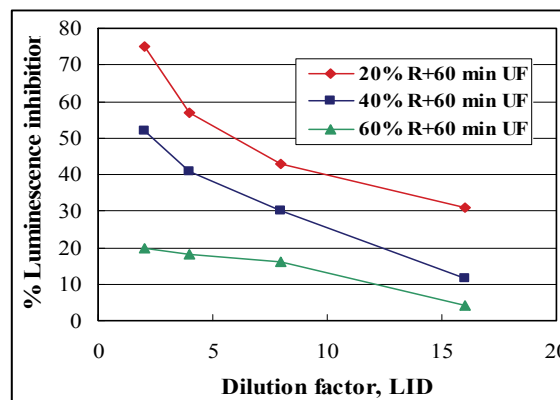

Fig. 13. Luminescence inhibition percentage depending on LID for 60min UF for R1, R2 and R3 effluents

Table 3. The toxicity evolution of the combined oxidation - ultrafiltration effluent

Reaction	*% H₂O₂*	*LID[1], initial value*	*LID[2], final value*	*Observation*
R1	20	32	32	Insignificant reduction of toxicity
R2	40	16	16	Reduction of toxicity-
R3	60	8	8	Reduction of toxicity-no toxicity of the effluent
R4	90	2	2	Insignificant values of toxicity

[1]-after reaction, [2]- after reaction+60 min UF

It can be observed that, when LID=16, the effluent presents a negligible toxicity (luminescence inhibition < 20%). The toxicity becomes negligible for R3 and R4 reaction as presented in Table 3.

After an analysis of data obtained in these studies, there is a concordance between the evolution of the removal efficiency and the final effluent toxicity. This behavior indicates that toxicity, expressed as percentage inhibition of luminescence in the Microtox[®] test can be used to describe the biological effectiveness of the combined processes studied. The ultrafiltration process does not contribute significantly to reduce the effluent toxicity, although it removes significantly the high molecular weight compounds.

5. Conclusions

The experimental results confirmed that the combined catalytic oxidation (homogeneous Fenton process) and ultrafiltration process can be used to eliminate priority organic pollutants from wastewater. Regarding catalytic oxidation process, stoechiometric ratio 4-CP: H_2O_2 increased from 20 to 90%, led to an increase in the removal efficiencies for COD from 47 to 60%, for TOC 51 to 53%, and for 4-CP from 95 to 100%. The toxicity of effluents from the catalytic oxidation process significantly decreases with increasing stoechiometric molar ratio of 4-CP: H_2O_2.

Regarding the ultrafiltration process, it was found that this process has high efficiency, especially for removing high molecular weight compounds derived from 4-chlorophenol degradation during the oxidation process when substoechiometric ratio 4-CP: H_2O_2 are used. The removal efficiency was 67% for ultrafiltration of the effluent resulted from catalytic oxidation with stoechiometric ratio value of 20% R. Also, for the same effluent were obtained the following values of the removal efficiencies: 52% for 4-chlorophenol, 26% for COD and 40% for TOC. The results of the toxicity tests revealed that ultrafiltration does not contribute significantly to reducing effluent toxicity.

The best removal efficiencies for the Fenton catalytic oxidation stage are obtained at the highest doses of hydrogen peroxide, nevertheless the dose should be carefully selected, considering the fact that the best removal efficiencies expressed as COD indicator for the ultrafiltration stage were obtained at the lowest doses, so an optimization between these process conditions should be made.

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