# Fe-Zn-ZVT CATALYST USED IN ADVANCED OXIDATION PROCESSES OF ORGANIC POLLUTANTS FROM WASTEWATERS

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Advanced chemical oxidation of organic biorefractory compounds is a very important process used in industrial wastewater treatment. This paper presents experimental results obtained in phenol advanced oxidation process from wastewaters using heterogeneous Fenton, hydrogen peroxide solution in excess (100%) and a Fe-Zn-zeolitic volcanic tuff catalyst (Fe-Zn-ZVT). Catalyst quantity and temperature influence over the process efficiency were studied and activation energy for the phenol total oxidation (H_2O_2 and Fe-Zn-ZVT catalysts) were calculated based on experimental values. Maximum oxidation conversions ($X_{total} = 95.90\%$, $X_{phenol} = 100\%$) were obtained for 4 g catalyst (100 cm^3 phenol wastewater) and 60°C.
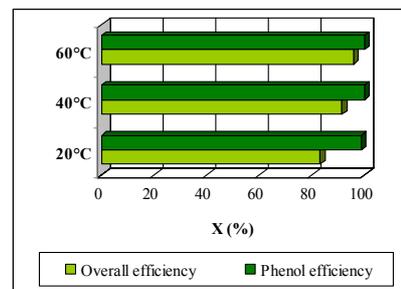
INTRODUCTION

Organic pollutants from wastewaters (phenol and phenolic compounds, pesticides, hydrocarbons) modify properties of water such as taste and smell, reduce dissolved oxygen quantity and have a toxic effect, sometimes carcinogenic or mutagenic, being bioaccumulated in living organisms. Due to their high toxicity and frequent occurrence in wastewaters, phenol and phenolic compounds have been in scientists' attention for more then twenty years. The phenol pollution sources of waters are: petrochemical industry, chemical industry (fabrication of phenol formaldehyde resins, fabrication of caprolactam, production of coke, diluting agents, paints, cosmetics and rubber) or metallurgy. Phenol and phenolic compounds are very toxic to human organisms as well as for aquatic organisms.[1,2] According to the Roumanian legislation, the maximum allowable concentration in surface waters is 1 µg fenol/dm^3.[3]

Purification of wastewater containing phenols can be achieved by non-destructive processes (extraction, steam entrapment, coagulation with chemical reactive, adsorption on active carbon), processes that cannot reduce phenol concentration under the maximum allowable level for discharge in surface waters, and destructive processes (biological processes, incineration, oxidation under high temperature and pressure, catalytic oxidation with oxygen from the air, advanced oxidation processes).[4-14]

Mild oxidation with oxygen from air can be utilized in case of wastewaters containing small quantities of stable organic compounds and it is realized at relatively low temperature and pressure. Advanced chemical oxidation with different oxidizing agents (ozone, hydrogen peroxide, ozone/hydrogen peroxide, and/or UV radiation, Fenton reagent, UV radiation/Fenton reagent) is a treatment method used in case of wastewaters with relatively small COD (chemical oxygen demand) content (COD < 5 g/L). Many oxidation processes

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of organic compounds in aqueous phase are catalytic processes. This can be supported by the fact that non-catalytic processes require longer reaction periods and severe operating conditions (200-450°C, 70-250 atm). Catalysts used in the oxidative processes are usually in solid state and can be metallic oxides (Fe_2O_3, ZnO, CeO_2, etc.), metals deposited on different supports (Rh, Pt on TiO_2 carrier, carbon aerogel, Al_2O_3), Cu^{2+}, Fe^{2+} or Fe^{3+} ions in solution or immobilized on clay minerals, or on natural or synthetic zeolites.[15-20]

Fenton reagent (hydrogen peroxide and Fe^{2+} ion as catalyst) can be used for removal of toxic organic compounds from wastewaters, resistant to traditional biological treatments. This reagent has proved to be more efficient in oxidative processes than oxygen, ozone or hydrogen peroxide.[21-25] The oxidation of organic pollutants with Fenton reagent is a fast and non-selective reaction based on the formation of HO· and HOO· highly reactive radicals. The heterogeneous Fenton method, which uses Fe^{2+} ion immobilized on a carrier, presents multiple advantages by comparison to the classic method, homogeneous Fenton, namely: it is not necessary to modify the wastewater pH to maintain the iron ions in solution, can be operated at relatively low temperature, and the catalyst can be easily separated and recycled in the oxidation processes.[26]

In this paper, we studied the possibility to use a Fe-Zn-ZVT catalysts obtained by modification of a zeolitic volcanic tuff, in the advanced oxidation of phenol from wastewaters, through heterogeneous Fenton process. We studied the influence of catalyst quantity and temperature over the process efficiency and we calculated, using experimental values, the activation energy for phenol total oxidation with H_2O_2 and Fe-Zn-ZVT catalyst.

RESULTS AND DISCUSSION

Catalyst characterization

Natural zeolitized volcanic tuffs were collected from Pâglişa (ZVT) deposit (Cluj County, Transylvania, Romania). The pyroclastic rocks belong to the Dej Tuff Complex, of a Lower Badenian age. The main petrographical component of this complex is represented by white and grey volcanic tuff that may be interlayered with clays, marls and clayey sandstones.[27-30] The intensive alteration processes that affected these tuffs, locally led to the formation of economically valuable accumulations.[31]

Representative samples from Pâglişa were investigated using optical (polarized light) microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transformed infrared (FTIR) spectroscopy, surface specific area (BET) and wet chemical analyses.[32]

The volcanic tuffs from the studied occurrences generally have a vitric and vitric crystal texture and are zeolitized. They consist of 70-90% of volcanic glass, 10-25% of crystals and lithic fragments in subordinate amounts (2-5%). The X-ray diffraction measurements performed on random powder of the whole material indicated the massive presence of clinoptilolite as the main zeolite species (65-70%). Scanning electronic microscopy (SEM) revealed that zeolites are present as tabular clinoptilolite crystals, micron- and submicron-sized crystals, or as larger crystals in the pores or voids. The bulk chemical analyses performed on tuff samples indicate the presence of a small quantity of iron. The analysis of the prepared catalyst showed that zinc and iron contents are 1.52 mg Zn^{2+}/g and 11.41 mg Fe_{total}/g. FTIR spectra of the zeolitic volcanic tuff sample, indicates the presence of specific zeolite peaks. BET specific surface areas for the zeolitic volcanic tuff sample and the Fe-Zn-ZVT catalyst were determined to be 16.8 and 15.3 m^2/g, respectively. Full characterization of the zeolite volcanic tuff used as catalyst support is presented elsewhere.[2, 31-33]

Catalyst quantity influence

The influence of catalyst quantity upon the advanced oxidation process of phenol was studied at 20 ºC temperature, pH 5.5-6 using 2, 3 and 4 g catalyst and 100 cm^3 phenol solution. We established that phenol concentration in the samples decreases fast in dynamic regime for all the three catalyst quantities, reaching 0.86 g/L (2 g catalyst), 0.59 g/L (3 g catalyst) and 0.41 g/L (4 g catalyst), towards the initial 1.33 g/L concentration, after 3.5 hours, Fig. 1. The minimum concentration of phenol was reached after about 48 hours if 4 g catalyst was used (0.01 g phenol/L), after about 75 hours if 3 g catalyst was used (0.05 g phenol/L), respectively 100 hours if 2 g catalyst was used (0.31 g phenol/L).

From the experimental results we can conclude that phenol oxidation is incomplete, the oxidative degradation process takes place with the formation of secondary oxidation products. A decrease of chemical oxygen demand from the initial value of 7710.4 mg $KMnO_4/L$ to 1611.6 mg $KMnO_4/L$ (2 g catalyst), 1453.6 mg $KMnO_4/L$ (3 g catalyst), and 1295.6 mg $KMnO_4/L$ (4 g catalyst) was observed in the samples collected at the end of the experiment, Fig. 2.

Maximum values for the overall efficiency in the phenol oxidative degradation process for 2, 3 and 4 g catalyst at 20 °C were calculated to be 76.47%, 81.14% and 83.19%, respectively (Fig. 3). Phenol efficiency has greater values compared to the overall efficiency for all four considered catalyst quantities, considerable differences were observed in case of the experiments where we used 3 and 4 g catalyst. The difference between the two efficiencies could indicate the fact that phenol was transformed in various organic intermediates, which were not completely oxidized (mineralized) during the process. Maximum oxidative efficiencies at 20 ºC were obtained for 4 g catalyst after circa 48 hours ($X_{total} = 83.16\%$, $X_{phenol} = 98.82\%$), Fig. 3.
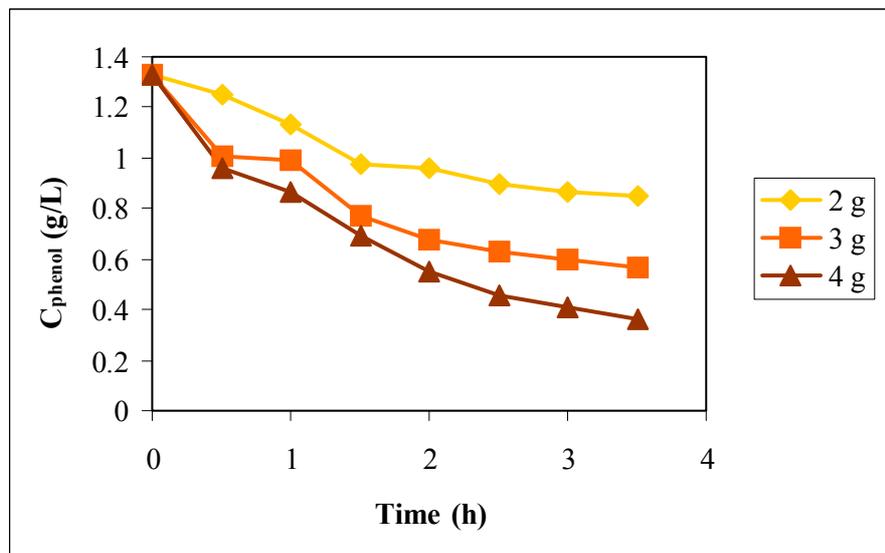

Fig. 1 – Catalyst quantity influence over the variation of phenol concentration in time, dynamic regime, 20°C.
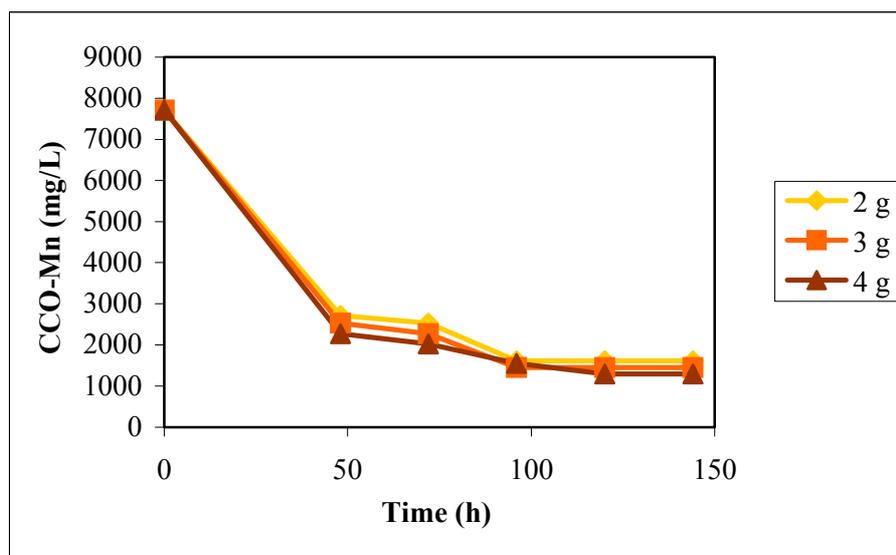

Fig. 2 – Catalyst quantity influence over the chemical oxygen demand evolution
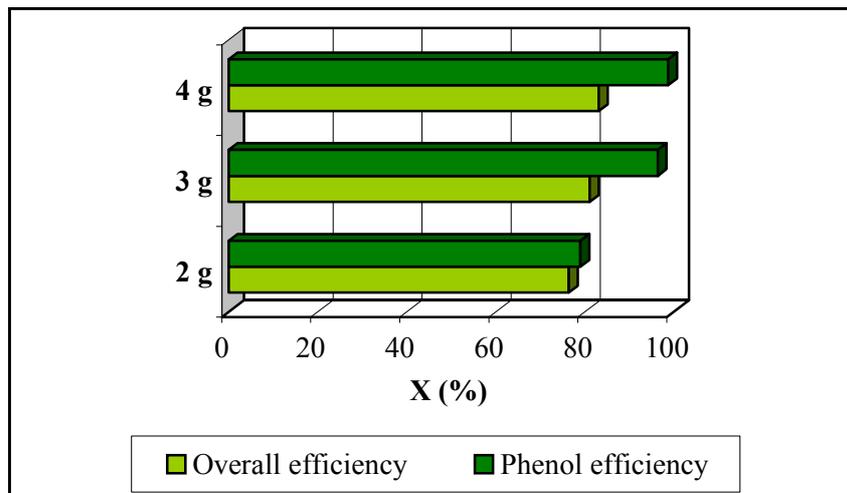for the entire working interval (0.5-3.5 hours in dynamic regime; 3.5-96 hours in static regime), 20°C.

Fig. 3 – Maximum values for phenol efficiency and overall efficiency,
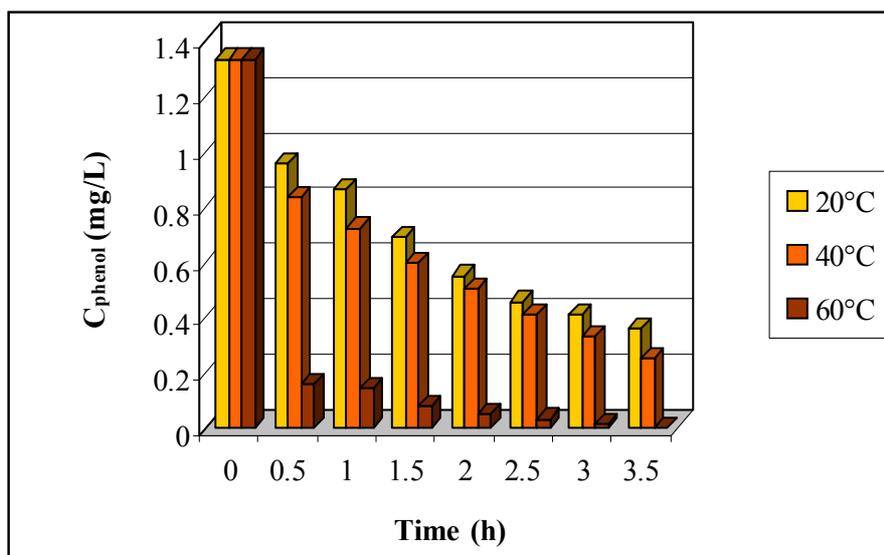20°C temperature, pH 5.5-6, catalyst quantity influence.

Fig. 4 – Temperature influence over the variation
of phenol concentration in time, dynamic regime, 4g catalyst.

Temperature influence

The study of the temperature influence upon phenol oxidation process was conducted using 4g catalyst and 100 cm^3 of phenol solution at temperatures of 20, 40 and 60 ºC. It has been observed that the rate of phenol oxidation from the wastewater increases with the working temperature, phenol concentration in water samples collected after three hours from the beginning of the experiment decreased with 66.41%, 75.30% and 98.82% at 20, 40 and 60 ºC,

respectively, Fig. 4. Maximum phenol efficiency, 100%, was reached at 60 ºC after 3.5 hours. Overall efficiency reached values greater than 80% in the first 30 minutes at 60 ºC, while at 20 and 40 ºC values higher than 80% where reached only after longer time intervals, approximately 24 hours, Fig. 5. In Fig. 6 are presented by comparison maximum values of phenol efficiency and overall efficiency for the three working temperatures. Maximum values were obtained at 60 ºC using 4 g catalyst (X_{total} = 95.90%, X_{phenol} = 100%).
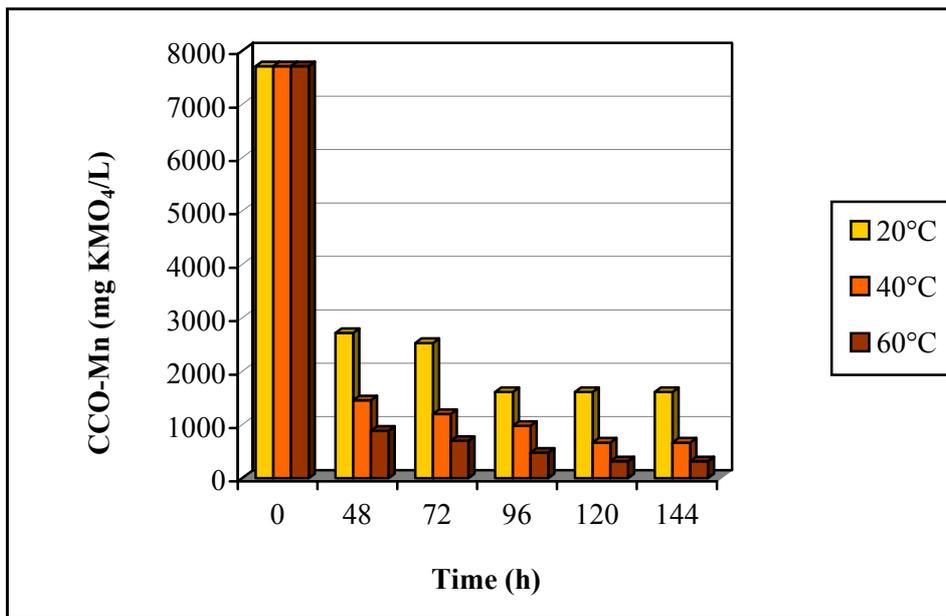
Fig. 5 – Temperature influence over the chemical oxygen demand variation
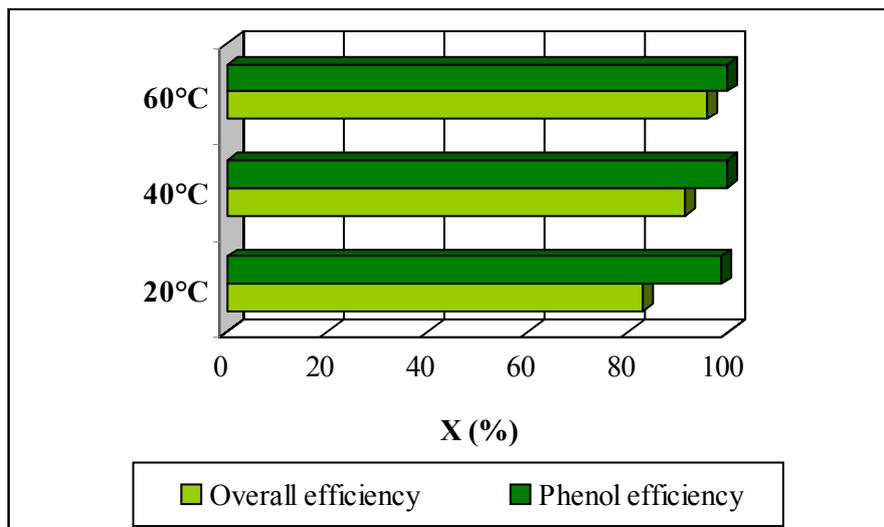for the entire working interval, 4 g catalyst.

Fig. 6 – Comparison of maximum values for phenol efficiency
and overall efficiency for the three temperatures considered, 4 g Fe-Zn-ZVT catalyst.

Assuming a first order kinetic for the phenol removal, we used the obtained results to calculate rate constants and activation energy. The $\log[1/(1-X_{phenol})] = f(time)$ kinetic curves where drawn for the working temperatures, Fig. 7. From the slopes of the kinetic curves, we calculated the rate constants, which are presented in Table 1. Using rate constant values and Arrhenius equation we represented the influence of temperature over the rate constant for phenol oxidation process,

$\ln k = f(1000/T)$, Fig. 8. From the slope of this plot we calculated the activation energy for phenol oxidation process with hydrogen peroxide in the presence of Fe-Zn-TZV catalyst to be $E_A = 19.58$ kJ/mol. According to literature data, lower values for the activation energy are considered to be more characteristic for total oxidation, while the higher ones probably resulted from polymerisation to tars rather than from true oxidation.[21]
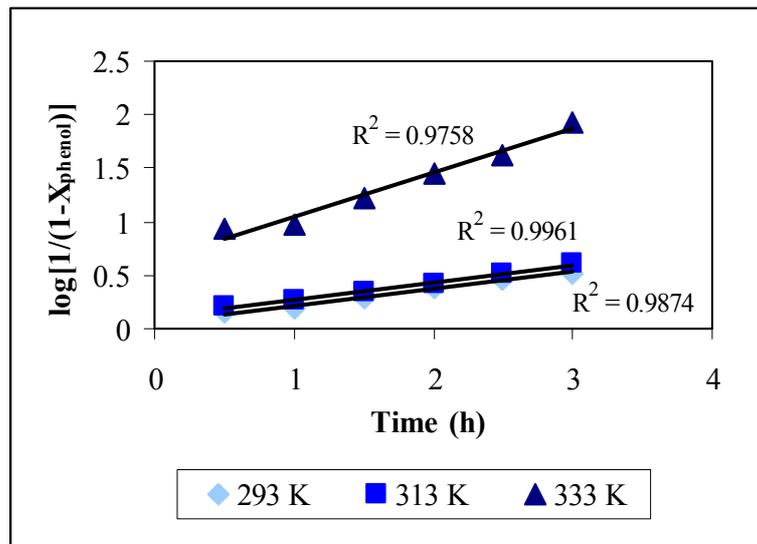
Fig. 7 – Kinetic curves obtained for phenol degradative oxidation
in a heterogeneous Fenton type process, 4 g Fe-Zn-ZVT catalyst.

Table 1

Rate constants for phenol degradative oxidation in a heterogeneous Fenton process, Fe-Zn-ZVT catalyst

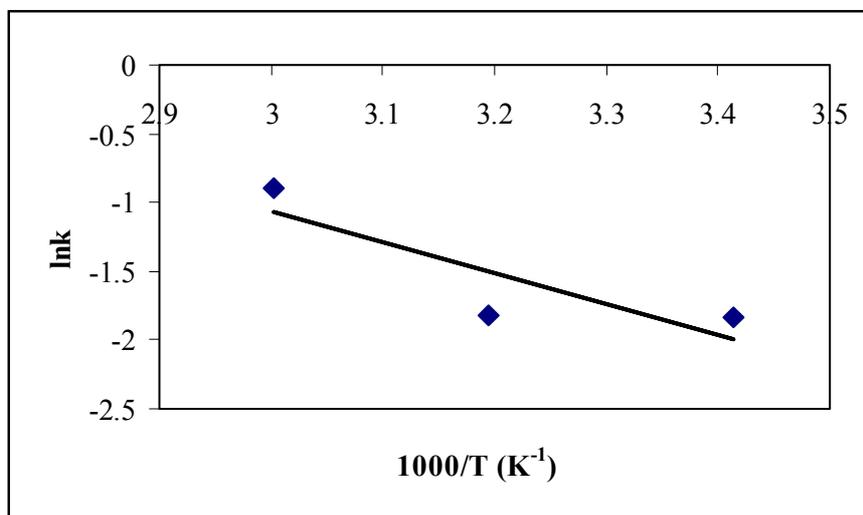| T (K)	k (min^{-1})	1000/T (K^{-1})	lnk
293	0.1591	3.4129	-1.8382
313	0.1616	3.1949	-1.8226
333	0.4104	3.0030	-0.8906

Fig. 8 – Arrhenius plot for phenol advanced degradative oxidation
in a heterogeneous Fenton type process, 4 g Fe-Zn-ZVT catalyst.

EXPERIMENTAL

The ionic exchanger, zeolitic volcanic tuff from Pâglişa deposit, Cluj County, was brought to a granulation of 0.2-0.6 mm by grinding and size separation, then washed with distilled water, dried at 105 ºC and used for treatment of wastewater resulted from electrochemical plating. The exhausted ion exchanger was calcined at 400 ºC for 4 hours, when the Fe-Zn-ZVT catalyst was obtained. Synthetic phenol solutions containing 1.33 g/L were used. Phenol concentration from the water samples was determined volumetrically (bromate-bromine method), while the presence of secondary degradation products of phenol was determined by chemical oxygen demand as CCO-Mn. Taking into account the fact that in this stage of the research we were interested to see how this type of material acts as catalyst for total oxidation of phenol we used KMnO$_4$ chemical oxygen demand, CCO-Mn, method in

order to establish the final concentration of the organics in solution. This determination is currently used in environmental laboratories for wastewaters characterization (STAS 3002/85, SR ISO 6060/96) according to Romanian legislation.[34]

The oxidation reagent, 30% hydrogen peroxide, was added in excess of 100% by comparison to the stoichiometric necessary amount for phenol oxidation. The experiments were conducted in dynamic regime, in a thermostated reactor with mechanical stirring, until the change in phenol concentration of the samples could be neglected (3.5 hours), then in a static regime, until equilibrium. We worked with 2, 3 and 4g catalyst, 100 cm^3 phenol solution at 20, 40 and 60 ºC and pH between 5.5-6 (the pH of the phenol solution). In order to establish process evolution, samples were taken every 30 minutes for 3.5 hours, and then every 24 hours.

The evolution of phenol advanced oxidation process was followed by means of overall efficiency, X_{total} (calculated using chemical oxygen demand values as CCO-Mn at a moment t and the initial CCO-Mn value), and phenol efficiency, X_{phenol}, eq. (1):

$$X = \frac{C_i - C_t}{C_i} \cdot 100 \qquad (1)$$

where,

C_i is the CCO-Mn / phenol initial value, in mg/L

C_t is the CCO-Mn / phenol value at moment t, in mg/L.

Overall efficiency, X_{total}, refers to all organic compounds which are present at a certain point in time in solution, obtained as oxidation intermediates from phenol. Phenol efficiency, X_{phenol}, refers to the phenol transformed in various compounds (intermediates and CO_2), during the oxidation process.

CONCLUSIONS

The Fe-Zn-TZV catalyst shows catalytic activity in the heterogeneous Fenton oxidation process of phenol, high phenol oxidation efficiencies (> 76%) were obtained for all three quantities of catalyst (2, 3 and 4g) and also for the three different working temperatures (20, 40 and 60 ºC). Maximum oxidation efficiencies were obtained for 4 g catalyst at 60 ºC after approximately 48 hours (X_{total} = 95.90%, X_{phenol} = 100%). A small quantity of phenol and secondary oxidation products were not completely oxidized (mineralized), the chemical oxygen demand decreases from the initial value of 7710.4 mg KMnO$_4$/L in the initial phenol solution to 316 mg KMnO$_4$/L in the samples collected at the end of the process, in case of the experiment conducted at 60°C using 4g catalyst.

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