

TREATMENT OF PHENOLIC EFFLUENTS BY PP-CWAO OVER Cu/13X CATALYST

O. WITTINE¹, S. KEAV², K. MADUNA VALKAJ¹, J. BARBIER, JR² and S. ZRNČEVIĆ¹

¹University of Zagreb, Department of Reaction Engineering and Catalysis, Marulićev trg
19, 10000 Zagreb, Croatia

²Laboratory of Catalysis in Organic Chemistry (LACCO) University of Potiers, 40 Avenue
du Recteur Pineau, Franc
e-mail: szrnce@fkit.hr

EXTENDED ABSTRACT

The increasing complexity of wastewater streams as well as the unfavourable public opinion about some conventional waste management techniques, e.g. incineration and adsorption is forcing the development of cost-competitive and environmentally acceptable waste treatments. To overcome the inconveniences of conventional treatment methods various chemical oxidation techniques have emerged in the past last decades. Wet air oxidation (WAO) is an attractive method for the treatment of waste streams which are too diluted to incinerate and too toxic to treat biologically. The use of catalysts makes the process more attractive by achieving high conversion at considerably lower temperature (353 – 473 K) and pressure (1-10 MPa). An alternative process which allows oxidation at the ambient or close-to-the-ambient conditions, thus limiting the investment costs, involves hydrogen peroxide as an oxidant in the so-called catalytic wet peroxide oxidation (CWPO). The main objective of this work is to integrate the benefits CWAO and CWPO in an intensified process, named Peroxide Promoted Catalytic Wet Air Oxidation (PP-CWAO) keeping high conversion of pollutant in wastewater and to give an effluent that could be easier biologically treated. The catalyst choice is the core for an efficient and cost competitive performance. Activity and stability of prepared Cu/13X catalyst was tested in CWAO, CWPO and PP-CWAO of phenol in aqueous medium.

The catalyst was prepared from the protonic forms of commercial 13X zeolite (13X-APG Molsiv™ UOP Italy, SiO₂/Al₂O₃ = 3.2) by ion exchange method and was calcined in air at 1023 K for 5 hours to increase its stability. The catalyst was characterized by BET, XRD and AAS in order to obtain information about their physical and chemical properties. The catalytic tests were carried out in a modified stainless steel Parr reactor in batch operation mode at constant temperature (333 K), different hydrogen peroxide concentration (0.01 - 0.14 mol dm⁻³) and different air pressure (2 - 20 bar). The catalyst weight was 0.1 g dm⁻³ and the initial concentration of phenol 0.01 mol dm⁻³.

It was found that the PP-CWAO process leads to higher pollutant removal conversions than the CWAO and CWPO processes. The results were influenced by the Ph: H₂O₂ : air molar ratio. A synergistic effect was found when H₂O₂ is combined with air which leads to higher mineralization of the phenol.

KEYWORDS: phenol, hydrogen peroxide, catalytic oxidation, promoting effect.

1. INTRODUCTION

There is no doubt that water pollution, especially by a large number of different organic chemical species is continuing and even growing problem that arises from human activities. No unique solution seems possible for destroying all these types due to the heterogeneous composition of real wastes as well as the diversity of the pollutants chemical properties. Some waste treatment methods such as adsorption transfer the toxic component from one phase to another. While this may serve to concentrate the waste in a more readily disposable form, it does not alter the chemistry of pollutant. Other processes use chemical reactions to transform the waste into less toxic by-products or harmless end products such as water and CO₂.

There is a clear need to test and set-up emerging alternative technologies that can deal with highly concentrated and/or toxic non-biodegradable organic water pollutants such as phenol and its derivatives. Phenol can be removed from wastewater by physical, biological and chemical treatment, while the choice of the method depends on source and quantity of the pollutant, quantity of wastewater to be purified, desired reduction level of organic compounds as well as economical factors (Busca *et al.*, 2008). In most cases concentration of phenol in wastewaters is in the range of 1.5 to 4000 mg dm⁻³ which is too concentrated for direct biological treatment, and on the other hand too diluted for some of the physical processes of wastewater treatment (Kremmer, 1988). In such cases liquid phase chemical oxidation methods promise to overcome the existing drawbacks of the above mentioned treatment methods. Several emerging liquid phase oxidation methods can be distinguished in terms of different oxidants, catalysts and operating conditions selected.

The non-catalytic wet oxidation (WO) can be defined as the oxidation of organic and inorganic compounds in an aqueous solution or suspension by air or oxygen (WAO) at high temperature and pressure: 423-573 K and 2-15 MPa. In order to reduce the severity of WAO operating conditions, catalytic wet air processes have been developed (CWAO) (Kolaczkowski *et al.* 1999). The reaction mechanism of CWAO is thought to be similar to the mechanism of WAO, and function of catalyst is essentially that of promoting the formation of free radical. Although CWAO is an efficient technique to eliminate organic compounds such as phenols, reaction is performed at high operating pressure (1-10 MPa) and temperature (353-475 K) makes investment rather costly.

The catalytic wet peroxide oxidation process (CWPO) first adapted from the classical Fenton's reagent allowed high oxidation efficiencies (up to 95%) under mild conditions ($T \leq 323$ K, $p = 0.1-0.3$ MPa), using hydrogen peroxide and a homogeneous Fe²⁺ catalyst. Even though the systems show an effective elimination of organic pollutants, two main drawbacks limit its application: a narrow range of pH, usually around 3.0 and the difficulties to recovering the catalyst that may lead to a secondary pollution.

The use of heterogeneous catalysts could be an alternative method of these problems. Recently, a great number of materials containing iron and copper as precursors supported/intercalated on/in oxides (Cuzzola *et al.*, 2002), pillared clays (Guélou *et al.*, 2003), zeolite (Calleja *et al.*, 2005; Maduna Valkaj *et al.*, 2007, 2008, 2011), carbon (Reye *et al.* 2009) and polymers (Liou *et al.*, 2005; Castro *et al.*, 2009) as active catalysts for Fenton-type reactions have been proposed to remove organic compounds. These catalysts exhibit the advantages of heterogeneously catalyzed process and got relatively higher oxidation efficiency as well as a lower sensitivity to pH compared with homogeneous catalysts at the same reaction conditions. However, most of them could not be used due to its lack of stability in aqueous media. A leaching of the active

elements or/and the support was often observed (Calleja *et al.*, 2005; Maduna Valkaj *et al.*, 2007, 2008, 2011; Zazo *et al.*, 2006).

The objective of this work is to investigate promoted wet air oxidation of phenol through the addition of hydrogen peroxide as a source of free radicals. The results obtained in CWAO of phenol using Cu/13X catalyst have been compared to those found for CWPO process. After analyzing the feature of both catalytic oxidation processes, a CWAO-CWPO treatment named "Hydrogen peroxide promoted catalytic wet air oxidation" (PP-CWAO) was performed and analyzed.

2. EXPERIMENTAL

2.1. Catalyst synthesis and characterization

The catalysts were prepared by ion exchange from commercial 13X zeolite (13X-APG Molsiv™ UOP Italy, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.2$, $w_{\text{N}_2\text{O}} = 20$ wt. %) in form of extrudates (cca. 2x3 mm). Detailed description of preparation procedure is found elsewhere (Maduna Valkaj *et al.*, 2011). Post synthesis thermal treatment consisted in calcinations of prepared Cu/13X samples at temperature of 1273 K for 5h (ramp 5 K min^{-1}) in order to obtain zeolite based materials that exhibit higher stability to the loss of active metal component during the reaction.

Textural characterization of the catalyst samples was performed by means of nitrogen adsorption/desorption isotherms at 77 K using Micromeritics ASAP 2000 instrument. Crystalline structures of prepared catalysts were checked by X-ray diffraction analysis. XRD patterns were obtained with Philips PW 1830 diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation operating at 40 kV and 30 mA. The patterns were recorded over $5^\circ < 2\theta < 40^\circ$ range using a step size of 0.02° . Stability of used catalysts was monitored through the extent of copper leaching. Copper content on fresh and used catalyst and in the reaction mixture was determined by atomic absorption spectrometry using Perkin Elmer AAS 3110.

2.2. Catalytic evaluation

The catalytic tests were carried out in a modified stainless steel Parr reactor in batch operation mode at the constant temperature 333 K, mass of catalyst ($0.1 \text{ g} / 200 \text{ cm}^3$), stirrer speed (600 rpm) and different air pressure (2-20 bar). The initial concentration of phenol was 0.01 mol dm^{-3} while the concentration of hydrogen peroxide was varied from 0.01 mol dm^{-3} to 0.14 mol dm^{-3} . A detailed description of the apparatus and the experimental procedure for CWAO, CWPO and PP-CWAO processes was found elsewhere (Wittine *et al.*, 2010). Phenol conversion was analyzed with HPLC chromatograph equipped with a Waters Spherisorb ODS2C column. Total organic carbon (TOC) was determined with TOC-V CSN Shimadzu analyzer.

3. RESULTS AND DISCUSSION

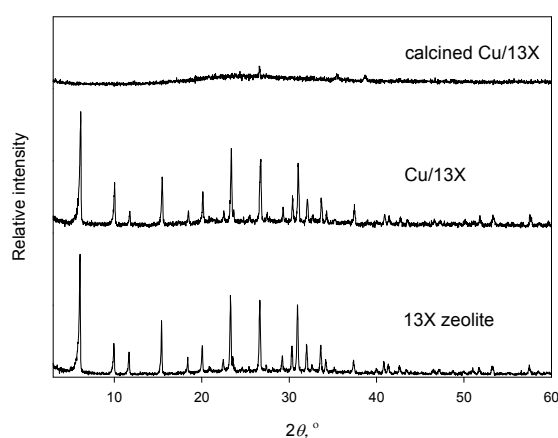
3.1. Catalyst characterization

In the Table 1 physical and chemical properties of prepared catalysts are shown. The incorporation of copper on 13X zeolite did not have a significant effect on the measured surface area and pore volume since the values obtained for 13X and Cu/13X are in good accordance. On the other hand, the thermal treatment at 1023 K caused the decrease of both BET surface area and pore volume. The change of physical properties, including the loss of mass during heating can be attributed to ceramization process that occurs during thermal treatment in the course of which a change in crystalline structure occurs. Copper content was around 7.26 wt. % and wasn't affected by thermal treatment.

Table 1. Physical and chemical properties of prepared catalysts

Sample	Method of preparation	BET surface area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Mass loss after calcination (wt. %)	Cu content (wt. %)
13X	-	498.91	0.33	-	-
Cu/13X	ion exchange	494.67	0.31	-	7.66
Cu/13X-K1023	ion exchange + calcination 1023 K	9.27	0.02	21.6	7.26

In order to check the crystallinity of the samples before and after ion exchange with copper and the possible formation of copper oxides, XRD patterns were recorded. As can be seen in Fig. 2 no significant difference was found between the diffractograms of the parent zeolites and the catalysts after ion exchange.

**Figure 2.** X-ray diffraction patterns of 13X and Cu/13X samples before and after thermal treatment.

Copper bearing zeolite calcined at 1023 K exhibits a change in number, intensity and position of peaks which mean that catalyst undergoes phase transformations – amorphization. The change in dominant crystal phase of samples thermally treated is accompanied by significant drop in measured BET surface area and pore volume as presented in table 1.

2.3. Catalytic evaluation

The time-dependent phenol degradation at various air pressures when reaction was performed on calcined Cu/13X catalyst is shown in Fig. 3. As can be seen CWAO of phenol at condition used in this work is practically negligible because the conversion of phenol depending on air pressure was between 1 to 5 %.

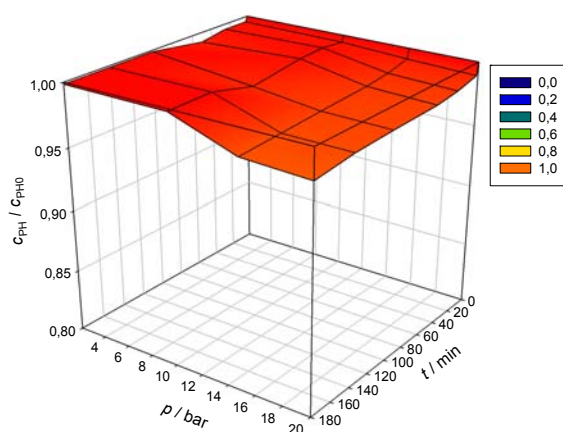


Figure 3. Dependence of phenol degradation rate on air pressure at $T = 333 \text{ K}$, $c_{\text{Ph}} = 0.01 \text{ mol dm}^{-3}$, $m_{\text{cat}} = 0.1 \text{ g}/200 \text{ cm}^3$.

It is well known that conditions for typical CWAO process are the high temperature (353 – 473 K) and pressure (1-10 MPa). In accordance with Henry's law, at conditions used in this work (i.e. 333 K and 15 bar) solubility of oxygen was $3.3 \cdot 10^{-5} \text{ mol O}_2/\text{bar}$, which means that the concentration of oxygen in reaction mixture was only $5.73 \cdot 10^{-3} \text{ mol dm}^{-3}$. This is the reason of very low phenol conversion.

Fig. 4 shows normalized concentrations of the remaining phenol versus time in the experiments performed at different initial hydrogen peroxide concentration on calcined Cu/13X catalyst (CWPO process).

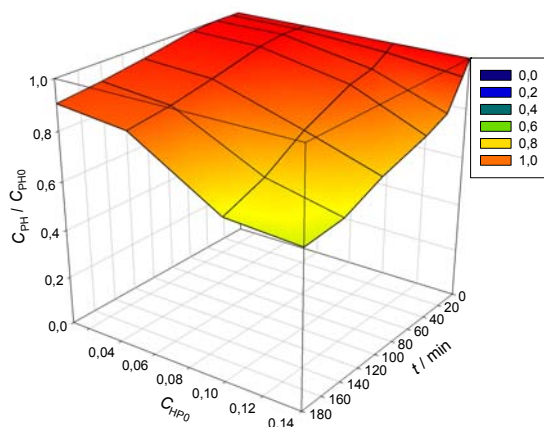


Figure 4. Influence of initial concentration of hydrogen peroxide on phenol oxidation and at 333K , $c_{\text{Ph}} = 0.01 \text{ mol dm}^{-3}$, $m_{\text{cat}} = 0.1 \text{ g}/200 \text{ cm}^3$.

As it can be seen the rate of phenol oxidation increase with increasing concentration of hydrogen peroxide but it is much lower than in the case when powdered catalyst was used ((Maduna Valkaj *et a.*, 2011). In the case of pellets of Cu/13X, there was assumed that the rate of phenol oxidation and peroxide decomposition is limited by diffusion. The external mass transfer was eliminated by high mixer's turning.

Fig. 5 shows phenol concentration profile obtained from PP-CWAO test at different air pressures and different hydrogen peroxide concentrations when reaction was performed at 333 K.

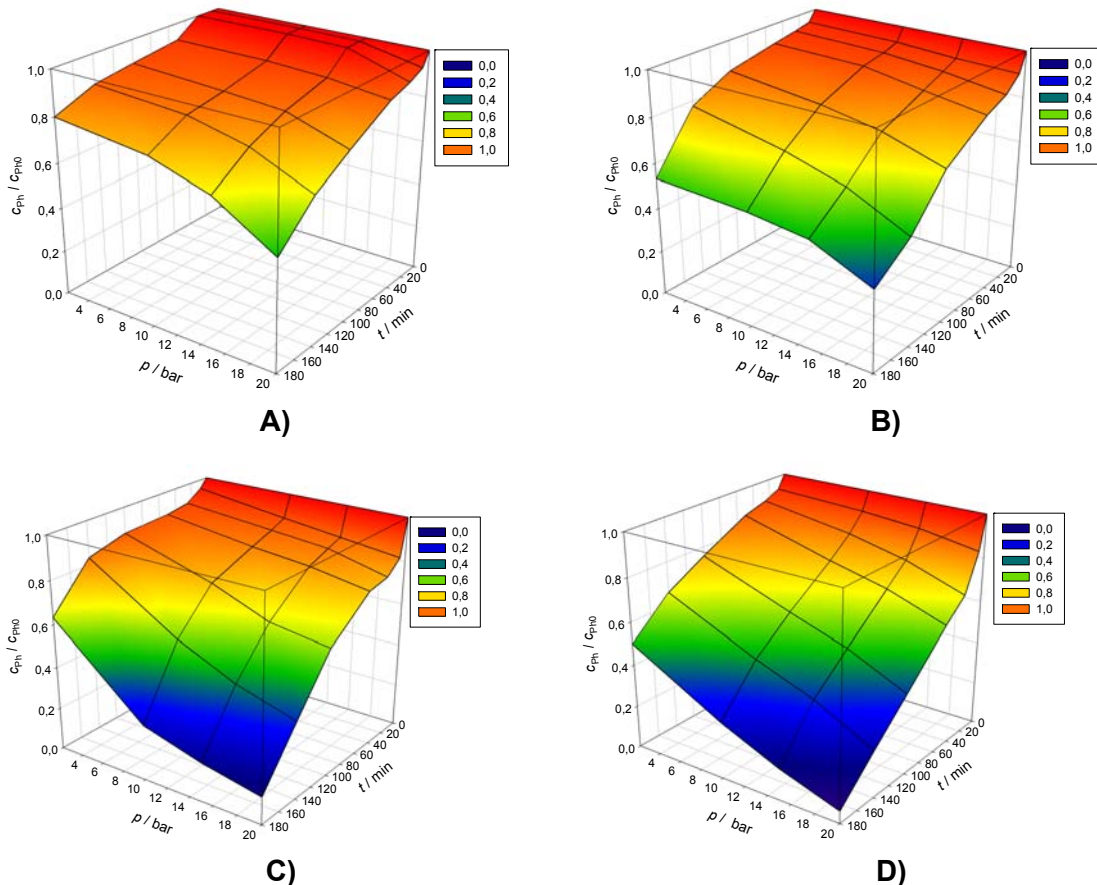


Figure 5. Influence of pressure and hydrogen peroxide concentration (A-0.01 mol dm⁻³; B-0.05 mol dm⁻³; C-0.1 mol dm⁻³; D-0.14 mol dm⁻³) on phenol oxidation at 333 K, $c_{Ph} = 0.01 \text{ mol dm}^{-3}$, $m_{cat} = 0.1 \text{ g/200 cm}^3$.

As can be seen the activity of Cat+Air+H₂O₂ system is much higher than that of non-promoted-CWAO (Fig. 3) and CWPO system (Fig.4). Comparing phenol conversion obtained after 180 min of reaction in CWPO and PP-CWAO test it could be seen that conversion of phenol in PP-CWAO is much higher than in CWPO process. These results prove that even small concentration of oxygen used in this work also plays a role in the initiation of the reaction and that there is synergistic effect of both oxidants.

Table 2 shows final values of TOC conversion after 180 min of phenol degradation using the different processes for the runs shown in Figures 3, 4 and 5.

Table 2. TOC conversion after 180 min of reaction for different processes (*CWAO; **CWPO, PP-CWAO)

TOC conversion					
$P_{air}, \text{ bar}$	$C_{HP}, \text{ mol dm}^{-3}$				
	$\downarrow 0^*$	0,01	0,05	0,1	0,14
$0^{**} \rightarrow$	1.00	10.41	14.64	19.74	23.99
2	1.38	16.85	18.55	22.12	44.79
10	2.93	22.48	21.14	27.26	54.58
15	3.50	23.77	24.17	36.08	73.60
20	4.23	25.41	26.80	44.84	80.99

In Table 2 is noticeable that PP-CWAO process provided the best performance of all used processes, giving TOC conversion about 80 % at highest air pressure and stoichiometric amount of hydrogen peroxide needed to oxidize the phenol. At the same time the TOC conversion in CWAO process at highest air pressure is only 4.23 % and in CWPO process at stoichiometric Ph:H₂O₂ ratio (1:14) is cca. 24%. These results also confirm above conclusion that contribution of oxygen concentration in PP-CWAO process is high although its concentration is small. The TOC removal rate is less than the phenol elimination rate, clearly showing that phenol oxidation take place in multiple steps and results in several by-products rather than only CO₂-only formation.

Leaching determinations of the copper species from the Cu/13X heterogeneous catalyst were carried out in order to ascertain how strongly held the copper is by the 13X zeolite matrix to take into account the possibility of recovery and reuse of the catalyst. Fig. 6 shows the percentage of copper leached-off with respect to the initial amount of Cu in the fresh catalyst for phenol oxidation using different processes.

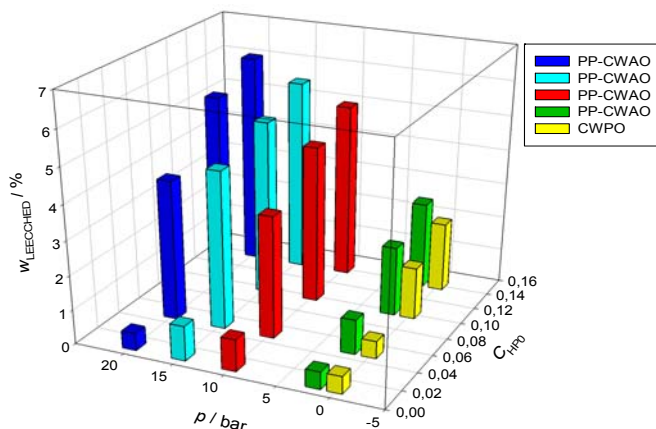


Figure 6. The effect of air pressure and hydrogen peroxide concentration on stability of Cu/13X catalyst at 333 K $c_{Ph} = 0.01 \text{ mol dm}^{-3}$, $m_{cat} = 0.1 \text{ g/200 cm}^3$.

It can be seen that in CWPO process Cu leaching increase with increasing hydrogen peroxide concentration but leaching is much smaller then in the case of non-calcined catalyst which was cca. 58% (Maduna Valkaj *et al.*, 2011). The amount of copper lost from the catalyst in PP-CWAO of phenol is maximal 10 % and increase with increasing air pressure and H₂O₂ concentration. The amount of leached Cu in CWAO process was negligible and therefore is not presented in Fig. 6.

5. CONCLUSIONS

It can be stated from the presented experimental results that the best catalytic oxidation of phenol was performed by PP-CWAO process carried out at highest pressure and H₂O₂ concentration due to the 94 % phenol conversion, 80% TOC conversion and relatively low leaching. The stability measurements showed that thermal treatment stabilizes the Cu/13X catalyst from leaching.

REFERENCES

1. Busca G., Berardinelli S., Resini C. and Arrighi C. (2008) Technologies for the removal of phenol from fluid streams: A short review of recent developments. *J. Hazard. Mater.*, **160**, 265-288.
2. Kremmer F.N., (1988) *The NALCO Water Handbook*, 2nd, ed.; McGraw Hill: New York.

3. Kolaczowski S.T., Babikov A.F., Beltran J., Rivas F.J. and McLurgh, D.B. (1999) Wet air oxidation: a review of process technologies and aspects in reactor design, *Chem.Eng.J.* **73**, 143-160.
4. Cuzzola A., Bernini M. and Salvadori P. (2002) A preliminary study on iron species as heterogeneous catalysts for the degradation of linear alkylbenzene sulphonic acids by H₂O₂ *Appl. Catal. B Environ.* **36**, 231-237.
5. Guélou E., Barrault J., Fournier J. and Tatibouët J.M. (2003) Active iron species in the catalytic wet peroxide oxidation of phenol over pillared clays containing iron *Appl. Catal. B Environ.* **44**, 1-8.
6. Calleja G., Melero J.A., Martinez F. and Molina R. (2005) Activity and resistance of iron-containing amorphous zeolitic and mesostructured materials for wet peroxide oxidation of phenol, *Water Res.* **39**, 1741-1750.
7. Maduna Valkaj K., Katović A. and Zrnčević S. (2007) Investigation of the catalytic wet peroxide oxidation of phenol over different types of Cu/ZSM-5 catalyst, *J. Hazard. Mat.* **144**, 663-667.
8. Maduna Valkaj K., Katović A., Tomašić V. and Zrnčević S. (2008) Characterization and activity of the Cu/ZSM5 catalysts for the oxidation of phenol with hydrogen peroxide, *Chem. Eng. Tech.* **31**, 1-7.
9. Maduna Valkaj K., Katović A. and Zrnčević S. (2011) Catalytic properties of Cu/13X zeolite based catalyst in catalytic wet peroxide oxidation of phenol, *Ind.Eng.Chem.Res.*, in press.
10. Rey A., Faraldos M., Casas, J.A., Zazo J. A., Bahamonde A. and Rodriguez J.J. (2009) Catalytic wet peroxide oxidation of phenol over Fe/AC catalysts: influence of iron precursor and activated carbon surface. *Appl. Catal. B: Environmental* **86**, 69-77.
11. Liou R.M., Chen, S.H., Hung M.Y., Hsu C.S. and Lai J.Y. (2005) Fe (III) supported on resin as effective catalyst for the heterogeneous oxidation of phenol in aqueous solution, *Chemosphere* **59**, 117-125.
12. Castro I.U., Stüber F., Fabregat A., Font J., Fortuny A and Bengoa C. (2009) Supported Cu(II)polymer catalysts for aqueous phenol oxidation, *J. Hazard. Mater.* **165**, 809-815.
13. Benaliouche, F., Boucheffa, Y., Ayrault, P., Mignard, S. and Magnoux, P. (2008) NH₃-TPD and FTIR spectroscopy of pyridine adsorption studies for characterization of Ag- and Cu-exchanged X zeolites, *Micropor. Mesopor. Mat.* **111**, 80-88.
14. Wittine O., Keav, S., Barbier jr* J. and Zrnčević S. (2010) Hydrogen Peroxide Promoted Catalytic Wet Air Oxidation of Phenol, *CHISA 2010*, 28 August - 1 October 2010 Prague, Czech Republic.