STUDIA UBB CHEMIA, LX, 3, 2015 (p. 237-246)
(RECOMMENDED CITATION)

Dedicated to prof. dr. I. C. Popescu
on the occasion of his 70th anniversary

CATALYTIC WET AIR OXIDATION OF PHENOL USING METAL MODIFIED ZEOLITIC VOLCANIC TUFFS

RALUCA PLEŞA CHICINAŞ[a], ZOLTÁN ZSEBE[a], HOREA BEDELEAN[b], MIRCEA DARABANTU[a], ANDRADA MĂICĂNEANU[a,*]

ABSTRACT. Zeolitic volcanic tuff modified with metals (Cu, Ce, Co, Ni, Zn, Mn and Fe) by ionic exchange was tested as catalyst in wet air oxidation process for phenol removal from aqueous solutions. The influence of temperature, air flow, catalyst quantity, phenol concentration, reaction time and catalyst grain size were considered. Also, the reaction was tested in two reactor types: batch and fixed bed. In the case of the batch reactor maximum value for the process efficiency, about 34%, was reached in the following conditions: 60°C, 60 L/h, 4 g catalyst, 1000 mg/L and 6 h reaction time. In case of the fixed bed reactor higher efficiencies were obtained, in the same reaction conditions.

Keywords: *zeolite, phenol, catalytic wet air oxidation, chemical oxygen demand*

INTRODUCTION

Zeolites are highly porous hydrated aluminosilicates with different cavity structures [1]. They are defined as crystalline substances with a structure characterized by a network of chained tetrahedrons [2]. The water from their structure can be easily removed by heating, without modification of the crystalline structure. After dehydration, zeolites become extremely receptive to receive other molecules in the blanks thus created [3]. Also, due to their negatively charged lattice balanced by mono and divalent

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[a] *Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos st., RO-400028, Cluj-Napoca, Romania.*

[b] *Babeş-Bolyai University, Faculty of Biology and Geology, 44 George Bilascu st., RO-400015, Cluj-Napoca, Romania.*

[*] *Corresponding author: andrada@chem.ubbcluj.ro*

exchangeable cations, zeolites exhibit ion exchange property. Therefore, they can be used in a number of areas: waste water purification (urban, mining industry, radioactive, from the manufacture of detergents, the sugar factories), softening of industrial water etc. [3].

Zeolites consist of a wide variety of species, more than 40 natural species being known. The most abundant species is clinoptilolite, member of the heulandite group. Clinoptilolite is component of the zeolitic volcanic tuffs, which is a low cost material, widespread in many places of the world. Clinoptilolite has been shown to have high selectivity for certain pollutants with characteristics as high ion-exchange capacity, high specific surface area, rigid porous structures and low cheap prices. These characteristics make clinoptilolite a promising material for use in wastewater remediation [1, 4].

Catalytic wet air oxidation (CWAO) is an efficient technique designed to eliminate organic compounds from wastewaters when their concentration is small and other techniques are not feasible from the economic point of view [5]. Synthetic zeolite, ZSM-5, modified with metals (Fe, Cu) were previously tested in catalytic wet peroxide oxidation (CWPO) of phenol, reaching, in the case of Fe-ZSM, total organic carbon (TOC) efficiency of 45% (80°C and 7 h) [6,7], while mixt metal catalyst, Cu-Fe-ZSM, was used in oxidative degradation of Rhodamine 6G [8]. Previous tests realized on zeolitic volcanic tuff (Aluniş, Cluj County) modified with iron, Fe-ZVT, showed high phenol removal efficiencies in CWAO under mild conditions (atmospheric pressure, 60°C) [9].

Phenol, commonly chosen as “model” molecule for studies on catalytic oxidation of organic compounds in dilutes aqueous solutions, is considered as one of the most toxic pollutants, harmful to human health and to aquatic organisms [10]. According to the Romanian legislation [11], the maximum concentration of phenol in surface waters must be 1 $\mu g/dm^3$.

Hence, the aim of the present work was to study the possible use of metal (Cu, Ce, Co, Ni, Zn, Mn and Fe) modified zeolitic volcanic tuff (ZVT) as catalyst in the wet air oxidation of organic compounds. The influence of the reaction parameters (temperature, air flow, catalyst quantity, phenol concentration, reaction time), and of catalyst grain size (<0.2, 0.2-0.4 and 0.4-0.6 mm) were considered.

RESULTS AND DISCUSSION

A representative sample of zeolitic volcanic tuff (ZVT) collected from Măcicaş deposit (Cluj County, Transylvania, Romania) was used. Complete characterization of ZVT was included in a previous work [12]. The high quantity of secondary and hydrated material is indicated by the high value of loss of ignition (12%). The samples under investigation showed a remarkable homogeneity in their mineralogical and chemical composition with a small variation in SiO_2 content. Also, the ZVT is low in Na and K content, but high in Ca. The main component of the ZVT is represented by volcanic glass (70-80%) as fragments with angular edges, pyrogenic materials also include K-feldspars, plagioclases, quartz, micas, amphiboles and opaque minerals. ZVT X-ray diffraction patterns obtained indicated the massive presence of clinoptilolite as the main zeolite species. The semi-quantitative estimation from XRD patterns indicated that the zeolite content reached values up to 80% from the crystallized fractions of the tuff. The ZVT contains abundant tabular clinoptilolite crystals that formed by the replacement of the vitric fragments. Finally, FTIR spectra of the ZVT samples indicated the presence of specific zeolite peaks [12].

Phenol CWAO results in batch reactor

The study of the temperature influence upon phenol oxidation process was conducted using 4 g Cu1-Z catalyst, 100 mL of phenol solution (1000 mg/L) and 20 L/h air flow at 40, 50 and 60°C, for 6 h. The results obtained in these conditions are presented in Figure 1. As expected, COD efficiency increased with the increase of temperature.

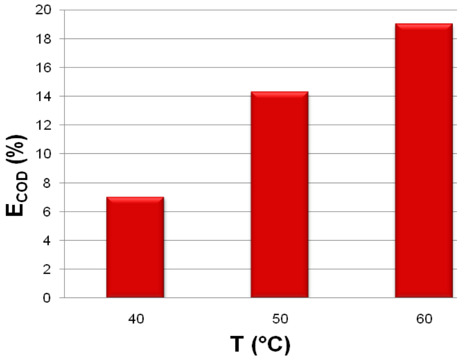


Figure 1. Temperature influence over the COD efficiency variation in the phenol CWAO process, for Cu1-Z catalyst (20 L/h, 4 g, 1000 mg/L, 6 h).

The influence of air flow upon the COD efficiency in the phenol oxidation process was studied at constant temperature 20°C, with the use of 100 mL (1000 mg/L) phenol solution, 4 g Cu1-Z catalyst at 20, 30, 40, 50, and 60 L/h air flow, for 6h. Maximum value of the COD efficiency, 33.73%, was calculated at 60 L/h. With an increase of the air flow, COD efficiency also increased, suggesting that oxygen diffusion process could be the rate determining step in the catalytic oxidation process. Maximum E_{COD} values thus obtained for all air flows are presented in Figure 2.

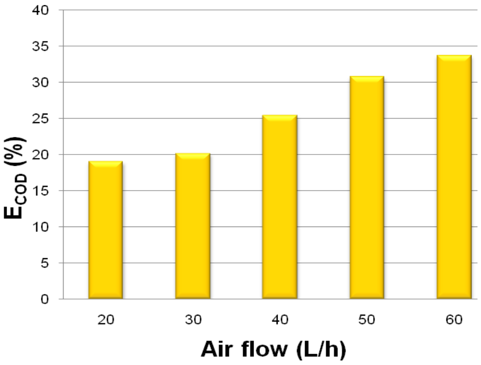


Figure 2. Variation of COD efficiency in the phenol CWAO process, at different air flows and constant temperature (60°C), for Cu1-Z catalyst (4 g, 1000 mg/L, 6 h).

The results obtained when various quantities of catalyst (2-5 g Cu1-Z) were used are presented in Figure 3.

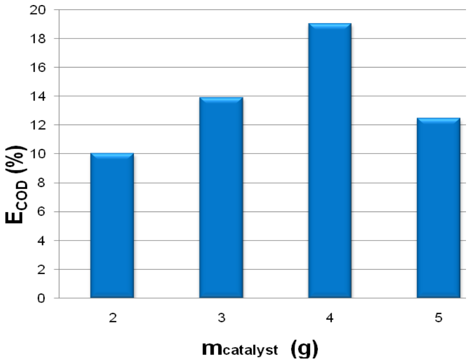


Figure 3. Catalyst quantity influence over the COD efficiency variation in the phenol CWAO process, for Cu1-Z catalyst (20 L/h, 60°C, 1000 mg/L, 6 h).

Thus, an increase in catalyst quantity led to an increase of COD efficiency up to 4 g due to an increase in active centers number on the catalyst surface. Further increase of the catalyst quantity led to a decrease in COD efficiency, probably due to the agglomeration of the catalyst grains, which results in an increase of the diffusion limitation.

Phenol initial concentrations used were 250, 500, 750 and 1000 mg/L. As one can observed from Figure 4, an increase of phenol initial concentration led to an increase of the COD efficiency.

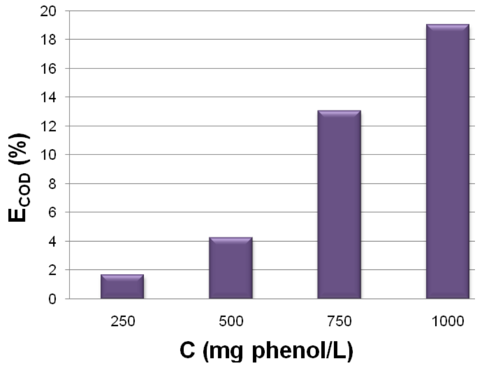


Figure 4. Variation of COD efficiency in the phenol CWAO process, at different phenol concentrations and constant temperature (60°C), for Cu1-Z catalyst (4 g, 20 L/h, 6 h).

The influence of the reaction time on the oxidation process of phenol was also investigated. Reaction conditions were chosen as: 20°C, 60 L/h air flow, 100 mL (1000 mg/L) phenol solution, using 4 g Cu1-Z catalyst and reaction time of 3, 4, 5 and 6 h. As expected, the acquired results, (Figure 5), showed that an increase of the reaction time led to an increase of COD efficiency.

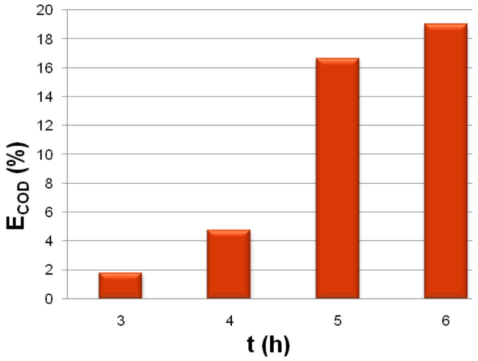


Figure 5. Time influence over the COD efficiency variation in the phenol CWAO process, for Cu1-Z catalyst (20 L/h, 60°C, 4 g, 1000 mg/L).

COD efficiency of the modified ZVT with various metals in the phenol CWAO process, in batch reactor, are presented in Figure 6. COD efficiencies reached for the considered catalysts have values in 19.76-33.72% range, with maximum value obtained for Cu1-Z.

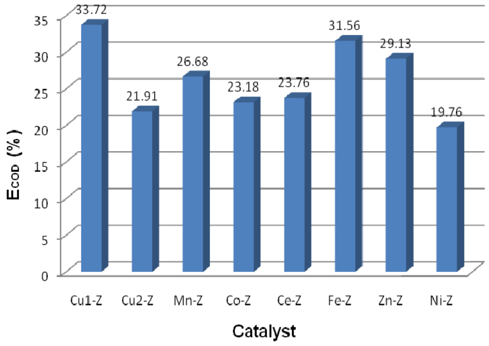


Figure 6. COD efficiency in the phenol CWAO process, for various catalysts (60°C, 60 L/h, 4 g, 1000 mg/L, 6 h).

Phenol CWAO results in fixed bed reactor

The study of the CWAO process using the catalyst in fixed bed showed an improved COD efficiency, an increase of about 50% by comparison with batch conditions, was observed for the same reaction parameters (60°C, 20L/h, 1000 mg/L, 6 h, catalyst:solution = 1:25). When different grain sizes were used, a very small difference was observed, in favor of Cu4-Z (0.4-0.6 mm), Figure 7.

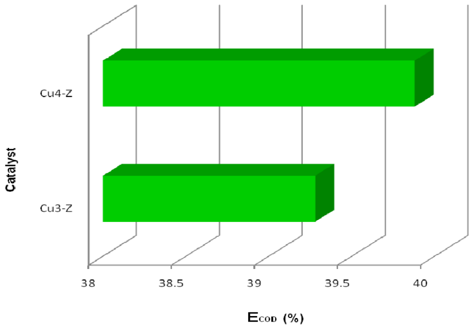


Figure 7. COD efficiency in phenol CWAO, in fixed bed reactor, for Cu3-Z and Cu4-Z catalyst (20 L/h, 60°C, 1 g, 1000 mg/L, 25 mL, 6 h).

CONCLUSIONS

The influences of temperature, air flow, phenol initial concentration catalyst quantity and time of reaction over the process efficiency were studied in the CWAO process using catalysts prepared by ionic exchange on ZVT. An increase of the temperature, air flow, time, catalyst quantity, phenol concentration and time led to an increase of the process efficiency.

In the case of the batch reactor maximum value for the process efficiency, about 34%, was reached in the following conditions: 60°C, 60 L/h, 4 g catalyst, 1000 mg/L and 6 h reaction time. In case of the fixed bed reactor higher efficiencies were obtained, in the same reaction conditions.

Further studies will be performed in order to identify the optimum conditions for fixed bed reactor and oxidation pathways on this type of catalysts.

EXPERIMENTAL SECTION

Materials

In this work, a representative sample of ZVT collected from Măcicaş deposit (Cluj County, Transylvania, Romania) was used.

All reagents (organic and anorganic) were of analytical purity and used as received. Distilled water was used throughout this work.

Catalysts preparation

Ion exchange method used for catalysts preparation used by Măicăneanu *et al.* was applied with some modifications [9].

The stages involved in the preparation of the ZVT were as follows: crushing, grinding, size separation (< 0.2, 0.2-0.4 and 0.4-0.6 mm), washing with distilled water, drying at 105°C for 24 hours, treatment with NaCl 1 M under stirring (330 rpm) for 2 hours with a solid:solution weight ratio of 1:10, washing with distilled water (until chlorine ions were no longer detected with AgCl solution) and finally drying at 105°C for 24 hours. At the end of the above treatment, the ZVT-Na form was obtained. ZVT-Na form was used for further catalyst preparation taking into account that the ionic exchange process efficiency is improved by comparison with the raw ZVT sample [13, 14].

$$Z + NaCl \leftrightarrows Z\text{-}Na + Cl^- \qquad (1)$$

In order to obtain the chosen catalysts, ZVT-Na sample was further on subjected to an ionic exchange process upon treatment with a 0.5 N solution containing the desired metal ions, using a solid:solution weight ratio of 1:10. The ionic exchange reaction that takes place during this process is:

$$n(Z\text{-}Na) + M^{n+} \leftrightarrows (Z)_nM^{n+} + nNa^+ \qquad (2)$$

Depending on the ZVT-Na grain size and in order to avoid particle erosion, the ionic exchange procedure was conducted using magnetic stirring (500 rpm) in case of < 0.2 mm particle size and 3D stirring for 0.2-0.4 and 0.4-

0.6 mm particle size. The ionic exchange process was conducted for 24 h. After stirring, samples were separated from the precursor solution by centrifugation for 5 minutes at 5000 rpm (< 0.2 mm) and settling (0.2-0.4 and 0.4-0.6 mm). After separation, samples were washed several times with distilled water, dried at 105°C (24 h) and calcined 250°C (4 h, with a heating rate of 4°C/min). The obtained catalysts are listed in Table 1.

Table 1. Catalyst name, precursor and ZVT sample.

Catalyst label	Precursor	ZVT sample
Cu1-Z	$CuSO_4 \cdot 5H_2O$	ZVT-Na, <0.2 mm
Cu2-Z	$Cu(NO_3)_2 \cdot 3H_2O$	ZVT-Na, <0.2 mm
Cu3-Z	$CuSO_4 \cdot 5H_2O$	ZVT-Na, 0.2-0.4 mm
Cu4-Z	$CuSO_4 \cdot 5H_2O$	ZVT-Na, 0.4-0.6 mm
Ni-Z	$Ni(NO_3)_2 \cdot 6H_2O$	ZVT-Na, <0.2 mm
Zn-Z	$Zn(NO_3)_2 \cdot 6H_2O$	ZVT-Na, <0.2 mm
Co-Z	$Co(NO_3)_2 \cdot 6H_2O$	ZVT-Na, <0.2 mm
Mn-Z	$Mn(NO_3)_2 \cdot 4H_2O$	ZVT-Na, <0.2 mm
Ce-Z	$Ce(NO_3)_3 \cdot 6H_2O$	ZVT-Na, <0.2 mm
Fe-Z	$Fe(NO_3)_3 \cdot 9H_2O$	ZVT-Na, <0.2 mm

CWAO experiments

In case of the catalysts prepared using ZVT-Na < 0.2 mm, the CWAO process was carried out in a thermostated batch reactor, figure 8a, equipped with a magnetic stirrer (500 rpm) at atmospheric pressure. For a typical run, 100 mL of phenol solution (1000 mg/L) and 4 g catalyst were loaded into the reactor and the oxidation conditions were maintained for 6 h. Reaction temperature and air flow were 60°C and 20 L/h, respectively. For Cu1-Z catalyst, various reaction parameters were considered: temperature (40-60°C), catalyst quantity (2-5 g), phenol concentration (250-1000 mg/L), 20-60 L/h air flow and 3-6 h reaction time.

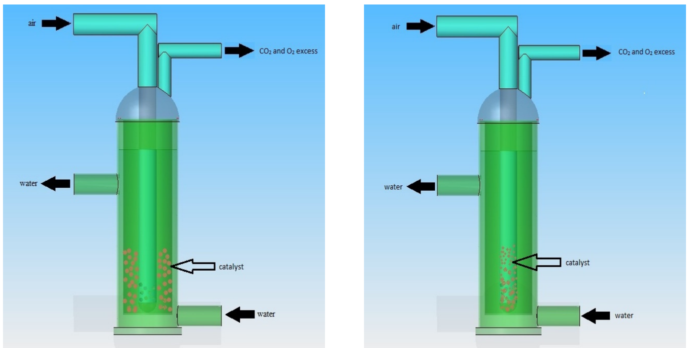
The catalysts prepared using 0.2-0.4 and 0.4-0.6 mm grain size (Table 1) were tested in a thermostated fixed bed reactor, figure 8b, placed on a 3D shaker (50 rpm), at atmospheric pressure. Typical conditions were: 25 mL phenol solution (1000 mg/L), 1 g catalyst, 60°C and 20 L/h air flow. The oxidation conditions were maintained for 6 h.

A blank sample (ZVT-Na), was also tested in the same reaction conditions. All the experiments were realized in triplicate, the presented values are averaged values.

The evolution of phenol oxidation process was followed by means of efficiency, calculated using $KMnO_4$ chemical oxygen demand (COD) values [9] obtained for the initial solution and at the end of CWAO reaction.

$$E_{COD},\% = \frac{COD_i - COD_f}{COD_i} \cdot 100 \qquad (3)$$

where, COD_i is the initial value and COD_f is the final value at the end of CWAO reaction, in mg $KMnO_4$/L.



(a) (b)

Figure 8. Reactors used in CWAO experiments: (a) thermostated batch reactor, (b) thermostated fixed bed reactor.

ACKNOWLEDGMENTS

This paper is a result of a doctoral research made possible by the financial support of the Sectoral Operational Program for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project POSDRU/159/1.5/S/132400 - “Young successful researchers - professional development in an international and interdisciplinary environment”.

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