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Fe/ZVT CATALYSTS FOR PHENOL TOTAL OXIDATION

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ABSTRACT. Zeolitic volcanic tuffs collected from Aluniş (A-ZVT) area (Cluj County, Romania) modified by ionic exchange with iron ions were tested, as catalysts, in the wet air oxidation process in order to remove phenol from synthetic wastewaters. The zeolitic volcanic tuff samples used as support for the oxidation catalysts were characterised by means of optical microscopy, scanning electron microscopy (SEM), X ray diffraction (XRD), chemical analysis and Fourier transformed infrared spectroscopy (FTIR). In order to realize phenol catalytic wet air oxidation we used a synthetic solution containing 1g phenol/dm^3 (100 cm^3), which was contacted with 4 grams of Fe/ZVT catalyst in a batch reactor with magnetic stirring. Air was introduced in the reactor using a glass frit at different flow rates. Effect of reaction conditions, temperature and air flow rate, over the phenol conversion and the overall efficiency of the oxidation process were investigated. With the increase of temperature and air flow rate we observed an increase of the oxidation process efficiency. Activation energy was also calculated.

Keywords: *zeolitic volcanic tuff, clinoptilolite, wastewaters, phenol, catalytic wet air oxidation (CWAO)*

INTRODUCTION

Pollutants removal from wastewaters and water disposal in nature or recycling in the economic circuit is one of the main strategies applied to avoid environmental pollution.

Effluents containing organic pollutants from chemical, petrochemical or pharmaceutical industries can create many problems in choosing an appropriate method to remove them. Many times, concentration of these pollutants is too small to make recovery profitable but too high to be treated by conventional methods. Between pollutants, which create problems due to their difficulty to remove by conventional methods (mechanical and biological treatment) are refractory organic pollutants [1-3].

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Because of their toxicity and the frequency of their presence in industrial wastewaters, phenol and phenolic compounds have gained increased attention in the last two decades. Moreover, phenol is considered to be an intermediate in the oxidation route of higher molecular weight aromatics and so usually is taken as a model compound in research studies [4].

Phenol is produced through both natural and anthropogenic processes. It is naturally occurring in some foods, in human and animal wastes, in decomposing organic material and it is produced endogenously in the gut from the metabolism of aromatic amino acids. Currently, the largest use of phenol is as an intermediate in the production of phenolic resins (which are used in the plywood, adhesive, construction, automotive, appliances industries), synthetic fibbers (nylon) and as epoxy resins precursors. Phenol is toxic to bacteria and fungi, and is used as a slimcide and disinfectant. The greatest potential source for exposure to phenol is in the occupational setting, where phenol is used in manufacturing process. People are also exposed via consumer products, such as medicines and lotions, some foods and tobacco smoke. Phenol was also found in drinking water. Phenol is readily adsorbed by the inhalation, oral and dermal routes. Once adsorbed, phenol is widely distributed in the body [5]. A wide range of adverse effects has been reported following well-documented human exposure to phenol. Gastrointestinal irritation has been reported following ingestion. Local effects following dermal exposure range from painless blanching or erythema to corrosion and deep necrosis. Systemic effects include cardiac dysrhythmias, metabolic acidosis, hyperventilation, respiratory distress, acute renal failure, renal damage, dark urine, methaemoglobinaemia, neurological effects (including convulsions), cardiovascular shock, coma and death. The lowest reported dose resulting in a human death was 4.8 g by ingestion (death occurred within 10 minutes). Symptoms associated with inhalation of phenol included anorexia, weight loss, headache, vertigo, salivation and dark urine.

Adequate human data on the carcinogenicity of phenol are not available [6]. Aquatic life can also be affected if wastewaters containing phenol are discharged in surface waters. At extremely low phenol values, there are two effects apparent in phenol-contaminated waters: toxicity to aquatic life, and the generation of an unpleasant taste in fish and shellfish [7].

Different methods for treating industrial wastewaters containing organic pollutants, including phenol, have been reported. The choice of treatment depends on the concentration, economics, efficiency, easy control and reliability [8].

Several processes for phenol removal have been studied, such as adsorption-floculation [9], adsorption on activated bentonites [10], activated carbons [11], membrane-based solvent extraction [12], separation techniques using composite membranes [13], electrochemical treatment [14-15], sonochemical processes [16], biodegradation [17, 18], photochemical degradation [19,20], wet air oxidation [21], advanced oxidation processes [22-24] and supercritical water oxidation [25].

Chemical oxidation with all its alternatives is widely used for treatment of wastewaters in order to remove organic pollutants, and has as final objective the mineralization of the organic contaminants to CO_2, H_2O and inorganics or, at least at their transformation into harmless products [22].

A reference parameter in case of using chemical oxidation as treatment process is the chemical oxygen demand (COD). Only waters with relatively small COD contents ($< 5 g \cdot L^{-1}$) can be suitably treated by means of advanced oxidation processes (AOP) since higher COD contents would require the consumption of too large amounts of expensive reactants. In those cases, it would be more convenient to use wet oxidation or incineration. Wastewaters with COD higher than $20\ g \cdot L^{-1}$ may undergo with wet oxidation, while those with COD > $200\ g \cdot L^{-1}$ are suitable for incineration [26].

Many of the oxidation processes are catalytic processes and are used for the oxidation of organic pollutants in dilute aqueous solutions, using air or oxygen as oxidation agent. Non-catalytic aqueous-phase oxidations requires long residence times and relatively severe temperatures (200-450°C) and pressures (70-250 atm) [27], therefore the catalytic processes become useful alternative processes. Catalysts used to destroy, organic pollutants including phenol, comprise Ru, Rh, Pt, Ir, Ni, Ag supported on TiO_2, CeO_2, Al_2O_3 [27, 28], metal oxides CuO, CoO, Cr_2O_3, NiO, MnO_2, Fe_2O_3, ZnO, CeO_2 [8, 27, 29, 30] and activated carbon [31]. Synthetic zeolites [32, 33], pillared clays [34, 35], on which iron or copper ions are immobilised, are also used as efficient catalysts for total phenol oxidation.

Zeolites are a group of hydrated aluminosilicates of the alkali or alkaline earth metals (sodium, potassium, magnesium, calcium). They have a particular crystal structure of a tectosilicate-type, characterised by pores with larger size than those of the ions (molecules) that pass through. Mono- and divalent cations such as Na^+, K^+, Ca^{2+} or Mg^{2+} compensate the negative charge that exist in the zeolite crystalline network due to isomorph replacement of silicon (IV) with alumina (III). These counter ions are mobile and can be total or partial exchanged during ionic exchange processes [36-38].

More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are known. Zeolites - both natural and synthetic, may be used as ionic or molecular filters due to this particular micro-porous structure.

Zeolitic volcanic tuff is the main rock-type containing zeolites. These volcanoclastic deposits contain the largest concentrations of zeolites, which result from the transformation of magmatic products such as volcanic glass and primary aluminosilicate minerals [39].

Clinoptilolite is a hydrated aluminosilicate member of the heulandite group and it is one of the more useful natural zeolites. Applications for clinoptilolite-bearing rocks include use as additives to cement, deodorization of ammonia-polluted environments [40], treatment of municipal and industrial wastewaters [41], and preparation of lightweight aggregates [42]. Clinoptilolite is well suited for these applications because of its large amount of pore space and ionic exchange capacity, and because of its high resistance to extreme temperatures and its chemically neutral basic structure.

The best represented zeolite species in altered volcanic tuffs from Romania are clinoptilolite; besides mordenite, natrolite, phillipsite, laumontite, stilbite, and analcime were also identified, but in lower quantities.

The aim of this work was to modify a zeolitic volcanic tuff from Aluniş (Cluj County), by ionic exchange with iron ions in order to test it as catalysts for phenol catalytic wet air oxidation (CWAO). We used two samples from the area mentioned before, labelled A1 and A8. Preliminary tests performed on both samples showed that the results are quite similar. Therefore this paper presents the results obtain for the A8 zeolitic volcanic tuff sample, a fine-pelitic tuff, with a relative homogeneous composition and structure.

EXPERIMENTAL SECTION

Zeolitic volcanic tuff compositional investigations

Natural zeolitized volcanic tuffs were collected from Alunis area (Cluj County). 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 [43]. Most of the tuffs from the studied area have a vitric texture and are extensively altered. The intensive alteration processes – mainly represented by zeolitization, silicification, bentonitization, and calcification – that affected these tuffs, locally led to the formation of economically valuable accumulations.

At Aluniş, the Dej Tuff is present as polysequential sedimentary rhythms characterized by several granulometric types building up a normal succession that point up to a pulsating volcanic activity. The rocks are white in colour and the texture is either compact or vacuolar.

Representative samples from Aluniş (Cluj County) were investigated by using optical microscopy, scanning electron microscopy (SEM), X ray diffraction (XRD), chemical analysis and Fourier transformed infrared spectroscopy (FTIR).

The petrographic observations were made using an optical microscope (Zeiss AxioLab) on thin sections. The study was focussed on the identification of the different mineralogical phases, on their quantification, and on the structural description of the material. The micromorphological features of the zeolitic tuffs were examined in silver-coated, fresh surfaces of the selected samples with a JEOL JSM 5510LV scanning electron microscope (SEM).

The chemical analyses on bulk rocks were performed at ICEI Cluj-Napoca using usual analytical methods for silicate materials [44].

The X-ray diffraction analyses were performed on a Siemens Bruker, with Cu Kα anticathode. The diffractograms were recorded from 10°to 70°2 θ. The analytic conditions were 40 A, 40 kV, step of 2 degrees.

Fourier transformed infrared spectra were realised on a JASCO-615 apparatus on 400-4000 cm^{-1} domain, resolution 2 cm^{-1}.

Catalyst preparation

A zeolitic volcanic tuff sample from Aluniş (Cluj County), A-ZVT, granulation d < 0.2 mm, brought in –Na form was contacted with a solution containing iron ions in order to obtain the desired catalyst – Fe/ZVT.

The stages involved in the zeolitic volcanic tuff preparation are as follows: crushing, grinding, size separation, washing with distilled water, drying at 105°C for 6 hours, treatment with 1M HCl in a stirring reactor with a zeolite : acid solution ratio of 1:10, washing with distilled water to pH = 7 and finally drying at 105°C for 6 hours. At the end of this sequence we obtained the zeolite in -H form (Z-H). Also, during the treatment with HCl, zeolite channels are cleaned and pores opened [45]. To bring the zeolite in -Na form which proved to be more efficient in the ionic exchange process [45-48], the zeolititic volcanic tuff sample was subjected subsequently to an alkaline treatment with a strong Na^+ solution (1M NaCl solution brought to pH = 10 with a 1M NaOH solution) according to equation (1). After the alkaline treatment the zeolitic volcanic tuff sample was washed again with distilled water to pH = 7 and dried for 6 hours at 105°C.

$$\text{Z-H} + \text{NaCl} \rightleftharpoons \text{Z-Na} + \text{HCl} \tag{1}$$

The zeolite prepared as described before was subsequently brought in Z-Fe form using a $FeSO_4 \cdot 7H_2O$ 0.5N solution. The ionic exchange process, equation (2), was realised in a batch reactor in static regime using 35 g zeolitic volcanic tuff in –Na form and 70 ml solution containing iron ions. Solid and solution were kept in contact for 24 hours. After impregnation, iron modified zeolitic volcanic tuff sample was separated by filtration, dried for 6 hours at 105°C and then calcinated at 400°C for 4 hours. We obtained in this way the wet air oxidation catalyst, containing 0.33 mg Fe/g solid, labelled Fe/A-ZVT. The initial and final concentration of iron ions in the solution was determined using $KMnO_4$ volumetric method.

$$2\text{Z-Na} + \text{Fe}^{2+} \rightleftharpoons \text{Z}_2\text{-Fe} + 2\text{Na}^{+} \tag{2}$$

Catalytic wet air oxidation – operating conditions

Phenol total oxidation, catalytic wet air oxidation (CWAO), was carried out in a thermostated stirred batch reactor (magnetic stirrer) at atmospheric pressure, using different air flows (20, 40 and 60 L/h) and temperatures of 20, 40 and 60°C. In the reactor were introduced 4 g of Fe/ZVT catalyst and 100 cm^3 phenol solution, containing approximately 1 g phenol/dm^3. Phenol was measured with $KBrO_3$-KBr in excess of KI in acidic medium (bromate-bromide method). The initial concentration of phenol was determined to be 1.05 g/dm^3. During the experiment phenol determination was carried out every 1 hour. Also, we determined the chemical oxygen demand using CCO-Mn method. The experiment was carried out for 360 minutes.

The evolution of phenol oxidation process was followed by means of phenol conversion (calculated from values of phenol concentration at a moment *t* and initial concentration of phenol, equation 3) and overall oxidation process efficiency calculated using chemical oxygen demand values (as CCO-Mn).

$$X_{phenol} = \frac{C_i - C_t}{C_i} \cdot 100 \tag{3}$$

where,

C_i is the phenol initial concentration, in mg/L
C_t is the phenol final concentration, in mg/L.

RESULTS AND DISCUSSIONS

Petrographic results

The volcanic tuffs from all the beds cropping out in the study area have mostly a vitric and vitric crystal texture and they are zeolitized.

The rocks consist of 70-85% volcanic glass, 15-25% crystals, and lithic fragments in subordinate amounts (2-3%). Petrographically the samples can be defined as rhyodacitic tuffs.

The main component is represented by volcanic glass as fragments with angular edges (glass shards). Pyrogenic crystal fragments include quartz, K-feldspar, acid plagioclases, biotite, hornblende and opaque minerals (figure 1). The quantitative composition is as follows: zeolites 65%, quartz 7%, phyllosilicates 5%, feldspars 8%.

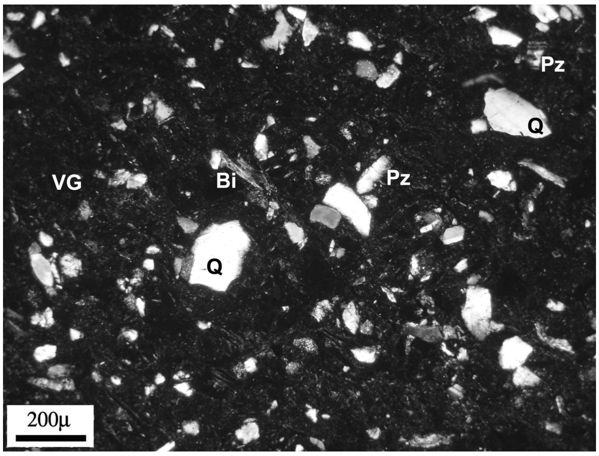

Figure 1. Details of the vitric crystal tuff from Aluniş (Cluj County), N+, optic microscope, polarized light; Q = quartz, Pz = plagioclase, Bi = biotite, VG = volcanic glass.

Significant amounts of volcanic glass in the pyroclastic sequence from Aluniş have been replaced by zeolites (between 60-70%), which consist mainly of clinoptilolite (figure 2).

These alterations are attributed to the diagenesis of the volcanic glass (vitreous matrix and glass shards) into zeolite minerals, opal-CT and probably clay minerals.

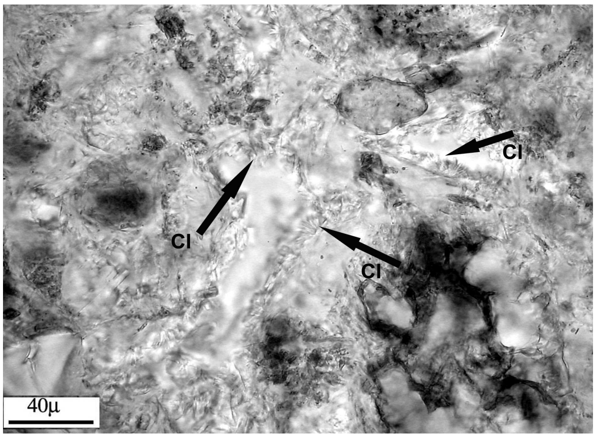

Figure 2. Pseudomorphic replacement of a glass shard by zeolites (clinoptilolite); vitric crystal tuff, Aluniş (Cluj County), 1N; optic microscope, polarized light Cl = clinoptilolite.

Scanning electronic microscopy (SEM) shows that the tuff commonly contains crystals of clinoptilolite of micron- and submicron- size or as larger crystals in the pores or voids (figures 3, 4). The zeolite crystals are about 2-10 microns in size; rarely do they reach 40-50 microns. Subordinately fibrous crystals of mordenite and opal-CT spheres occur (figure 3).

Opal-CT forms thin bladed crystals that aggregate locally into small lepispheres and commonly coexist with clinoptilolite.

Some clusters of a fibrous mineral are present with clinoptilolite and opal-CT. There is no specific evidence in the XRD pattern, probably due to the low quantities, but the fibrous habit suggests that the mineral is most likely mordenite.

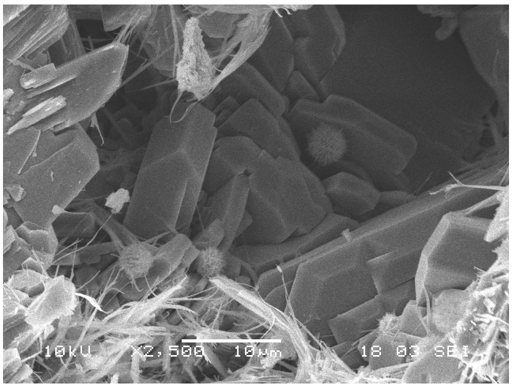

Figure 3. SEM image of a tuff sample from Aluniş (Cluj County). Tabular clinoptilolite crystals with minor amounts of fibrous crystals (most likely mordenite); Opal-CT lepispheres rarely occur (central, down left).

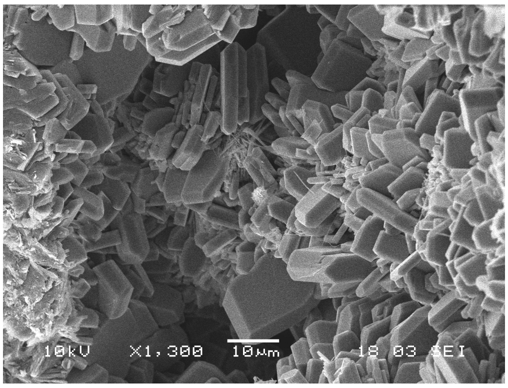

Figure 4. SEM image of a tuff sample from Aluniş (Cluj County). Clinoptilolite euhedral tabular crystals.

The X-ray diffraction patterns obtained on random powders of the whole material show the massive presence of clinoptilolite as the main zeolite species (figure 5). The semi-quantitative estimation from the X-ray diffractograms indicates that the zeolites reach between 60% and 70% from the crystallized fractions of the tuff from Aluniş. According to the microscopic observations, other minerals identified are quartz, feldspar, and clay minerals.

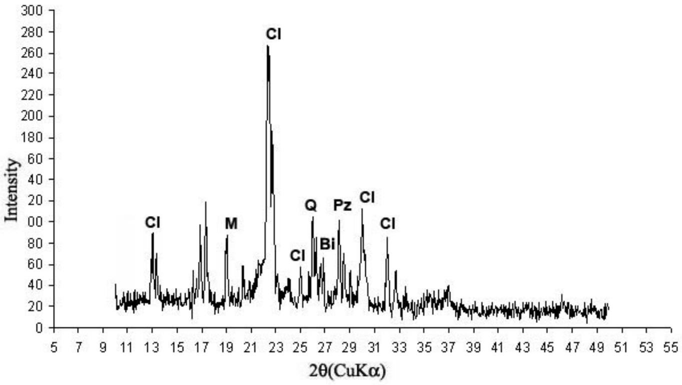

Figure 5. Powder X-ray diffractogram of a volcanic tuff sample from Aluniş (Cluj County); Cl = clinoptilolite, Pz = plagioclase, Q = quartz, Bi = biotite, M = montmorillonite.

The bulk chemical analyses performed on tuff samples are presented in table 1. The chemical composition is very similar with that of samples of volcanic tuffs from other occurrences that belong to the Dej Tuff Complex in Cluj County. The high concentration of secondary and hydrated material (zeolite and clay minerals) is indicated by the high values of L.O.I (loss of ignition), 14.23%. Considering an average 15% L.O.I., attributed mainly to the zeolitic minerals, the amount of clinoptilolite in the samples from Aluniş may be estimated around 60%.

Table 1.

Chemical composition of the zeolitic tuff from Aluniş (Cluj County).

Oxides, [%]	**SiO_2**	**TiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**L.O.I.**
Aluniş	62.06	0.34	14.07	1.61	5.72	0.96	0.35	0.86	14.23

FTIR spectra of the zeolitic volcanic tuff sample, figure 6, indicates the presence of specific zeolite peaks [49, 50]. Were identified peaks corresponding to O-H bond stretching (3446.17 cm^{-1}), angular deformation of H-O-H

(1635.34 cm^{-1}), an intense band of T-O asymmetric stretching (1064.51 cm^{-1}), three weaker bands of T-O external symmetric stretching (794.53, 721.26 and 669.18 cm^{-1}), a medium intense band (605.54 cm^{-1}) corresponding to external vibrations of tetrahedrical units coupled in rings and a peak corresponding to O-T-O angular deformation (464.76 cm^{-1}); T indicates the tetrahedrical position of Si and Al.

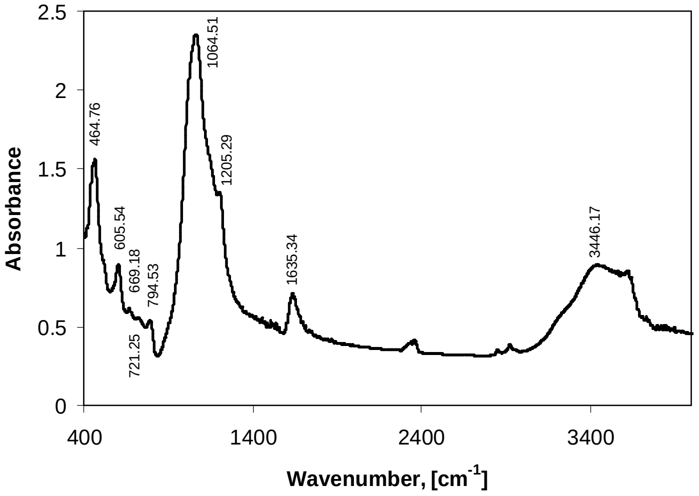

Figure 6. FTIR spectra of a tuff sample from Aluniş (Cluj County).

The volcanic tuffs from Aluniş formed due to the cementation of the explosive products of acidic and subordinately intermediary character, during the explosive stage of the Tertiary volcanism [43].

The process of zeolitization, of a sin- and diagenetic nature (halmyrolysis), took place in a marine, alkaline environment at a pH > 7, and it was a one-way process: primary material (glass, crystalloclasts) → zeolites [51]. It was mainly the volcanic glass that was substituted by zeolites, due to its high instability in the marine environment. The resulted zeolitic species were dependent on temperature, pressure and the variable chemical parameters, such as Si:Al ratio, Ca^{2+}, Na^+ and K^+ ratios and the pressure-dependent H_2O (P_{H2O}) and CO_2 (P_{CO2}) activities [51].

The amount of zeolite is directly correlated to the original amount of volcanic glass. Based on mineralogical (XRD and SEM) analyses, the studied volcanic tuffs from Alunis contain exclusively the zeolite clinoptilolite (heulandite group).

The petrographic and chemical analyses of the vitric tuff from Alunis suggest that zeolite may reach up to 65% of the whole rock. Glass shards have been leached and the resulting molds are partly filled by clinoptilolite crystals (figures 3, 4). This suggests that the processes of zeolitization involved direct dissolution of glass and precipitation of clinoptilolite. The opal-CT represents, probably, the silica that was left over after the formation of zeolite from the glass shards, which being of acid composition, are silica rich (> 60% SiO_2).

Catalytic wet air oxidation results

Phenol catalytic wet air oxidation was conducted at: (a) a constant oxygen flow rate of 20 L/h and different temperatures of 20, 40, 60℃, and (b) a constant temperature of 20℃ and different air flows of 20, 40, 60 L/h.

The influence of operating temperature over the phenol concentration variation in time is presented in figure 7. As expected, phenol concentration decreases significantly with the increasing of the temperature. In case of the operation at 20 and 40℃ phenol concentration drops from the initial 1.05 g/dm^3 to 0.7 and 0.5 g/dm^3, while in case of the higher temperature (60℃) a steep drop down to 0.06 g/dm^3 was recorded. The presented values are calculated after a reaction time of 360 minutes. Maximum values for phenol conversion for the three temperature used in the phenol oxidation process are presented in figure 8. The highest phenol conversion value was 94.03%, obtained at 60℃.

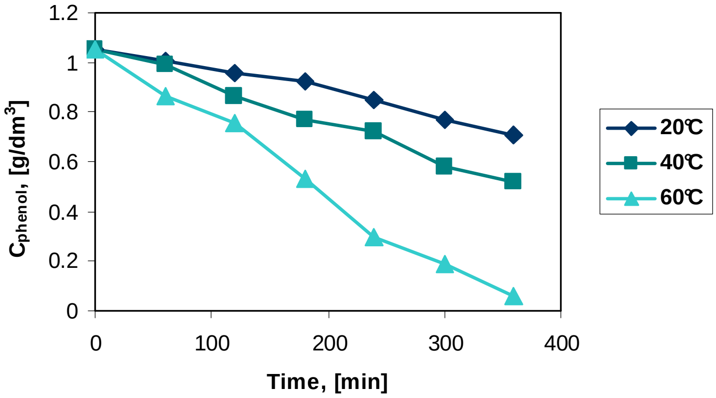

Figure 7. Concentration of phenol as a function of time at different temperatures and constant air flow rate, 20 L/h.

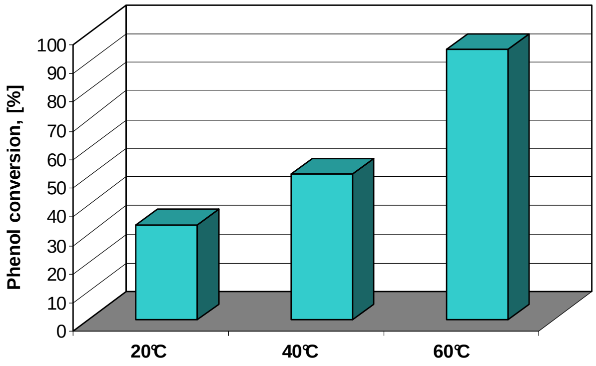

Figure 8. Maximum conversions for phenol CWAO at different temperatures and constant air flow rate, 20L/h.

Variation of phenol concentration in time, when different air flows were used is presented in figure 9. The decrease of phenol concentration is not as steep as in the case of temperature variation. After 360 minutes the final concentration reached for the three air flows are as follows: 0.7, 0.6 and 0.4 g/dm^3, respectively for 20, 40 and 60 L/h faced to the initial

1.05 g/dm^3 concentration. The maximum value obtained for phenol conversion in this case was 56.72%, figure 10, therefore we can conclude that an increase of the flow rate will lead to a small increase in the phenol oxidation process efficiency.

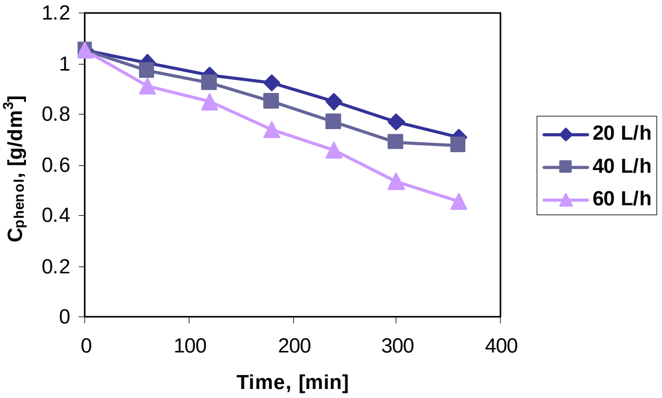

Figure 9. Concentration of phenol as a function of time at different air flow rates and constant temperature, 20℃.

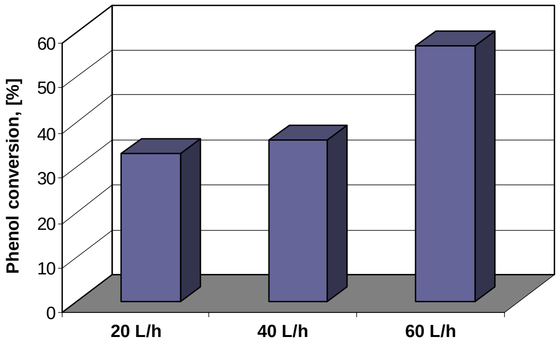

Figure 10. Maximum conversions for phenol CWAO at different air flow rates and constant temperature, 20℃.

During the oxidation process we also determined the chemical oxygen demand as CCO-Mn and we calculated the overall efficiency of the oxidation process using the CCO-Mn values, as mg $KMnO_4/dm^3$, calculated during the process. If we compare phenol conversion values with overall efficiencies, figure 11, we can conclude that phenol oxidation took place with formation of oxidation secondary products. This effect is more important at lower temperatures, 20 and 40℃, where phenol conversion is higher that overall efficiencies. At 60℃, phenol and other oxidation products are removed in proportion of 94, respectively 93%.

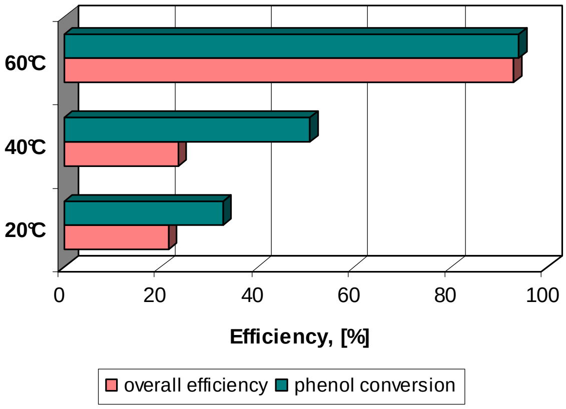

Figure 11. Maximum values for overall efficiency of the oxidation process, after 360 minutes at different temperatures and constant air flow rate, 20L/h.

Assuming a first order kinetic for the phenol removal, we used these results to calculate rate constants and activation energy. From the slopes of the kinetic curves for phenol catalytic wet air oxidation, figure 12, log[1/(1-X_{phenol})]=f(t), we calculated the rate constants for phenol removal. Results are presented in table 2.

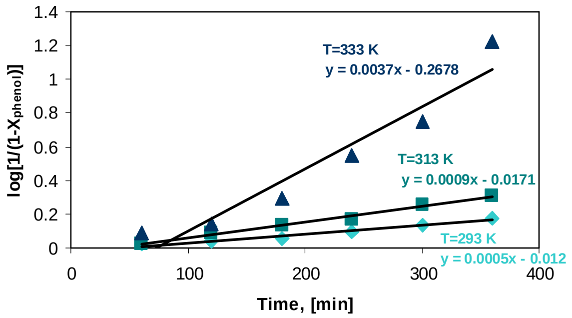

Figure 12. Kinetic curves for phenol catalytic wet air oxidation on Fe/A-ZVT.

Table 2.

Rate constants for phenol removal on a Fe/ZVT catalyst.

T, K	k, min^{-1}	1000/T, K^{-1}	lnk
293	0.5×10^{-3}	3.4129	-7.6009
313	0.9×10^{-3}	3.1949	-7.0131
333	3.7×10^{-3}	3.0030	-5.5994

Using rate constant values and Arrhenius equation we represented lnk=f(1000/T), effect of the temperature on the rate constant for phenol removal (figure 13). From the slope of this plot we calculated the activation energy to be E_A=40.19 kJ/mol.

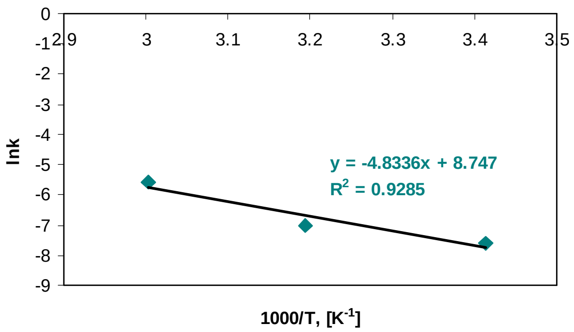

Figure 13. Arrhenius plot for phenol wet air oxidation on Fe/A-ZVT.

For the wet hydrogen peroxide oxidation of phenol [24] on a CuY-5 catalyst, E_A was calculated to be 90.32 kJ/mol, while E_A values from literature varied from 55 to 175 kJ/mol. The lower values are considered to be more characteristic for total oxidation, while the higher ones probably resulted from polymerisation to tars rather than from true oxidation [24]. Using a crude bentonite sample Barrault and co-workers [35] prepared samples of Al-Cu pillared clays using different techniques. They found that the rate of phenol oxidation into carbon dioxide using hydrogen peroxide as oxidation agent, increased after the addition of copper mainly due to a heterogeneous oxidation rather than to a homogeneous Fenton-like oxidation.

CONCLUSIONS

We prepared a catalyst containing iron using a natural zeolitic volcanic tuff from Aluniş (Cluj County), Fe/ZVT. This type of catalyst can be used in catalytic wet air oxidation process for wastewaters treatment at lower temperatures by comparison with non-catalytic processes [27].

The influence of temperature and air flow rate over the phenol conversion and overall process efficiency was studied. An increase of the operating temperature led to an increase in phenol conversion and overall process efficiency. Phenol conversions up to 94.03% were reached. The maximum value for process efficiency was calculated to be 93% using CCO-Mn values. An increase of the air flow rate led to a small increase in the phenol oxidation process efficiency.

Further studies will be performed in order to establish the catalyst reproducibility and lifetime, the influence of the catalyst quantity over the process efficiency. Other catalysts using different type of natural supports and different metal ions will be also prepared and studied.

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