



## Original Article

# Catalytic Ozonation of Phenol Using Copper Coated Pumice and Zeolite as Catalysts

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## ABSTRACT

**Background:** Catalytic ozonation has recently been applied as a new method of contaminant removal from water and wastewater. In this study, copper coated pumice and zeolite were used to catalyze the ozonation of phenol as a target pollutant from aqueous solutions.

**Methods:** The pumice and zeolite stone were modified by  $\text{CuSO}_4$  (1N). Modified pumice and zeolite were characterized by Adsorption/Desorption Porosimetry (BET) and Scanning Electron Microscope analyses. Ozonation and catalytic ozonation experiments were performed in a 1 L semi-batch reactor containing a prepared phenol solution. The efficiency of catalytic ozonation was investigated by different variables: pH value, contact time, initial phenol concentration, catalyst dose, and radical scavenger.

**Results:** Experimental data indicated that as the pH solution increased, phenol removal increased. pH = 8 was measured as the optimum pH. The removal efficiency in single ozonation process (SOP) was 32% and in the catalytic ozonation process (COP) using modified zeolite and pumice was 51% and 63%, respectively. Moreover, these processes showed a great ability to mineralize phenol (up to 30%). Using the radical scavenger determined the indirect oxidation as the main pathway of phenol removal in both catalytic processes.

**Conclusion:** The copper modified zeolite and pumice had good performance to remove phenol through catalytic ozonation method.

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## Introduction

Phenol is an organic pollutant known as some specific characterizations like high toxicity, carcinogenicity, and refractory properties as well<sup>1,2</sup>. Due to various uses, it can be found in agricultural effluents and some industrial wastewaters such as pharmaceutical, petrochemical, and fossil fuel power plants<sup>3</sup>. The danger of the presence of phenol in the environment, has led to use effective methods to remove it from aqueous solutions. Several methods, such as biological processes<sup>3</sup>, wet air oxidation<sup>4</sup>, wet peroxide oxidation<sup>1</sup>, adsorption<sup>5-8</sup> and advanced oxidation processes (AOPs)<sup>9-11</sup> have been used for the removal of phenol from wastewater. Among these methods, AOP is the most extensively used and a promising technique for the removal of biorecalcitrant and resistant to biodegradation<sup>11</sup>. A recent ozone-based AOP is recognized as the COP. According to the literature, in the COP, catalytic materials are added to the SOP as a catalyst for the decomposition of  $\text{O}_3$  and thus generate reactive radicals. These radicals result in more degradation and mineralization of the refractory organic matter and toxic compounds compared to

SOP<sup>12</sup>. Based on the type of catalyst used, the COPs are divided into homogeneous and heterogeneous processes.

The main advantages of a heterogeneous over a homogeneous catalytic ozonation are the ease of catalytic retrieval from the reaction media, simplicity of operation, non-residual catalyst in the reaction media, lower cost and reduced inhibition effect of radical scavengers. In this regard, capability of modified pumice and zeolite as catalysts was evaluated in this work<sup>13,15,16</sup>.

Pumice is a light, highly porous volcanic stone which has been extensively applied in various fields like agriculture and industries<sup>17, 18</sup>. Because of having properties like capital cost advantages and availability it has been investigated lately,<sup>18, 19</sup>. Moreover, Clinoptilolite ( $(\text{Na}, \text{K})_6\text{Si}_3\text{O}_7\text{Al}_2\text{O}_7 \cdot n\text{H}_2\text{O}$ ) is a natural zeolite belonging to Heulandite group and owing to its availability, abundance and cheapness, it has found an important position in environmental works<sup>20, 21</sup>.

The main objective of this work was to develop and investigate an AOP-based process in water with modified pumice. The catalytic effect of modified pumice and zeolite the important parameters in this catalytic process on phenol decomposition (e.g., solution pH, scavenger effect and modified pumice dosage) were investigated.

## Methods

The efficiency of catalytic ozonation by using copper modified zeolite and pumice for phenol removal from aqueous solutions was studied. This aim was done by different variables including initial concentrations of phenol (100, 200, 300, 400 and 500 mg/L), contact times (2.5, 5, 7.5, 10, 15, 20, 25, and 30 min), the modified pumice and zeolite doses (2, 5, 10 and 15 g) as well as acetic acid as the radical scavenger. The experiment was conducted in 2011.

All materials were prepared by Merck (Hohenbrunn, Germany). An ARDA ozone generator (model COG-1A, 5 g/h) was used and the tests were carried out in a 500 mL (DURAN®-Germany) ozonation reactor. Meanwhile ozone dose in all experiments was constant (0.54 mg/min). All methods were based on the "Standard methods for Water and wastewater Examinations" book<sup>22</sup>. At first, a 1000 mg/L stock solution of phenol was prepared. Then the applicable solutions (100, 200, 300, 400 and 500 mg/L) were daily prepared from that. Spectrophotometer UV/VIS (model Hatch-DR 5000) was used to measure the concentrations of phenol in the standard and unknown samples.

### Collection, Preparation and Modification of Catalysts

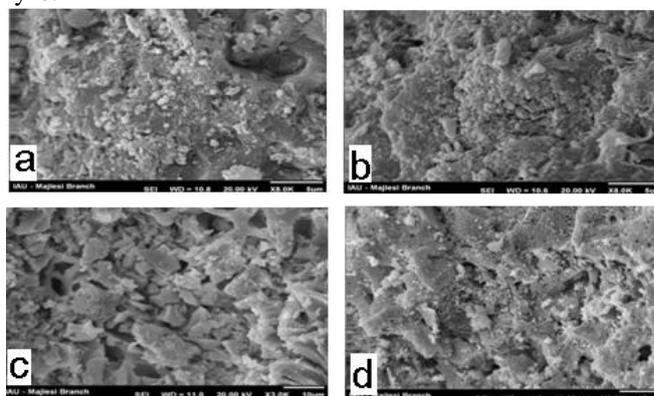
The used zeolite was extracted from zeolite mines located in Semnan Province, Iran, and bought from Afrand Toosca Company. Pumice stone was taken from Tikmeh Dash region of Azarbayejan Province, Iran. The samples were first crushed and sieved into 20-40 mesh (0.4-0.8 mm), coated by  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (1N) solution in according with Kitis et al. and Rezaee et al. methods<sup>18, 23</sup> with a few modifications, rinsed with DDW several times and then dried and pretreated in acid solution (HCl, M=1) for 24 h and were washed out with DDW again and put in distilled water for 24 h. Next, they were rinsed by acetone solution and dried in an oven at 110 °C for 14 h. A stock solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (1N) was prepared and added to the samples. pH of mixture was adjusted at 9.5 by NaOH (3N) solution over mixing and then boiled for half an hour. In the next stage, boiled mixture was laid stable for 72 h and dried at 105 °C for 14 h. Finally, the mixture was washed out with DDW many times, dried at 110 °C for 14 h and kept in a container for next usages.

### Characterization of modified pumice and zeolite

The modified pumice and zeolite samples were characterized by X-ray diffraction (XRD) and X-ray fluorescence (Philips, Model X PER MPD). The operational parameters of Cu k $\alpha$  radiation, a voltage = 40 kV and an A = 40 mA were used. The Brunauer -Emmett-Teller (BET) characterized other surface features of modified catalysts. The catalysts surface morphology was analyzed using a Philips model XL-30 scanning electron microscope (SEM) with energy-dispersive X-ray microanalysis. pH of point of zero charge ( $\text{pH}_{\text{ZPC}}$ ) of each catalysts was determined as one of the main catalyst characteristics according to Dastgheib et al. reports<sup>24</sup>.

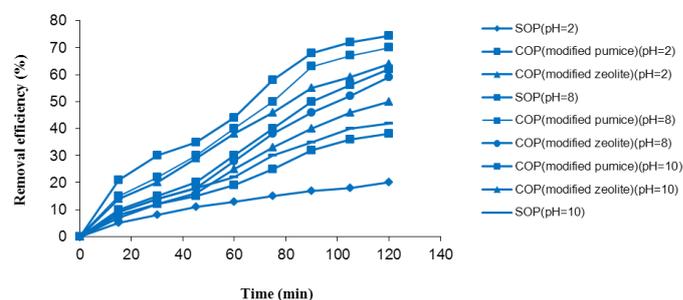
## Results

The results of X-ray Fluorescence (XRF) analysis for zeolite were as follows: silica (66.5%), alumina (11.81%), different metal oxides of potassium, sodium, iron. This analysis for pumice showed the following results (65.21%), alumina (15.46%), LOI (8.07%),  $\text{K}_2\text{O}$  (2.68%),  $\text{Fe}_2\text{O}_3$  (2.61%), CaO (2.51%) and  $\text{Na}_2\text{O}$  (1.81%). The SEM micrographs of both catalysts are shown in Figure 1, which shows that the porosity of both catalysts has increased after modification; this can provide the required surface to stabilize more metal-copper.  $\text{pH}_{\text{ZPC}}$  of raw and modified zeolite were determined 7.2 and 7.5 and for raw and modified pumice it was determined 7.5 and 7.16, respectively. The specific surface area (9, 13.7  $\text{m}^2/\text{g}$  for raw and modified pumice and 13.7, 21  $\text{m}^2/\text{g}$  for raw and modified zeolite) and total pore volume (0.05  $\text{cm}^3/\text{g}$  for both raw and coated pumice and 3.12 and 0.06  $\text{cm}^3/\text{g}$  for raw and modified zeolite) of both catalysts were determined by using BET analyze.



**Figure 1:** SEM images of raw zeolite (a), modified zeolite (b) raw pumice (c) and modified pumice (d)

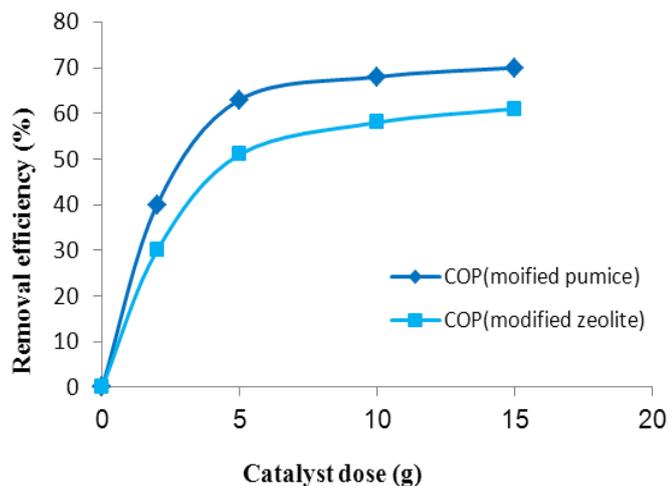
Figure 2 shows the percentage of phenol degradation achieved. Accordingly after 120 min in SOP, along with increasing in pH values, phenol removal increased from 20% to 42%. In the case of ozonation with modified pumice and zeolite, changing the pH values from 2-10, raised the phenol removal from 62% to 74% and 50% to 62%, respectively.



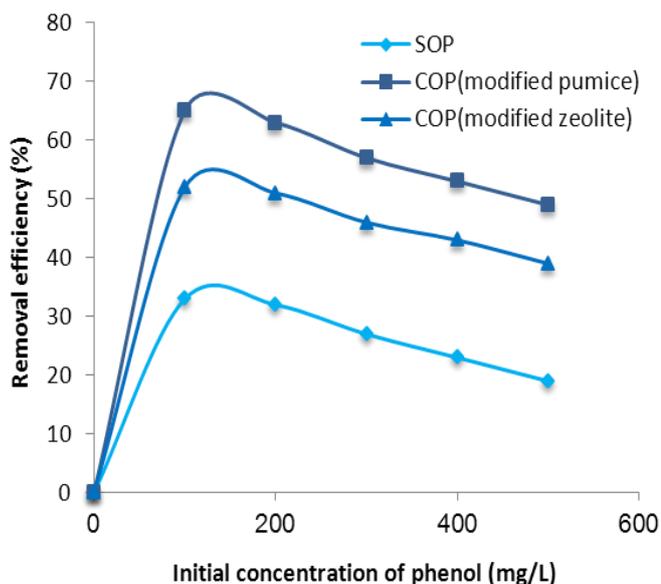
**Figure 2:** Effect of pH and contact time on catalytic ozonation of phenol (initial concentration of phenol=200 mg/L, copper coated pumice 10 g/L, copper coated zeolite 20 g/L)

Phenol removal efficiency increased through rising catalyst dose from 2 to 15 grams in the contact time of 90 min (Figure 3) which led to an increase of 40 to 70% and 30 to 60% respectively once the amount of modified pumice and zeolite increase from 2 to 15 grams. Additionally, the optimum doses of copper-modified zeolite and pumice were determined 10 and 5 grams in a 500 milliliter reaction tank.

As can be seen from Figure 4, in a 90 min contact time along with increasing the initial concentration of phenol from 100 to 500 mg/L, the removal efficiency in SOP and in both COPs using modified pumice and zeolite decreased from 33% to 19%, 65% to 49% and 52% to 39%, respectively. And also the optimum phenol concentration was 100 mg/L.



**Figure 3:** Effect of catalyst dose on catalytic ozonation of phenol (initial concentration of phenol=200 mg/L, pH=8, contact time 90 min)

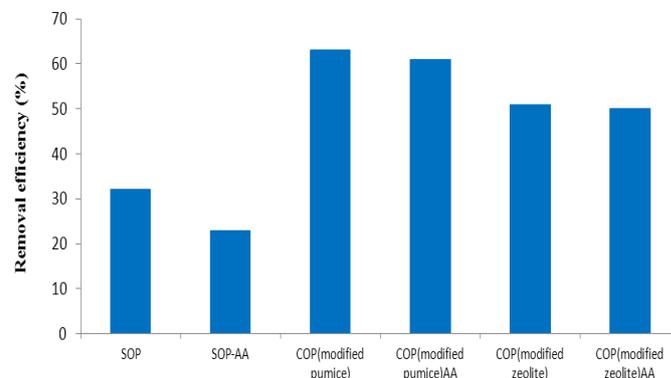


**Figure 4:** Effect of initial concentration of phenol (initial concentration of phenol=200 mg/L, copper coated pumice 10 g/L, copper coated zeolite 20 g/L, pH=8, contact time 90 min)

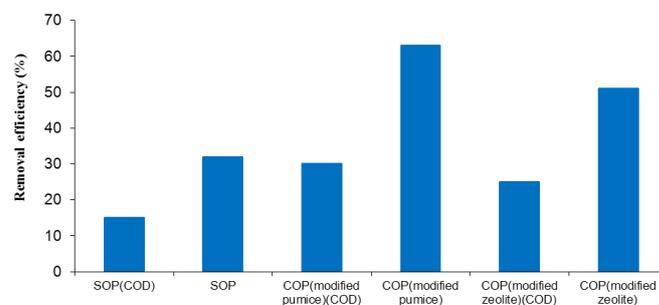
One of the problems in AOPs was the existence of interfering factors during the reaction period. These factors, radicals consuming agents, are things like sulfate carbonate chloride and nitrate occurring in natural waters and decrease the efficiency of AOPs. The removal amount in the absence of acetic acid (AA) (0.1 M) in SOP was 32% and in the COPs using modified zeolite and pumice was 51% and 63% respectively, while the presence of acetic acid changed these figures to 23%, 50% and 61% respectively (Figure 5).

As one of the most vital parameters in wastewater treatment, COD was investigated. Figure 6 indicates the degree of mineralization (COD reduction) of phenol in the developed COP. The initial COD concentration was 501 mg/L. Referring to Figure 6 shows the COD removal efficiency in SOP and

COP with modified zeolite and pumice were 15%, 25% and 30%, respectively. The COP not only efficiently degraded the phenol as a recalcitrant compound, but also attained a high degree of COD reduction and thus mineralization of the degradation intermediates.



**Figure 5:** Effect of radical scavenger (AA) on catalytic ozonation of phenol (acetic acid: 0.1 mol, initial concentration of phenol=200 mg/L, copper coated pumice 10 g/L, copper coated zeolite 20 g/L, pH=8, contact time 90 min)



**Figure 6:** Effect of catalytic ozonation on COD removal (initial concentration of phenol=200 mg/L, copper coated pumice 10 g/L, copper coated zeolite 20 g/L, pH=8, contact time 90 min)

## Discussion

With increasing pH, the removal efficiency increased. It can be because of the phenol structure, the structure of modified pumice and zeolite as well as  $pH_{ZPC}$  of both of them. Since  $pH_{ZPC}$  of the modified zeolite and pumice in this research was 7.16 and 7.5 respectively, the results showed that if the pH is higher than  $pH_{ZPC}$ , the functional groups are deprotonation on pumice surface and their nucleophilic property will increase. In such condition, the deprotonation functional groups on pumice surface boost the ozone reaction rate. In comparison with SOP, COPs had better performance at contact time of 90 min. In all pH values the COPs had better performance compared with SOP. High removal efficiency in COPs under acidic condition is because of the adsorption, and direct and indirect oxidation. If pH is less than 3, hydroxyl radicals are not produced and pH does not have any effect on the degradation of ozone and consequently pollutants. Some researchers reported that such increase in catalytic ozonation process in acidic conditions is related to the production of non-hydroxyl active radicals<sup>3, 25, 26</sup>.

In view of the economic issues arisen from increasing or decreasing the pH, the experiments were continued with pH=8. In catalytic ozonation using volcanic sand on benzothiazole removal, Valdes et al. (2008) showed the increase of pH from 2 to 7 increased removal rate.  $pH_{ZPC}$  of volcanic sand was deter-

mined 6.8. They explained that this removal increase is because of the fact that pH is more than  $pH_{ZPC}$  (at  $pH = 7$ ), ozone had a strong affinity to interact with Lewis acids and metal oxides available on volcanic sand surface<sup>24</sup>. Additionally, in catalytic ozonation of phenol with non-polar bonded alumina, Erol et al. reported that, the phenol removal efficiency was higher in alkaline pHs ( $pH 13$ ) than acidic ones ( $pH 2.5$ ). This is related to the formation of hydroxyl radicals in high pH values<sup>25</sup>.

As indicated in Figure 3, phenol degradation was increased as catalysts dose increased. Such increase in phenol degradation in COPs stems from the increase of ozone decomposition on pumice and zeolite surface leading to the increase of radical density on both catalyst surface and solution bulk<sup>12</sup>. Increasing catalyst dose raises both surface area and active sites which lead to increase of ozone adsorption on the surface. This adsorption increases surface reactions and radical production in catalytic ozonation process.

Valdes et al. have investigated the rate of ozone decomposition using volcanic sand. Results showed that reactions mostly happened under heterogeneous condition (conditions in which reactions take place on catalyst surface not in bulk solution). It is because the catalyst surface is suitable to adsorb ozone and change it into surface radicals<sup>16</sup>. In catalytic ozonation and integrated catalytic ozonation/biological processes in phenol removal from saline wastewaters, Moussavi et al. have tested activated carbon as catalyst in ranging from 2.5 to 20 g/L in degradation of phenol. Results depicted that the phenol removal efficiency increased from 50% to 97% in a 5-min time period and the optimum catalyst dose 20 g/L<sup>3</sup>.

As showed in Figure 5, by increasing the initial concentration of phenol, the number of phenol molecules goes up in reaction environment. On the other hand, because the amount of hydroxyl radicals (which are resulted from ozone decomposition on catalyst surface) is constant, the degradation of highly-concentrated phenol solution is done slowly. This problem can be solved by increasing the ozonation dose either by increasing ozonation rate or by ozonation duration<sup>3</sup>.

Acetic acid as a radical scavenger was used to reveal the main pathway of reaction. The ability of acetic acid to react with hydroxyl radical ( $k_{OH} = 1.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ ) was higher than its ability to react with ozone molecule ( $k_{O_3} = 3 \times 10^{-5} \leq \text{M}^{-1}\text{s}^{-1}$ )<sup>16</sup>. Dissociation of functional groups on pumice surface causes nucleophilic property among them. Such dissociated functional groups act as Lewis acid. Ozone molecule, because of its resonance structure, is dramatically inclined to react with active sites on catalyst surface<sup>15</sup>. When pH is higher than  $pH_{ZPC}$ , ozone reacts with these acidic functional groups acting as Lewis acid and this can accelerate the decomposition rate and radical production<sup>16</sup>. Actually, interfering factors act as Lewis base competing with ozone to react with surface functional groups which act as Lewis acid. Therefore, in view of the concepts of Lewis acid and ozone special structure, ozone molecule acts better than the interfering factors in reacting with active sites, so the catalytic ozonation process is not influenced by such interfering factors<sup>3, 16</sup>.

Investigating the effect of COPs on COD removal, as one of the most important parameters of process efficiency showed that pumice modification increases the catalytic property of pumice so it can mineralize phenol more. Since COD is an index for degradation of organic pollutants (both biodegradable

and non-biodegradable) these results show that catalytic ozonation process, instead of partial degradation, leads to a complete degradation of the major part of the phenol, but commonly-used oxidants like ozone degrade the pollutants partially and in some cases increase COD. Since in industrial wastewaters the discharge effluent standards are based on COD, the combination of this process with biological processes can provide the desired standards of different institutions. Catalytic ozonation using brucite to remove Brilliant red X-3B dye, Yuming Dong et al. showed 89% of the dye and 32.5% of COD removal after a 15 minute reaction time<sup>27</sup>. Accordingly, it can be concluded that the developed modified pumice and zeolite are efficient and active catalysts in the degradation and mineralization of phenol using the catalytic ozonation technique.

## Conclusion

The copper-modified zeolite and pumice had a good performance in removing the phenol over catalytic ozonation method. Indirect oxidation and production of hydroxyl radicals were the principal mechanisms of phenol degradation in the work. Catalytic ozonation is less affected by interfering factors compared with conventional ozonation. Hence, it leads to more complete phenol removal. To sum up, regarding the cheapness and availability of zeolite and pumice minerals and as well as the high catalytic ability of the copper, the copper modified zeolite and pumice can be used as catalyst in water and wastewater treatment applications.

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## Conflict of interest statement

The authors declare that they have no conflicts of interest.

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