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Performance of the catalytic ozonation process with pumice in removal of humic acids from aqueous solutions

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ABSTRACT

Aims: This study was conducted to evaluate the feasibility of applying pumice as a catalyst in the ozonation process for removal of humic acids from aqueous solutions.

Materials and Methods: The molecular structure and chemical composition of pumice were determined using X-ray fluorescence (XRF) and X-ray diffraction (XRD). The catalytic ozonation experiments were performed in a semi-batch reactor and the mass of ozone produced was measured by means of iodometric titration methods. Concentration changes in humic acid were determined using a spectrophotometer, at an absorption wavelength of 254 nm. To evaluate the performance of catalytic ozonation in humic acid removal, effects of different parameters including pH, contact time, pumice dosage, and t-butyl alcohol (TBA) were examined.

Results: The catalytic ozonation results showed that the use of pumice as a catalyst increased the decomposition of humic acid eight times, and the removal efficiency increased as the pH changed from 4 to 12 and catalyst dosage changed from 0.25 to 10 g/l. The catalytic ozonation with considerable efficiency (90%) removed humic acid in less time (10 minutes) than the sole ozonation process (SOP). Moreover; the results indicated that the catalytic ozonation process (COP), compared to conventional SOP, was less affected by the radical scavenger.

Conclusions: Due to the low cost, easy access, and remarkable performance of pumice as a catalyst, it can be used in conventional sole ozonation processes for removing organic pollutants.

Key words: Catalytic ozonation, humic acids, pumice, sole (single) ozonation

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INTRODUCTION

Ozone is considered as an oxidant for removal of natural organic compounds and trihalomethanes precursors, due to its oxidation and high disinfection power.[1,2] Although ozone has numerous advantages as a chemical oxidant, its application in water treatment has been limited, due to some disadvantages, like its low solubility, instability, high cost of production, and partial decomposition of organic compounds.[3,4] The reaction of ozone with organic compounds leads to the formation of aldehydes and carboxylic acids, which do not interact with ozone. This is one of the most important limitations in the application of sole ozonation causing the catalytic ozonation process, particularly heterogeneous catalytic ozonation, to be regarded as a new technology. In recent years, the researchers have paid attention to this method due to its

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easy operation, low cost, increasing ozone solubility, and capability of separating the catalyst from the environment and using it again.[3-5] Catalytic ozonation is a controlled process for changing ozone to free radicals, which is regarded as an advanced oxidation process (AOPs), although there are some differences between them. The studies in this regard used solid substances and adsorbents like zeolite, sand, and activated alumina as catalysts in combination with ozone.[4] Pollutant removal in AOPs is based on the production of hydroxyl-free radicals, with high oxidation power, that converts many organic chemical compounds into mineral materials. These radicals are unstable and highly active and produced through chemical and photochemical reactions.[2] Radical scavenger inhibitors prevent the full-scale application of this process. Catalytic ozonation is a new approach of advanced oxidation processes, which increases the efficiency of the ozonation process, decreases the contact time and the required amount of ozone, and develops different forms of advanced oxidation processes. These processes increase the production of hydroxyl radicals, superoxide, and hydroperoxyl, which have a higher oxidation potential than ozone.[6,7]

Pumice is a light, porous, volcanic stone with a large surface area. It is easily and cheaply found in nature or some kinds of wastes. Pumice is composed of highly micro-vesicular pyroclastic glass with very thin, translucent bubble walls of extrusive igneous rock. Pumice is commonly pale in color, ranging from white, cream, blue, or gray, to greenish brown or black. It is formed when volcanic gases exsolving from viscous magma nucleate bubbles, which cannot readily decouple from the viscous magma, prior to the chilling to glass. It is a common product of explosive eruptions (plinian and ignimbrite-forming) and commonly forms zones in the upper parts of silicic lavas. Pumice has an average porosity of 90%, and initially floats on water. Italy ranks the first in producing 40% of the total pumice stone and Turkey ranks second in manufacturing pumice products. This stone is easy accessible in our country due to its frequency and low cost.[8] It is also applied in the water and wastewater industry, especially as a sludge maintenance bed, as investigations show that the price per cubic meter of pumice used as a bed is about 2% of the price of a commercial bed per cubic meter.[8,9]

Chlorination is the most common method of disinfection in water treatment plants across the world. The studies on the waters disinfected with chlorine, show that the reaction of chlorine with naturally present organic compounds in water forms a group of chlorinated organic compounds known as disinfection byproducts. Most of the byproducts of disinfection with chlorine are trihalomethanes and haloacetic acids. These compounds are toxic, carcinogenic, and mutagenic, of

which trihalomethanes cause cancers of the bladder, kidney, colon, and intestine.[10-12] The presence of organic matters in water sources cause many problems in water treatment, especially in the conventional water treatment method. Natural organic matters are effective in different aspects of water treatment, including, the performance of oxidation processes, coagulation, absorption, and the most important one being the reaction of these matters with chlorine and formation of chlorination byproducts. It has been proved that the formation of chlorination byproducts depends on the concentration of natural organic compounds, which is the main agent in the reaction. Conventional processes for water treatment including clarification, coagulation, flocculation, sedimentation, filtration, and disinfection only remove 30% of the trihalomethanes precursors. The most frequent organic matters naturally present in surface waters are humic and fulvic acids.[12,13] Humic acids constitute 60 to 90% of the natural organic compounds. The presence of organic compounds in purified water causes re-growth of pathogenic microorganisms in the water distribution network, obstructs the membranes and anionic resins, and prevents iron and manganese oxidation.[11] Application of new approaches such as the ozonation process, as an urgent process, is recommended in order to overcome the limitations of the conventional water treatment. In this study, the pumice stone has been used as a catalyst due to its low cost and easy accessibility. Therefore, the effect of parameters of ozonation, contact time, pH, catalyst dosage, and the interfering factors in the production of hydroxyl radicals were analyzed in the catalytic ozonation process.

MATERIALS AND METHODS

This experimental study was conducted in a batch system. The samples were prepared of humic acid produced in Sigma-Aldrich Company, and other materials were provided by Merck Company in Germany. To conduct the experiment, 1000 mg/l of humic acid stock solution was prepared and then used for making water samples with specific humic acid concentration. In this study, in order to conduct water and wastewater experiments, the ultraviolet (UV) absorption at wavelength of 253.7 (254) nm was measured using a UV visible spectrophotometer (model PU8700, Philips) according to the 5910B standard methods.[14] The pumice stone was taken from the mines in Tikmedash, Boostanabad, Iran, and other materials were supplied from Merck and Aldrich companies. At first, the pumice stone were crushed up and granulated using standard sieves with a mesh size of 20 (0.85 mm). The composition of the pumice was determined using X-ray diffraction (XRD) and X-ray fluorescence (XRF) (model X Pert MPD, Holland) [Table 1]. One property of the pumice

Table 1: The results by XRF experiment (%)

SiO$_2$	Al$_2$O$_3$	K$_2$O	Na$_2$O	Fe$_2$O$_3$	CaO	MgO	LOI	Others	Total
73.98	14.1 2	4.2	3.15	1.4	1.14	0.37	1.06	1.2	100

XRF - X-ray fluorescence, LOI - Loss of Ignition

that was specified in this study was the point of zero charge (pH_{PZC}).[15] To determine pH_{PZC}, 0.01 M NaCl solution was used as an electrolyte and 0.1 M HCl and NaOH solutions were used as controlling factors. Electrolytic solution of 30 ml was poured into each 50 ml Erlenmeyer flask (eight flasks) and the pH of the eight flasks was adjusted using HCl and NaOH solutions in the range of 2 – 12. The amount of 0.5 g of pumice was added to the each flask. The flasks were placed on a shaker at 150 rpm and were shaken for 24 hours. Following that, the final pH of the flasks, after filtration, was determined, using a pH meter (Sense Ion 375). The pH_{PZC} was specified after drawing a curve for the pH shifts versus the initial pH.[15] Ozone was generated from pure oxygen by an ARDA ozone generator (Model AEGCOG-5S), and it was fed continuously to the ozonation reactor at 0.5 mg-minute / l. The mass of ozone produced was measured by iodometric titration methods.[14]

In this study, the effects of parameters of ozonation contact time, pH, catalyst dosage, and the interfering factors in production of hydroxyl radicals (0.2 mol t-butyl alcohol) were analyzed in the catalytic ozonation process. The kinetics of humic acid decomposition in SOP and COP was examined in the rest of the study. Each experiment was repeated thrice and the mean results are presented.

RESULTS

Properties of the catalyst
As shown in Figure 1, the main part of the pumice structure consists of quartz with a chemical formula of SiO_2. The structure was determined based on the experiment and the curve's peak using the standard cards. The results by XRF of the sample [Table 1] showed the chemical compositions of pumice as silica, alumina, potassium oxides, sodium, and so on. According to Figure 2, the pH_{ZPC} of modified pumice was determined as 7.7.

The effect of pH on humic acid removal
The results of the effect of pH[4,6,8,10,12] on SOP and COP are shown in Figure 3. As shown in Figure 3, in SOP, over 30 minutes of ozonation humic acid removal efficiency increased from 40 to 60% as the pH increased. In COP, humic acid removal efficiency increased from 70 to 90% as the pH increased. The results showed that in all pH regions, COP performed better than the SOP. Considering the economical problems arising from increasing and decreasing pH, the rest of experiments were done at pH: 8.

The effect of the catalyst dosage on humic acid removal
In order to study the effect of catalyst dosage on humic acid removal, the dosage of the catalyst changed from 0.25 to 10 g. It was shown that as the pumice dosage increased, the humic acid removal percentage increased from 50 to 99% [Figure 4].
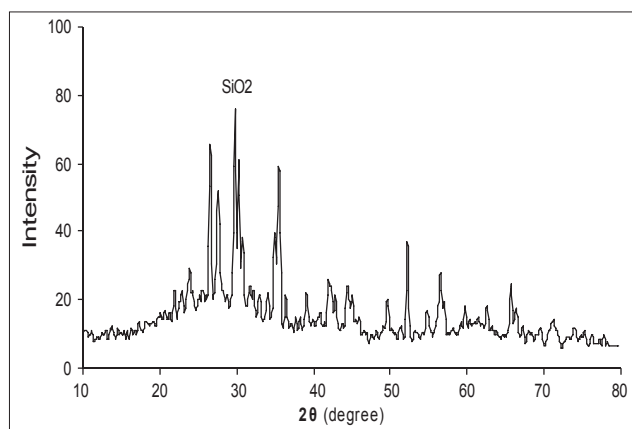

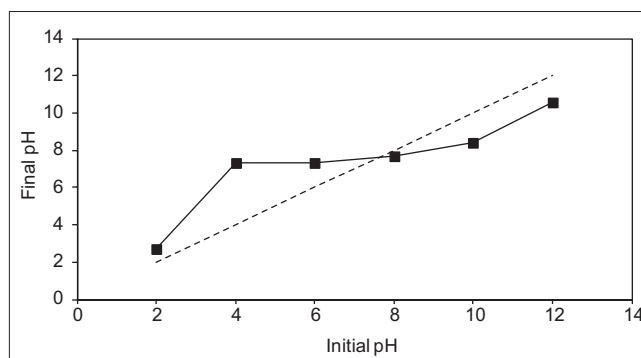**Figure 1:** XRD of the pumice sample used in this study

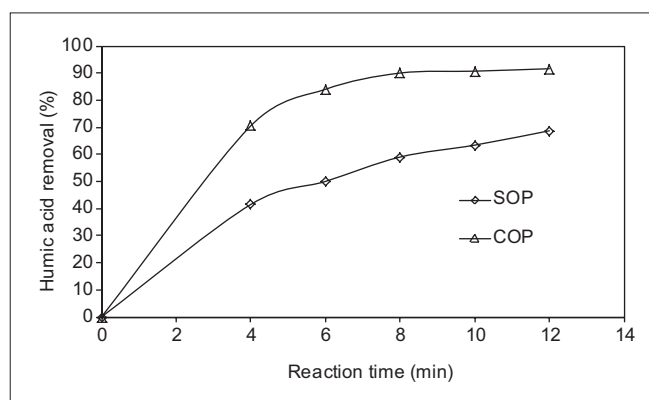**Figure 2:** Determining pH_{ZPC} of pumice

Figure 3: The effect of pH on humic acid removal in the sole ozonation and catalytic ozonation processes (initial concentration of humic acid = 30 mg / L, input ozone dosage = 0.45 mg / minute, catalyst dosage = 2 g, and contact time = 30 minutes)

The effect of t-butyl alcohol on humic acid removal
In order to study the effect of t-butyl alcohol on humic acid removal, 0.2 mole of alcohol was added to the humic acid samples. The obtained compound may react with the ozone and hydroxyl radical with a velocity of 3×10^{-5} mol / second and 8×10^8 mol / second, respectively.[16] The results of the effect of t-butyl alcohol on the sole ozonation and catalytic
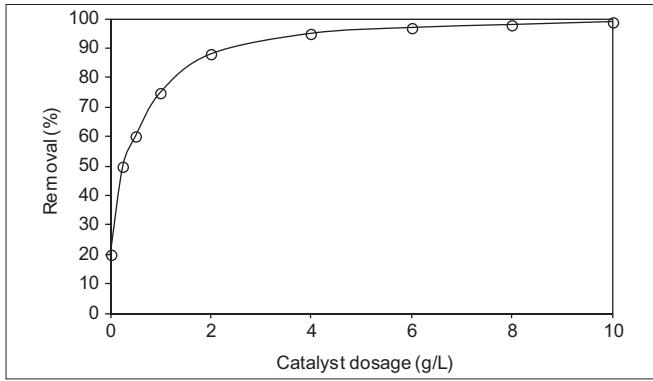
Figure 4: The effect of catalyst dosage on humic acid removal in the catalytic ozonation process (concentration of humic acid = 30 mg / l, pH = 8, input ozone concentration = 0.45 mg / minute, and contact time = 30 minutes)
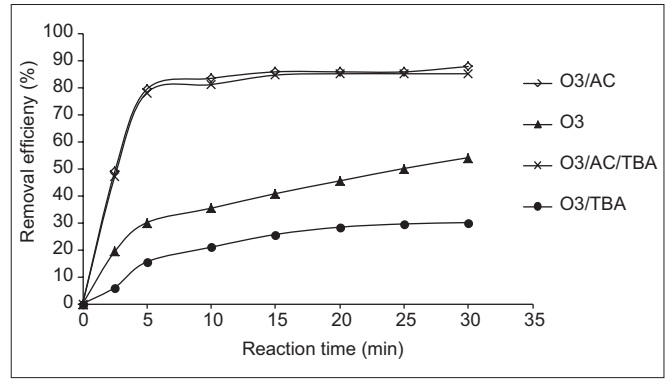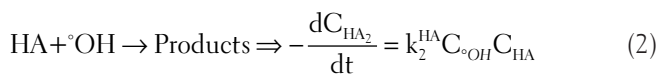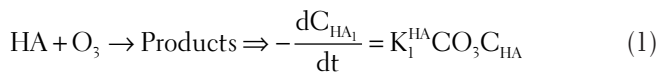

Figure 5: The effect of t-butyl alcohol on humic acid removal in the sole ozonation and catalytic ozonation processes (concentration of humic acid = 30 mg / l, pH = 8, and catalyst dosage = 2 g in catalytic ozonation with input ozone dosage of 0.45 mg / minute)

ozonation processes are shown in Figure 5. According to these results, the humic acid removal efficiency in catalytic ozonation decreased only by 5%, while in sole ozonation, it decreased by 50%.
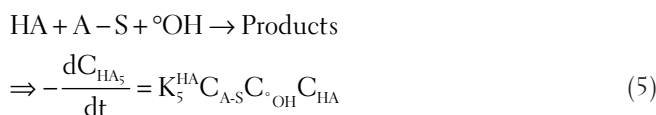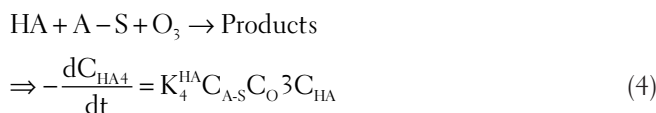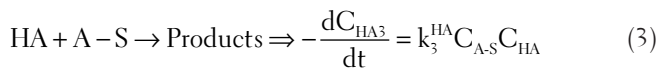
Kinetics of humic acid decomposition

In this study, the humic acid decomposition rate in sole ozonation and the catalytic ozonation processes was determined. The results showed that decomposition of humic acid in sole ozonation and the catalytic ozonation processes followed the first-order reactions. Decomposition of humic acid in the presence of pumice is the result of homogenous and heterogeneous reactions. Liquid humic acid is decomposed in direct reaction with the ozone molecule and in indirect reaction with the produced radicals.[16] These two reactions take place in liquid volume on the pumice surface and can be shown with following simple equations.

Homogeneous reactions:

$$HA + O_3 \rightarrow Products \Rightarrow -\frac{dC_{HA_1}}{dt} = K_1^{HA}CO_3C_{HA} \qquad (1)$$

$$HA + ^{\circ}OH \rightarrow Products \Rightarrow -\frac{dC_{HA_2}}{dt} = k_2^{HA}C_{\circ OH}C_{HA} \qquad (2)$$

Heterogeneous reactions:

$$HA + A - S \rightarrow Products \Rightarrow -\frac{dC_{HA3}}{dt} = k_3^{HA}C_{A\text{-}S}C_{HA} \qquad (3)$$

$$HA + A - S + O_3 \rightarrow Products$$
$$\Rightarrow -\frac{dC_{HA4}}{dt} = K_4^{HA}C_{A\text{-}S}C_O3C_{HA} \qquad (4)$$

$$HA + A - S + ^{\circ}OH \rightarrow Products$$
$$\Rightarrow -\frac{dC_{HA_5}}{dt} = K_5^{HA}C_{A\text{-}S}C_{\circ OH}C_{HA} \qquad (5)$$

A – S indicates the active sites, functional groups, and metal active sites on the pumice surface. Therefore, the total decomposition rate of humic acid can be written as follows:

$$-\frac{d[C_{HA_{overall}}]}{dt} = r_{homo}^{HA} + r_{hetero}^{HA} = (k_{homo}^{HA} + k_{hetero}^{HA}C_{A\text{-}S})C_{HA} \qquad (6)$$

Where, k_{homo}^{HA} is the reaction rate constant in the liquid volume or homogeneous conditions, which are obtained by:

$$k_{homo}^{HA} = k_1^{HA}C_{O3} + K_2^{HA}C_{\circ OH} \qquad (7)$$

Moreover, k_{hetero}^{HA} is the reaction rate constant on the catalyst surface or a heterogeneous condition which is obtained by:

$$k_{hetero}^{HA} = K_3^{HA}C_{O3} + K_4^{HA} + K_5^{HA}C_{\circ OH} \qquad (8)$$

Assuming $C_{HA} = C_{HA0}$, equation 8 can be written as follows:

$$Ln\frac{C_{HA}}{C_{HA0}} = -(k_{homo}^{HA} + k_{hetero}^{HA}C_{A\text{-}S})t = -K_{Overall}^{HA}t , \qquad (9)$$

In this equation k is obtained by:

$$k_{overall}^{HA} = k_{homo}^{HA} + k_{hetero}^{HA}C_{A\text{-}S} , \qquad (10)$$

$\frac{d[C_{HA_{overall}}]}{dt}$ indicates the changes in humic acid concentration over time, C_{HA} is the humic acid concentration (mg / l), and $K_{Overall}^{HA}$ is the first-order reaction rate constant over time. In the sole ozonation process, humic acid is decomposed through two reactions (direct and indirect reactions).[17] These direct and indirect reactions are shown by the following reactions:

$$-\frac{d[HA]}{dt} = K_O[HA][O_3] + K_{OH}[HA][^{\circ}OH] \qquad (11)$$

$$-\frac{d[HA]}{dt} = (K_O + K_{OH}[OH])[HA] \qquad (12)$$

$$-\frac{d[HA]}{dt} = K_{Overall}[HA] \qquad (13)$$

$K_{Overall}^{HA}$ is determined by drawing the curve for $Ln(\frac{C}{C_0})$ versus time. The HA degradation rates are presented in Table 2. The results show that as the pH changes from 4 to 12, $K_{Overall}^{HA}$ increases from 0.25 to 0.85 per minute in the catalytic ozonation process, and from 0.05 to 0.11 in the sole ozonation process. The ratio of K_{COP} / K_{SOP}, under acidic conditions, is 5. Under alkaline conditions, the K_{COP} / K_{SOP} ratio increases to 8. Therefore, this result shows that the addition of pumice to SOP increases the decomposition rate of humic acid five times in the acid region and to eight times in the alkaline region.

DISCUSSION

The efficiency of COP depends on various parameters. The important parameters affecting the heterogeneous ozonation process are the kind of surface properties of the catalyst and pH of the solution. Surface properties and chemical compositions are among the most significant features of a catalyst that are involved in the conversion of ozone into active radicals.[3,4,18] According to the XRF [Table 1] results, the pumice chemical compound consists of metal oxides. These metals as active sites are involved in ozone decomposition and formation of functional groups on the pumice surface. When placing pumice in water, these metals are covered by decomposed water molecules and form metallic functional groups on the pumice surface.[17,19] The presence of these functional groups causes the pumice to act as an electron donor and acceptor according to the pH, and as a Lewis acid or base in the conversion of ozone into

active radicals.[3,4] At a pH higher than pH_{PZC}, the surface functional groups are deprotonated (equation 14) and at a pH lower than pH_{PZC}, these surface functional groups are protonated (equation 15).

$$S-OH + OH^- \leftrightarrow S-O^- + H_2O \qquad (14)$$

$$S-OH + H^+ \leftrightarrow SOH_2^+ \qquad (15)$$

Protonation and deprotonation of the surface functional groups cause the pumice to act as a Lewis acid or base and this is one of the most important and phenomenal catalytic functions of pumice.[17,20] Based on the results of this study and other studies, it can be concluded that the chemical properties of the heterogeneous catalytic ozonation process must be studied specifically due to their importance. pH is one of the significant factors affecting the catalytic ozonation process, by influencing the structure of humic acid, catalyst surface charge, and formation and performance of the functional groups.[19] As shown by the results [Figure 3], the humic acid removal rate increases as the pH increases. The increase in humic acid efficiency along with the pH increasing may arise from the acceleration of the ozone mass transfer and ozone decomposition rate, with a pH that results in the formation of highly active radicals specially the hydroxyl radical. The more the pH increases, the more is the amount of radicals that increase.[2,3] Therefore, the removal efficiency will increase. The removal efficiency of humic acid in all regions of pH in the catalytic ozonation process has been more than that of the sole ozonation process. Humic acid removal increases as the pH increases. In the acidic regions, the three processes of adsorption, direct, and indirect oxidation, are involved in humic acid removal in the catalytic ozonation process. Ozone may be adsorbed by the pumice surface in acidic regions. The removal efficiency of humic acid in the acidic regions, in the catalytic ozonation process, increases compared to the SOP, due to ozone chemical adsorption on the catalyst surface, which results in the formation of active radicals reacting with the unadsorbed humic acid, chemical adsorption of humic acid on the catalyst surface, its reaction with molecular ozone and active radicals in the liquid volume, and simultaneous adsorption of ozone and humic acid and their interaction on the catalyst surface. Moreover, a part of the humic acid is removed by direct reaction of the ozone molecule. A study by Valdes *et al.*,[19] on the performance of a zeolite as a catalyst, in the removal of benzothiazole showed that in the acid region, ozone was adsorbed by a carbon surface and converted into radicals on the surface when they reacted with the functional groups and metal oxides, and also a part of the adsorbed benzothiazole on the surface was decomposed through surface reaction and all these circumstances increased the efficiency of the removal.

In the alkaline regions at high pH, especially higher than pH_{PZC}, the dominant mechanism in the catalytic ozonation process is a radical one (indirect reactions). The reason (of

Table 2: Kinetics of humic acid removal for different pH values in COP and SOP

Processes	Parameters		
	pH	$K_{Overall}^{HA}$ (min^{-1})	R^2
SOP	4	0.05	0.98
	6	0.07	0.99
	8	0.08	0.99
	10	0.98	0.99
	12	0.11	0.99
COP	4	0.25	0.98
	6	0.36	0.99
	8	0.4	0.99
	10	0.68	0.98
	12	0.85	0.99

SOP - Sole, ozonation process, COP - Catalytic, ozonation process

efficiency removal increase in the alkaline region) is related to the humic acid structure, the pumice structure, and the pH_{PZC} of the pumice used. The pH_{PZC} of the activated carbon used was 7.7 [Figure 2]. This is one of the most important properties of the catalyst's surface. Normally, most of the surface electric charge on the various catalysts' surface may be positive or negative, depending on the surface properties of the catalyst's specially functional groups and its components. A region of pH in which the positive and negative electric charges are equal is pH_{PZC}. As the pH changes, the dominant electric charge on the catalyst surface will change inversely to that of pH_{PZC}. Although the pH is higher than pH_{PZC}, the dominant electric charge will be negative, and when the pH is lower than pH_{PZC}, the dominant electric charge will be positive.[4,19]

Studies show that at a pH higher than pH_{PZC}, the functional groups are decomposed on the pumice surface and the nucleophilicity of these groups increases. Under these conditions, the decomposed functional groups on the pumice increase the velocity reaction with ozone. Loss of an electron in these acidic functional groups leads to the transfer of the electron to the ozone molecule and the reaction progress, and conversion of ozone, into highly active radicals on the pumice surface. This electron transfer causes the formation of an ozonide anion and this radical cycle continues.[21] Therefore, humic acid is the removed part, with an indirect reaction in the liquid volume and a part of the reaction with the surface radicals. Thus, the pH increasing and the reaction of ozone with the surface functional groups cause the production of active radicals with a concentration higher than that of SOP at a high pH. In fact, the pH increasing and surface reactions have a synergistic effect on humic acid removal. As the pH increases, the concentration of the hydroxyl ion increases in the liquid volume. This ion is one of the triggers of the ozone decomposition reaction and its conversion into radicals. Furthermore, while the pH increases, the ozone mass transfer is accelerated and the decomposition rate increases. Therefore, humic acid removal efficiency increases remarkably in COP compared to SOP. These results confirm the dominance of indirect reactions.

As mentioned earlier, while the catalyst dosage increased, the efficiency removal increased too [Figure 4]. This efficiency increase in COP is due to an increase in ozone decomposition on the pumice surface resulting in an increase in the concentration of radicals on the surface and in the liquid volume.[21] An increase in catalyst dosage increases the surface area and active sites, and therefore, the adsorption of ozone increases. As the adsorption increases, the surface reactions and radical production in the catalytic ozonation process increase.[21,22] One problem in the advanced oxidation processes are the interfering factors. These interfering or consuming factors include sulfate, carbonate, chloride, and nitrate, which are present in natural waters and highly decrease the efficiency of the advanced oxidation processes.[21,23] According to the results

[Figure 5], humic acid removal efficiency in the catalytic ozonation decreases by only 5%, while in sole ozonation, it decreases by 50%, that is, catalytic ozonation is less affected by radical scavengers. Radical scavengers act as a Lewis base, competing with the ozone in the reaction with the surface functional groups, which act as the Lewis acid. Regarding the ozone-resonant structure and high density of the electron in one the ozone's molecules, it has a strong inclination to react with the Lewis acid, thus, catalytic ozonation is less affected by radical scavengers. Moreover, radicals other than hydroxyls are produced in catalytic ozonation, which do not react with t-butyl alcohol and also these reactions may take place on the catalyst surface, so as not to be affected by the radical consuming factors.[17] Some researchers have shown that radical production in SOP, in the presence of radical scavengers such as t-butyl and acetic acid, ceased, and the removal efficiency decreased greatly.[4] The results of this study have conformed with the results of the other studies, although the experiment conditions in this study have differed from theirs. According to the results, as the heterogeneous catalytic ozonation process is less affected by radical scavengers, it can be a replacement for SOP.

CONCLUSION

The present study has explained the first reported characterization of pumice. The findings of this study revealed that prepared pumice mainly consisted of SiO_2 and had a pH_{zpc} of 7.7. Pumice was composed of metal oxides such as silica, alumina, potassium oxides, sodium, and so on. Furthermore, the results showed that as the catalyst dosage increased, the decomposition rate of humic acid increased, too. The decomposition rate of humic acid in catalytic ozonation processes followed the first-order reactions. The results from the kinetic study indicated that the addition of pumice to SOP increased the decomposition rate of humic acid to five times in acid region and eight times in the alkaline region. Based on the results, pumice is an inexpensive and easily accessible substance, which has the desired potential as a catalyst. Pumice stone can be used in water and wastewater treatment for removing pollutants, especially humic acid, which is one of the main factor of trihalomethanes precursors.

ACKNOWLEDGMENT

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