Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20452

67 (2017) 117–124
March

Natural organic matter removal by catalytic ozonation using original and surface-modified waste and natural materials

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Received 21 August 2016; Accepted 18 December 2016

ABSTRACT

Natural organic matter (NOM) removal efficiency of natural and waste materials used both as the catalyst and as the adsorbent was investigated altogether. The influence of important parameters such as temperature, presence of radical scavengers and NOM source on the efficiency of catalytic ozonation was examined. Moreover, the various processes such as (catalytic hydrogen peroxide oxidation, hydrogen peroxide only, adsorption only, single ozonation and catalytic ozonation processes) were compared. According to experimental results, the application of iron-coated pumice to the ozonation process enhanced the efficiency of NOM removal when compared with single ozonation and adsorption only. However, steel slag and original red mud particles from waste materials did not exhibit any catalytic activity for NOM degradation on catalytic ozonation process. The addition of *tert*-butanol remarkably decreased the removal efficiency of NOM in iron-coated pumice catalyzed ozonation, which suggested that NOM degradation follows the mechanism of hydroxyl radical oxidation. The obtained NOM removal was greater in the humic acid solution than in the low specific UV absorbance natural water by catalytic ozonation. However, approximately 60% UV absorbance removals were achieved by iron-coated catalyzed ozonation in natural waters. In low catalyst dose, the catalytic ozonation showed better performance for removal efficiency of NOM than the catalytic hydrogen peroxide oxidation did.

Keywords: Catalytic ozonation; Catalytic hydrogen peroxide oxidation; Iron oxide; Pumice; Natural organic matter

1. Introduction

Natural organic matter (NOM), which is a heterogeneous mixture of organic compounds such as carbohydrates, amino acids, proteins, humic and fulvic acids, originates from autochthonous (created within the water bodies as decomposition products of organism such as bacteria and algae) and allochthonous sources (transported to the water as the results of decomposition of plant and animal residues in terrestrial environments) [1,2]. NOM affects many aspects of potable water quality and water treatment processes [3]. The presence of NOM not only influences characteristics of potable water such as colour, taste and odour but also impacts the removal of other contaminants in water, disinfectant and coagulant demand and the reuse of water. Furthermore, NOM contributes to corrosion, biological re-growth in distribution systems and membranes fouling, as well [1,3]. Yet, there appears a more serious problem among these effects which is the disinfection by-products (DBP) formation. The application of disinfectants such as chlorine in water containing NOM causes to the formation of DBP [4].

One of the recommended treatment technologies for removal of NOM from drinking water is the advanced oxidation process (AOP) [5]. There is an increasing attention to AOPs such as O_3/H_2O_2, UV/H_2O_2, UV/O_3, UV/TiO_2 and Fe^{2+}/H_2O_2 using a combination of oxidant, radiation and catalysis (e.g. transition metals, metal oxides) [6–10]. AOPs aim to produce the hydroxyl radicals to mineralize organic pollutants in waters [11]. Hydroxyl radicals are generated in situ, and they are

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highly unstable, unselective and reactive radicals, which can degrade organic pollutants and recalcitrant compounds [12,13]. It is known that catalytic ozonation and Fenton-like processes are classified as an AOP providing to reduce total organic carbon (TOC) concentration and UV absorbance of water improving the degradation of organic pollutants [9]. Fenton-like processes have some advantages such as reuse of catalysis, the less iron oxide sludge formation and a wider operating pH range over classical Fenton process [14]. Catalytic ozonation process enhances production of OH· radicals which is effective in mineralization of the organic pollutants improving ozone decomposition and reaction rate of the single ozonation process [15,16]. In addition, catalytic ozonation process can operate within a wider pH (in the acidic and alkaline conditions) [17].

The aims of this study were to: (1) evaluate the catalytic ozonation performance using natural and waste materials catalysts in terms of NOM degradation and (2) to compare the performance of catalytic ozonation and the other process (single ozonation, catalytic hydrogen peroxide oxidation, adsorption only and hydrogen peroxide only). The used natural and waste materials for this purpose were red mud, steel slag (SS) and pumice. In addition to these materials, goethite and hematite were also used to compare its catalytic performance. Red mud is a toxic by-product produced in the aluminum production industry, and it is classified as hazardous because of its caustic nature [18]. The random store of the produced red mud in large amounts is a very serious environmental problem. For this reason, alternatives are sought to evaluate red mud. Red mud contains iron oxide like goethite and hematite, and this makes it useful to apply in water treatment. SS is an inert by-product formed during iron and steel production, containing mainly iron (Fe) and calcium oxide (CaO) [19,20]. Pumice is a light, porous, volcanic and natural material with a large surface area and low hardness. Because of these properties, pumice is suitable for use in water treatment as adsorbent or catalyst. The use of this low-cost natural and waste materials offers cheaper alternatives and sustainable solutions in the water treatment. Moreover, the reuse of these waste materials can provide an advantage in terms of economic and environment.

2. Materials and methods

2.1. Materials

In this study, natural water (Isparta drinking water supply) and synthetic humic acid (HA) solution were used as NOM sources. HA isolate was purchased from Acros organics (Belgium). Dissolved organic carbon (DOC) concentration of HA solution was adjusted as 3.5 mg/L to ensure the same experimental conditions with Isparta drinking water supply. Isparta drinking water supply presents water with low specific UV absorbance (SUVA) while HA solution presents water with high SUVA. Before experiments, raw water was filtered as 0.45 µm to remove suspended particles, and it was stored at +4°C. The physicochemical characteristics of the water samples are given in Table 1. Hydrogen peroxide (30%, Merck, Germany) and the chosen *tert*-butanol as radical scavenger were purchased from Merck (Germany). Ozone was generated from pure oxygen by using an ozone generator (Triogen, Lab2B).

In experiments, original red mud (ORM), SS and Isparta pumice particles were used as both adsorbent and catalyst. ORM particles were provided by the Etibank-Seydisehir Aluminum Production Plant, Turkey, and were washed with distilled and deionized water (DDW) and dried at 80°C before it was used in experiments. ORM particles were also used by activating the acid [21]. The preparation method of acid activated red mud (AARM) can be found in reference [19]. Particle size fraction of both ORM and AARM was <250 µm. SS particles were obtained from Eregli Iron and Steel Production Plant, Turkey. The sieved SS particles of 250–500 µm were used in experiments after it was washed with DDW to remove any impurities. Pumice particles were supplied at Pumice Research and Application Center at Suleyman Demirel University, Isparta. This pumice particles were sieved to <63 µm particle size. In order to coat with iron oxide, this natural pumice particles were used to the methods reported by Kitis et al. [22]. The details of the coating process were reported in our previous study [19]. Commercial goethite (FeOOH, 71063) and hematite (Fe_2O_3, 31005) particles were provided from Sigma-Aldrich (USA) and used as received. The physicochemical characteristics such as Brunauer–Emmett–Teller (BET) surface area, adsorption average pore width, iron content and pH_{pzc} of the tested adsorbents/catalysts can be seen in Table 2. The characterization of the all used particles were inclusively discussed in our previous study [19].

2.2. Analytical methods

The surface area, pore volume and pore size distributions of particles were determined by means of BET method by using a Micromeritics Gemini V analyzer. The total iron content on the surface of the particles was determined by using acid digestion analysis mentioned in reference [23]. In acid digestion analysis, 5 g adsorbent/catalyst and 50 mL 6 N HCl solution were mixed for 24 h. After 24 h, solution was filtered through a filter paper. Total iron concentrations in solutions were measured by using phenanthroline method [19]. DOC was determined by using the TOC analyzer (TOC-L, Shimadzu) according to high-temperature combustion method (Standard Method 5310B). UV absorbance was measured at 254 and 280 nm using UV-visible spectrophotometer (UV-1700, Shimadzu, Japan). Hydrogen peroxide concentration was measured with a titrimetric test kit (22917-00, Hach, USA). Dissolved ozone concentration

Table 1
The physicochemical characteristics of the tested waters

Parameters	Isparta drinking water[a,b]	Humic acid solution[a]
DOC (mg/L)	3.7	3.5
UV_{280} Abs (cm^{-1})	0.026	0.287
UV_{254} Abs	0.038	0.365
$SUVA_{280}$ (L/mg DOC.m)	0.7	8.2
Conductivity (µS/cm)	412	10
Total hardness (mg $CaCO_3$/L)	214	17
Alkalinity (mg $CaCO_3$/L)	235	20
pH	8.9	6.86

[a] The values are averages of triplicate measurements.
[b] The raw drinking water was filtered as 0.45 µm before water quality analysis and experiments.

Table 2
Some physicochemical characteristics of the tested particles

	BET surface area (m^2/g)	Adsorption average pore width (nm)	Iron content (mg Fe/g)	pH_{pzc}
Original (untreated) samples				
Isp (<63)	14.2	NA	2.1	9.0
SS	<2	NA	23.2	11.4
ORM	10.1	18.40	20.7	9.9
Goethite	13.7	11.12	27.1	6.3
Hematite	3.1	14.52	589.2	6.2
Modified samples (treated)				
Isp (<63) IC	9.2	NA	16.2	6.2
AARM	266.4	4.40	41.5	3.9

Note: NA: Not available. Codes for particles: Isp, Isparta pumice; ORM, original red mud; SS, steel slag; AARM, acid activated red mud; IC, iron oxide coated. Values reported above are the average values of duplicate measurements.

was analyzed with test kits (25180-25, Hach) according to the methods of indigo.

2.3. Experimental procedure

All experiments (adsorption only, single ozonation, catalytic ozonation and catalytic H_2O_2 oxidation experiments) were performed in completely mixed batch reactors by using amber glass (vials) bottles, 40 or 100 mL, with Teflon-lined screw caps and at 25°C. Synthetic HA experiments were studied at original pH (6.86), and the pH of natural raw water was also adjusted by adding HCl and NaOH.

- Adsorption experiments: Kinetic experiments were performed to find the time needed for adsorption and tested periods 1, 4, 8, 12, 24, 48, 96, 120 and 144 h at a constant adsorbent dose (3 g/L). Kinetic experiments indicated that the necessary time to reach equilibrium was 24 h, and therefore, 24 h was chosen for the adsorption isotherm experiments. In isotherm experiments, amber glass bottles were filled with an adsorbent (0.05, 0.2, 0.5, 1, 3, 6 and 10 g/L) and HA solution and then stirred at 150 rpm at a constant temperature of 25°C for 24 h. After adsorption for a predetermined time, the samples were filtered by using a filter (0.45 μm pore size).
- Catalytic H_2O_2 oxidation experiments: In the kinetic experiments, constant catalyst dosage of 3 g/L and hydrogen peroxide dosage of 300 mg/L were tested. The durations were selected as 1, 4, 8, 12, 24, 36, 48, 72, 96, 120 and 144 h. According to the results of the kinetic experiments, it was found that 24 h was adequate to reach equilibrium, and therefore, further experiments were carried out at 24 h. For the catalytic H_2O_2 oxidation experiments, different concentrations of hydrogen peroxide (50, 150, 300 and 1,000 mg/L) were applied to glass vials containing HA solution and various amounts of catalyst for 24 h. In addition to catalytic H_2O_2 oxidation experiments, peroxide only experiments were conducted. In the peroxide only experiments, peroxide was added alone without catalyst to determine NOM removal. Samples taken after a specific time were analyzed for residual hydrogen peroxide, and sodium sulphite was added to quench residual peroxide. The samples were filtered by using 0.45 μm filter prior to pH, UV absorbance and TOC analysis.
- Catalytic ozonation experiments: Ozonation and catalytic ozonation experiment were carried out by adding the predetermined amounts of ozone stock solution to samples. For this, the given amount of HA solution/natural water was immediately mixed with ozone-containing water to be DOC: O_3 ratio of 1:1. Kinetic experiments of catalytic ozonation process were tested with 3 g/L constant catalyst dosage and 3.5 mg/L of constant ozone dosage. The durations were selected as 5, 10, 15, 20, 30, 60, 90 and 120 min. The results showed that NOM removals did not significantly change after 60 min of reaction time and equilibrium was reached within 60 min. Similarly Park et al. [24] selected 40 min of reaction time in the goethite-catalyzed ozonation of NOM. Therefore, based on the literature and the obtained results, in the further ozonation experiments' reaction time was selected as 60 min. Catalytic ozonation reactions were initiated by addition of an ozone stock solution to the HA solution/natural raw water containing catalyst. The tested catalyst doses were 0.05, 0.2, 0.5, 1, 3, 6 and 10 g/L. The initial DOC concentration was about 3.5 mg/L. The samples then were mixed at 150 rpm and 25°C. Single ozonation procedure was performed in the same procedure as catalytic ozonation but without catalyst.

Moreover, the influence of parameters such as temperature and the presence of radical scavenger on the catalytic ozonation process was investigated. The applied temperature values to determine the effect of temperature are 25°C and 35°C. *tert*-Butanol was chosen as radical scavenger to verify the hydroxyl mechanism in the catalytic ozonation process. The used *tert*-butanol concentration in ozone studies in the literature ranged from 10^{-3} M to 0.1 M [25–27]. Therefore, in the experiments conducted in the presence of radical scavenger, a concentration of 10^{-3} M of *tert*-butanol was used.

3. Results and discussion

3.1. Catalytic ozonation experiments

Fig. 1(a) shows UV_{280} absorbance removals, and Fig. 1(b) shows the NOM removal efficiency by single ozonation, adsorption only and catalytic ozonation process from HA solution (with iron-coated Isparta pumice). 47% UV_{280} absorbance removal and 10% DOC removal were obtained by single ozonation process in the HA solution (Figs. 1(a) and (b)). Similar trends were also observed in the natural water experiments. 38% UV_{280} absorbance and 4% DOC removal were obtained by single ozonation process from Isparta drinking water (not shown). This result is the expected situation since it is known that ozone is not completely oxidized by dissolved organic matter and it provides a minor reduction of DOC concentration. [28,29]. Molnar et al. [30] found a DOC decrease of 6% from groundwater in the ozonation experiments while Gracia et al. [31] found 13% DOC and 52% UV absorbance removal by single ozonation process in Ebro River.

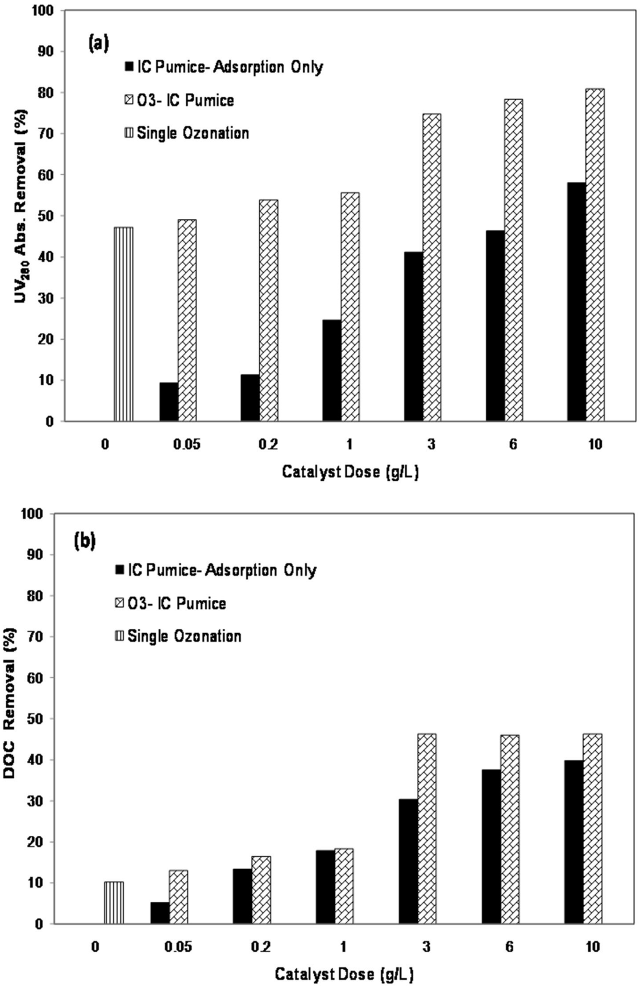

Fig. 1. The effect of catalyst dose on: (a) UV_{280} absorbance removals and (b) DOC removals for the humic acid solutions by single ozonation, adsorption only and catalytic ozonation process (which uses iron-coated pumice) (<63 μm pumice fraction, *T*: 25°C, reaction time: 24 h, pH: 6.86, ozone dose: 3.5 mg/L, IC: iron coated).

As shown in Fig. 1(a), the lowest UV absorbance removal efficiency is obtained by the adsorption only. On the other hand, iron-coated Isparta pumice and ozone used together (catalytic ozonation) significantly enhanced NOM removal efficiency. The obtained removal by catalytic ozonation is greater than the obtained one in terms of both single ozonation and adsorption only process. For example, 75% of UV_{280} absorbance was achieved by the catalytic ozonation, while the adsorption only process removed only 41% (using 3 g/L iron-coated pumice). The obtained DOC removals are consistent with UV_{280} absorbance removals for all the process (Fig. 1(b)). While 30% DOC removal was obtained with adsorption only process by using iron-coated pumice 3 g/L dosage, the catalytic ozonation process achieved 46% DOC removal. Yuan et al. [32] reported that the degradation efficiency of *p*-chloronitrobenzene (*p*-CNB) was significantly enhanced by pumice-catalyzed ozonation while adsorption only had no significant contribution on degradation of *p*-CNB. The maximum UV_{280} absorbance and DOC removal efficiency by catalytic ozonation as using iron-coated pumice (10 g/L pumice dose) were, respectively, 81% and 46% (Figs. 1(a) and (b)). Similar catalytic effect had also been observed in the natural water experiments. Despite adsorption only process was ineffective in NOM removal from Isparta drinking water (removals under 5%), NOM removals were enhanced by catalytic ozonation process. Besides, ozonation in the presence of iron-coated pumice was higher than both adsorption on the iron-coated pumice and single ozonation. For example, 55% of UV_{280} absorbance was achieved by the catalytic ozonation by using 3 g/L iron-coated pumice (not shown). The provided maximum UV_{280} absorbance and DOC removals with iron-coated pumice catalyzed ozonation in Isparta drinking water were, respectively, 59% and 14% (at constant 10 g/L) (not shown).

As a general trend, the found NOM uptake in the Isparta drinking water with low SUVA by the all tested particles was lower than the provided NOM uptake in the HA solution by catalytic ozonation. For example, the obtained UV_{280} absorbance removal for the HA solution and Isparta drinking water supply by catalytic ozonation using Isp IC particle were 78% and 59%, respectively (at 6 g/L catalyst dose). Similarly, Kaplan Bekaroglu et al. [33] studied NOM removal in natural waters with different SUVA values, and they found that NOM removal went up by increasing from 1.41 to 3.64 L/mg DOC.m of SUVA values of the natural waters.

SUVA value of Isparta drinking water source was 0.7 L/mg DOC.m, which has low SUVA value (Table 1). SUVA value describes the composition of water in terms of hydrophilic and hydrophobic, and it shows that NOM is mostly hydrophilic when SUVA values are lower than 3 L/mg DOC.m. Therefore, it is possible to say that NOM in Isparta drinking water source, which has low SUVA value, is hydrophilic character. Iron oxide surface is effective at removing preferably hydrophobic fractions of NOM. For this reason, catalytic ozonation process was more effective at removing NOM in the HA solution. But still remarkable removals were achieved by catalytic ozonation process in Isparta drinking water supply. It stems from the fact that ozone has a high oxidation potential and it is effective at removing different NOM fractions. The ozone, which is a strong oxidant, is effective at removing not only hydrophobic fractions but also hydrophilic fractions in Isparta drinking water with low SUVA value. Zhang et al. [34] stated that goethite catalyzed ozonation was effective at removing both hydrophobic and hydrophilic fractions and of the river water.

The temperature dependence of the catalytic ozonation process was investigated in synthetic HA solution. The effect of temperature on the catalytic ozonation process is given in Fig. 2. During the first 20 min reaction period, the NOM removal efficiency significantly increased from 25°C to 35°C. UV_{280} absorbance removal increased from 56% to 63% with temperature from 25°C to 35°C at 10 min. However, after 30 min, NOM removal reached the highest level, and after the mentioned time, the increasing of the temperature did not cause a significant change. It is known that the increase of temperature affects catalytic ozonation process in different ways. Ozone molecules are quickly transformed to OH· radicals promoting the decomposition of ozone with increasing temperature; on the other hand, ozone concentration in the solution is reduced with the rise of temperature [17].

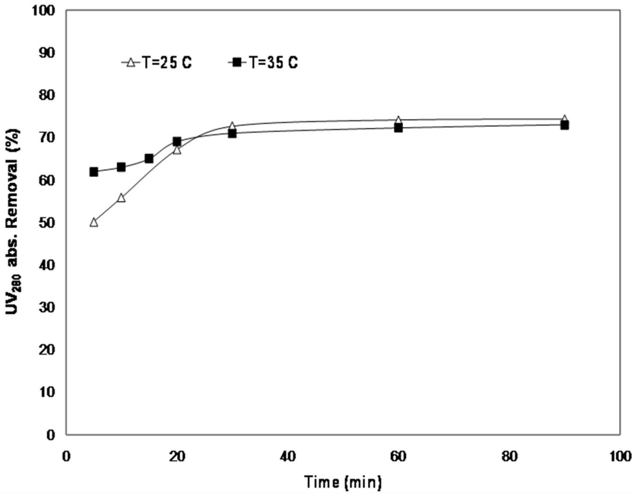

Fig. 2. The temperature effects on the UV_{280} absorbance removals by catalytic ozonation process in the humic acid solution (iron-coated Isparta pumice, <63 μm particle size fraction; pumice dose: 3 g/L; *T*: 25°C; pH: 6.86).

Therefore, in the first minutes, NOM removal increased with the increase in temperature because the transformation of ozone to OH· radicals was fast. But then it was observed that the temperature had no effect on the NOM removal by catalytic ozonation. These findings are consistent with other observations in literature. Huang et al. [35] stated that TOC removal increased from 45.6% to 94.5% with temperature in the catalytic ozonation process by using iron-loaded mesoporous material as catalyst but TOC removal was suppressed to 84% at temperature above 35°C.

The experiments were conducted in the absence and presence of the *tert*-butanol in order to determine reaction mechanism of NOM removal by the single ozonation and catalytic ozonation process. *tert*-Butanol is a well-known radical scavenger that reacts faster with hydroxyl radicals ($k_{\mathrm{OH}\bullet} = 4.56 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) when compared with ozone ($k_{\mathrm{O3}} = 0.18\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) [36].

Fig. 3 shows the effect of the addition of *tert*-butanol on the NOM removal by single ozonation and catalytic ozonation (ozonation with iron-coated pumice). It is seen that the presence of *tert*-butanol affects NOM removal by the single ozonation and catalytic ozonation. Single ozonation process with the addition of *tert*-butanol slightly influenced by showing a reduction in the UV removals from 47% to 42%. This shows that NOM removal by single ozonation takes place with direct reaction by ozone molecules. The addition of the *tert*-butanol to catalytic ozonation process also exhibited similar trends to single ozonation. However, it is clear that it is the addition of *tert*-butanol that influences catalytic ozonation process according to single ozonation much more. UV_{280} absorbance removal decreased from 73% to 63% with the addition of *tert*-butanol for the catalytic ozonation at the 30 min reaction time. In light of this information, it is possible to say that the obtained NOM removal by both of the processes (catalytic and single ozonation) declines the presence of *tert*-butanol. This situation reveals that iron-coated pumice catalyzed ozonation enhances the NOM removal creating OH· radical on the pumice surface through a radical mechanism.

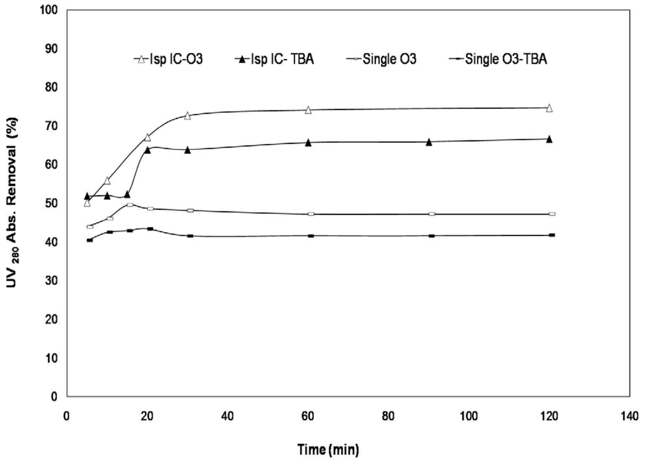

Fig. 3. The effect of *tert*-butanol on NOM removals by single ozonation and catalytic ozonation process (pH: 6.86; pumice dose: 3 g/L; ozone dose: 3.5 mg/L; *tert*-butanol concentration: 10^{-3} M; IC: iron-coated, TBA: *tert*-butanol).

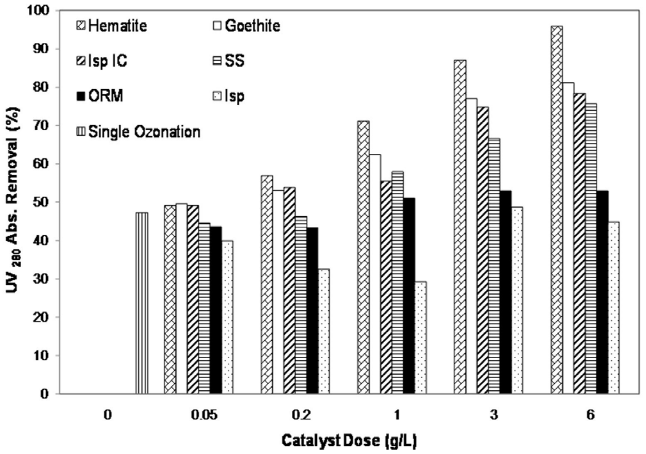

Fig. 4. The compairison of UV_{280} absorbance removal efficiency various catalysts by the catalytic ozonation process in the humic acid solution (ozone dose: 3.5 mg/L; pH: 6.86; *T*: 25°C; IC: iron-coated; Isp: Isparta pumice; SS: steel slag; ORM: original red mud).

The obtained findings are consistent with the results in the degradation of nitrobenzene by the goethite-catalyzed ozonation, in the *p*-CNB and HA removal by pumice-catalyzed ozonation, catalytic ozonation of refractory organics with alumina [32,37–39].

3.2. The comparison of the effectiveness of the catalysts for catalytic ozonation process

Ozonation with other catalysts (hematite, goethite, original/iron-coated pumice, ORM and SS particles) were compared according to their effectiveness of NOM uptake. Fig. 4. shows the obtained UV_{280} absorbance removal efficiency by catalytic ozonation process using ORM, SS original and iron-coated pumice, hematite and goethite. As shown in Fig. 4, the use of ozone with the catalysts except for the ORM and original pumice enhances the removal of NOM.

ORM does not have any catalytic activities for NOM removal because the catalytic ozonation process did not enhance NOM removal according to both the adsorption only and single ozonation. For example, 51% UV_{280} absorbance removal was provided by the catalytic ozonation while the obtained UV_{280} absorbance removal of single ozonation and adsorption only process were 47% and 45%, respectively. This is due to the structure of caustic red mud and complex nature of NOM, which prevents the formation of OH· radicals. Similar observations were obtained in the catalytic ozonation by using AARM. Similarly to ORM and AARM, original pumice did not show a catalytic activity even at the highest dose in the catalytic ozonation process. Moreover, the obtained removals by original pumice-catalyzed ozonation are lower than the obtained removals by single ozonation. However, it is clear that NOM uptake increased by improving the ozone decomposition after the pumice was coated with iron. In the literature, it is emphasized that iron oxides enhance the catalytic activity in the removal of various pollutants in the catalytic ozonation process [40,41]. In this case, it is possible to say that iron-coated pumice particles are effective as commercial iron oxides in NOM removal by catalytic ozonation. The using of SS particles as catalyst in the catalytic ozonation process seems to develop NOM uptake when compared with single ozonation process. However, it is seen that SS is not successful to catalyze NOM degradation when SS catalyzed ozonation compared with adsorption only process (Fig. 6). SS inhibits the formation of OH· radical, and in consequence of decreasing ozone decomposition, it can be assumed that it was probably all due to its basic surface character.

Commercial hematite and goethite-catalyzed ozonation exhibit a similar trend with iron-coated pumice. Among the tested catalysts, hematite catalyst is the most effective catalyst in the catalytic ozonation of NOM showing the highest UV_{280} absorbance removal. Ozonation with hematite enhanced NOM uptake about 50% when compared with single ozonation (at the 6 g/L dose). 81% UV_{280} absorbance was obtained by goethite particles showing similar trends to hematite particle. These results indicate that catalysts' activity relies on the production of OH· radical in the removal of NOM by catalytic ozonation by using the iron oxides. The used iron oxides in the catalytic ozonation process increase ozone decomposition and provide OH· radical formation. In the OH· radical mechanism, dissolved ozone primarily adsorbed to catalyst surface, and then OH· radicals formed NOM oxidizing [42]. There are many studies concerning NOM removal by iron oxide catalyzed ozonation based on OH· radical mechanism [24,40,43,44].

3.3. The comparison of the effectiveness of the different processes

Fig. 5 compares NOM removal efficiency by the hydrogen peroxide only, single ozonation, adsorption only, catalytic hydrogen peroxide oxidation and catalytic ozonation process in terms of the UV_{280} absorbance removal. It is possible to say that the obtained removals by hydrogen peroxide only process are low and are not effective processes in NOM removal. 11% UV_{280} absorbance removal was obtained even the highest hydrogen peroxide dose (1,000 mg/L) by hydrogen peroxide only process for HA solution. 47% UV_{280} absorbance removal efficiency was provided in the single ozonation process carried out without iron-coated pumice. In the single ozonation, the higher NOM uptake was obtained than hydrogen peroxide only process, because ozone (2.1 V) has a stronger oxidation potential than hydrogen peroxide (1.8 V).

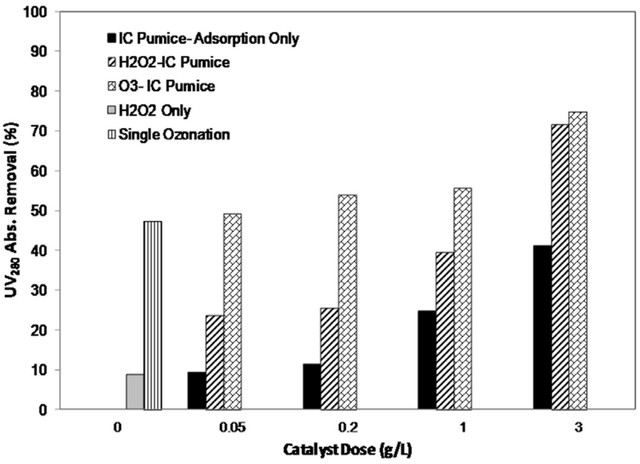

Fig. 5. The comparison of NOM removal efficiency of the advanced oxidation process used iron-coated Isparta pumice as catalyst in the humic acid solution (H_2O_2 dose: 1,000 mg/L; ozone dose 3.5 mg/L; Isparta pumice particle size fraction: <63 μm).

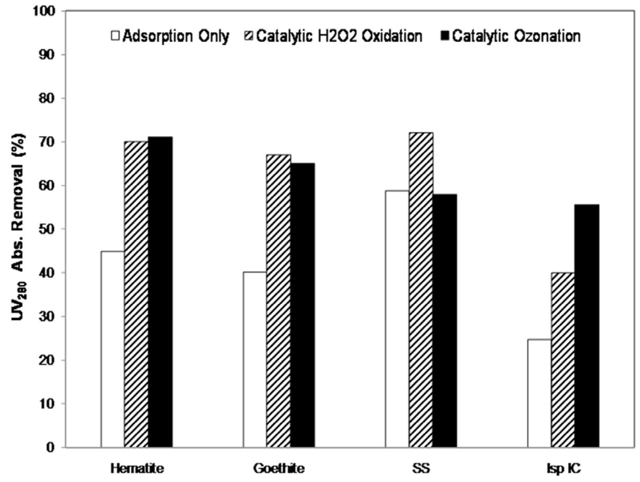

Fig. 6. The comparison of adsorption only, catalytic hydrogen peroxide oxidation and catalytic ozonation process for the tested particles in the humic acid solution (ozone dose: 3.5 mg/L, H_2O_2 concentration: 1,000 mg/L, catalyst dose: 1 g/L, T: 25°C, pH: 6.86).

On the other hand, the use of ozone or hydrogen peroxide with iron-coated pumice significantly increased NOM removal efficiency according to hydrogen peroxide only, single ozonation and adsorption only process. For example, catalytic ozonation process increased 31% while catalytic hydrogen peroxide oxidation UV_{280} absorbance removal went up to 15% according to the adsorption only using 1 g/L iron-coated pumice. Furthermore, catalytic ozonation process is more effective than catalytic hydrogen peroxide oxidation in terms of NOM removal until the 3 g/L pumice dose even if hydrogen peroxide is used at the highest dose (1,000 mg/L) (Fig. 6). However, at 3 g/L, the obtained NOM removal efficiency by catalytic hydrogen peroxide oxidation and catalytic ozonation process were almost the same because of particle dose effect. The obtained UV_{280} absorbance removal by catalytic hydrogen peroxide oxidation and catalytic ozonation using 3 g/L iron-coated pumice were, respectively, 71% and 75%.

Fig. 6 shows the NOM removal efficiency for hematite, goethite, SS and iron-coated pumice (for the adsorption only, catalytic ozonation, catalytic hydrogen peroxide oxidation process). In low catalyst dose and hydrogen peroxide dose, catalytic ozonation process is the most effective process for the NOM removal for the almost all tested catalyst when it was compared with the other processes. However, the NOM removal efficiency of catalytic ozonation and catalytic hydrogen peroxide oxidation were almost in the same degree with increasing of catalyst dose owing to particles dose effect. Hematite from all the tested particles has the highest NOM removal in all the processes (adsorption only, catalytic hydrogen peroxide oxidation and catalytic ozonation). Catalytic ozonation process is more effective when catalytic hydrogen peroxide oxidation and catalytic ozonation process were compared together using Isp IC particle. However, in the highest doses, the obtained NOM removals by catalytic hydrogen peroxide oxidation and catalytic ozonation process were almost similar with the hematite and goethite. Catalytic hydrogen peroxide oxidation using the SS particle was very effective according to adsorption only process. But SS and ozone, which were used together, failed to catalyze, and the obtained removals were close to the provided removals by adsorption only.

4. Conclusions

Surface-modified natural and waste materials were used as catalyst in catalytic ozonation process for the NOM degradation. The performed single ozonation without addition of catalyst removed 10% DOC in the HA solution. On the other hand, the combined use of iron-coated pumice and ozone significantly enhanced the removal of NOM. Moreover, the higher removals by the catalytic ozonation process were obtained when compared with adsorption only. The maximum 46% DOC removal by iron-coated catalyzed ozonation was achieved in the HA solution. SS and ORM waste materials do not have the ability to catalyze NOM degradation due to its surface properties. In the conducted natural water experiments with Isparta drinking water were also observed similar trends. High NOM removals were achieved by catalytic ozonation using iron-coated pumice while iron-coated pumice was ineffective in the NOM removal by adsorption only. The provided maximum DOC removals by catalyzed ozonation using iron-coated pumice in Isparta drinking water were 14%. No significant change was observed in NOM removal efficiency for tested temperatures. The addition of *tert*-butanol in the iron-coated pumice catalyzed ozonation process decreased from 73% to 63% removal of UV_{280} absorbance and the formation of OH· radicals were proven. It is deduced that iron-coated pumice catalyzed ozonation process was governed through a radical type mechanism in contrary to single ozonation, which followed direct reaction mechanism with ozone. In iron oxide catalyzed ozonation process, activity of the catalyst depends on the production of OH· radicals. The iron oxide surfaces on iron-coated pumice improve ozone decomposition and thus enable hydroxyl radical generation. Reduced NOM removals were found in Isparta drinking water when compared with HA solution. It is shown that catalytic ozonation process is more effective than catalytic hydrogen peroxide process in order that ozone has a higher oxidation potential when compared with hydrogen peroxide. Besides, ozone is more effective because it removes both hydrophobic and hydrophilic fractions of NOM. However, the obtained removals by the catalytic ozonation and catalytic hydrogen peroxide were almost the same in the higher doses, which were the results of particle dose effects. These iron-coated pumice particles can be used as low-cost and sustainable catalysts for the NOM removal in the catalytic ozonation process.

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