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Catalytic Ozonation for The Removal of Humic Acid in Water with Iron Coated Zeolite (ICZ)

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Abstract

This study examined the catalytic ozonation of humic acid (HA) with iron coated zeolite (ICZ) and hydrogen peroxide (H_2O_2). The results were evaluated by DOC that specify organic matter, UV_{254}, $SUVA_{254}$ (Specific Ultraviole Absorbance at 254 nm), and A_{436}. When ozonation was used alone, DOC removal was obtained as 21.4% at ozone concentration of 10 mg/L, pH 6.50 and oxidation time of 60 min. DOC removal was found to increase by the the addition of H_2O_2 in ozonation process. The use of ICZ as catalyst increased the decomposition of humic acid compared to ozonation alone. DOC removal efficiency was obtained as 62.0% at pH 6.5, at catalyst loading of 0.75 g/L, and oxidation time of 60 min. In catalytic ozonation process DOC removal slightly incresed, when H_2O_2 was added. 64.6% DOC removal was obtained at ozone concentration of 10 mg/L, catalyst dosage of 0.75mg/L and H_2O_2 concentration of 1 mg/L. The catalytic ozonation enhanced the destruction of the aromatic and UV-absorbing structures compared with ozonation alone. However, increasing ozone concentrations did not increase removal efficiencies significantly in the catalytic ozonation processes.

Keywords: Humic acid, ozonation, hydrogen peroxide, catalytic ozonation

Sulardan Humik Asit Gideriminde Demir Kaplı Zeolitle (DKZ) Katalitik Ozonlama

Öz

Bu çalışmada hidrojen peroksit ve demir kaplı zeolitle katalitik ozonlama ile humik asit giderimi incelenmiştir. Sonuçlar çözünmüş organik karbon (ÇOK), UV254, SUVA254 (254 nm'de (spesifik Ultraviyole absorbansı) ve renk absorbansı (A436) parametreleri ölçülerek değerlendirilmiştir. 60 dakikada pH 6.5'da 10 mg/L ozon konsantrasyonunda yalnız başına ozonlama ile %21,4 ÇOK giderimi elde edilirken demir kaplı zeolitle (0,75 mg/L) katalitik ozonlama deneylerinde %62 ÇOK giderimi elde edilmiş, katalitik ozonlama sistemine 1 mg/L hidrojen peroksit ilavesiyle de (%64,6 ile) çok hafif bir artış gözlenmiştir. katalitik ozonlama yalnız başına ozonlamaya kıyasla UV absorplayan aromatik yapının parçalanmasına katkıda bulunmuş ve ÇOK giderimini de iyileştirmiştir ancak katalitik ozonlama sistemlerinde ozon konsantrasyonunun artışı giderim veriminde kayda değer bir artış sağlamamıştır.

Anahtar Kelimeler: Humik asit, ozonlama, hidrojen peroksit, katalitik ozonlama

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1. Introduction

“Water resources usually include natural organic matter depending on the hydrological cycle and the interaction between the biosphere and the geospher[1]. Natural organic substances are composed of heterogeneous and complex structures such as humic acid, polysaccharide, amino sugar, protein, peptide, lipid, small hydrophilic acids, and others”[1 ve 2]. “The presence of NOM, in surface waters is a concern not only for their adverse environmental impact on aquatic ecosystems, but also for their potential harmful effects on human health resulting from halogenated organic disinfection byproducts such as trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles, haloketones, haloaldehydes, and halogenated furanones” [3].

“NOM contained mainly of humic substances serves as the major precursor to the formation of DBPs. It has been proved that the formation of DBPs depends on the concentration of NOM which is the main agent in the reaction” In general, rising NOM levels in chlorinated drinking waters raises the formation of disinfection by-products[4]. It is therefore necessary to remove humic substances or to reduce their concentration.

Recently, catalytic ozonation has been proved its effectiveness for the degradation of refractory pollutants in water and wastewater. “During the catalytic ozonation process, the catalysts play an important role in generating hydroxyl radicals and degrading pollutants. Some of the catalysts have been developed for the catalytic ozonation of refractory pollutants in wastewater such as FeOOH” [5 ve 6]. ,Fe/MgO [7], TiO_2,[8], pumice [9] and metals composites [10]. Among these catalysts, ICZ has been demonstrated to be effective for the catalytic degradation of humic acid [11].

The objective of the study was to examine the effect of ozone concentration and hydrogen peroxide on iron coated zeolite (ICZ) catalyzed ozonation for the removal of humic acid from aqueous solution.

2. Materials and Methods

2.1 Chemicals

The stock humic acid solution (commercially purchased sodium salt, Sigma-Aldrich) was obtained by dissolving 1 g HA in 1 L DDW using the ultrasonic sonication bath. The characteristics of HA and detailed experimental procedure can be found in our previos study [11].

2.2 Preparation and Characterization of ICZ

The zeolite (clinoptilolite) samples used in our study were received from the Gördes region in Manisa of Turkey. The zeolite was first ground and then sieved to +45-35 mesh particle size fractions. The zeolite samples were covered by iron using reagent grade $FeCl_3.6H_2O$, employing the method notified by Lai and Chen (2001), Lai et al. (2000) and Kitiş et. al., (2007) [12 ve 14].

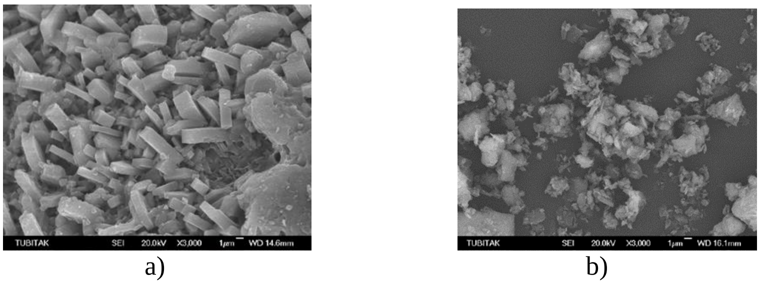
2.3 Ozonation and Catalytic Ozonation Procedure

The ozone gas is generated at the concentration of 0.01-20 mg/L from dried air with an ozone generator (8 g/h capable of producing ozone, TeknoOzone. After HA solution placed in to the ozonation reactor the ozonation process was initiated. Hydrogen peroxide and/or catalyst were added at desired concentrations in the catalytic ozonation experiment. The reactor (2 L) and content of the reactor was mixed by a mechanical stirrer at 150 rpm during the reaction (24±^{o} C). The effluent O_3 gas, was absorbed by potassium iodide (KI) solution. Removal of humic acid was monitored by spectroscopic measurements such as A_{436} (absorbance at 436 nm) and UV_{254} (absorbance at 254 nm). The extent of mineralization was determined by dissolved organic carbon (DOC) measurements" [11].

3. Results and Discussion

3.1 Properties of the Catalyst

The surface morphology of iron coated zeolite and natural zeolite were examined with the aid of SEM micrographs as depicted in Figure 1(a) and 1(b). The SEM image of ICZ indicated that this surface was covered with newborn iron oxides.



a) b)

Figure 1. a) SEM photographs of ICZ (x3000) b) SEM photographs of natural zeolite(x3000)

"According to XRD results, ICZ sample contained 49.531% O, 36.299% Si, 6.3% Al, 2.132% Fe, 3.470% K and trace amounts of other elements. Iron content increased from 0.779% to 2.132% with coating procedure. Zeolites are naturally negatively charged, and have a high ion exchange capacity[15]. However, due to the positive charge of oxide covering layer [16], surface properties of zeolite have changed".

3.2 The Effect of Ozone Concentration on Catalytic Ozonation of Humic Acid

Catalytic ozonation experiments were carried out at various ozone concentrations, ranging from 10 to 20 mg/L, at a constant HA concentration of 30 mg/L and a constant pH of HA and a constant catalyst dosage of 0.75 g/L.

The effect of ozone concentration on catalytic ozonation of HA is shown in **Figure 2**. It was observed that DOC removal efficiency increased from 62.01% to 66.4% with increasing ozone concentration from 10 to 20 mg/L. UV_{254} removal efficiency increased from 95.8 to 97.5%, and A_{436} removal efficiencies were almost 100% in all ozone concentrations. $SUVA_{254}$ value decreased from 0.93 to 0.63. As can be seen from Figure 3, HA removal efficiencies increased with the oxidation time.

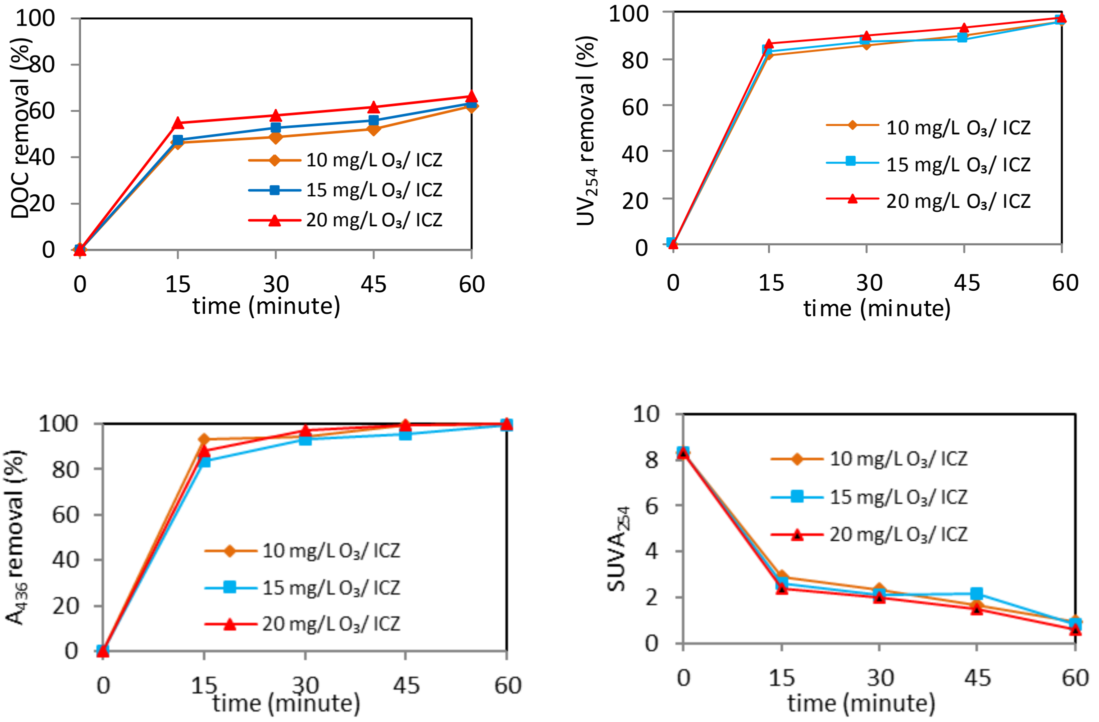


Figure 2. The effect of ozone concentration on catalytic ozonation of HA removal
(concentration of HA = 30 mg/L, pH = 6.5, IZC=0.75 g/L T = 24 ± 1°C)

3.3 Effect of H_2O_2 on Catalytic Ozonation of Humic Acid

The effect of H_2O_2 concentration was investigated at ozone concentration of 10 mg/L, a constant H_2O_2 dose of 1 mg/L (H_2O_2:O_3=0.1), ICZ concentration of 0.75 g/L and pH 6.5. Comparison of the results were shown in Figure 3.

DOC, UV_{254}, $Color_{436}$ removal efficiencies were 21.4%, 72.8%, 93.0%, respectively and $SUVA_{254}$ value was and 2.88 at oxidation time of 60 min. for ozonation alone. When 1 mg/L of H_2O_2 added the DOC and UV_{254} removal efficiency increased from 21.4 to 38.8% and from 72.8 to 76.2% at ozonation time of 60 min. It was found that DOC, UV_{254}, $Color_{436}$ removal efficiencies were 62.0%, 95.8%, 100%, respectively and $SUVA_{254}$ value was and 0.93 at oxidation time of 60 min for catalytic ozonation with ICZ. When 1 mg/L of H_2O_2 added to ICZ/O_3 process the DOC removal efficiency increased from 62.0 to 64.6% and UV_{254} removal efficiency decreased from 95.8 to 94.5% and $SUVA_{254}$ value increased from 0.93 to 1.29 at ozonation time of 60 min.

O_3/H_2O_2 process was more efficient compared to O_3 alone at pH 6.5. However, O_3/ICZ/H_2O_2 process was not efficient compared to O_3/ICZ at pH 6.5. So, the addition of H_2O_2 did not have any significant effect on HA catalytic ozonation with ICZ.

"Ozone reacts with NOM by an electrophilic addition to double bonds. This reaction is very selective. In addition to the direct reaction of ozone with NOM, a non-selective and fast reaction occurs with $OH^{\bullet}$ radicals that are formed when ozone decomposes in water. There are several solutions to promote the $OH^{\bullet}$ radical production in the ozonation process" [11 ve 17].

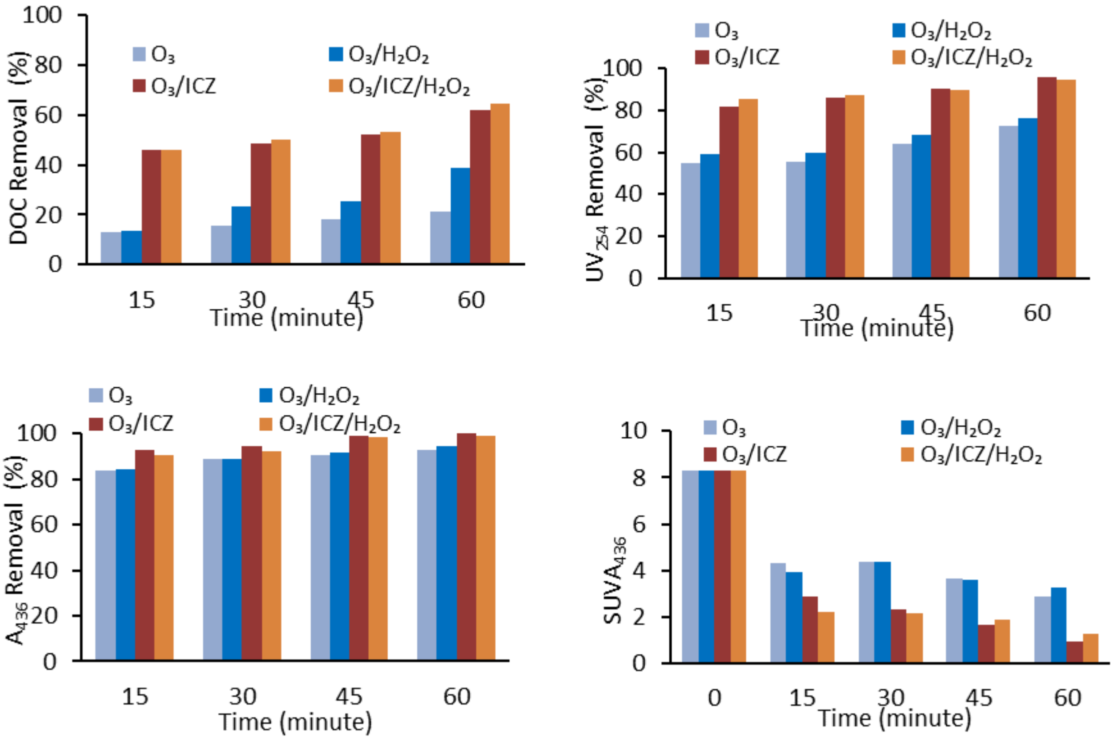


Figure 3. Comparison of ozone, ozone/ICZ, ozone/H_2O_2, ozone/ICZ/H_2O_2 processes for HA removal (concentration of HA=30 mg/L, catalyst dosage=0,75 g/L, pH= 6.5 and ozone concentration= 10mg/LO_3, dose of H_2O_2 of 1 mg/L)

“It has also been reported that the removal efficiency of organic compounds in the O_3/H_2O_2 system depends on the degree of $OH^{\bullet}$ generation”[18]. “The O_3/H_2O_2 process has been used to enhance the oxidation of the ozone refractory organic pollutants [19], but, most of the studies have proved that the H_2O_2 addition is of little contribution in wastewater treatment”[20 ve 24]. “It should be noted that high concentrations of H_2O_2 in the solution may act as $OH^{\bullet}$ scavenger[25] , therefore, reducing the treatment efficiency” [26].

4. Conclusions

In the present study, catalytic ozonation of humic acid (HA) with ICZ and hydrogen peroxide was investigated. It was found that 62.01% of DOC removed by catalytic ozonation with ICZ as the catalyst at ozone concentration of 10 mg/L and oxidation time of 60 min. Increasing ozone concentrations did not increase removal efficiencies significantly in the catalytic ozonation processes. H_2O_2 contributed to the individual ozonation process. However, it contributed to the catalytic ozonation process only a slight decrease of DOC. DOC removal was obtained as 38.8% and 64.6% at H_2O_2 concentration of 1mg/L in ozonation anad catalytic ozonation process.

5. Acknowledgment

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