

## Catalytic Potential of Nano-Magnesium Oxide on Degradation of Humic Acids From Aquatic Solutions

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Received: November 20, 2014; Revised: November 30, 2014; Accepted: December 2, 2014

Catalytic ozonation is a new and promising process used to remove the contaminants from drinking water and wastewater. This study aimed to evaluate the catalytic potential of nano-magnesium oxide (nano-MgO) for the removal of humic acids (HA) from water. Mg (NO<sub>3</sub>)<sub>2</sub> solution was used to prepare MgO powder by the calcination method. In a semi-batch reactor, the catalytic ozonation was carried out. The effects of the various operating parameters, including pH, reaction time, T-butyl alcohol (TBA) and phosphate on HA degradation were evaluated. Experimental results indicated that degradation of HA was increased as the pH solution and reaction time were increased. Maximum HA degradation was obtained at pH = 10 and the reaction time of 10 minutes in the catalytic process. The calculated catalytic potential of nano-MgO on ozonation of HA was 60%. Moreover, catalytic ozonation process was not affected by TBA and the main reaction on HA degradation HA have effect take place on MgO surface. According to the results of this study, the developed MgO catalyst is the active and proficient catalyst in HA degradation using the catalytic ozonation process.

**Keywords:** Catalytic; Ozonation; Humic Acids; Magnesium Oxide

### 1. Introduction

In water treatment plants across the world, chlorination is the most common method for disinfection of water and wastewater (1). During chlorination, natural organic material reacts with chlorine and then forms a group of chlorinated organic compounds known as disinfection byproducts (DBPs), such as trihalomethanes and haloacetic acids. The formation of DBPs is a major concern regarding water disinfected with chlorine. Disinfection byproducts are toxic, carcinogenic, and mutagenic cause cancers of the bladder, kidney, colon, and intestine (1-3). Humic substances (HS) signify up to 90 percent of natural organic material and are believed to be first-class precursors of DBPs. Approximately 30 percent of organic matter eliminated in the most conventional water treatment systems (1). Several processes including membrane, adsorption, coagulation and oxidation have been intended for natural organic matter (NOM) removal from the surface water. The addition of ozone before chlorination is the most promising NOM removal process among the processes suggested for controlling DBP precursors.

Ozone in water and wastewater treatment is used for many different purposes. The application of single-ozonation processes in water treatment due to instability, high cost of production, partial decomposition of organic compounds, slow reactions with some organic compounds and relatively low solubility in water has been

limited. heterogeneous catalytic ozonation as a promising advanced oxidation process has been investigated for degradation of recalcitrant compound in water and wastewater (4-10).

Presently, the nanoparticle technology employed as an effective interest method for a large number of useful applications. Nanoparticle technology provided high surface area materials. Metal oxides, particularly nano-sized alkaline earth due to their destructive sorbence are very important for catalyst applications. As reported in literature (10, 11), the application of magnesium oxide (MgO) as a catalyst in removal of dye and phenol indicated that it is an efficient catalyst in the catalytic ozonation. Actually, MgO is hard, insoluble in water and it has high surface reactivity (10-12). Moreover, MgO is not a toxic compound; thus, if it releases in water, it does not cause any contamination. Therefore, due to this property, it is used in combination with ozone as a catalyst to degrade humic acid (HA) in water in this study. According to the literature, the arrangement of ozone and MgO nano-crystal in heterogeneous catalytic ozonation applied for HA degradation has never been reported.

This study aimed to evaluate MgO nano-crystal as a catalyst and the important parameters in this catalytic ozonation process (COP) (solution pH, scavenger effect, and catalytic potential of MgO nano-crystal).

## 2. Materials and Methods

The MgO nano-crystal powder was prepared using the calcination method. For preparation of the catalyst, Mg (NO<sub>3</sub>)<sub>2</sub> solution was first dried at 100 °C for 8 hours. The dried powder was then calcined at 500 °C for 2 hours in an electrical furnace (13). As a final point, to ensure that the nano-MgO was obtained, the prepared nano-particle was characterized for the average size of particle, surface area, surface morphology and volume and size of pores. Catalytic ozonation performed in a 1-L reactor containing a prepared HA solution. Ozone was generated from the pure oxygen by an ARDA ozone generator (Model AE-5S), and it was fed continuously to the ozonation reactor at 0.5 mg-min/L. Water samples were collected from the reactor during the ozonation period. The ultraviolet (UV) absorbance at wavelength of 254 nm was measured before and after the catalytic ozonation to determine the HA concentration according to the 5910B standard methods (14). The catalytic ozonation potential of the MgO on HA degradation was obtained from the subsequent Equation 1.

$$(1) \quad \begin{aligned} &\text{Catalytic ozonation potential} \\ &= [\text{degradation HA in catalytic ozonation} \\ &- (\text{degradation HA in single-ozonation} \\ &+ \text{adsorption HA on MgO})] \end{aligned}$$

To better illustrate the effects of nano-MgO on HA degradation, the degradation kinetics were investigated. The degradation kinetics of humic substances has been expressed using a pseudo-first-order Equation 2. The kinetics of degradation in the ozonation processes can be written as (15).

$$(2) \quad -\frac{d[\text{HA}]}{dt} = K_{\text{HA}} C_{\text{MgO}}$$

However, as  $C_{\text{MgO}}$  is constant, a second constant phrase can be defined as revealed in Equation 3.

$$(3) \quad K_{\text{obs}} = K C_{\text{MgO}}$$

Consequently, the equation can be written as Equation 4.

$$(4) \quad -\frac{d[\text{HA}]}{dt} = K_{\text{obs}} C_{\text{HA}}$$

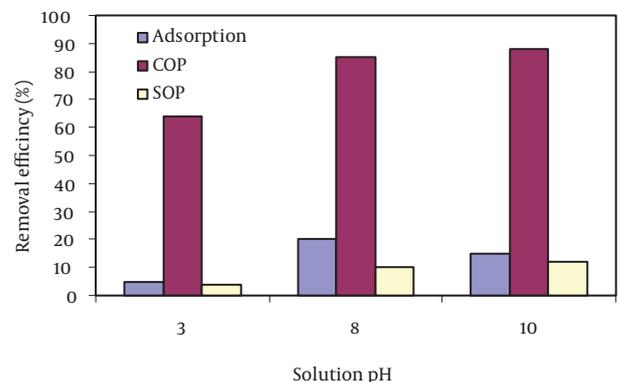
$K_{\text{obs}}$  represents the pseudo-first-order rate constants (min<sup>-1</sup>). The data from both COP and sole ozonation processes (SOP) fitted well to the pseudo-first-order kinetics.  $K_{\text{sop}}$  was calculated via the method as reported by Asgari et al. (15).

## 3. Results and Discussion

The mean size of synthesized MgO was found to be 55 nm. The BET surface area analysis (data not shown) showed that the MgO had a BET of 120 m<sup>2</sup>/g and a total pore volume of 0.166 cc/g. The pH<sup>pzc</sup> of the synthesized powder was determined to be 7.2. The influence of pH on single, catalytic ozonation and HA adsorption on MgO presents in Figure 1. The results of this study indicated that as the pH increased, the HA removal efficiency in

COP, adsorption and SOP increased from 65% to 85%, 5% to 25% and 4% to 15%, respectively. As the results indicated (Figure 1), the HA degradation in SOP and COP was considerably affected by pH of the solution. The pH value of the solution is a key factor that influencing the structure of target contaminates, on the properties of the catalyst surface and on the transfer of ozone from the gas to the liquid phase (15, 16). Actually, the increase pH solution that cause the acceleration of the ozone mass transfer and ozone decomposition rate through both heterogeneous (catalytic) and, homogeneous reaction. These reactions resulted in the formation of highly active radicals (hydroxyl radical and others radicals such as OH, HO<sub>2</sub> and HO<sub>3</sub> and therefore can enhance the degradation rate of HA (17, 18). In all values of pH (3, 8, 10), in the COP, the HA degradation has been more than that of the SOP and adsorption process. In COP, HA was removed by the adsorption, direct, and indirect oxidation processes. Assessment of the HA adsorption onto the MgO and HA degradation in single ozonation at different pH solution indicated that adsorption and SOP removed the maximum HA approximately 20% and 15%, respectively. This result implies that HA is mainly degraded in COP and MgO has low adsorption capacity in HA. Measuring the potential of COP demonstrates a significant catalytic potential for MgO on ozonation in HA degradation. Additionally, the pH<sub>pzc</sub> of MgO was approximately 7.2 and the maximum removal efficiency attained at pH of the solution (10) demonstrates that the functional groups are decomposed on the MgO and the nucleophilicity of these groups increases. Therefore, the rate of reaction with ozone was increased and ozone was converted into highly active radicals, such as an ozonide anion and this radical cycle continued on the MgO surface. Therefore, the HA degradation was increased considerably in COP compared to SOP.

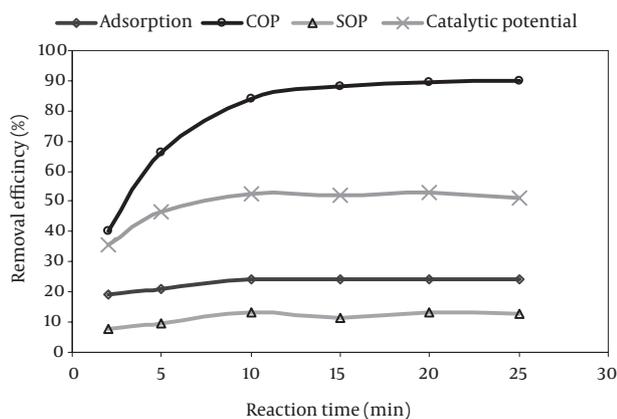
**Figure 1.** The Effect of the pH Solution on Humic Acid Removal in Adsorption, Catalytic Ozonation Process and Single Ozonation Process



HA = 25 mg/L; MgO Dose = 0.1 g; Ozone Flow Rate 0.5 mg-min/L and Reaction Time (minute) = 10.

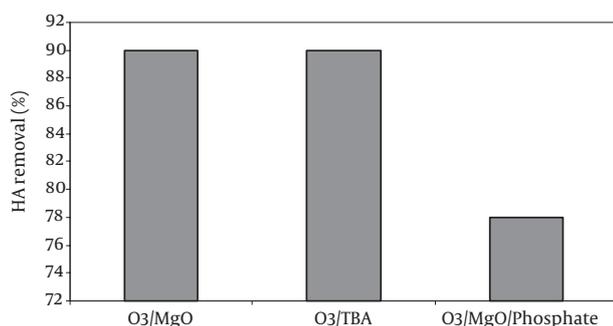
Figure 2 showed the calculated potential of MgO to catalyze the HA using the Equation 1 and the effect of reaction time on HA degradation in catalytic ozonation. As seen in Figure 2, the degrees of HA removal via adsorption onto MgO and by single-ozonation were both less than 22%. The catalytic potential of MgO increased from 40% to 90% with an increase in the reaction time from 2 to 25 minutes. The results showed that MgO considerably accelerated the rate of HA degradation and it is consequently an excellent catalyst to be applied for catalyzing the ozonation of model refractory compounds. This catalytic potential of MgO in HA degradation may result in the presence of high density of basic functional groups that results in the decomposition of ozone on the surface of MgO and in the formation of active radicals (4).

**Figure 2.** Potential of Magnesium Oxide to Catalyze of the Humic Acid and the Effect of Reaction Time on Removal of Humic Acid in Catalytic Ozonation, Single Ozonation Process and Adsorption



Humic Acid = 25 mg/L; Magnesium Oxide Dose = 0.1 g; Ozone Flow Rate 0.5 mg-min/L and pH= 8.

**Figure 3.** The Effect of Scavenger t-butyl Alcohol, Phosphate on Humic Acid Removal and Mechanism of Humic Acid Degradation



Reaction Time (Minute) = 25, Humic Acid = 25 mg/L; Magnesium Oxide Dose = 0.1 g; Ozone Flow Rate 0.5 mg- min/L.

The data of the presence of phosphate and t-butyl alcohol on COPs are indicated in Figure 3. According to these data, the HA removal efficiency in catalytic ozonation in the presence of t-butyl alcohol was not decreased, while HA removal efficiency, in the presence of phosphate was decreased by 12% (Figure 3). This result suggested that COP with MgO is an excellent process as compared with other advance oxidation process. The results of this study confirmed that the main reaction in HA degradation took place on the surface of MgO and was not affected by the OH radical scavenger. Results from the evaluation of presence of phosphate in COP reconfirmed the previous suggestion. Bonded phosphate with the functional groups on the MgO surface resulted in decreasing the HA degradation on the surface of the catalyst. The results of this study are in accordance with those of the other studies (10-12).

The HA degradation rates are presented in Table 1. As shown in Table 1, the HA degradation rate constant in both processes under the given conditions was increased with increasing pH. Table 1 further illustrates that the COP process performed better than SOP. At each pH level, MgO had a greater effect on HA decomposition or degradation rates compared to SOP. The pseudo-first-order rate ( $k_{SOP}$ ) of SOP was increased from 0.06 min<sup>-1</sup> to 0.13 min<sup>-1</sup>, while the COP  $K_{obs}$ -value was increased from 0.2 min<sup>-1</sup> to 0.45 min<sup>-1</sup> when pH was increased from 3 to 10. The ratio of  $k_{obs}/k_{SOP}$  under acidic conditions is 3.3. Hence, the presence of MgO increased the rate of reaction 3.3-fold in acidic conditions. Under alkaline conditions, the  $K_{obs} / k_{SOP}$  ratio increased to 3.64 (at pH 8) and 3.5 (at pH 10). This confirms that MgO acts as a catalyst promoting HA degradation. This findings demonstrate that catalytic ozonation with MgO is a valuable process in degradation of HA from water. According to the results of this study, the heterogeneous catalytic ozonation process is an excellent process for the replacement of SOP and other AOP.

**Table 1.** Kinetics of Humic Acid Removal for Different pH Values in Catalytic Ozonation Process and Single Ozonation Process<sup>a,b</sup>

Process, pH	Parameters	
	$K_{SOP}, \text{min}^{-1}$	$R^2$
<b>SOP</b>		
3	0.06	0.95
8	0.11	0.96
10	0.13	0.99
<b>COP</b>		
3	0.2	0.98
8	0.4	0.99
10	0.45	0.98

<sup>a</sup> Abbreviations: COP, Catalytic Ozonation Process; SOP, Single Ozonation Process.

<sup>b</sup> Conditions: Reaction time (min) = 25, HA = 25 mg/L; Magnesium Oxide dose = 0.1 g; Ozone Flow Rate 0.5 mg-min/L

## 4. Conclusions

The findings revealed that the prepared catalysts had a  $pH_{zpc}$  of 7.2, the average size 55nm and the specific surface area of 120m<sup>2</sup>/g. The HA degradation was mainly done through a series reaction on surface nano-particles. COP is an efficient process in HA degradation and it can be applied in field condition. Moreover, MgO is the simply accessible matter and has the desired potential as a catalyst. Accordingly, MgO can be employed in water and wastewater treatment to mineralize the recalcitrant pollutant.

## Acknowledgements

The authors are grateful for the financial assistance provided by the Hamadan University of Medical Sciences (Grant number 901216208) in conducting this research.

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