Chemical Engineering Journal 152 (2009) 1–7

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Degradation and biodegradability improvement of the reactive red 198 azo dye using catalytic ozonation with MgO nanocrystals

Gholamreza Moussavi*, Maryam Mahmoudi

Department of Environmental Health, School of Medical Sciences, Tarbiat Modares University, Tehran, Iran

ARTICLE INFO

Article history:
Received 11 January 2009
Received in revised form 2 March 2009
Accepted 5 March 2009

Keywords:
Dye removal
Catalytic ozonation
MgO/O_3
Decolorization
COD removal

ABSTRACT

The catalytic ozonation of RR198 solution in the presence of MgO nanocrystal catalysts was investigated in a laboratory scale batch reactor. The effects of solution pH (2–12), reaction time, MgO dosage (1–6 g/L), and initial dye concentration (100–500 mg/L) on color and COD removal were evaluated, and the findings were compared to those of ozonation without a catalyst. The results indicate that adding MgO nanocrystals into the ozonation reactor greatly accelerated the rate of RR198 degradation, thereby reducing the reaction time and improving the reduction of color and COD compared to conventional ozonation. The optimum pH and catalyst dosage values were determined to be 8 and 5 g/L, respectively. The complete removal of color was observed in COP at this optimum condition for an RR 198 concentration of 200 mg/L at a reaction time as short as 9 min, while the time required to attain the same performance at single ozonation was 30 min. Furthermore, the COP could markedly increase the ratio of BOD_5 to COD from below 0.1 in raw solution to 0.63 to 0.38 for dye solutions of 100 and 500 mg/L, respectively; thus, RR 198 was converted to biodegradable compounds. Therefore, the COP on MgO nanocrystals is considered as an effective and feasible process for pre-treating the azo dye-laden solutions, making possible a post-treatment of the effluent in a biological system.

1. Introduction

Dyes are synthetic aromatic compounds used to colorize products of many different industries, including textiles, tanneries, pharmaceuticals, pulp and paper, paint, plastics, food, and electroplating [1–4]. Generally, a significant quantity of the consumed dyes finds its way to the industrial effluent [2,5]. Since most of the dye molecules are toxic, recalcitrant, and chemically and photochemically stable and impart undesirable color to the receiving waters [5–7], their release to the environment may pose many serious aesthetical, ecological, environmental and health hazards. Different physical, chemical, and biological methods, or combinations thereof, have been investigated for removal of color from dye-laden wastewater via pretreatment, main treatment and post-treatment processes [8–13]. Due to the complexity of the dyes' aromatic molecular structure, the conventional biological and physical–chemical processes are less suitable for their efficient treatment and mineralization [6,14,15]. Therefore, researchers are faced with the challenge of presenting a viable and efficient technique for treating the dye-containing wastewater, specifically one designed to mineralize the dye molecules. A review of the literature shows a growing interest in developing advanced oxidation processes (AOPs) for the treatment of liquid streams containing toxic and xenobiotic compounds, including dyes. The AOPs' simplicity, low cost, and high efficacy all factor into the their increasing popularity as a new technique for dye removal [8,16]. Interestingly, the AOPs can completely stabilize the organic compounds into water and carbon dioxide [17]. So far, several AOPs have been developed and investigated for use in the water and wastewater treatment industry [18], most of which are based on using ozone as the principal oxidant. Although single ozonation has been shown effective for color removal, it has little effect on dye mineralization [19]. Hence, considerable attention has recently been paid to investigating the catalytic ozonation process (COP) as a novel AOP. Indeed, adding a catalyst to the ozonation reaction leads to an increased oxidation rate and decreased reaction time, thereby reducing the treatment cost [20]. However, the effectiveness of the COP depends on operational variables, including solution pH and temperature, structure of the target compound(s), type and dose of the catalyst, dose of ozone, and reactor configuration. The COP can be used either homogenously or heterogeneously [16,21,22], with each way mineralizing organic molecules by direct oxidation with ozone molecules and/or by indirect radical oxidation [20,23,24]. Heterogeneous catalytic ozonation is an appealing wastewater treatment process due to its low cost, potential for catalyst reclamation, and lack of secondary pollution [25]. Several reports have been published

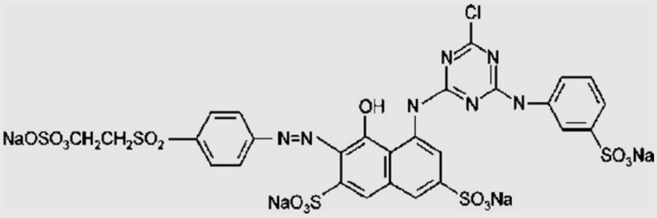
---

* Corresponding author at: Department of Environmental Health, School of Medical Sciences, Tarbiat Modares University, P.O. Box 14115-331, Tehran, Iran. Tel.: +98 21 82883827.

E-mail address: moussavi@modares.ac.ir (G. Moussavi).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.03.014

Table 1
Main properties of the model azo dye (RR198).

Parameter	Characteristic
Chemical formula	$C_{27}H_{18}C_{l}N_7Na_4O_{15}S_5$
Class	Azo
C.I. number	18221
Molecular weight (g/mol)	967.5
λ_{max} (nm)	518
Molecular structure	

in the last decade on using catalytic ozonation for dye removal [20–22,26–30], describing the COP as a promising and effective process for the removal and mineralization of persistent organic wastewater contaminants such as dye molecules. Most efforts in recent years have been focused on preparing and studying new catalysts to improve COP efficiency in removing different contaminants.

Nanosized alkaline earth metal oxides are very promising materials for catalyst applications due to their destructive sorbence [31,32], high surface reactivity, and adsorption capacity [33]. He et al. [23] observed that using magnesium oxide (MgO) along with ozonation could accelerate phenol and COD removal from solution. However, the catalyzing capabilities of MgO in the COP for dye removal have not been reported.

This work focused on the preparation and application of MgO nanocrystals as catalysts in the COP, comparing the performance with ozonation alone in the removal of reactive red 198 (RR198) as the model azo dye. The effect of the main operational variables, including pH, reaction time, catalyst dose, and initial dye concentration, on the COP's performance will be compared to the performance of ozonation alone under the same conditions.

2. Materials and methods

2.1. Materials and catalyst preparation

The selected model dye was obtained from the DyStar Co. (Germany) through a local textile company and used as received. The chemical structure and maximum absorbance wavelength of the selected dye are given in Table 1. All chemicals and reagents used were of analytical grade and purchased from Merck. Distilled water was used in the preparation of all solutions used in these experiments. MgO nanocrystal powder was prepared by calcinating a $Mg(NO_3)_2$ solution. The $Mg(NO_3)_2$ solution was first dried at 100 °C. The remaining material was calcinated in air at 500 °C for 2 h, producing the final MgO nanocrystals. The surface morphology and textural properties of the catalyst were studied.

2.2. Experimental apparatus and procedure

The experimental set-up was composed of a Pyrex cylindrical sparger as the ozone contactor, an ozone generator, a sintered glass diffuser to distribute the ozone to the solution, an air pump with the control valve, a flow meter, an ozone off-gas destruction system, and valves and tubing. The catalytic ozonation reactor was a magnetically stirred column with a total volume of 150 mL. The experiments were performed at a temperature of 23 ± 3 °C under batch reaction, with 100 mL of dye solution in each run throughout the study. Different operational variables, including pH of the dye solution, dye concentrations, catalyst dose, and reaction time, were investigated. MgO nanocrystals were used as the ozonation catalyst for oxidation of the reactive azo dye. As stated previously, the RR198 was selected as the model azo dye. In addition, control experiments were performed with ozonation alone to verify the catalytic nature of the catalyst. Ozone was generated from the air by a commercial generator (ARDA, model AEGCOG-5S). The dose of ozone was considered constant at 0.2 g/h throughout the experiment. The ozone in the off-gas stream of the reactor was quenched and destructed in a 2% KI solution.

2.3. Analytical methods

The powder produced was characterized for specific surface area, average particle size, particle surface morphology, and the volume and size of pores. The specific surface area and pore characteristics of the particles were determined by the nitrogen adsorption technique (Micromeretics/Gemini-2372). Average pore size was determined from the following equation [34]:

$$D_p = \left(\frac{4V}{S}\right) \times 10^3 \qquad (1)$$

where, D_p is the mean pore diameter (nm), V is total pore volume (cc/g), and S is the BET surface area (m^2/g).

The morphology of the particles was investigated using scanning electron microscopy (SEM) images from a Philips–XL30 Electron Microscope. In order to assess the performance of catalytic ozonation in degrading RR198 and its corresponding organic content, samples were taken from each experimental run at the beginning and end of the reaction. The samples were analyzed for RR198, chemical oxygen demand (COD), and pH. The residual dissolved ozone was quenched by adding sodium thiosulfate solution to the samples prior to dye analysis. The concentration of RR198 was determined using a Unico-UV 2100 UV–vis spectrophotometer at its maximum absorbance wavelength of 518 nm. The color removal in each experiment was calculated from the difference of initial (before reaction) and final (after reaction) concentrations of RR198. COD was measured by the standard method of potassium dichromate oxidation [35]. pH was determined using an electrode (Sense Ion 378, Hack). The ozone concentration in the inlet gas stream was analyzed by iodometric titration [35]. To ensure the reproducibility of data, each experiment was conducted in duplicate and the average of the two measurements was reported.

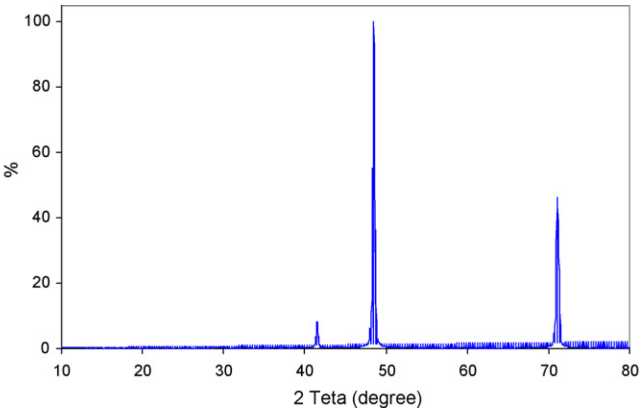


Fig. 1. XRD pattern of the fabricated powder.

3. Results and discussion

3.1. Catalyst characteristics

The pattern of the synthesized MgO is given in Fig. 1, which shows the cubic and pure periclase MgO crystalline particles in the powder [32]. The average size of crystals, calculated from Scherrer's equation, was found to be 65 nm. The SEM image shown in Fig. 2 is used to visualize the surface morphology of the synthesized MgO; the image indicates porous, agglomerated and honey-combed nanocrystals. The nitrogen adsorption–desorption isotherm (data not shown) indicated that the synthesized powder had a BET surface area of 118 m^2/g and a total pore volume of 0.156 cc/g. The mean size of the pores calculated from the Eq. (1) was found to be 5.3 nm. These findings reveal that the fabricated powder was composed of mesoporous nanocrystals that had a high specific surface area.

3.2. Effect of initial pH and reaction mechanism

Since solution pH plays an important role in the contaminant degradation mechanism during an oxidation process, it is relevant to evaluate the effect of pH in catalytic ozonation of the selected model dye. Therefore, the effect of the dye solution's initial pH on degradation and COD removal of RR198 was studied at pH values ranging from 2 to 12, under constant reaction time and ozone dosing, in both non-catalyzed ozonation and catalytic ozonation with MgO nanocrystals. Fig. 3 shows the removal percentages of color and COD as a function of initial pH in non-catalyzed and catalytic ozonation, respectively. As seen in Fig. 3a, the percentage of color removal in the non-catalyzed ozonation process at an acidic pH of 2 was 91%, and it decreased to 85% when pH was increased to 6. The high color removal at a pH of 2 is related to the direct oxidation of ozone with dye molecules, which is best performed at a more acidic pH [22]. The removal of color from the solution increased for a pH above 6 and reached a maximum value of 97% at a pH near 10, which is 12% higher than that at a pH of 6. As pH increases to alkaline conditions, the rate of ozone decomposition accelerates, resulting in the production of more reactive radicals [36]. Hence, most of the degradation of RR198 molecules, and thus color removal, at alkaline pHs likely occurs by indirect oxidation with radicals. However, some direct oxidation with non-decomposed ozone molecules also might occur. Erol and Özbelge [22] observed higher dye removal rates by ozonation at alkaline conditions (pH 13) than acidic conditions (pH 2.5), and they attributed this result to the formation of hydroxyl radicals at high pH. In contrast, Arslan [26] showed that the removal of color by the ozonation of simulated dispersed dye-bath water performed better at acidic pH than alkaline pH. Predicting the mechanism of dye molecule oxidation by an ozonation process depends on the structure and solubility of the target dye molecule at different pHs [26] and thus requires determining the ozone and OH radical concentrations in the reactor, as well as the rate of reaction of the target compound with both ozone and OH radicals [36]. Fig. 3a also illustrates the trend of COD removal of RR198 as a function of the solution pH. Removal of COD had almost the same trend as color with the value around 46% at a pH of 10, where the highest color removal was observed. It can be inferred

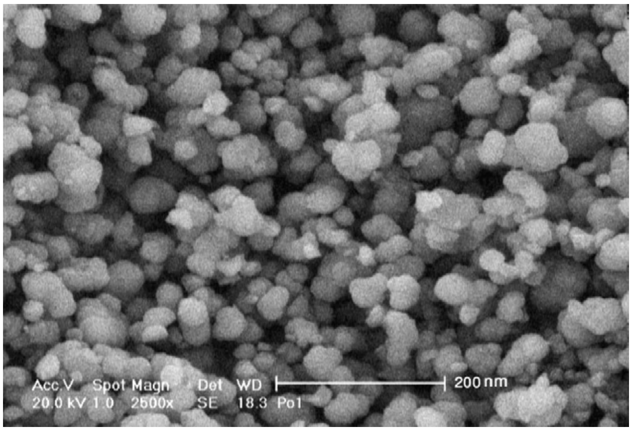


Fig. 2. SEM images of fabricated MgO particles.

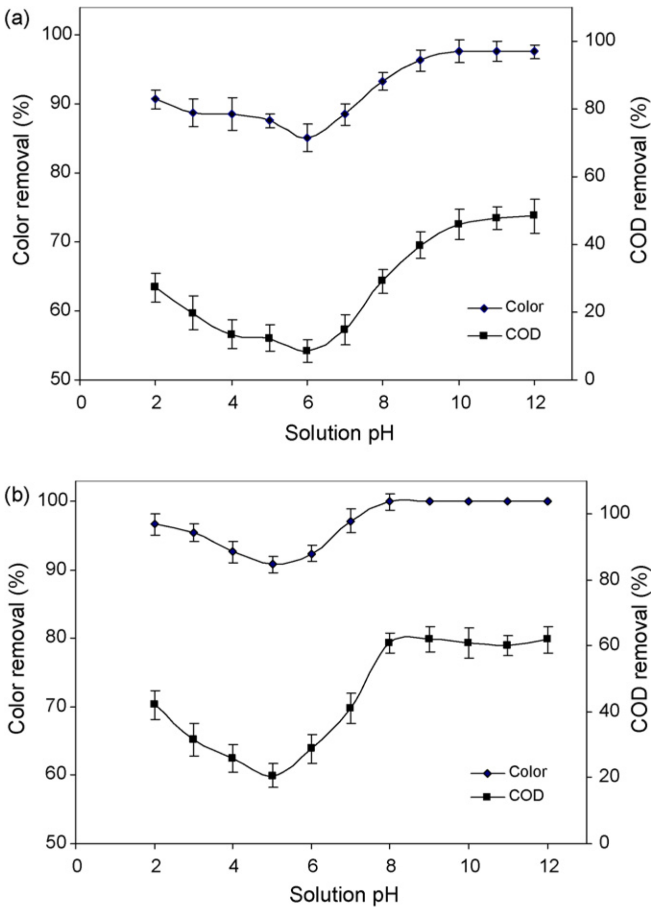


Fig. 3. Effect of initial pH on color and COD removal from RR198 solution in: (a) the conventional ozonation reactor (RR198 concentration = 200 mg/L, reaction time = 20 min), and (b) the COP (RR198 concentration = 200 mg/L, MgO dosage = 5 g/L, reaction time = 10 min).

from the relationship between COD removal and pH that radical oxidation was likely the predominant mechanism involved in oxidizing the intermediates and thus reducing COD. Fig. 3b presents the color and COD removal of RR198 by catalytic ozonation with MgO nanocrystals. It shows that a removal of 97% color was attained at a pH of 2, but the degradation reduced to 91% when the pH was lowered to 6. This reveals that the removal of RR198 with catalytic ozonation under acidic pH was due to direct oxidation by the ozone molecules, as was the case with non-catalyzed ozonation. The removal of color began to increase with the increase of pH above 6, reaching a maximum of 100% at a pH of 8. For COD removal of RR198 versus solution pH in the catalytic ozonation experiments (Fig. 3b), the results indicated a trend similar to that of color removal, although with a lower rate. COD removal decreased from 42% at a pH of 2 to around 21% at a pH of 5, and it then increased to 61% when the pH was increased to 8. Since hydroxyl radicals are mainly generated at pHs above 10 [23,37,38], the maximum COD and color removal obtained at pH of 8 can be explained by the formation of radical species other than hydroxyls, and/or the MgO has reduced the optimum pH for generation of hydroxyl radicals. The percent of removed COD remained almost unchanged with the increase of pH to 12. It is presumed that, at this high pH, hydroxyl radicals are the predominant species providing higher degradation and COD removal of RR198. These findings imply that the pH of the dye solution acts as an important factor in both non-catalyzed and catalytic ozonation of RR198, and that catalytic ozonation performed better in color and COD removal of RR198 with a much lower reaction time. Dong et al. [21] found a negative effect for pH in the ozonation of brilliant red X-3B.

The increased removal percentage of color and COD corresponding to alkaline pH can be further attributed to the resulting increase in available hydroxide ions and acceleration of the ozone decomposition [39,40], which thereby increases the formation of oxidative radicals such as hydroxyl and MgO-hydroxyl radicals. Following mechanisms were assumed to account for radical formation in the presence of ozone and MgO: the action of MgO as an initiator for radical formation in the bulk solution, and the adsorption of ozone on the surface of MgO, which causes its decomposition into active radicals.

$$O_3 + (MgO - s) \rightarrow (MgO - s^{O_3}) \tag{2}$$

$$(MgO - s^{O_3}) \rightarrow (MgO - s^{O^\bullet}) + O_2 \tag{3}$$

$$(MgO - s^{O^\bullet}) + 2H_2O + O_3 \rightarrow (MgO - s^{^\bullet OH}) + 3^\bullet OH + O_2 \tag{4}$$

(The suffix *s* in MgO-s denotes the Lewis acid site on the surface of MgO).

As seen in Eqs. (2)–(4), several radicals are generated in the reaction, all leading to improvement in RR198 oxidation. These radicals caused indirect oxidation of the RR198 molecules with higher rates than those seen with single ozone oxidation [30,41] and in turn enhanced the degradation of organics in the solution. Similar mechanisms were proposed by Faria et al. [42] for catalytic ozonation of oxamic and oxalic acids on activated carbon. Addition of *tert*-butanol to the COP resulted in a marked reduction of color and COD removal percentages, confirming that degradation of RR198 followed the radical oxidation mechanism. Direct oxidation of the RR198 dye by ozone molecules might also occur in the catalytic ozonation, as is seen with non-catalytic ozonation. Wu et al. [30] reported that the degradation of reactive red 2 in the UV/TiO_2/O_3, O_3/Mn(II) and O_3/MnO_2 processes occurred mainly via radical, surface and radical type mechanisms, respectively.

As shown in Fig. 3, the removal of color in both non-catalyzed and catalytic ozonation was greater than the removal of COD. A possible explanation for this is that the azo bonds (N═N) are more easily destroyed than the aromatic bonds [20], so the azo RR198 dye present in the ozone-based oxidation processes is preferentially decolorized by cleavage of the chromophore and by breaking down the azo bond in the dye molecule structure into the more simple intermediates [8,43]. The resultant organics subsequently underwent further oxidation and mineralization, directly by ozone and/or indirectly by the generated radicals, which led to the reduction of COD. The oxidation of the dye molecules and intermediates might be taking place both in bulk solution and on the catalyst surface, using both radicals and molecular ozone. Because of the large specific surface area of the catalyst in these experiments, the degradation on the surface of the catalyst likely played a significant role in the dye degradation. Gül et al. [29] investigated the catalytic ozonation of reactive red 194 and reactive yellow 145 in aqueous solution on granular activated carbon (GAC) and concluded that, although hydroxyl radicals were formed on the surface of GAC, the primary oxidative reactions responsible for degrading organic structures took place in the bulk solution.

It is known that the ozonation of a solution with pH higher than 10 can result in the formation of strong oxidative radicals, mainly hydroxyl radicals [23,37,38]. Fig. 3 clearly shows this phenomenon for conventional ozonation of RR198. A comparison of conventional and catalytic ozonation with MgO nanocrystals (seen in Fig. 3) revealed that MgO could reduce the pH at which radicals form in the ozonation process. It can be further inferred that MgO nanocrystals effectively catalyzed the decomposition of ozone and accelerated the formation of oxidative radicals, resulting in an increased oxidation rate and thereby a reduction in the required reaction time. These are very important features from both operational and economical standpoints. Although a few researchers [e.g., 23,30,44–46] have previously indicated that metal oxides are active catalysts that decompose ozone in solution to form oxidative radicals, the order of chemical reactions and the type of radical formed depends greatly on the type of metal oxide and the reaction conditions. Since the color and COD removal of RR198 in COP was highest at a pH of 8, this was selected as the optimum value in the subsequent ozonation experiments.

3.3. *Effect of reaction time*

One of the important variables affecting the design and operation of an oxidation process is the reaction time, which is the time required to attain the desired goals of the treatment. Accordingly, the second phase of this experiment was to investigate the removal of color and COD of RR198 by catalytic ozonation as a function of reaction time, under the optimum initial pH value of 8 and a dye concentration of 200 mg/L, compared with the non-catalyzed process operated at the similar condition. Fig. 4 depicts the color and COD removal of RR198 versus the reaction time under the specified conditions in conventional and catalytic ozonation processes, respectively.

Referring to Fig. 4, it can be observed that removal of both color and COD increased with an increase in reaction time for both processes, although at a rate higher for color than COD removal, and higher for catalytic than conventional ozonation processes. For conventional ozonation process, the color removal of RR198 increased from zero at the beginning of the experiment to around 78% after 10 min of ozonation (Fig. 4a). Increasing the reaction time to 30 min led to 98% color removal. A similar trend was observed for COD removal in the non-catalyzed ozonation process. The COD removal of RR198 was 20% after 10 min of ozonation, and it increased to 50% after 30 min of ozonation (Fig. 4a). The results indicate that the RR198 degradation in the conventional ozonation process was best fitted with a pseudo-first-order reaction, with a reaction constant of approximately 0.16/min.

Fig. 4b presents the results of decomposition and COD removal of RR198 in the catalyzed ozonation using MgO nanocrystals. As observed, the COP could achieve 83% color removal after a reaction

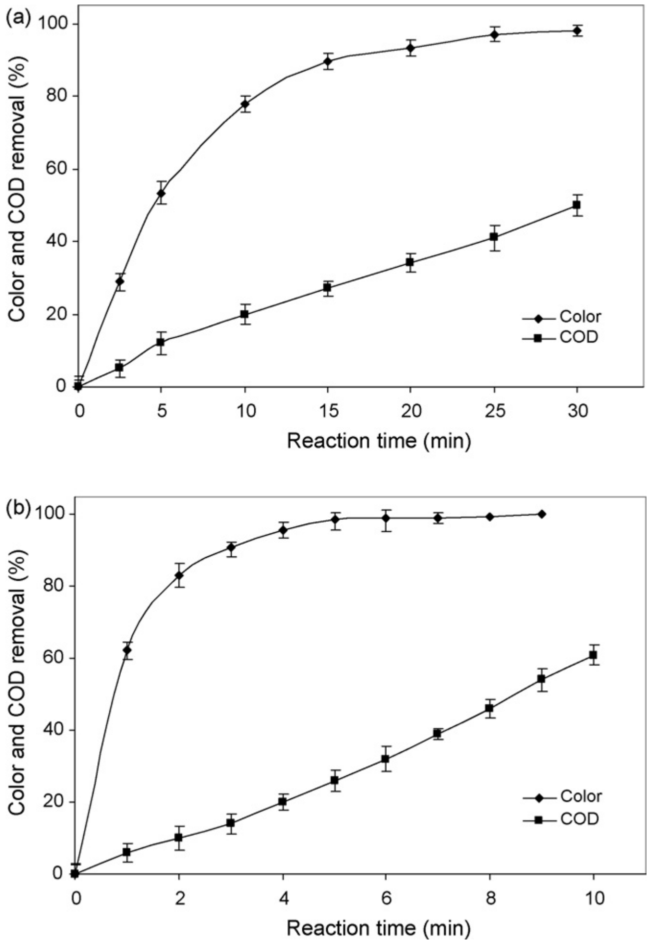


Fig. 4. Effect of reaction time on color and COD removal from RR198 solution in: (a) the conventional ozonation reactor (RR198 concentration = 200 mg/L, initial pH 8), and (b) the COP (RR198 concentration = 200 mg/L, initial pH 8, MgO dosage = 5 g/L).

time of only 2 min. The percentage of color removal increased to 99% after 5 min and to 100% after 9 min of the reaction. In addition, the COP achieved 61% removal of COD from the solution after 10 min of the reaction. Similar to the conventional ozonation process, the degradation of RR198 in the COP was found to be a pseudo-first-order reaction with constant of 0.63/min. Comparing the results indicates that adding MgO nanocrystals to the ozonation reactor could significantly accelerate the decomposition rate of RR198. Overall, the higher the rate of the oxidation reaction, the shorter the time required to complete the reaction and, in turn, the smaller the required reactor size and treatment cost.

No previously published report could be found on catalytic ozonation of dyes using MgO for comparison with results of the present work. The findings presented here imply that MgO nanocrystals are very promising catalysts for application in ozonation of dye-containing solutions. Due to their high surface area and reactivity [33,47], destructive ability [31], and the simplicity of their production from an abundant natural mineral (brucite), MgO nanocrystals are preferable catalysts from both technical and economical points of view for the augmented degradation of organic compounds from wastewaters.

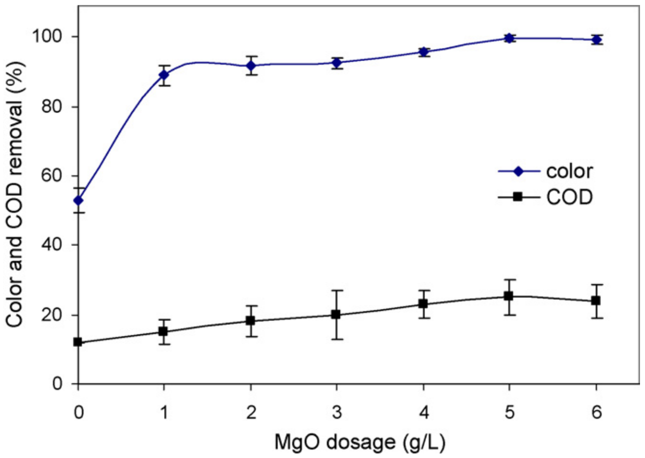


Fig. 5. Effect of MgO dosage on color and COD removal from RR198 solution in the COP (RR198 concentration = 200 mg/L, initial pH 8, reaction time = 5 min).

3.4. *Effect of MgO dosage*

The catalytic ozonation of RR198 solution in the presence of various concentrations of MgO nanocrystals (ranging between 0 and 6 g/L) was evaluated, and the relative performance in the degradation and COD removal of RR198 was determined. All experiments in this phase were carried out at the constant reaction time of 5 min (at which the previous experiments showed 99% color removal), at an RR198 concentration of 200 mg/L, and at the optimum pH of 8. Fig. 5 shows the color and COD removal of RR198 as a function of catalyst concentration in the solution under reaction, revealing an improving effect of MgO in the ozonation process. As illustrated in Fig. 5, the color removal increased from 53% in the absence of catalyst to 89% in the presence of 1 g/L MgO powder. Thereafter, it improved slightly to over 99% when the MgO dosage was increased to 5 g/L. A further increase in MgO dosage to 6 g/L did not increase the color removal. Thus, relatively a small dosage of MgO is needed to catalyze and enhance the degradation of RR198. This can be explained by the high surface area of MgO, which allows a small amount of MgO to provide the required reactive surface for the ozone added to the reactor to induce and propagate the chain of radical reactions [41]. The removal of COD showed a different trend with the dosage of MgO (Fig. 5). As shown in Fig. 5, removal of COD increased almost linearly from 12% to 25% with the increase of MgO dosage from zero to 5 g/L at a constant contact time; further increasing the catalyst dosage caused no significant change in the removal of COD. Low COD removal at these experimental conditions is due to short reaction time. On the basis of these results, 5 g/L was selected as the optimum dosage of MgO for the subsequent experiments.

He et al. [23] observed that adding 5 g/L of MgO powder to a phenol solution in an ozonation reactor accelerated the oxidation efficiency. Similarly, other researchers have reported increased oxidation efficiency in metal-based COPs with increased catalyst dosage [26,48]. However, the optimum catalyst dosage depends significantly on the type of catalyst, the reactant(s), and the reaction conditions. Comparing the removal of color and COD against applied MgO dosage shows that the effect of MgO dosage on COD removal is apparently more significant than its effect on decolorization. In addition, the degradation of RR198 was revealed to occur mainly in the bulk solution, whereas its degradation intermediates were primarily oxidized on the catalyst surface.

3.5. *Effect of initial dye concentration*

Despite the fact that industrial wastewaters often contain different concentrations of dye, most of the studies on catalytic ozonation have been carried out using a specific target compound concentration. Therefore, it is very important from a practical point of view to study how the initial dye concentration affects the performance of a COP in the removal of color and organics. The effect of initial

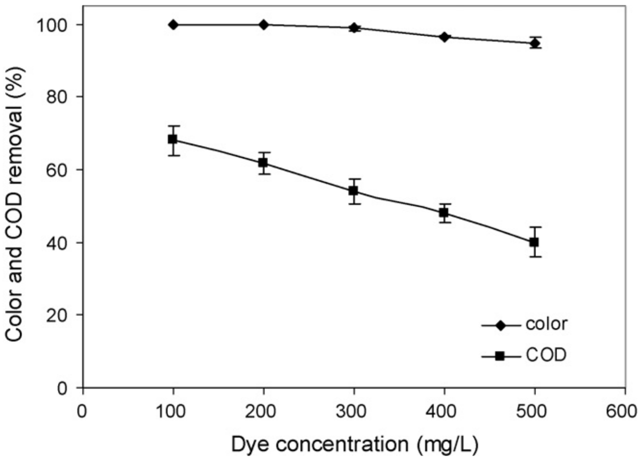


Fig. 6. Effect of initial dye concentration on color and COD removal from RR198 solution in the COP (initial pH 8, reaction time = 10 min, MgO dosage = 5 g/L).

RR198 concentrations of 100–500 mg/L on color and COD removal in the COP was investigated at an initial pH of 8 and reaction time of 10 min. Fig. 6 depicts the color and COD removal of RR198 at various initial concentrations.

As shown in Fig. 6, the color removal efficiencies in COP for initial concentrations of 100, 200, 300, 400 and 500 mg/L were 100%, 100%, 99%, 97% and 95%, respectively, indicating a trend of reduced removal with increasing initial dye concentration. The COD removal efficiency for the corresponding dye concentrations were 69%, 62%, 54%, 48% and 40%, respectively, showing a similar reduction trend. The rate of reduction in COD removal efficiency was more noticeable than that for color, suggesting that more ozone is required to oxidize the intermediates from the dye degradation. This can be supplied by increasing the ozonation dose either via increased ozone flow rate and/or increased ozonation time.

These findings show that the dye concentration in the range tested had no significant influence on the RR198 degradation (color removal). However, it markedly affected the COD removal efficiency. A possible explanation for this finding might be a greater affinity of the ozone for dye compounds than for their intermediates; therefore, as more organic intermediates were likely being generated and accumulated in the reactor with the increase of initial dye concentration, they contributed to the COD measurement and thereby decreased the measured COD removal.

3.6. Biodegradability enhancement of the COP effluent

The biodegradability of a wastewater is usually evaluated in terms of the BOD_5 to COD ratio [49]. The biodegradability of raw and COP-treated RR 198 solutions was investigated at different concentrations in order to show the capability of using biological treatment for the post-treatment of COP effluents. The results are given in Fig. 7. It should be noted that the ratio of BOD_5 to COD in raw solution at all dye concentrations was below 0.1, indicating that RR 198 is a recalcitrant compound. As shown in Fig. 7, the BOD_5 to COD ratio of the dye solution at all experimental concentrations after passing the pretreatment step in COP (under condition of pH 8, MgO dose = 5 g/L and reaction time = 10 min) increased and ranged from 0.38 to 0.63. This indicates that the biodegradability of RR198 significantly improved after a short reaction time in COP and was converted to a biodegradable waste. The enhancement of the biodegradability is related to cleavage of the azo bonds and aromatic rings and thus the conversion of the dye molecules into simple and more degradable intermediates such as acetic acids, aldehydes, ketones, etc. [50]. Since a wastewater having the BOD_5 to COD ratio of 0.4 and higher is considered easily biodegradable

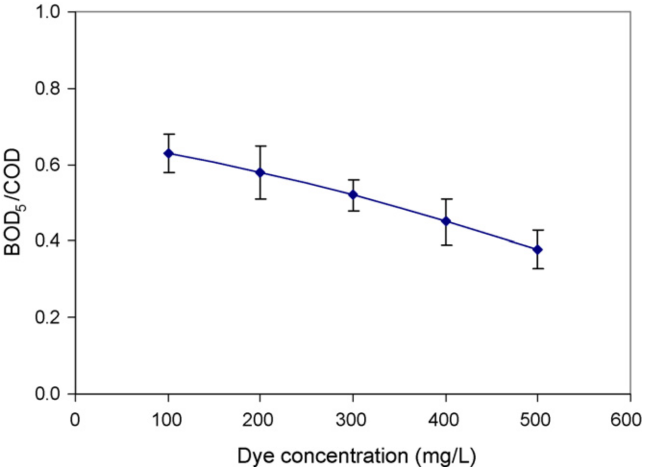


Fig. 7. Effect of catalytic ozonation on biodegradability of different concentrations of (initial pH 8, reaction time = 15 min, MgO dosage = 5 g/L).

[51], it can be concluded from these results that the effluent from catalytic ozonation with MgO nanocrystals treating azo dyes is biodegradable enough to be easily post-treated in a biological reactor.

4. Conclusions

This paper presents the results of experiments performed using MgO as a catalyst in the ozonation processe for degrading RR198 as the selected reactive azo dye. The MgO nanocrystals exhibit unique features of a particularly high specific surface area, increased destructive ability, and simplicity of production, demonstrating their promise as a catalyst for catalytic ozonation of dye-containing wastewater. MgO nanocrystals were demonstrated to be effective catalysts in the catalytic ozonation of dye-containing solutions since it notably accelerates decolorization and COD removal and reduces the required oxidation time compared to non-catalyzed ozonation. The catalytic ozonation with MgO nanocrystals could also significantly improve the biodegradability of the selected dye, making possible the post-treatment of the effluent in a bioreactor.

Acknowledgement

The authors gratefully acknowledge the financial and technical support provided by the Tarbiat Modares University, Tehran, Iran.

References

[1] P. Nigam, G. Armour, I.M. Banat, D. Singh, R. Marchant, Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues, Bioresour. Technol. 72 (2000) 219–226.
[2] Z. Aksu, G. Karabayır, Comparison of biosorption properties of different kinds of fungi for the removal of Gryfalan Black RL metal-complex dye, Bioresour. Technol. 99 (2008) 7730–7741.
[3] E. Demirbas, M. Kobya, M.T. Sulak, Adsorption kinetics of a basic dye from aqueous solutions onto apricot stone activated carbon, Bioresour. Technol. 99 (2008) 5368–5373.
[4] V.K. Gupta, I. Ali, V.K. Saini, Adsorption studies on the removal of Vertigo Blue 49 and Orange DNA13 from aqueous solutions using carbon slurry developed from a waste material, J. Colloid Interface Sci. 315 (2007) 87–93.
[5] B.-T. Low, Y.-P. Ting, S. Deng, Surface modification of Penicillium chrysogenum mycelium for enhanced anionic dye removal, Chem. Eng. J. 141 (2008) 9–17.
[6] M.A. Khalaf, Biosorption of reactive dye from textile wastewater by non-viable biomass of Aspergillus niger and Spirogyra sp., Bioresour. Technol. 99 (2008) 6631–6634.
[7] F. Renault, N. Morin-Crini, F. Gimbert, P.-M. Badot, G. Crini, Cationized starch-based material as a new ion-exchanger adsorbent for the removal of C.I. Acid Blue 25 from aqueous solutions, Bioresour. Technol. 99 (2008) 7573–7586.
[8] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour. Technol. 77 (2001) 247–255.

[9] E. Forgacs, T. Cserháti, G. Oros, Removal of synthetic dyes from wastewaters: a review, Environ. Int. 30 (2004) 953–971.
[10] F.P. van der Zee, S. Villaverde, Combined anaerobic–aerobic treatment of azo dyes—a short review of bioreactor studies, Water Res. 39 (2005) 1425–1440.
[11] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, Bioresour. Technol. 97 (2006) 1061–1085.
[12] A.B. dos Santos, F.J. Cervantes, J.B. van Lier Santos, Review paper on current technologies for decolourisation of textile wastewaters: Perspectives for anaerobic biotechnology, Bioresour. Technol. 98 (2007) 2369–2385.
[13] G. Crini, P.-M. Badot, Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature, Prog. Polym. Sci. 33 (2008) 399–447.
[14] Y. Fu, T. Viraraghavan, Removal of a dye from an aqueous solution by fungus Aspergillus niger, Water Qual. Res. J. Can. 35 (2000) 11–95.
[15] F. Yi, S. Chen, C. Yuan, Effect of activated carbon fiber anode structure and electrolysis conditions on electrochemical degradation of dye wastewater, J. Hazard. Mater. 157 (2008) 79–87.
[16] M.H. Khan, J.Y. Jung, Ozonation catalyzed by homogeneous and heterogeneous catalysts for degradation of DEHP in aqueous phase, Chemosphere 72 (2008) 690–696.
[17] F. Harrelkas, A. Paulo, M.M. Alves, L. El Khadir, O. Zahraa, M.N. Pons, F.P. van der Zee, Photocatalytic and combined anaerobic–photocatalytic treatment of textile dyes, Chemosphere 72 (2008) 1816–1822.
[18] J.C. Crittenden, R.R. Trussell, D.W. Hand, K.J. Howe, G. Tchobanoglous, Water Treatment: Principals and Design, second ed., MWH, John Wiley and Sons. Inc., 2005.
[19] O.S.G.P. Soares, P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Ozonation of textile effluents and dye solutions in the presence of activated carbon under continuous operation, Sep. Sci. Technol. 42 (2007) 1477–1492.
[20] C.-H. Wu, C.-Y. Kuo, C.-L. Chang, Homogeneous catalytic ozonation of C.I. Reactive Red 2 by metallic ions in a bubble column reactor, J. Hazard. Mater. 154 (2008) 748–755.
[21] Y. Dong, K. He, B. Zhao, Y. Yin, L. Yin, A. Zhang, Catalytic ozonation of azo dye active brilliant red X-3B in water with natural mineral brucite, Catal. Commun. 8 (2007) 1599–1603.
[22] F. Erol, T.A. Özbelge, Catalytic ozonation with non-polar bonded alumina phases for treatment of aqueous dye solutions in a semi-batch reactor, Chem. Eng. J. 139 (2008) 272–283.
[23] K. He, Y.M. Dong, Z. Li, L. Yin, A.M. Zhang, Y.C. Zheng, Catalytic ozonation of phenol in water with natural brucite and magnesia, J. Hazard. Mater. 159 (2008) 587–592.
[24] L.F. Liotta, M. Gruttadauria, G. Di Carlo, G. Perrini, V. Librando, Heterogeneous catalytic degradation of phenolic substrates: catalysts activity, J. Hazard. Mater. 162 (2009) 588–606.
[25] Y.-F. Zeng, Z.-L. Liu, Z.-Z. Qin, Decolorization of molasses fermentation wastewater by SnO_2-catalyzed ozonation, J. Hazard. Mater. 162 (2009) 682–687.
[26] I. Arslan, Treatability of a simulated disperse dye-bath by ferrous iron coagulation, ozonation, and ferrous iron-catalyzed ozonation, J. Hazard. Mater. 85 (2001) 229–241.
[27] Z. Parisheva, L. Nusheva, Catalytic ozonation of aqueous model solutions of reactive dye Blue-1, Environ. Protec. Eng. 29 (2003) 5–15.
[28] K. Yong, J. Wu, S. Andrews, Heterogeneous catalytic ozonation of aqueous reactive dye, Ozone Sci. Eng. 27 (2005) 257–263.
[29] Ş. Gül, Ö. Özcan, O. Erbatur, Ozonation of C.I. Reactive Red 194 and C.I. Reactive Yellow 145 in aqueous solution in the presence of granular activated carbon, Dyes Pigments 75 (2007) 426–431.
[30] C.-H. Wu, C.-Y. Kuo, C.-L. Chang, Decolorization of C.I. Reactive Red 2 by catalytic ozonation processes, J. Hazard. Mater. 153 (2008) 1052–1058.
[31] I.V. Mishakov, A.F. Bedilo, R.M. Richards, V.V. Chesnokov, A.M. Volodin, V.I. Zaikovskii, R.A. Buyanov, K.J. Klabunde, Nanoparticleline MgO as a dehydrohalogenation, J. Catal. 206 (2002) 40–48.
[32] B. Nagappa, G.T. Chandrappa, Mesoporous nanoparticleline magnesium oxide for environmental remediation, Microporous Mesoporous Mater. 106 (2007) 212–218.
[33] R. Richards, R.S. Mulukutla, I. Mishakov, V. Chesnokov, A. Volodin, V. Zaikovski, N. Sun, K.J. Klabunde, Nanocrystalline ultra high surface area magnesium oxide as a selective based catalyst, Scripta Mater. 44 (2001) 1663–1666.
[34] S. Altenor, B. Carene, E. Emmanuel, J. Lambert, J.-J. Ehrhardt, S. Gaspard, Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation, J. Hazard. Mater. (2008), doi:10.1016/j.jhazmat.2008.10.133.
[35] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 21st ed., Washington DC, 2005.
[36] U. von Gunten, Ozonation of drinking water: part I. Oxidation kinetics and product formation: review, Water Res. 37 (2003) 1443–1467.
[37] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1999) 51–59.
[38] S. Esplugas, J. Gimeĭnez, S. Contreras, E. Pascual, M. Rodrıĭguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.
[39] A.R. Freshour, S. Mawhinney, D. Bhattacharyya, Two-phase ozonation of hazardous organics in single and multi component systems, Water Res. 30 (1996) 1949–1958.
[40] J. Wu, K. Rudy, J. Spark, Oxidation of aqueous phenol by ozone and peroxidase, Adv. Environ. Res. 4 (2000) 339–346.
[41] B. Kasprzyk-Hordern, M. Ziolek, J. Nawrocki, Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, Appl. Catal. B: Environ. 46 (2003) 639–669.
[42] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Catalytic ozonation of sulfonated aromatic compounds in the presence of activated carbon, Appl. Catal. B: Environ. 79 (2008) 237–243.
[43] P. Peralto-Zamora, A. Kunz, S. Gomez de Morales, R. Pelegrini, P. de Capos Moleiro, J. Reyes, N. Duran, Degradation of reactive dyes. I. A comparative study of ozonation, enzymatic and photochemical processes, Chemosphere 38 (1999) 835–852.
[44] B. Dhandapani, S.T. Oyama, Gas phase ozone decomposition catalysts, Appl. Catal. B: Environ. 11 (1997) 129–166.
[45] C. Heisig, W. Zhang, S.T. Oyama, Decomposition of ozone using carbon supported metal oxide catalysts, Appl. Catal. B: Environ. 11 (1997) 117–129.
[46] T. Sreethawong, S. Chavadej, Color removal of distillery wastewater by ozonation in the absence and presence of immobilized iron oxide catalyst, J. Hazard. Mater. 155 (2008) 486–493.
[47] F. Khairallah, A. Glisenti, Synthesis, characterization and reactivity study of nanoscale magnesium oxide, J. Mol. Catal. A: Chem. 274 (2007) 137–147.
[48] S. Christoskova, M. Stoyanova, Degradation of phenolic wastewaters over Ni-oxide, Water Res. 35 (2001) 2073–2077.
[49] J. Wu, H. Doan, S. Upreti, Decolorization of aqueous textile reactive dye by ozone, Chem. Eng. J. 142 (2008) 156–160.
[50] M. Khadhraoui, H. Trabelsi, M. Ksibi, S. Bouguerra, B. Elleuch, Discoloration and detoxicification of a Congo red dye solution by means of ozone treatment for a possible water reuse, J. Hazard. Mater. 161 (2009) 974–981.
[51] M.R. Ghezzar, F. Abdelmalek, M. Belhadj, N. Benderdouche, A. Addou, Enhancement of the bleaching and degradation of textile wastewaters by Gliding arc discharge plasma in the presence of TiO_2 catalyst, J. Hazard. Mater. 164 (2009) 1266–1274.