Application of carbon-doped nano-magnesium oxide for catalytic ozonation of real textile wastewater: fractional factorial design and optimization

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ABSTRACT

This study was aimed to prepare carbon-coated magnesium oxide (C-MgO) nanoparticles and investigate the catalytic activity of C-MgO in catalytic ozonation process (COP) for treating a real textile wastewater. A fractional factorial design was conducted to assess the interactions between operating parameters (pH, ozone flow rate, catalyst dose, reaction time) for the catalytic treatment of the textile wastewater via the C-MgO catalyst. The experiments of degradation and mineralization results matched well with those attained by the predicted models. Fractionate of the contribution reactive oxygen species (ROSs) and O_3 in COD removal indicated that ROSs had a dominant role in the mineralization of the recalcitrant compound in examining the textile wastewater sample. C-MgO showed better potential catalytic activities (synergetic effect = 57%) as compared with plain nano MgO and O_3 alone in COD elimination. The catalytic activity findings demonstrated that the mineralization rate of the COP with the C-MgO catalyst was 5.7 times that of the plain nano MgO/O_3 process. Based on the results, this report showed that the C-MgO catalyst could be applied in COP for treating real textile wastewaters.

Keywords: Textile wastewater; Catalytic ozonation; Fractional factorial design; Nano-magnesium oxide

1. Introduction

Since the textile wastewater contains large quantities of recalcitrant and toxic compounds, its discharge into the environment without sufficient treatment may be harmful to humans and the environment [1,2]. Textile wastewater has variable constituents such as different dyes (about 100,000 synthetic dyes), high turbidity, inorganic salts, and other chemicals. It usually has low biological degradability of organics (the biological oxygen demand [BOD_5]/chemical oxygen demand [COD] ratio < 0.1) [3,4]. Therefore, the treatment of recalcitrant organics in textile wastewater is a major concern; thus, certain methods such as advanced oxidation processes (AOPs) must be applied to increase the performance of the methods. In comparison with conventional wastewater treatment methods, AOPs have significant advantages such as the lack of production

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of large quantities of sludge, production of a large amount of highly reactive and non-selective hydroxyl radicals that are more powerful (E_0: 2.80 eV) [5–8]. Ozonation alone is not enough for the mineralization of refractory COD in textile effluent and generated by-products in the O_3 system are difficult to be removed. A common objective of AOPs is increasing the removal of COD and more mineralization of refractory compounds in industrial wastewater. One of the efficient processes of the AOPs is the catalytic ozonation process (COP) [9,10]. The type of catalyst and the surface characteristics are the main factors directly affecting the efficiency of ozone decomposition and radical formation rate in the COP [11]. So as to find novel types of catalysts with an active, stable material and higher abilities to improve the effectiveness of ozonation, more research is required. In this regard, the COP, in homogeneous and heterogeneous modes, with a variety of solids, metals and metal in single or composite have been evaluated as catalysts to enhance the efficiency of ozonation. Nano-sized magnesium oxide (MgO), as a catalyst in COPs, has been attracting great attention due to some advantages such as simplicity and inexpensive synthetic methods. MgO is not toxic and one of its unique features is high stability in water. It is also environmentally friendly and would not cause water pollution if it is leaked into water [9,10,12]. Oxygen vacancy defects of nano-sized magnesium oxide help the catalytic activity of it in the COP. In earlier studies, it has been revealed that nanoparticles coated with nonmetal elements (such as sulfur, fluoride) have more catalytic activity [12–15]. Therefore, the catalytic potential of nano-sized magnesium oxide can be improved via doping non-metal elements. As a result, we focused on preparing C-MgO nanosize by a couple synthesis method. To our best knowledge, applying C-MgO as a catalyst and its potential in treating real textile wastewater has not yet been reported.

The main purpose of performing the bench-scale study was to obtain the maximum removal of pollutants from the environment, as well as find conditions under which maximum removal would occur. Therefore, the optimization of operating parameters to obtain the best results is of great importance. Two methods can be used to determine the optimal conditions in each experiment. Classical (one factor at a time) and design of experiments (DOE) methods are used for an experimental plan. The first method is a trial and error procedure and does not follow a specific standard. By contrast, in DOE, the DOE involves a sequence of examinations that intentionally change the input variables of the experiment; in this way, the extent to which the changes in response to the output of the experiments are evaluated, observed and detected. The DOE is based on a series of standards. In DOE, interaction among factors is investigated with performing fewer experiments but final optimum points of the parameters can be reached [16].

In this study, the fractional factorial design (FFD) experiment was used to determine the optimal conditions of COP with C-MgO in the treatment of the textile wastewater. The new data were evaluated using a polynomial regression model to understand the main and interaction outcome of factors on the COP.

2. Materials and methods

2.1. Materials

The real textile wastewater samples were taken from a local dyeing and finishing plant in the west of Iran and used without any treatment for the COP experiments. Table 1 indicates the properties of the real textile wastewater.

Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) was obtained from Merck Co. (Germany). Other materials were purchased from local suppliers. The nano C-MgO was synthesized and completely considered as described in detail by Asgari and Salari [12] and Asgari et al. [15]. To prepare the nanosized C-MgO, 3 g of sucrose and 10 g of magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$) were dissolved in 200 mL of deionized water. Then, NaOH (0.5 M) was added under constant stirring until the pH value reached to the optimum value (10.5). Next, the solution was stirred and heated on a hot plate for about 2 h. The prepared $Mg(OH)_2$/sucrose precursor was heated from room temperature to optimum calcination temperature (550°C) for 2 h. Then, the furnace was switched off and C-MgO was collected and cooled at room temperature. The surface morphology of C-MgO was analyzed using the scanning electron microscopy (SEM) technique Philips-XL30 electron microscope (FEI Company, Netherlands). Similarly, the elemental composition was considered using the SEM technique integrated with energy dispersive analysis of X-rays (EDAX) and EDAX elemental mapping Philips-XL30 electron microscope (FEI Company, Netherlands). The surface area of C-MgO was identified using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method using the Belsorp mini II instrument. The crystalline phases of C-MgO were evaluated by X-ray diffraction (XRD) analysis of the scattering angles from 5° to 80°, with a scanning speed of 2° per minute. The Rigaku (Rigaku, Japan) miniFlex diffractometer device was employed to generate CoKα radiations at 30 kV and 15 mA.

2.2. Experimental setup and procedure

The COP experiments were conducted using a pyrex cylindrical reactor. Ozone was generated from pure oxygen by an ARDA ozone generator (Model AEGCOG-5S) and introduced into the reactor from the bottom through a sintered glass diffuser to distribute the ozone to the solution. In the ozonation experiment, the ozone flow rate, solution pH, catalyst concentration and reaction time (hydraulic retention time) were regarded as operating parameters (Table 2) to investigate the treatability of the actual textile wastewaters via the process. At the end of each run, aliquots were regularly collected and dye concentration and COD were detected. In each aliquot, dye concentration (American Dye

Table 1
Characteristics of real textile wastewater

COD (mg/L)	1,400
BOD (mg/L)	250
ADMI	1,450
pH	10.45
BOD_5/COD	0.12

Table 2
Operating independent variables, response, FFD design, residual and predicted value for different experimental conditions

Parameter	Unit	Symbol	Levels		
			−1	0	1
pH	A	–	3	7	11
Ozone concentration *	B	mg/L	4	10	16
Catalyst concentration	C	g/L	0.5	1.75	3
Reaction time	D	min	5	17.5	30

					Removal efficiency (%)					
Run	A:pH	B:O_3 (mg/L)	C:C-MgO (g/L)	D:Time (min)	COD			ADMI		
					Experimental (%)	Predicted (%)	Residual	Experimental (%)	Predicted (%)	Residual
1	3.00	10.00	1.75	30.00	61.4	61.52	−0.12	70.40	70.29	0.11
2	7.00	10.00	1.75	17.50	58.2	58.17	0.033	70.20	70.30	−0.100
3	7.00	10.00	0.50	5.00	37.5	37.50	−0.004	47.80	47.81	−0.013
4	7.00	16.00	3.00	17.50	80.4	80.32	0.083	89.40	89.63	−0.22
5	3.00	4.00	1.75	17.50	42.7	42.54	0.16	51.60	51.70	−0.096
6	11.00	10.00	1.75	5.00	49.3	49.38	−0.083	59.50	59.56	−0.058
7	7.00	16.00	1.75	30.00	79.7	79.68	0.021	87.50	87.55	−0.046
8	3.00	10.00	1.75	5.00	44.3	44.28	0.017	55.60	55.36	0.24
9	7.00	4.00	1.75	30.00	52.6	52.68	−0.079	62.30	62.26	0.038
10	11.00	10.00	3.00	17.50	65.4	65.68	−0.28	75.70	75.40	0.30
11	7.00	10.00	3.00	30.00	72.7	72.42	0.28	83.50	83.46	0.038
12	7.00	4.00	3.00	17.50	53.6	53.62	−0.017	64.70	64.64	0.058
13	7.00	10.00	3.00	5.00	58.3	58.14	0.16	70.50	70.53	−0.029
14	11.00	16.00	1.75	17.50	71.5	71.39	0.11	78.40	78.28	0.12
15	7.00	16.00	0.50	17.50	59.5	59.68	−0.18	66.30	66.31	−0.008
16	3.00	10.00	0.50	17.50	43.1	42.90	0.20	50.10	50.48	−0.38
17	3.00	16.00	1.75	17.50	66.6	66.64	−0.038	74.50	74.23	0.27
18	11.00	10.00	1.75	30.00	63.2	63.42	−0.22	72.10	72.29	−0.19
19	7.00	10.00	0.50	30.00	54.6	54.49	0.11	62.60	62.55	0.054
20	7.00	16.00	1.75	5.00	62.4	62.40	0.004	71.80	71.91	−0.11
21	11.00	4.00	1.75	17.50	45.1	44.79	0.31	53.60	53.85	−0.25
22	7.00	10.00	1.75	17.50	57.9	58.17	−0.27	70.40	70.30	0.10
23	7.00	4.00	1.75	5.00	38.6	38.70	−0.096	50.20	50.23	−0.029
24	3.00	10.00	3.00	17.50	60.6	60.83	−0.23	71.50	71.65	−0.15
25	11.00	10.00	0.50	17.50	45.2	45.05	0.15	53.00	52.93	0.071
26	7.00	10.00	1.75	17.50	58.4	58.17	0.23	70.30	70.30	0.000
27	7.00	4.00	0.50	17.50	35.4	35.68	−0.28	44.60	44.32	0.28

*2 mg/min (0.1 L/min = 10 mg/L), 4 mg/min (0.2 L/min = 20 mg/L), 8 mg/min (0.3 L/min = 40 mg/L), 16 mg/min (0.4 L/min = 80 mg/L)

Manufacturers Institute [ADMI]) and COD were determined through the methods explained in the Standard Methods, respectively [17]. The degrees of degradation (in terms of ADMI removal) and mineralization efficiency (in terms of COD removal) of the wastewater with making catalyst in COP were calculated through Eqs. (1) and (2), respectively.

$$\text{Degradation efficiency}\left(\%\right) = \frac{\left(ADMI_0 - ADMI_t\right)}{ADMI_0} \times 100 \qquad (1)$$

where $ADMI_0$ and $ADMI_t$ are the concentration of dye before and after the reaction in COP, respectively.

$$\text{Mineralization efficiency}\left(\%\right) = \left(1 - \frac{COD_t}{COD_0}\right) \times 100 \qquad (2)$$

where COD_0 and COD_t are the COD of the wastewater before and after the reaction in the COP with C-MgO, respectively.

2.3. Experimental design and statistical analysis

In order to evaluate the statistical significance of the effects of four different factors and their interactions on the performance of the COP, a three-level regular FFD was designed. FFDs, compared with one-factor-at-a-time (OFAT), provide information on interaction effects [16,18]. A 3^{K-1} FFD was conducted to plan an experimental series. A three-level FFD is a special type of factorial design in which the number of experiments is greatly reduced through neglecting some insignificant information. In this design experiment, three-factor interactions are assumed negligible and these main effects or components of two-factor interactions were evaluated. The advantage of the fraction method is that it allows for the examination of additional factors without increasing the number of tests. Color and COD removal were selected as the response variable. The experimental FFD and the randomized order of the experiments run are presented in Table 2.

A second-order polynomial regression was used to model curvilinear response using quantitative predictor variables (Eq. (3)) [16]. In this study, we developed an empirical model that includes each predictor raised for the first, and third powers along with all interaction terms.

$$\widehat{Y(\%)} = \beta_0 + \sum_{i=1}^{K}\beta_i x_i + \sum_{i=1}^{K}\beta_{ij} x_i^2 + \sum_{i=1}^{k-1}\sum_{j=i+}^{k}\beta_i x_i x_j + \varepsilon \quad (3)$$

where $Y(\%)$ is the % predicted response, β_0 is the constant term, β_i is (i = 1,2,3) the main-effects, β_{ij}s and β_{ij}ks ($i < j < k$ = 1,2,3,4) are the interaction-effects, β_{ij} is the quadratic effects. Actually, Eq. (3) shows the relation between the predicted response (ADMI, COD) as the dependent variable and independent factors A, B, C and D. The analysis of variance (ANOVA) was used for the analysis of the FFD and the independent variables. For assessing the goodness of fit of the final model, correlation coefficient (R^2), adjusted correlation coefficient and adequate precision were used [16].

3. Results and discussion

3.1. Model equations, their validation, and selection of optimal levels and estimation of optimum response characteristics

In Table 3, the statistical analysis consequences and regression factors for the experimental and predicted result in degradation and mineralization of dye in textile wastewater have been indicated. As ANOVA results indicate, the p-values for the used models are less than 0.05 illustrating that the models were significant to expect mineralization (COD removal) and dye degradation (ADMI reduction) from the textile wastewater by catalytic ozonation with C-MgO, respectively. Moreover, as seen in Table 3, the P-values of the lack of the fit models were 0.1345 and 0.5864 for dye degradation and COD removal, respectively. High P-values (>0.05) of the lack of the fit of the used models indicated the models

Table 3
Analysis of variance and adequacy of the model for COD and dye removal

Source	Sum of squares		Df		Mean square		F-value		p-value	
	COD	ADMI	COD	ADMI	COD	ADMI	COD	ADMI	COD	ADMI
Model	3,898.75	3,830.30	14	14	278.48	273.59	4,270.66	4,673.48	<0.0001	<0.0001
A-pH	36.75	28.83	1	1	36.75	28.83	563.58	492.47	<0.0001	<0.0001
B-O$_3$	1,927.87	1,654.40	1	1	1,927.87	1,654.40	29,564.74	28,260.23	<0.0001	<0.0001
C-C-MgO	1,115.54	1,427.90	1	1	1,115.54	1,427.90	17,107.34	24,391.19	<0.0001	<0.0001
D-Time	733.20	574.08	1	1	733.20	574.08	11,244.01	9,806.41	<0.0001	<0.0001
AB	1.56	0.90	1	1	1.56	0.90	23.96	15.42	0.0004	0.0020
AC	1.82	0.42	1	1	1.82	0.42	27.95	7.22	0.0002	0.0198
AD	2.56	1.21	1	1	2.56	1.21	39.26	20.67	<0.0001	0.0007
BC	1.82	2.25	1	1	1.82	2.25	27.95	38.43	0.0002	<0.0001
BD	2.72	3.24	1	1	2.72	3.24	41.75	55.35	<0.0001	<0.0001
CD	1.82	0.81	1	1	1.82	0.81	27.95	13.84	0.0002	0.0029
A^2	40.95	117.81	1	1	40.95	117.81	627.94	2,012.47	<0.0001	<0.0001
B^2	4.73	6.31	1	1	4.73	6.31	72.53	107.74	<0.0001	<0.0001
C^2	16.96	47.60	1	1	16.96	47.60	260.11	813.11	<0.0001	<0.0001
D^2	2.97	8.00	1	1	2.97	8.00	45.50	136.71	<0.0001	<0.0001
Residual	0.78	0.70	12	12	0.065	0.059				
Lack of fit	0.66	0.68	10	10	0.5864	0.068	1.04		0.5864	0.1345
Pure error	0.13	0.020	2	2	COD		ADMI			
Cor total	3,899.54	3,831.01	26	26	R^2	0.9998	R^2		0.9998	
Std. dev.	0.45	0.24			Adjusted R^2	0.9996	Adjusted R^2		0.9996	
Mean	50.23	65.86			Predicted R^2	0.9963	Predicted R^2		0.9990	
C.V. %	1.23	0.37			Adeq precision	105.4521	Adeq precision		251.190	

were not significant. The lack of the fit of a model should not be significant. In other words, if the lack of the fit of the model is significant, it indicates the inefficiency of the model in providing information points in the tested domain. The high correlation coefficient ($R^2 > 0.99$) in both models used to expect COD and ADMI reduction indicated that there is a good agreement between the experimental and predicted data. The "adequate precision" of the model measures the signal to noise ratio and represents the difference between the predicted value of the model and the predicted error value. An adequate precision greater than 4 is desirable. As seen, adequate precision values of the selected models were 105.452 and 251.190 for COD and ADMI reduction, respectively, indicating an adequate signal. Hence, this result suggested that these selected models can be used to navigate the space defined through the FFD. After the exclusion of insignificant terms, at *p*-value less than 0.05 (95% confidence levels), the final experiential models, based on Eqs. (4) and (5) for ADMI reduction and COD removal, respectively, can be indicated as follows:

Degradation (%) = + 70.30+1.55*A*+11.74*B*+10.91* *C*+6.92*D*+ 0.47*A B*+0.33*AC*–0.55*AD*+0.75*BC*+0.90*BD*– 0.45*CD*–4.70*A*^{2}–1.09*B*^{2}–2.99*C*$_2$–1.23*D*^{2} (4)

Mineralization (%) = + 58.17+1.75*A*+12.67*B*+9.64*C*+7.82*D*+0.6 2*AB*+0.68*AC*-0.80*AD*+0.68*BC*+0.83*BD*- 0.68*CD*-2.77*A*^{2}+0.94*B*^{2}–1.78*C*^{2}–0.75*D*^{2} (5)

The results in Table 3 indicate that a high correlation coefficient of 0.999 was attained for the used models to expect the efficiency of catalytic ozonation in the real textile wastewater with C-MgO based on COD and ADMI reduction. The results show that only 1% of the total variations were not explained. The value of adjusted R-squared was also very high (0.99), which was close to the value of R^2, demonstrating a high significance of the model. The comparison of the selected model with a null model (model without any terms) except β_0 result to p-value < 0.001 (lower than 0.05) indicated the suitability of the factor used in predicting the dye degradation efficiency (%) and COD removal (%). The suitability of the used models was also evaluated through "residuals" plots. As results indicated in Figs. 1a and b, a plot of residuals against its theoretical values of standardized normal quintiles supports the normality assumption of residuals for COD and dye degradation, respectively. Similarly, Figs. 1c and d show a scatter plot of residuals against fitted values depicting fairly no trend and random scattering of residuals about zero. Therefore, it seems that the functional form of the
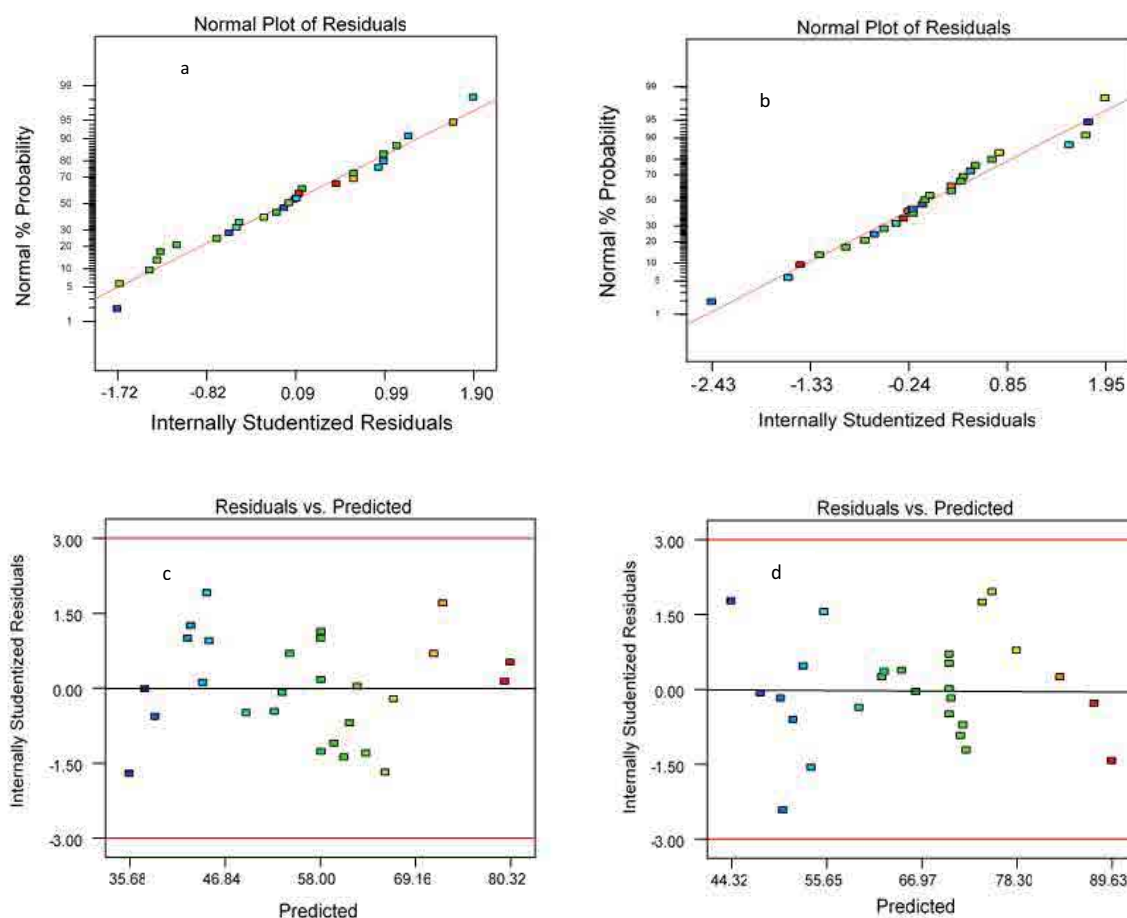
Fig. 1. (a,b) Plots of residuals against its theoretical values of standardized normal scatter and (c,d) plot of residuals against fitted values.

final model is appropriate, the error variance is constant and there are no considerable outliers. The main objective of the optimization is to determine the values of variables for the maximization of the dye degradation and mineralization efficiency with the COP. In optimization, the desired goal of the response (dye degradation and COD removal) was chosen for maximum possible value and the values of parameters of reaction time, catalyst dose, pH and the ozone flow rate were selected in their range to achieve this goal. The optimization results of the process variables for dye degradation and mineralization efficiency in the COP with the C-MgO catalyst were determined to be ozone flow rate = 15.74 mg/min, catalyst dose = 3 g/L, pH = 8 and reaction time = 19 min. Based on the model, the optimal amount of dye degradation and mineralization efficiency were predicted about 91% and 75%, respectively.

To confirm the model adequacy and the validity of the optimization procedure, additional experiments were performed under the projected optimal conditions. The average values of the two replicated experiments indicated that the COP with the C-MgO catalyst is applicable for 92% of dye degradation and 76% of COD removal under the optimum operating conditions. According to Eq. (6), the Pareto effect (percentage contribution) was calculated for each factor and displayed in Fig. 2.

$$P_i = \left[\frac{(b_i^2)}{\sum b_i^2} \right] \times 100 \tag{6}$$

where b represents the regression coefficient of each term in accordance with coded values. As seen from Fig. 2a, the contribution of each factor in COD removal under the COP was different; furthermore, the parameters of the ozone dose, catalyst concentration and contact time revealed the highest effect on the COP performance, respectively. The similar result was obtained in assessing the Pareto effect for the COP performance in the removal of ADMI, as observed in Fig. 2b.

3.2. Effect of main parameters on ADMI and COD removal

Three-dimensional graphs were used to better assess the effect of the main parameters (combined effects) on dye and COD removal by the C-MgO/ozone process. Figs. 3a and b present the effects of pH, C-MgO concentration, reaction time and ozone concentration on dye degradation in textile wastewater by this process. Also, in Figs. 3c and d the effects of pH, C-MgO concentration, reaction time and ozone concentration on COD removal from textile wastewater by the process have been indicated. The results clarified that the dye degradation efficacy increased from around 47% to 89% with increasing the catalyst concentration from 0.5 to 3 g/L and reaction time from 5 to 30 min (Fig. 3a). This trend can also be seen in Figs. 3b and c. As the results indicated, dye degradation efficacy increased to 90.5% with an increase in ozone concentration. As can be seen in Fig. 3b, the highest dye degradation was 91% achieved at pH = 8.5 and ozone concentration = 15 mg/L. Similarly, this trend can also be seen in Fig. 2d in the removal of COD. The pH increase leads to the conversion of ozone to hydroxyl radical which has an oxidation potential (E_0 = 2.80) higher than O_3 (E_0 = 2.07). With increasing ozone concentration and pH value, more ozone is converted to radicals and this trend increased the dye removal and mineralization efficiency of the C-MgO/O$_3$ process. As indicated, C-MgO has a high surface area (414 m^2/g) which provided available active sites for ozone transformation and the adsorption of dyes from wastewater in reaction reactor as well. With increasing catalytic, the number of active sites and the transformation of ozone to a very active radical in ozonation reactor increases. No report could be found on the degradation of real textile wastewater in the COP with C-MgO to compare the results. However, the study trend and the obtained results are in agreement with the study by Maljaei et al. [19], Jorfi et al. [20], and Pang et al. [21], in the treatment of real textile wastewater. It is well known that, in terms of aesthetic aspects, wastewater discharging into the environment should be free from color. According to existing standards, the textile industry wastewater should be pretreated before being discharged into municipal sewage collection systems and receiving waters. A pre-treated textile wastewater should have a color less than 120 (ADMI color unit) for the new source and the 220 (ADMI color unit) is the best available technology for existing sources [1,15]. As results indicated,
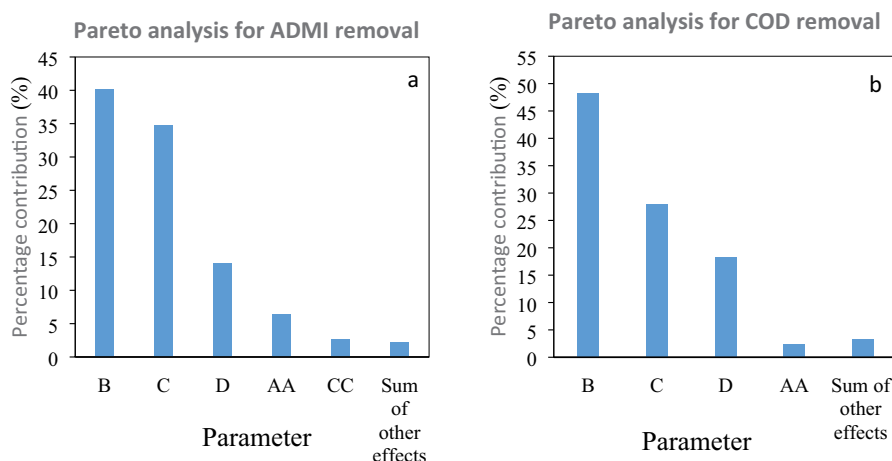

Fig. 2. Percentage contribution of each factor on (a) COD and (b) ADMI removal based on Pareto analysis.
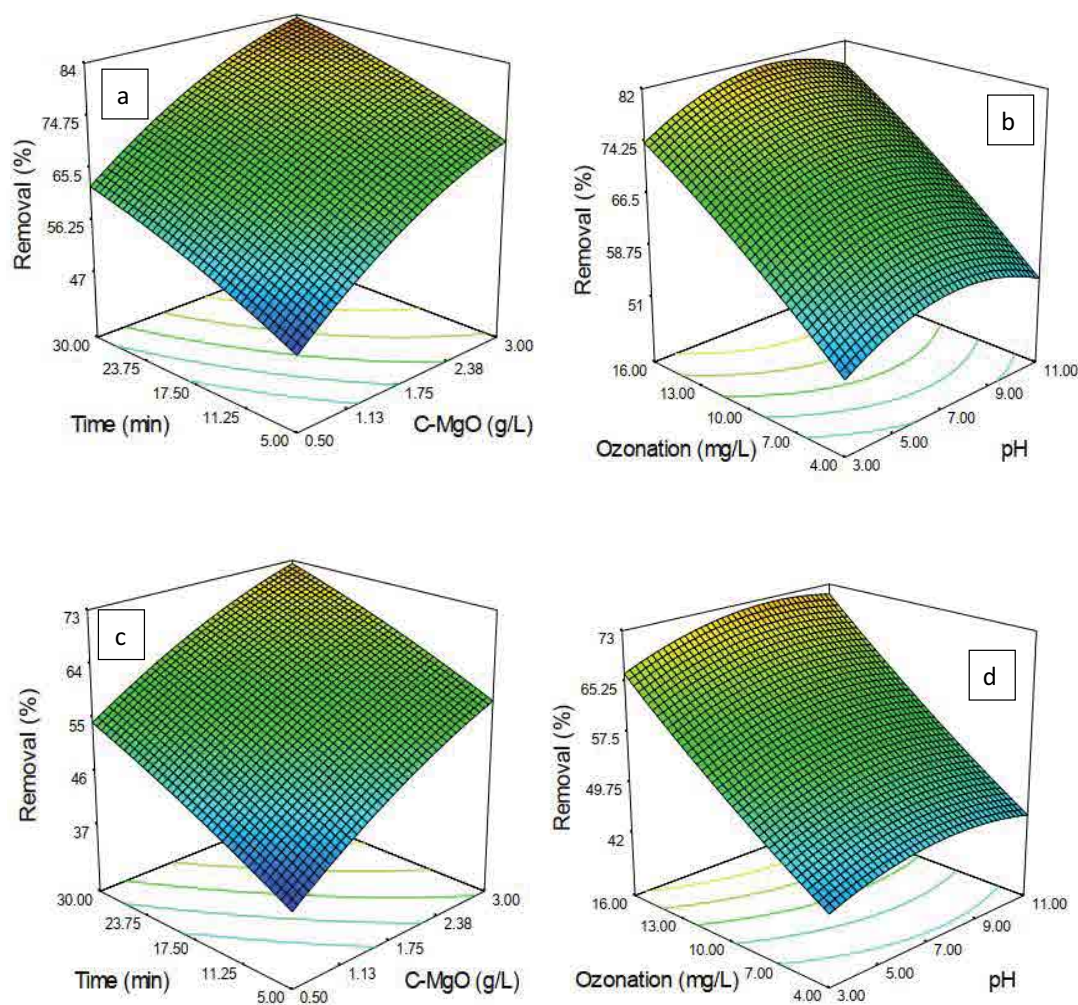
Fig. 3. (a,b) Response surface for dye degradation ADMI reduction and (c,d) mineralization (COD removal efficiencies as a function of ozone concentration, catalyst dosage, pH and reaction time).

the initial ADMI of the raw textile sample was reduced to 98 after treating via the COP with C-MgO. These findings indicate that the selected process meets the standard for discharging colored wastewater in municipal sewage collection systems and receiving waters.

3.3. Comparison of catalytic activity of C-MgO with plain MgO and SOP in dye degradation and mineralization under the optimum conditions

Dye degradation (in terms of ADMI removal) and its mineralization rate (in terms of COD) in COP with C-MgO are compared with plain MgO and SOP shown in Fig. 4. As seen in Fig. 4a, the maximum dye degradation (91%) and mineralization (75%) were achieved with the C-MgO catalyst in comparison with the plain MgO and SOP. This result clearly indicated that dye degradation efficiency was greater than mineralization efficiency in both tested (C-MgO/ozone and MgO/ozone) COP. This means that physical adsorption is not just the mechanism involved in treating the real wastewater by C-MgO. Indeed, if physical adsorption was the only mechanism, the percentage of dye degradation and mineralization

efficiency would be similar. During ozonation, the dye molecule being oxidized and mineralize by the attack of ozone on aromatic rings and unsaturated sites on dye molecules. It should be noted that opening and severing rings of the dyestuff can produce an organic or inorganic compound; this may show itself as COD-containing chemical molecules in treated wastewater. Consequently, as the results indicated, the main difference between the SOP and COP with C-MgO in COD removal is noticeable. In COP, some of the target pollutants adsorbed on the catalyst, thus, so as to evaluate the extent of pollutant adsorbed on the catalyst, three test runs were performed under the optimum conditions. The results of these three tests (influence the adsorption process on mineralization efficiency) have been indicated in Fig. 4b. As shown, 8% and 6% of COD were removed due to adsorption onto the C-MgO and plain MgO, respectively. Also, in SOP, COD removal was 10% (Fig. 4a). Also, 67% of 75% of total COD from textile wastewater was mineralized in the COP with the C-MgO catalyst and 8% of 75% of COD may have been adsorbed onto the C-MgO catalyst. Correspondingly, 10% of 75% of total COD of textile wastewater was removed in COP with the C-MgO catalyst may have been because of
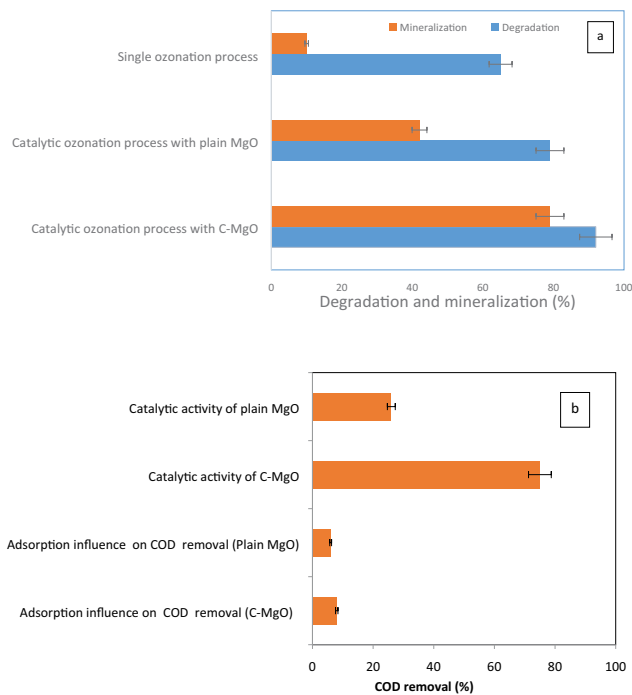
Fig. 4. (a) Comparison removal efficiency of C-MgO with plain MgO and SOP in dye degradation and mineralization and catalytic activity, (b) effect of adsorption process in COP with C-MgO with plain MgO under optimum conditions.

direct oxidation in the SOP. Therefore, the catalytic activity of the C-MgO catalyst in the mineralization of COD was 57% calculated as follows [22]:

Catalytic activity (%) = Total COD removal in COP –
(COD removal by adsorption onto
catalyst + COD removal in SOP)　(7)

Similarly, catalytic activity plain MgO in the mineralization of COD was estimated to be 10%. These results indicate that adsorption processes are not important in this catalytic system. It is suggested that supported C-MgO improved the degradation of target contaminants in COP, reduced shock loads due to adsorption and contributed to the radical generation in comparison with SOP. Also, the high catalytic activity of C-MgO implies that the intermediates of COD-containing chemical molecules could be better oxidized in the COP with the C-MgO composite than in SOP and even in COP with MgO. Moreover, as results indicated, the catalytic activity of C-MgO in mineralization of COD was about 5.7 ([catalytic activity of C-MgO]/[catalytic activity of plain MgO]) times the catalytic activity of plain MgO. This suggests that the use of the C-MgO composite as a catalyst improved the mineralization degree of the intermediates of COD-containing chemical molecules generated in SOP [23,24]. Therefore, the greater generated reactive radicals in the ozonation reactor are produced in the presence of the C-MgO catalyst. This proved that the COP with the C-MgO catalyst is more efficient for the mineralization of COD than the COP with plain MgO in the equal operational conditions and SOP.

Table 4
Kinetic information of textile wastewater treated with COP via C-MgO

K_{app} (1/min)	C-MgO (g/L)
0.51	0.5
0.85	1
1.2	1.75
1.35	2
1.5	3

3.4. Kinetic study and mechanism of mineralization

To highlight the catalytic ability of the C-MgO, the kinetics of COD removal was assessed based on the Langmuir-Hinshelwood equation (Eq. (8)). The COD experiments were done at various C-MgO doses (0.5–3 g/L) and under the optimum conditions.

$$\frac{d[COD]}{dt} = -kC_{COD}C_{catalyst} \tag{8}$$

Since the selected concentration of catalysts was high and remained constant during the kinetic tests, Eq. (9) has been reduced to a pseudo-first-order (PFO) rate equation ($K_{app} = KC_{catalyst}$).

$$\frac{d[COD]}{dt} = K_{app}C_{COD} \tag{9}$$

K_{app} denotes an apparent PFO rate constant (min⁻¹). It can be determined by:

$$\ln\frac{C_{COD_t}}{C_{COD_{t=0}}} = -K_{app}t \tag{10}$$

The K_{app} values obtained via the slope of the plot for $\ln\dfrac{C_{COD_t}}{C_{COD_{t=0}}}$ as a function of reaction time.

In Table 4, the kinetic information of the textile wastewater treated with COP via C-MgO has been indicated.

The results presented that the COD mineralization rate increased with increasing C-MgO dosage (Table 4). The mineralization rate with an increase in the concentration of the catalyst can be qualified to increased activation sites available to interact with the COD constant value. The high mineralization rate by C-MgO is related to changes in MgO surface properties (defects of oxygen vacancy), functional groups, and increased BET, after doping with carbon [15]. Mineralization mechanism for textile wastewater in the COP with C-MgO can be simplified as follows:

Dissolved oxygen adsorbed on C-MgO

$$O_2 + C-MgO \rightarrow [O_2 \dots C-MgO] \tag{11}$$

Adsorbed oxygen on C-MgO disassociated into $O_2^{\bullet-}$ and make superoxide radical (Eq. (12))

$$O_2 \dots C-MgO \rightarrow O_3 \rightarrow [O_2^{\bullet-} \dots C-MgO^+] \tag{12}$$
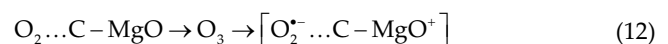
Mineralization was done through the strong superoxide radical $[O_2^{\bullet-}...C-MgO^+]$ (Eq. (13))

$$\left[O_2^{\bullet-}...C-MgO^+\right]+COD \rightarrow CO_2 + H_2O + \text{intermediates} \quad (13)$$

Also, mineralization of COD may take place by °OH in the bulk solution and on the C-MgO surface generated by reacting $[O_2^{\bullet-}...C-MgO^+]$ with water molecules (Eqs. (14) and (15)).

$$[O_2^{\bullet-}...C-MgO^+]+2H_2O \rightarrow [HO^{\bullet}...C-MgO^+]+3OH^+ \quad (14)$$

$$[HO^{\bullet}...C-MgO^+]+COD \rightarrow CO_2 + H_2O + C-MgO \quad (15)$$

Similarly, mineralization may take place by molecules O_3 in the bulk solution (Eq. (16)).

$$COD + O_3 \rightarrow CO_2 + H_2O + \text{intermediates} \quad (16)$$

For highlighting the contribution of °OH or active oxygen species dominating in the mineralization of textile wastewater in COP with C-MgO and plain MgO, the mineralization efficiency was obtained with/without the presence of salicylic acid. The results indicated that the mineralization efficiency of the COP with C-MgO was 90% and almost no change was seen in the presence of a radical scavenger. However, the mineralization efficiency of the COP with plain MgO decreased from 42% to 10% in the presence of a radical scavenger. It confirms that °OH was not the main reactive oxygen species (ROS) involved in the degradation and mineralization of the dye in the textile wastewater with C-MgO. Therefore, a dye might be degraded mainly via an ROS such as peroxides, superoxide, hydroxyl radical, singlet oxygen and alpha-oxygen [12].

This observation illustrates that the main mechanism in mineralization of textile wastewater may be because of the strong superoxide radical, reconfirming that synergetic effect happens between ozone and the catalyst; as a result, active oxygen species in COP with the C-MgO catalyst is produced. Moreover, the results established that the surface properties of plain MgO changed due to doping carbon and generation defects of oxygen vacancy on the MgO surface. Asgari and Salari [12], and Moussavi et al. [14] reported similar observations. They stated that generation defects of oxygen vacancy on the MgO surface due to doping of sulfur were the main reason for the degradation and mineralization of antibiotic tetracycline in the COP.

3.5. Biodegradability assessment

Average oxidation (AOS), carbon oxidation state (COS) and BOD_5/COD ratio are usually regarded as indices for the biodegradability of industrial wastewater. In this study, BOD_5/COD ratio, AOS and COS were used to evaluate the biodegradability of the textile wastewater after treatment in the COP with C-MgO. AOS and COS were considered by Eqs. (17) and (18) [20,25].

$$AOS = 4 - 1.5\frac{COD}{TOC} \quad (17)$$

$$COS = 4 - 1.5\frac{COD}{TOC_i} \quad (18)$$

COS and AOS were +2.8 and +2.12 in treating real textile samples, respectively, which indicate that initial COS = –0.38 increased to +2.8, as well as COS increased from 0.38 to +2.12. The AOS and COS results are in the range of indexes that have been applied for AOS and COS (–4 to +4 for methane [more reduced state of C] and carbon dioxide [more oxidized state of C]), respectively [20,25]. These data displayed that treated textile wastewater in COP with the C-MgO catalyst has more biocompatibility of the effluent. In the case of the COP, non-degradable compounds in textile wastewater are converted to degradable compounds. One of the main differences between industrial textile wastewaters and other industrial wastewaters containing dyes is the presence of non-biodegradable materials. The BOD_5/COD ratio of the raw textile wastewater was 0.12. The BOD_5/COD ratio data showed that the raw wastewater was challenging to be biodegraded [26,27]. After treating the textile wastewater through the COP with the C-MgO catalyst, BOD_5/COD ratio increased to 0.43. Thus, the treated sample of the textile wastewater can easily be treated with biological processes because the BOD_5/COD ratio of the treated samples was between 0.3 and 0.8.

3.6. Catalyst characterization

Fig. 5 shows the SEM (surface morphologies) of the synthesized nano C-MgO. The synthesized nano C-MgO is as magnesium oxide layers are placed on each other (Fig. 5a). Fig. 5b with the magnification of 200 kx and scale 200 nm clearly indicates the formation of nearly spherical and porous C-MgO particles.

The chemical composition (EDX analysis) of nano C-MgO has been presented in Fig. 6. The EDX analysis displayed that the nano C-MgO has main components such as magnesium (51.65%), oxygen elements (35.17%) and carbon (13.19%). Also, the BET results indicated that the synthesized nano C-MgO has BET = 414 m²/g, BJH = 454 m²/g, and Langmuir specific surface area = 450 m²/g. The BET of the C-MgO showed that 414 m² surface area per g of C-MgO can provide suitable sites for reaction adsorptions and ozone reactions on the surface of the catalyst.

The average pore size of the prepared nano C-MgO was calculated by BJH equation (data not shown). The calculated average pore size approved that the synthesized nano C-MgO is a mesoporous material based on IUPAC classification (2–50 nm) [13,15].

The XRD of nano C-MgO has been revealed in Fig. 7. As XRD data indicated, two positioned peaks at 2Θ nearly 50° and 73° correspond to (2 0 0) and (2 2 0) planes confirming the dominant presence of MgO in the synthesized powder. According to the Joint Committee on Powder Diffraction Standard (45-0946), these results are in a good agreement with the main peaks of the MgO particles [13,15]. The Debye–Scherrer formula (Eq. (19)) was used to calculate the average crystallite size of the C-MgO particles as follows:

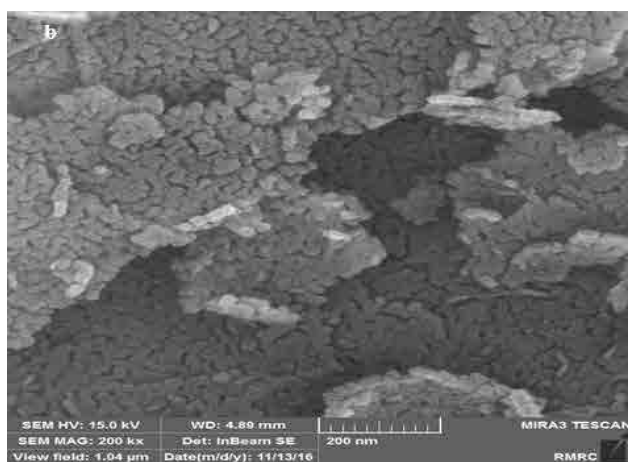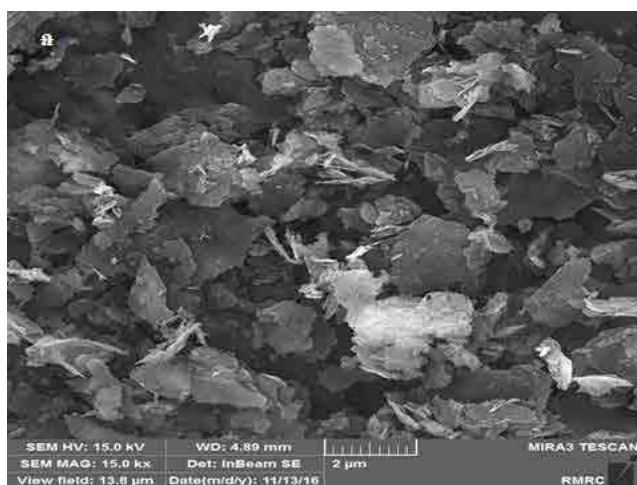$$D = \frac{K\gamma}{\beta \cos \theta} \quad (19)$$

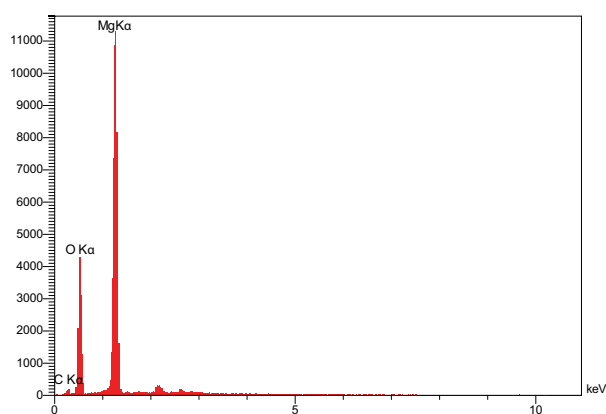Fig. 5. SEM images for synthesized C-MgO with different magnifications.

Fig. 6. EDX analysis for C –MgO.

where D is the average crystallite size, λ is the shape factor (0.9), λ is the wavelength of Co ka radiation, h is the angle of reflection and b is full width at the half-maximum height of a peak. The size of the C-MgO produced was 18.6 nm.
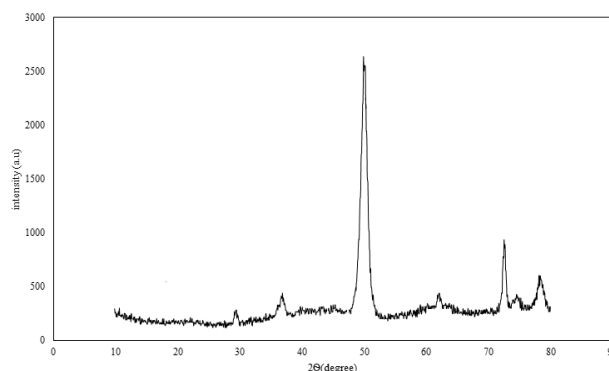

Fig. 7. XRD analysis for C–MgO.

4. Conclusions

Couple synthesis manner was considered to prepare the nano-C-MgO to be used as a catalyst in the catalytic treatment of a real textile wastewater. The catalytic activity of the nano-C-MgO in degradation and mineralization of dye and recalcitrant compounds in textile wastewater was compared with plain nano-MgO. The models' adequacy was shown by accomplishment of numerous statistical evaluates, approving that the suggested models can professionally expect the considered responses. The FFD design experiment and statistical evaluate indicated that the maximum catalytic activity of the nano-C-MgO was obtained at pH = 8.11, ozone concentration of 15.74 mg/min, catalyst dose = 3 g/L and reaction time = 19 min. In conclusion, the finding of this work suggests that the prepared C-MgO is an effective and capable material for elimination of dye compounds from the wastewater.

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