Global NEST Journal, Vol 18, No 2, pp 371-380, 2016

DECOLORIZATION OF METHYLENE BLUE AND METHYL ORANGE WITH Ag DOPED TiO_2 UNDER UV-A AND UV-VISIBLE CONDITIONS: PROCESS OPTIMIZATION BY RESPONSE SURFACE METHOD AND TOXICITY EVALUATION

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Received: 17/01/2016
Accepted: 13/04/2016
Available online: 13/05/2016

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ABSTRACT

MB decolarization with pure TiO_2 and Ag doped TiO_2 based photocatalytic system were investigated under UV-A and UV-Visible conditions. Different ratios of Ag were used as metal dopant. 1% Ag-TiO_2 increased the decolorization efficiencies of MB and MO dyes, also the k_{app} constant enhanced under UV-A and UV-Visible conditions. A central composite analysis showed the effect of initial dye concentration, pH, Ag-TiO_2 concentration and the reaction time of photocatalytic process under UV-A irridation in both dyes. The photocatalytic degradation pathways of both dyes by Ag doped TiO_2 catalyst were obtained in this study. According to these results, the application of Ag-TiO_2 catalyst are proved to be more effective than pure TiO_2 catalyst for both MB and MO removal. The toxicity test of Daphnia Magna shows that non toxic wastewater discharge to the receiving environment could be possible with photocatalytic degration by Ag-TiO_2 catalyst.

Keywords: dye, decolorization, doped TiO_2, optimization, photocatalytic, toxicity.

1. Introduction

Different dyes applied in many industries such as textile, paint, ink, plastics and cosmetics processing are mostly poorly biodegradable pollutants and cause serious environmental problem due to the toxicity and carcinogenicity (Mirkhani *et al.*, 2009; Çifçi *et al.*, 2015). Advanced Oxidation Processes are commonly used to remove of dyes and toxic chemicals (Zhang *et al.*, 2014; Pekakis *et al.*, 2006). In recent years, doping metals (e.g. Pd, Au and Ag) on the surface of TiO_2 is one of the common methods applied to increase the photocatalytic activity of TiO_2 under visible light and sunlights (Sun *et al.*, 2014). Among the metals, silver has attracted intense attention to increase photocatalytic activity and stability and can act as electron traps aiding electron–hole separation (Arabatzis *et al.*, 2003). Researches showed the improving in the efficiency of some dyes with Ag doped TiO_2 (Padikkaparambil *et al.*, 2012; Mirkhani *et al.*, 2009). However, there are a few reasearches about the examination of the effects of process parameters by statistical methods. Response surface methodology (RSM) is very useful, quick and cost-effective statistical method that are obtained optimization of different parameters and exhibits the interaction of these parameters (Khataee *et al.*, 2010; Kasiri *et al.*, 2011; Barka *et al.*, 2014).

The aim of this study is to evaluate MB and MO decolorization by pure TiO_2 and Ag doped TiO_2/UV process and also examining the effects of initial dye concentration, pH, catalyst concentration and time on photocatalytic degradation by using response surface methodology. Also, toxicity is evaluated at optimum

conditions by Daphnia Magna and identified the intermediate products and degradation pathways of both dyes.

2. Materials and methods

2.1.Chemicals and analytical methods

Methylene blue (MB, Cat No: 1.05045), methyl orange (MO, Cat No: 1.01322), silver nitrate ($AgNO_3$, Cat No: 1.01510), glacial acetic acid (Cat No: 1.00056), Ethanol (Cat No: 1.00986) hydrochloric acid (Cat No: 1.00314), and sodium hydroxide (Cat No: 1.06462) were purchased from Merck. Titanium (IV) butoxide (Cat No: 86910, purum ≥97.0%) was obtained from Fluka. All aqueous solutions were prepared by using deionized water. The determination of Methylene Blue (MB, λ = 664 nm) and Methyl Orange (MO, λ= 464 nm) at different irradiation times were analyzed by UV–vis spectroscopy in a Shimadzu UV-2401 PC instrument in standard quartz cells.

Residues and intermediates of MB and MO were determined by ESI-MS using an AB Sciex (Models 3200 QTRAP) and MS was operated in positive and negative ionization mode with electrospray source ionization (ESI). The positive ionization mode was operated under the following conditions: curtaing gas (CUR): 20, ion spray voltage (IS): 5500, DP: 90 and EP: 10. The negative ionization mode was operated under the following conditions: curtaing gas (CUR): 20, ion spray voltage (IS): -450, DP: -70 and EP: -12.

Pure and Ag doped TiO_2 catalysts were characterized by scanning electron microscope (SEM)-energy dispersive X-ray analyzer (EDX) and Fourier Transform Infrared Spectroscopy (FTIR). The particle morphology was observed by a scanning electron microscope (FEI-QUANTA FEG 250) with secondary electron detector (Everhardt Thornley ETD detector) operated at 5 kV, 2.5 spot and 60000x mag and equipped with an attachment for the Energy dispersive X-ray spectroscopy (EDX) was used for analysis of elemental compositions of the photocatalysts. FT-IR was performed at room temperature on a Bruker VERTEX 70 ATR and it was used to evaluate and identify the formation of functional groups formed during synthesis of the photocatalyst in the range of 400 to 4000 cm^{-1}. The pH_{pzc} of the samples was determinated according to the literature (Asgari *et al.*, 2013).

2.2.Preparation of pure and doped TiO_2

Pure TiO_2 and Ag doped TiO_2 catalysts were prepared by sol-gel technique at room temperature. Ethanol was slowly added to titanium (IV) butoxide and was stirred for 60 min (Ethanol:Titanium Butoxide: 10:1 v/v). A second solution was prepared mixing glacial acetic acid with deionized water (Glacial acetic acid:Distilled water: 1:3 v/v) and this solution was gradually added to titanium (IV) butoxide and ethanol solution and stirring continued for one hour. Ag-TiO_2 ratios (weigth%) were selected as 0.5, 1.0, 1.5 and 2.0% Ag (weight%) was added glacial acetic acid and deionized water solutions for Ag doped TiO_2. After that sol was dried at 105 °C for 12 hours and calcinated in muffle furnace at 450 °C for 2 hours. Pure TiO_2 was prepared by the same methods of metal doped TiO_2 without any metal additions.

2.3.Photocatalytic experiments

The photocatalytic experiments performed with 150 mL quartz beaker and carried out at Luzchem UV Photoreactor equipped with fifteen UV-A (Hitachi, 8W) or UV-Vis light lamps (Sylvania, 8W) at 30°C. Samples for analysis were collected at 3 ml and through 0.45 µm cellulose acetate membranes. NaOH and HCl solutions were used for pH adjustments in this study.

2.4.Central composite design (CCD)

CCD were used to evaluate the influence of operating parameters and to determine the optimum Ag/TiO_2 ratios for photodegradation of MB and MO. The CCD matrix was used in the experiments and designed by using the Design Expert. Four factors were investigated as inital MB or MO concentration (mg l^{-1}), pH, catalyst concentration (g l^{-1}) and reaction time (min.). Total number of experiments was 30 and the experimental design points consists of 2^n factorial points (2^4= 16), 2n axial points (2x4=8) and 6 replications

of central points (Table 1). The second-order polynomial equation was used in this study according to previous research (Zuorro *et al.*, 2013).

Table 1. Experimental factors and levels in the central composite design.

Factors	Levels				
	-2	**-1**	**0**	**+1**	**+2**
MB or MO Concentration (mg l^{-1}) (X_1)	5	10	15	20	25
pH (X_2)	3	5	7	9	11
Ag-TiO_2 Concentration (mg l^{-1}) (X_3)	0.125	0.25	0.375	0.50	0.625
Reaction time (min^{-1}) (X_4)	30	60	90	120	150

2.4.Toxicity by Daphia Magna

Acute toxicity of initial and photocatalytic treated samples of different times were done by Daphnia magna (new born daphnids <24 h) according to ISO 6341 Method (1996). Toxicity tests details were given at Cifci *et al.*, 2015. All samples were diluted by 50% and set at pH 8, also 20 ml effective volume was used in the test beaker.

3.Results and discussion

3.1.Characterization of pure TiO_2 and doped TiO_2 catayst

Figure 1 shows the SEM images of pure TiO_2 and 0.5, 1.0 and 2.0% Ag doped TiO_2 particles. All the morphologies of particles have different shapes of grains with irregular boundaries and exhibit aggregated particles with many smaller crystals. It can be seen that in 2.0% Ag-TiO_2 nanoparticles have increased the particle size of TiO_2 nanoparticles. The results of EDX analysis for elemental composition of pure TiO_2 and 0.5, 1.0 and 2.0% Ag-TiO_2 showed that the weight of Ti (titanium) and O (oxygen) were the main components of the nanoparticles. The atomic ratio of Ti and O in the nanoparticles were within the range of 8.7-10.5% and 90.1-91.3%, respectively. The atomic ratio of Ag in the 0.5, 1.0 and 1.5% Ag-TiO_2 were obtained 0.11%, 0.20% and 0.44%, respectively.

According to the FT-IR spectra of nanoparticles, four significant peaks were shown at ca. 400-500, 600-800, 1600-1700 and 2300-2400 cm^{-1}. The peak around 400-500 cm^{-1} assigned to the characteristic vibrations of Ti-O-Ti lattice and bending mode of vibrations and at ca. 700 and 800 cm^{-1} were attributed to the strecthing vibrations of Ti–O bonds in the TiO_2 lattice (Bezrodna *et al.*, 2004). Peak around 1600-1700 cm^{-1} represented the bending vibrations of the O–H bending which adsorb hydroxyl ions on the surface of catalyst plays an important role in increasing photocatalitic activity. Comparing the FT-IR spectra of the pure and Ag doped TiO_2, significant changes were observed at peaks around 600-800, 1600-1700 and 2300-2400 cm^{-1} when Ag doped the TiO_2 surface. The peaks increased with escalating Ag weight from 0.5% to 1.0%; however in 2.0% Ag-TiO_2 nanoparticles peaks decreased according to 1.0% Ag-TiO_2 nanoparticles. Furthermore, with doping Ag on to TiO_2 catalayst, there has become a new peak at around 1500-1600 cm^{-1}.

pH_{pzc} values of Ag-TiO_2 did not significantly change between 0-1% Ag-TiO_2 and they were 6.6, 6.33 and 6.25 in TiO_2, 0.5% Ag-TiO_2 and 1.0% Ag-TiO_2. However, at 2.0% Ag-TiO_2 pH_{pzc} values increased to 7.05. pH_{pzc} value is important due to positively surface charged ($pH<pH_{pzc}$) and negatively surface charged ($pH>pH_{pzc}$) of the particles (Khanna and Shetty, 2013).

3.2.Photocatalytic activity of MB and MO

In the study, photolysis can be ignored due to very low degradation of MB and MO in the absence of catalysts under UV-A conditions. MB removal efficiencies were not significantly changed by 0.5% Ag-TiO_2 while it was increased from %83 to %99 with %1 Ag doped the TiO_2 catalyst. A similiar result was also observed on MO removal. However, the MB or MO decolorization efficiencies decreased both UV-A and UV-Visible conditions when Ag amount increase than 1.0%. The high amount of Ag particles on the TiO_2 surface decrease the intensity of light through photocatalytic degradation. As a consequence, maximum

MB and MO decolorization were achieved at 1.0% Ag-TiO_2. Moreover, the irridation time decreased from 120 min. to 90 min with 1.0% Ag/TiO_2 catalyst under UV-A conditions.

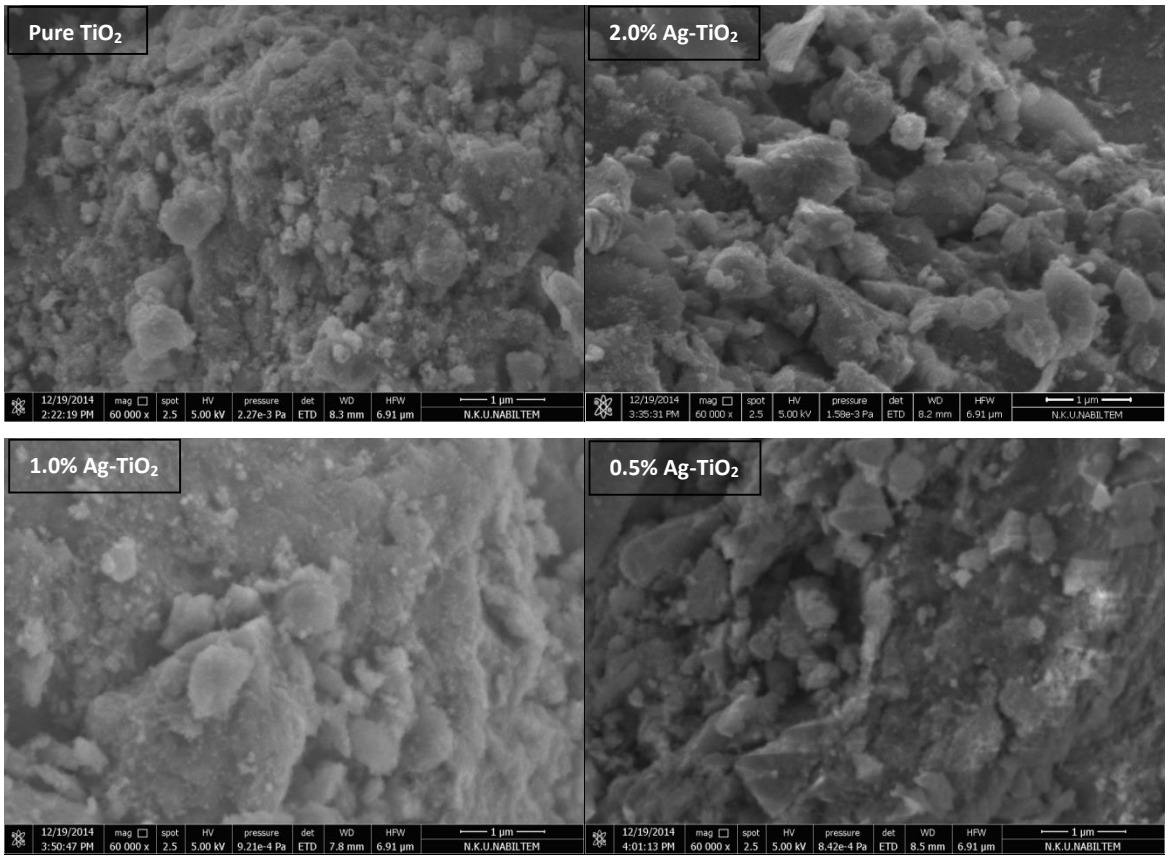

Figure 1. SEM images of pure TiO_2 and 2.0, 1.0 and 0.5% Ag-TiO_2 nanoparticles

In UV-Visible conditions, MB decolorization increased from 18% to 44% after 7 h. irridation with 1% Ag-TiO_2 nanoparticles while MO decolorization increased from 27% to 36%. Photocatalytic degradation of MB and MO were fitted to pseudo first order reaction kinetics for TiO_2/UV process. Pseudo first order kinetics were calculated according to Zaharieva *et al.*, 2015 and pseudo first order kinetic constants are given as k_{app}. According to results, k_{app} was obtained approximately 2 fold higher with 1.0% Ag-TiO_2 than pure TiO_2 catalyst in MB decolorization while its 3.5 fold higher in MO decolorization.

Table 2. MO and MB kinetics of Ag-TiO_2 catalyts under UV-A and UV-Vis conditions (MB or MO: 20 mg l^{-1}, pH 7.0, catalyst: 0.5 g l^{-1})

Catalyst	UV-A for MB		UV-Visible for MB		UV-A for MO		UV-Visible for MO	
	k_{app}*	Removal	k_{app}	Removal	k_{app}*	Removal	k_{app}	Removal
TiO_2	15.0	83.1	0.54	18.3	9.3	80.4	0.70	26.8
0.5% Ag-TiO_2	14.4	81.5	0.70	24.3	11.9	82.6	0.54	25.4
1.0 % Ag-TiO_2	34.1	99.2	1.41	44.5	33.2	99.6	1.02	36.5
1.5% Ag-TiO_2	25.7	96.8	0.84	30.6	17.0	95.4	0.85	34.8
2.0% Ag-TiO_2	22.7	95.1	0.73	25.9	14.8	92.8	0.63	29.5

*k_{app} values are min^{-1} *10^{-3} and Removal is %

3.3.Analysis of central composite design

Maximum photodegradation of MB and MO were found at the 1.0% weight ratio of Ag-TiO_2 catalyst and CCD experiment were done in photocatalytic degradation of MB and MO with UV-A conditions. The experimental and predicted results of MB and MO removal with variable matrix were shown in Table 3.

In the CCD experimental and predicted datas of Ag-TiO_2/UV-A process, the results of the quadratic regression model are fitted analysis of variance (ANOVA) at 95% confidence level ($p<0.05$). The Model F-value (15-18) and P value Prob > F (< 0.0001) imply that the model is significant. The larger the magnitude of the t-value and smaller the P-value, the more significant is the corresponding coefficient (Liu and Chiou, 2005). Moreover, the value of the determination coefficient (R^2) and the adjusted determination coefficient (adjusted R^2) are obtained 0.9519 and 0.9070 in MB decolarization and 0.9599 and 0.9225 in MO decolarization, respectively and it is recommended that R^2 should be more than 0.80 to fit the regression model (Daghrir *et al.*, 2013). The closing experimentals and predicted values are means that the model is a good fit in these experiments. MB and MO decolarization equations are given in Eq. 1 and Eq. 2, respectively.

Table 3. Experimental design matrix and response based on experimental and predicted value on MB and MO removal efficiency

Standard Order	X_1	X_2	X_3	X_4	MB Removal (%)		MO Removal (%)	
					Experimental	Predicted	Experimental	Predicted
1	-1	-1	-1	-1	53.6	57.8	78.5	81.0
2	1	-1	-1	-1	74.7	68.4	50.6	49.1
3	-1	1	-1	-1	96.3	96.7	71.0	69.0
4	1	1	-1	-1	74.0	77.1	33.8	37.6
5	-1	-1	1	-1	42.9	47.6	90.8	90.1
6	1	-1	1	-1	60.7	59.8	79.9	84.1
7	-1	1	1	-1	99.6	99.9	75.7	78.6
8	1	1	1	-1	79.2	82.0	78.6	73.2
9	-1	-1	-1	1	75.8	75.7	99.2	99.6
10	1	-1	-1	1	88.9	86.8	72.6	69.9
11	-1	1	-1	1	100.0	99.0	96.8	92.8
12	1	1	-1	1	82.0	80.1	67.9	63.6
13	-1	-1	1	1	77.2	72.3	98.1	94.6
14	1	-1	1	1	82.7	85.1	93.9	90.8
15	-1	1	1	1	100.0	109.0	91.9	88.4
16	1	1	1	1	97.7	91.8	87.5	85.2
17	-2	0	0	0	100.0	94.2	93.5	95.1
18	2	0	0	0	82.6	87.5	56.8	60.0
19	0	-2	0	0	45.6	47.6	84.2	84.0
20	0	2	0	0	96.0	93.1	61.4	66.4
21	0	0	-2	0	69.5	71.8	53.2	54.8
22	0	0	2	0	76.5	73.3	82.1	85.4
23	0	0	0	-2	78.5	74.8	78.0	73.8
24	0	0	0	2	99.6	102.4	95.3	100.3
25	0	0	0	0	94.1	93.5	93.1	93.3
26	0	0	0	0	93.1	93.5	93.4	93.3
27	0	0	0	0	94.1	93.5	93.7	93.3
28	0	0	0	0	92.9	93.5	93.5	93.3
29	0	0	0	0	93.1	93.5	93.4	93.3
30	0	0	0	0	93.6	93.5	92.6	93.3

X_1 MB or MO Concentration (mg l^{-1}), X_2 pH, X_3 Ag-TiO_2 Concentration (g l^{-1}), X_4 Reaction time (min)

The expression of MB decolarization percentage by following equation:

$$Y=93.46-1.68*X_1+11.38*X_2+0.37*X_3+6.90*X_4-7.52*X_1X_2+0.42*X_1X_3+0.14*X_1X_4+3.36*X_2X_3-3.88*X_2X_4+1.70*X_3X_4-0.66*X_1^2-5.78*X_2^2-5.23*X_3^2-1.22*X_4^2$$

(1)

According to Equation 1, pH value of solution affects the MB removal efficiency more than the other parameters and pH (X_2) and time (X_4) are important factors on MB decolarization. pH (X_2), Ag-TiO_2 concentration (X_3) and time (X_4) have possitive effect on the photocatalytic degradation of MB. It means that the photocatalytic degradation is the most suitable at high pH, high Ag-TiO_2 concentration and high reaction time (Fig. 2). Besides, MB removal decreased while the inital MB concentration (X_1) increased. Also, quadratic effect is observed in pH and Ag-TiO_2 concentration and synergy effect is observed between inital MB concentration and pH; pH and Ag-TiO_2 concentration; pH and time. MB removal efficiency is decreasing from 100% to 60% at low Ag-TiO_2 concentration and acidic conditions. MB removal obtained about 70% even increasing Ag-TiO_2 concentration from 0.125 to 0.625 g l^{-1} at pH 3. However, it could be increased to 90% with increasing pH to 9 at low Ag-TiO_2 concentration (0.25 g l^{-1}).

The expression of MO decolarization percentage by following equation:

$$Y=93.27-8.79*X_1-4.42*X_2+7.65*X_3+7.64*X_4+0.13*X_1X_2+6.49*X_1X_3+0.56*X_1X_4+0.16*X_2X_3+1.32*X_2X_4-3.51*X_3X_4-3.93*X_1^2-4.52*X_2^2-5.80*X_3^2-1.06*X_4^2$$

(2)

According to Equation 2, all factors have most effect on the response factors of MO decolarization and the effect of the independent parameters is counted as: inital MO concentration>Ag-TiO_2 concentration>oxidation time>pH. A similiar result was obtained at other research and it is explained that high dye concentration caused the reduction of penetration (Sahoo and Gupta, 2012). Ag-TiO_2 concentration (X_3) and time (X_4) have possitive effects on the photocatalytic degradation of MO, while the inital MB concentration (X_1) and pH (X_2) have negative. It means that the photocatalytic degradation is the most suitable at low inital MO concentration, low pH, high Ag-TiO_2 concentration and high reaction time (Fig. 3). The most important parameter to enhance the MO removal efficiency is initial MO concentration and the effects of Ag/TiO_2 and oxidation time are very close to the effects initial MO concentration. Besides, quadratic effect is observed in the inital MO concentration, pH and Ag-TiO_2 concentration and synergy effect is observed between inital MO concentration and Ag-TiO_2 concentration; Ag-TiO_2 concentration and reaction time. MO removal efficieny is decreased to 60% when pH 9 and Ag-TiO_2 concentration 0.25 g l^{-1} or pH 9 and 60 min oxidation time.

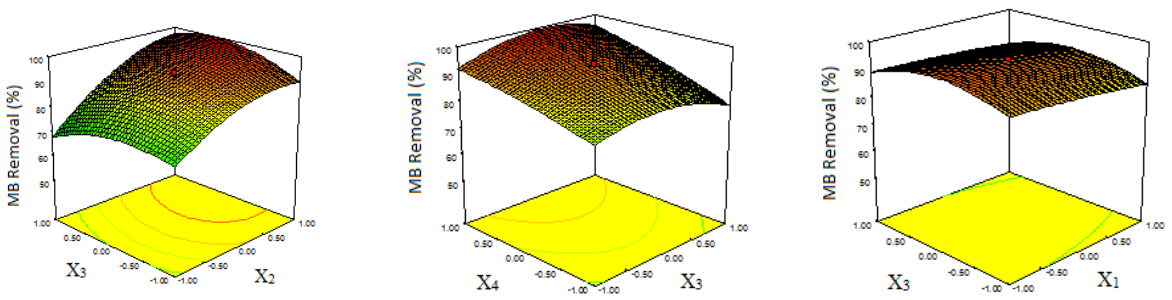

Figure 2. Response surface and contour plots of MB decolorization (%) between independent variables

MB and MO removal efficiencies decrease by increasing the inital MB and MO concentration. High MB decolarization was observed at 5, 10 and 15 mg l^{-1} MB concentration than 20 and 25 mg l^{-1} MB concentration. Xiao *et al.* (2008) observed similiar trends and MB degradation was decreased at 20 and 50 mg l^{-1} than 5 and 10 mg l^{-1} MB concentration. High MB concentrations cause the reduction of light penetration into solution and inhibite photogenerated holes or absorbe UV photons by the pollutants instead of TiO_2 photocatalyst (Xiao *et al.*, 2008; Daghrir *et al.*, 2013). Besides, according to MB removal, MO removal efficiency is affected more than the increase of MO concentration. MO removal efficiency was decreased to 56.8% at 25 mg l^{-1} MO concentratration while MB removal efficiency is 79.5% at 25 mg l^{-1} MB concentration.

Photocatalytic decolorization efficiency of MB increased with increasing the pH value and similar trends were observed in the literature (Xiao *et al.*, 2008; Lin *et al.*, 2006). Besides, the adsorption of MB increased with increasing pH (Lachheb *et al.*, 2002). In this study, maximum MB decolorization was observed at pH 9. On the other hand, maximum MO decolorization was observed in acidic condition at pH 5.

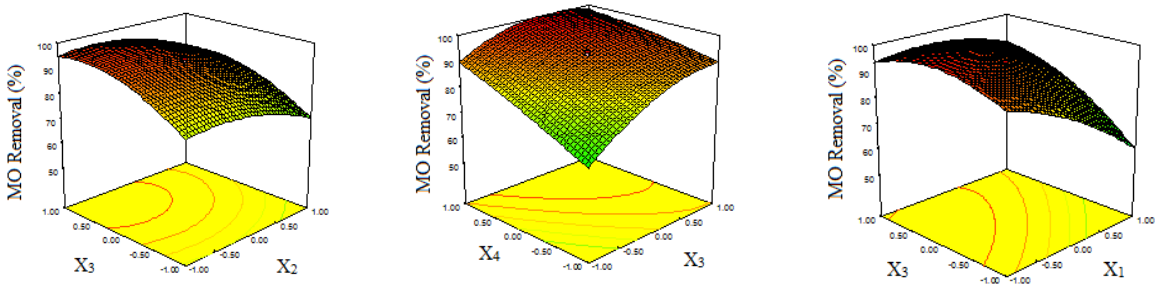

Figure 3. Response surface and contour plots of MO decolorization (%) between four independent variables at central level

The influence of Ag/TiO_2 concentration, within the range of 0.125–0.625 g l^{-1} is evaluated and the MB removal rate increased with the increasing Ag-TiO_2 concentration until 0.500 g l^{-1}. After 120 min irradiation, 71.9% MB decolarization efficiency was observed at 0.125 g l^{-1} Ag-TiO_2 concentration and it increased to 99.6% MB removal at 0.375 g l^{-1} Ag-TiO_2 concentration while it is slightly decreased to 93.4% MB removal at 0.625 g l^{-1} Ag-TiO_2 concentration. When the initial MB or MO concentrations increase, the reaction time increases in parallel due to the reducing the photogeneration of holes or OH radicals on the surface of catalyst.

3.4.Toxicity Evaluation at optimum conditions

Photocatalytic oxidation process must be evaluated by toxicity due to the understanding full of minerilization or the toxicity of intermediate by-products (Saien and Khezrianjoo, 2008). Toxicity assays by *Daphnia Magna* is benefical method for evaluation of toxicity in textile wastewater or dyes (Meriç *et al.*, 2005a; 2005b). Optimum conditions of MB and MO were selected to evaluate of toxicity by photocatalytic process. Toxicity of *Daphnia Magna* decreased with degrading the dye molecules in time and there was no observed toxicity after 60 min oxidation time while approximately 98-99% MB or MO removal and %38-40 TOC removal observed after 60 min photocatalytic oxidation. However, TOC removal was increased with oxidation time increased from 60 to 120 min and TOC removal was obtained as 83.3% for MO, while it is observed that 45.8% of TOC removal for MB after 120 min photocatalytic oxidation time (Fig. 4).

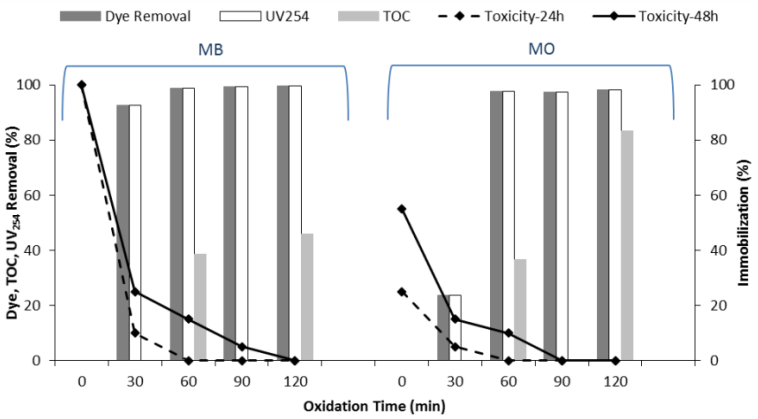

Figure 4. Decolorization and toxicity evaluation of optimum condition of MB (MB: 20 mg l^{-1}, pH: 9 and Ag-TiO_2: 0.375 g l^{-1}) and MO (MO: 20 mg l^{-1}, pH: 5 and Ag-TiO_2: 0.625 g l^{-1})

Decreasing *Daphnia Magna* immobilization with increasing oxidation time in both MB and MO dyes indicate that breaking of the long chain molecules of dyes and occured nontoxic by-products (Meriç *et al.*, 2005b). Besides, more than 95% UV_{254} removal showed the high dearomatization in both systems (Çifçi *et al.*, 2015).

3.3.Paracetamol Residues in treated samples by Ag doped TiO_2 catalysts

ESI-MS analysis was used to determine the aromatic by-products of MB and MO photo-oxidation and both of MB and MO degradation pathways are given in Figure 5 a-b. The MS analysis gives six significant m/z values which are 114.1, 101.7, 140.1, 123.9, 288.1 and 107.9 m/z in MB degradation while it is four significant m/z values which are 101.9, 240.7, 114.1 and 140.1 m/z in MO degradation.

MB was degraded to single ring structure products and three main single ring structure by-products were observed in the sample which were at 124 m/z (aminoquinone), 108 m/z (benzoquinone) and 140 m/z (Phenylsulfinate ion). Phenylsulfinate ion at 140 m/z was also observed photocatalytic degradation of methylene blue on nanocrystalline TiO_2 (Gnaser *et al.*, 2005).

MO was separated into two forms due to the hydroxyl radical attack the benzene containing SO_3 group and phenylsulfinate ion at 140 m/z was observed in the treated samples like MB treated samples. On the other hand, product at 241 m/z could be MO molecules (absence of SO_3) which was given in literature (Baiocchi *et al.*, 2002). Aromatic structure of intermadiates generate demethylation reactions by hydroxyl radicals and the molecule at 212 m/z (both methyl groups absence) was observed as by oxidation products (Mascolo *et al.*, 2007; Baiocchi *et al.*, 2002). After the seperation of methyl groups, the OH radicals attack has become to take place on the –N=N– double bond and the aromatic rings of products were degrading to single ring structures such as at 124 m/z (aminoquinone) and 108 m/z (benzoquinone).

114.1 and 101.7 m/z values were observed in both of the dyes which indicated that intermadiates were degrading to smaller molecules such as carboxylic acids group. At the end of the degradation of dyes, these carboxylic acids converted to inorgonic ions such as carbon dioxide, nitrate, sulfate, water and chlorine (Huang *et al.*, 2010; Ghauch *et al.*, 2012).

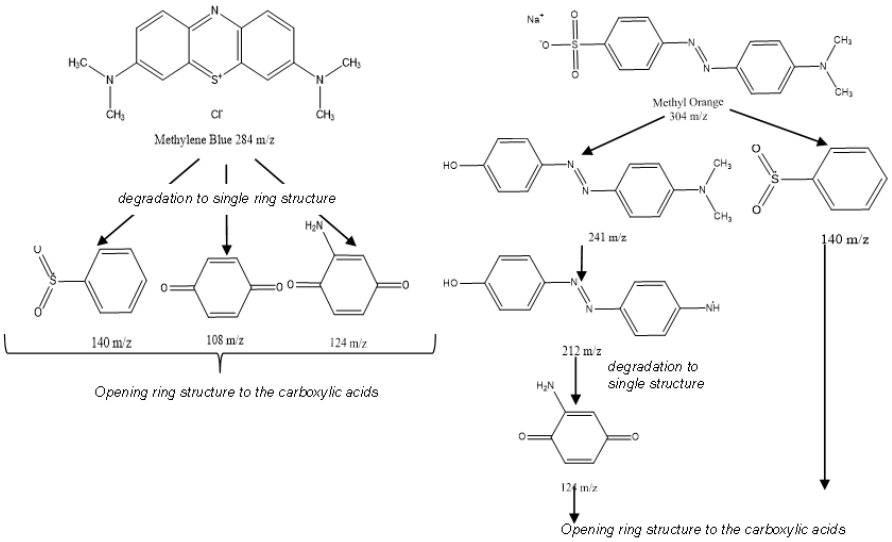

Figure 5. Possible degradation pathway of dyes by Ag doped TiO_2 MB (MB: 20 mg l^{-1}, pH: 9 and Ag-TiO_2: 0.375 g l^{-1}, oxidation time: 120 min) and MO (MO: 20 mg l^{-1}, pH: 5 and Ag-TiO_2: 0.625 g l^{-1}, oxidation time: 120 min)

4. Conclusion

In this study, photocatalytic degradation of methylene blue and methyl orange by using pure TiO_2 and Ag-TiO_2 were evaluated. Maximum MB decolarization was observed 1% Ag-TiO_2/UV-A process and it was

found that 1% (weight) Ag doped TiO_2 increased both the MB and MO removal efficiency from about 80% to 99% at 0.5 g l^{-1} catalyst concentration after 2 hour photocatalytic degradation. Furthermore, MB and MO photodegradation reaction kinetic constant increased approximately 2 and 3.5 fold higher by dopping 1% Ag on the surface of TiO_2 at TiO_2/UV process, respectively. The toxicity of Daphnia Magna was not observed in both dyes by Ag-TiO_2 catalyst after 2 h photocatalytic oxidation times and this means that both of the dyes can be degraded to non toxic degradation products. Also, it was examined that the effects of the inital MB concentration, pH, Ag-TiO_2 concentration and reaction time on MB decolarization in Ag-TiO_2/UV-A process. In MB decolarization, pH was the most important parameter for the photodegradation while initial MO concentration was the most effect the photocatalytic process in MO decolarization. The Response Surface Methodology approach was a useful method for estimation of the influence process operating conditions on MB and MO photodegradation. Metal doped TiO_2 could be enhanced the photocatalytic degradation of dyes and the residues products were the non toxic in aquatic environment.

Funding

This study was financed by Namik Kemal University Scientific Research Projects with project number NKUBAP.00.17.AR.14.01.

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