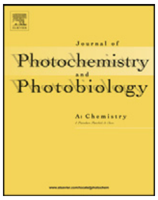
Journal of Photochemistry and Photobiology A: Chemistry 225 (2011) 26–35

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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



Response surface methodological approach for the assessment of the photocatalytic degradation of NOM

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ARTICLE INFO

Article history:
Received 20 April 2011
Received in revised form
16 September 2011
Accepted 24 September 2011
Available online 1 October 2011

Keywords:
Response surface methodology
NOM
Photocatalytic oxidation

ABSTRACT

In this paper, statistics-based experimental design with response surface methodology (RSM) was employed to investigate the effects of operational conditions on the photocatalytic oxidation of humic acid as a model compound of natural organic matter. Considering the vast number of the obtained experimental data, in this study, a correlative approach was employed for the assessment of the photocatalytic degradation efficiency of humic acids (HA) using an empirical method for the optimization of the key parameters such as photocatalyst dose, pH and humic acid concentration. The results of this study revealed that the regression analysis showed a close fit ($R^2 > 0.83$) between the experimental results and the model predictions. Maximum DOC removal was achieved as 89.3% under the experimental conditions of 30 mg/L humic acid, 2.0 mg/mLTiO_2 and pH = 7. Under acidic conditions (pH = 5), and in the presence of 1.0 mg/mLTiO_2 almost complete removal of UV absorbing centers were attained for 30 mg/L humic acid. Exhaustive decolorization was attained under alkaline conditions (pH = 8), for the photocatalyst loading of 1.5 mg/mLTiO_2 for 18.5 mg/L humic acid. The role of the irradiation period on the removal efficiency of the specified parameters were expressed by the relation between the predicted values attained for irradiation periods (40 min and 60 min) that were presented by the correlation coefficients as $R^2 = 0.847$, 0.691 and 0.700 for DOC, UV_{254} and $Color_{436}$ respectively. Moreover, model verification was also reported for a selected humic acid substrate and a specified photocatalyst specimen.

1. Introduction

Natural organic matter (NOM) is a complex heterogeneous aggregate of organic compounds defined as decaying material from plants, animals and their degradation products in terrestrial environments as well as in aquatic systems. NOM displays temporal and spatial heterogeneity with important impacts on energy and carbon dynamics. In aquatic systems dissolved organic carbon (DOC) constitutes the largest pool of reduced organic carbon displaying high reactivity and influencing ecosystem functions through many biogeochemical reactions, such as binding with metal ions and hydrous metal oxides. Humic substances (HSs) mainly humic acids (HAs) that are comprised of highly functionalized carbon rich polydisperse polyelectrolytes are the major fraction of naturally occurring organic substances [1]. Humic substances act as the main precursors for the formation of carcinogenic disinfection by-products (DBPs) during the chlorination process in water treatment systems. The treatment of water for potable use has traditionally focused on the removal of NOM by the application of conventional treatment methods and later by advanced treatment processes such as membrane filtration, ion exchange/adsorption and ozonation/biodegradation. Moreover, advanced oxidation processes have also been employed for the destructive removal of NOM. A significant interest has been devoted to the TiO_2-mediated photocatalytic oxidation of HAs as model compounds of NOM [2–6] The photocatalytic behavior of humic acids in diverse aqueous solution matrix conditions has also been extensively studied by Bekbolet and coworkers [5,7,8].

Recent works have proved that response surface methodology (RSM) could serve as a powerful statistical tool for optimization of the process parameters [9,10]. RSM application on the advanced oxidation processes have been reported by several research groups [11–16]. RSM methodology has also been employed to the photocatalytic degradation studies of various pollutants [17–26]. More specifically the application of RSM for the removal of humic acids has been reported for electrocoagulation [27], for coagulation [28] for membrane filtration [29] and for photoelectrocatalytic removal of fulvic acids [30]. Rodrigues and colleagues [31] employed experimental design based on RSM approach for the elucidation of the trihalomethane formation potential of fulvic acid during chlorination. Moreover, Frimmel and colleagues used factorial screening

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doi:10.1016/j.jphotochem.2011.09.021

design for the elucidation of the disinfection by-products by photocatalysis [32,33]. Performance of further investigations on this subject could be beneficial in order to find out the optimal settings of reaction parameters at lab-scale or pilot scale.

The objectives of this study could be visualized in dual perspectives; (i) the application of RSM methodology was assessed for the photocatalytic degradation efficiency of humic acids in terms of selected UV–vis parameters ($Color_{436}$ and UV_{254}) and DOC for the optimization of the key parameters such as photocatalyst dose, pH and humic acid concentration, ii. verification of the RSM model results were evaluated by the use of previously obtained "generic" data for the understanding of the applicability of the RSM methodology to the photocatalytic degradation efficiency.

2. Methodology

2.1. Materials

Aqueous humic acid (HA) solutions (sodium salt of humic acid was supplied from Aldrich) in the concentration range of 10–50 mg/L were prepared by the appropriate dilutions of the stock humic acid solution (1000 mg/L) prepared by using Milli-Q type ultrapure water. The pH of the humic acid solutions was adjusted by the addition of either $HClO_4$ or NaOH. Titanium dioxide, Degussa P-25 was used as the photocatalyst. The main physico-chemical characteristics of TiO_2 P-25 was reported as possessing a crystal structure composed of 70% anatase and 30% rutile with BET surface area of $55 \pm 5\ m^2/g$ and medium particle size of 30 nm. All chemicals used were of reagent grade.

2.2. Photoreactor and photocatalytic treatment

Photocatalytic degradation of humic acid was carried out using a bench scale system comprised of a 50 mL cylindrical Pyrex reaction vessel. Titanium dioxide Degussa P-25 loading was used in the range of 0.10–2.00 mg/mL at different pH conditions (pH 5–9) [2,4]. A 125 W black light fluorescent lamp (BLF) emitting radiation between 300 and 420 nm with a maximum at 365 nm was used as the light source. A photon generation rate of 2.85×10^{16} quanta s^{-1} was measured by a potassium ferrioxalate actinometer [34]. Prior to analysis, following the specified reaction periods, i.e. 60 min and 40 min that were applied for the assessment of the effect of irradiation time, TiO_2 was removed from the reaction medium by filtration through 0.45 μm Millipore membrane filters.

2.3. Analytical methods and specified parameters

UV–vis spectra (200–600 nm) were recorded on a Perkin Elmer λ 35 Spectrophotometer. Dissolved organic carbon (DOC, mg/L) contents of the samples were determined by using Shimadzu TOC-VWP Series (Wet oxidation/NDIR method) total organic carbon analyzer. pH was measured by using WTW pH 526 pH meter equipped with a combined electrode.

Humic acid removal was expressed by using spectroscopic parameters as UV_{254} (absorbance at 254 nm, cm^{-1}), and $Color_{436}$ (absorbance at 436 nm, cm^{-1}) and DOC removals. The removal efficiency (Y) is calculated by using the simple equation; $Y (\%) = ((X_0 - X)/X_0) \times 100$, where X represents, DOC, $Color_{436}$ and UV_{254} obtained after treatment and X_0 represents the initial conditions of DOC, $Color_{436}$ and UV_{254}.

3. Results and discussion

3.1. Characterization of humic acid and selection of parameters

Photocatalytic degradation of humic acid was followed by UV–vis spectroscopic parameters specified as UV_{254} and $Color_{436}$ as well as by DOC contents. Humic acid concentration was selected as 10–50 mg/L representing DOC concentration that could be present in natural water conditions. Operational parameters of photocatalytic degradation were selected as photocatalyst loading and pH [5,8]. TiO_2 loading was chosen as 0.1–2.0 mg/mL representing the widely studied photocatalyst range (0.1–1.0 mg/mL) as well as covering the higher photocatalyst loading (2.0 mg/mL) [35]. pH should be considered as an important operational parameter due to both pH dependent variations in surface properties of TiO_2 and deprotonation capacity of humic acid. Taking into account the main functional groups of humic acids as carboxylic groups ($pK_a = 3–5$) and phenolic groups ($pK_a = 7–9$) and neutral pH conditions of natural waters (pH 6–7), the pH range was selected as pH 5–9. The pH_{zpc} of TiO_2 was reported as 6.3; therefore the selected pH range would also cover both the acidic and basic surface properties of the TiO_2 oxide surface [36]. Referring to the previously published results, irradiation time was selected as 60 min [37] and for comparison purposes the results obtained for 40 min of irradiation time were also presented to express the effect of irradiation time.

3.2. Model parameters for the photocatalytic degradation of humic acid

In the present study, a Box–Wilson experimental design was employed to evaluate the combined effect of three independent variables; initial humic acid concentration, TiO_2 loading and initial pH, designated as X_1, X_2 and X_3, respectively, on the photocatalytic removal efficiency of humic acid as expressed by the DOC, UV_{254}, and $Color_{436}$ removal percentages. The minimum and maximum range of variables were investigated and experimental conditions determined by the Box–Wilson statistical design were presented in Table 1. The experiments consisted of six axial (A), eight factorial (F) and center points (C). The center point was repeated four times. Computation was carried out using multiple regression analysis using the least squares method.

Considering the general function expressing the interaction between the independent and dependent variables a second order model was employed;

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{iii} X_i X_j \tag{1}$$

where b_{ii} represents the coefficients of the quadratic parameter and $i < j$.

The following response function was used in correlating the humic acid removal efficiency (Y_{HA}) in terms of DOC (Y_{DOC}), UV_{254} ($Y_{UV_{254}}$) and $Color_{436}$ ($Y_{Color_{436}}$) removal efficiency with independent parameters (X_1, X_2, X_3).

$$\begin{aligned} Y = {} & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 \\ & + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \end{aligned} \tag{2}$$

The STATISTICA computer program was employed for the determination of the coefficients by regression analysis of the experimental data for each where; Y is predicted yield, b_0 is constant, b_1, b_2 and b_3 are linear coefficients, b_{12}, b_{13} and b_{23} are cross product coefficients and b_{11}, b_{22} and b_{33} are quadratic coefficients. The results attained by the photocatalytic degradation experiments that were performed under 60 min of irradiation period were used to determine the coefficients of the response functions, and the coefficients were further used in calculating predicted values of DOC, UV_{254} and $Color_{436}$ removal efficiencies (Eqs. (3)–(5)). The correlation coefficients (R^2) between the observed and predicted values were found to be 0.933 for DOC, 0.912 for UV_{254} and 0.834 for $Color_{436}$ removal

Table 1
Experimental conditions according to a Box–Wilson statistical design.

	X_1 HA	X_2 TiO_2	X_3 pH		X_1 HA	X_2 TiO_2	X_3 pH		X_1 HA	X_2 TiO_2	X_3 pH
	Axial points				Factorial points				Center points		
A1	50	1.0	7	F1	41.5	1.5	8	C1	30	1.0	7
A2	10	1.0	7	F2	41.5	1.5	6	C2	30	1.0	7
A3	30	2.0	7	F3	41.5	0.5	8	C3	30	2.0	7
A4	30	0.1	7	F4	41.5	0.5	6	C4	30	0.1	7
A5	30	1.0	9	F5	18.5	1.5	8				
A6	30	1.0	5	F6	18.5	1.5	6				
				F7	18.5	0.5	8				
				F8	18.5	0.5	6				

indicating a good agreement between the observed and predicted values.

$$\begin{aligned}\text{DOC removal, } \% = {} & -224.0959 + 4.1856\,(\text{HA}) + 70.0558\,(\text{TiO}_2) \\ & + 63.2270\,(\text{pH}) + 0.1230\,(\text{HA} \times \text{TiO}_2) \\ & -0.1893\,(\text{HA} \times \text{pH}) - 5.3118\,(\text{TiO}_2 \times \text{pH}) \\ & -0.04711\,(\text{HA})^2 - 11.7834\,(\text{TiO}_2)^2 \\ & -4.1950\,(\text{pH})^2 \end{aligned} \tag{3}$$

$$\begin{aligned}\text{UV}_{254}\text{ removal, } \% = {} & 269.1764 - 1.3543\,(\text{HA}) - 22.8069\,(\text{TiO}_2) \\ & -40.9156\,(\text{pH}) + 0.8192\,(\text{HA} \times \text{TiO}_2) \\ & -0.1511\,(\text{HA} \times \text{pH}) + 5.5280\,(\text{TiO}_2 \times \text{pH}) \\ & +0.01555\,(\text{HA})^2 - 12.1101\,(\text{TiO}_2)^2 \\ & +2.7141\,(\text{pH})^2 \end{aligned} \tag{4}$$

$$\begin{aligned}\text{Color}_{436}\text{ removal, } \% = {} & 182.5990 + 0.09794\,(\text{HA}) - 9.1079\,(\text{TiO}_2) \\ & -23.4907\,(\text{pH}) + 0.3015\,(\text{HA} \times \text{TiO}_2) \\ & -0.1519\,(\text{HA} \times \text{pH}) + 5.6790\,(\text{TiO}_2 \times \text{pH}) \\ & +0.007706\,(\text{HA})^2 - 14.5387\,(\text{TiO}_2)^2 \\ & +1.5147\,(\text{pH})^2 \end{aligned} \tag{5}$$

The factors in front of the model terms indicate the intensity and direction of the influence of the independent variable. A positive effect of a factor means that the response is improved when the factor level increases and a negative effect of the factor reveal that the response is inhibited when the factor level increases. On the basis of the coefficients given in Eqs. (3)–(5), it can be stated that the percent DOC removal or percent mineralization increases with concentration of humic acid (X_1), TiO_2 dose (X_2) and pH (X_3). According to Eq. (3), the variable TiO_2 dose exhibited the highest positive influence on percent DOC removal. The positive effect of pH could also be revealed as significant. UV_{254} removal decreases with HA concentration, TiO_2 dose and with a more profound effect of pH. On the other hand, $Color_{436}$ removal increases with the HA concentration while decreasing with TiO_2 dose and pH.

The examined independent variables of the process imply that the factors influencing the removal of DOC and the specified spectroscopic parameters may differ significantly from each other. Experimentally obtained results of the design matrix are presented in Table 2 together with the predicted responses obtained from the regression equations. The observed DOC removal efficiencies varied between 50.4% and 89.3%, UV_{254} removal efficiencies ranged from 49.9% to 100% and $Color_{436}$ removal efficiencies were between 62.6% and 100% after 60 min oxidation. Maximum DOC, UV_{254} and $Color_{436}$ removal efficiencies were found to be 89.3%, 100% and 100%, respectively. In most cases observed and predicted results were compatible with each other. These results were achieved at experimental conditions of A3 (30 mg/L humic acid concentration, 2.0 mg/mL TiO_2 loading and pH 7), A6 (30 mg/L humic acid concentration, 1.0 mg/mL TiO_2 loading and pH 5) and F5 (18.5 mg/L

Table 2
The observed and predicted DOC, UV_{254} and $Color_{436}$ removal efficiencies using Box–Wilson model.

No.	DOC removal, %		UV_{254} removal, %		$Color_{436}$ removal, %	
	Observed	Predicted	Observed	Predicted	Observed	Predicted
A1	70.4	65.7	78.5	78.8	92.2	94.6
A2	55.4	59.4	98.5	100	97.8	100
A3	89.3	82.6	93.9	89.9	95.5	91.6
A4	52.6	60.2	49.9	61.3	62.6	74.2
A5	50.4	51.7	88.0	92.8	97.7	99.2
A6	79.3	77.5	100	100	100	100
F1	61.9	65.8	93.1	91.8	99.9	99.1
F2	81.1	88.3	87.6	93.6	95.6	99.2
F3	57.7	56.7	63.9	60.6	81.6	79.3
F4	70.0	68.6	79.8	73.5	100	90.8
F5	63.2	65.1	100	100	100	100
F6	77.4	79.0	97.8	95.9	100	96.9
F7	65.6	58.8	100.0	88.7	100	90.9
F8	65.4	62.1	98.6	94.6	100	95.4
C1	83.4	81.4	90.6	85.7	95.6	95.5
C2	80.0	81.4	88.0	85.7	95.0	95.5
C3	86.0	81.4	83.0	85.7	97.0	95.5
C4	78.0	81.4	80.0	85.7	93.0	95.5

Table 3
ANOVA results for response surface quadratic model for 60 min oxidation.

Parameter	Source	Sum of squares	Degrees of freedom	Mean square	*F*-value	Prob > *F*
DOC removal	Model	2120.64	9	235.63	5.95	0.0098
	Residual	316.97	8	39.62		
	Lack of fit	279.10	5	55.82	4.42	0.1255
	Pure error	0.00	1	0.00		
	$R^2 = 0.9330$					
UV_{254} removal	Model	2568.95	9	285.44	4.40	0.0243
	Residual	519.24	8	64.91		
	Lack of fit	450.52	5	90.10	3.93	0.1445
	Pure error	0.00	1	0.00		
	$R^2 = 0.9120$					
$Color_{436}$ removal	Model	997.16	9	110.80	2.03	0.1652
	Residual	435.76	8	54.47		
	Lack of fit	427.49	5	85.50	31.02	0.0087
	Pure error	0.00	1	0.00		
	$R^2 = 0.8340$					

humic acid concentration, 1.5 mg/mL TiO_2 loading and pH 8). In order to see the precision of the predicted values, the experimental data were analyzed using the trial version of Design-Expert 7.0.0 software using user defined model and fitted to a second order model. Coefficient values similar to that obtained with STATISTICA programme were attained. The model adequacy check is an integral part of the data analysis as the approximating model functions would give poor or misleading results if the fit is inadequate. Table 3 shows the Analysis of Variance (ANOVA) results of the established model for percent DOC, UV_{254} and $Color_{436}$ removals.

The mean squares were obtained by dividing the sum of squares of each of the two sources of variation, the model and the error (residual) variance, by the respective degrees of freedom (DF). The model *F*-value (Fisher variation ratio), probability value (Prob > *F*) and adequate precision are the main indicators showing the significance and adequacy of the employed model. The model *F*-value was calculated by dividing the model mean square by residual mean square. Values of Prob > *F* less than 0.0500 imply that the model is significant, whereas the values greater than 0.1000 are usually considered as insignificant. Prob > *F* values of 0.0098 and 0.0243 denote the employed models are significant for percent DOC and UV_{254} removals, respectively. On the contrary, the high Prob > *F* value (0.1652) obtained for percent $Color_{436}$ removals reveal that the model is insignificant for the $Color_{436}$ removal response. The use of the $Color_{436}$ parameter signifies the decolorization efficiency rather than the removal of organic content of humic acid [8].

The correlation coefficients (R^2) value of the response variables followed the order of R^2 (DOC) > R^2 (UV_{254}) > R^2 ($Color_{436}$). The highest R^2 obtained for DOC removal efficiency indicates that 93.3% of the total variation could be represented by the established model expressing a satisfactory quadratic fit. Considering the above explained ANOVA test results, the model application explained the reaction quite well and can be employed to navigate the design space at least in terms of DOC and UV_{254} removal efficiencies.

The response surface plots of the model-predicted responses keeping one variable constant and varying the others within the experimental ranges were established. The interactive relationships between the process variables and treatment outputs for humic acid as a model compound of natural organic matter were presented below.

3.3. *Optimization of operational parameters*

3.3.1. *Effect of initial humic acid concentration*

The effect of initial HA concentration on the removal efficiency of DOC, UV_{254} and $Color_{436}$ at a constant TiO_2 concentration of 1.0 mg/mL, for different pH values were predicted by using response equations with determined coefficients (Eqs. (3)–(5)) as presented in Figs. 1–3.

DOC removal efficiencies displayed an increasing trend with respect to increasing pH conditions up to an initial humic acid concentration of 30 mg/L. Further increase in DOC removals could also be attained under pH conditions of pH 5–8 for 40 mg/L HA followed by a more significant decrease for an initial HA concentration of 50 mg/L HA irrespective of pH.

pH values close to the pH_{zpc}, the surface of TiO_2 is equally positively and negatively charged according to the following equations (Eqs. (6) and (7));

$$Ti^{IV}-OH + H^{+} \rightarrow Ti^{IV}-OH_2{}^{+} \quad K_{a1} \tag{6}$$

$$Ti^{IV}-OH + OH^{-} \rightarrow Ti^{IV}-O^{-} + H_2O \quad K_{a1} \tag{7}$$

the pH_{zpc} of TiO_2 can be calculated as $pH_{zpc} = (pK_{a1} + pK_{a2})/2 = 6.3$ [33,35,36].

Therefore, the resulting effect of the predominating negative–negative charge repulsion by reason of the presence of negative TiO_2 surface conditions ($pH > pH_{zpc} = 6.3$) and negatively charged humic moieties due to the deprotonation of both carboxylic ($pK_a = 3–5$) and phenolic groups ($pK_a = 7–9$) could be observed by the considerably lower DOC removal at pH 9. Moreover, under alkaline conditions humic acid exhibits a rather stretched conformational structure open to oxide surface interactions probably leading to surface saturation condition [37]. The light absorption capacity of TiO_2 is diminished due to the surface coverage thereby formation of reactive oxygen species primarily hydroxyl radicals is also hindered. Under neutral and slightly acidic conditions humic moieties display spherical coiled conformational structure leading to fractional surface coverage and open access to light interaction. The resulting effect of the aqueous reaction medium conditions could be visualized by the pH controlled removal efficiencies. The maximum DOC removal efficiency was obtained as 84% at pH 6 and HA concentration of 30 mg/L ($DOC_i = 10.5$ mg/L) (Fig. 1a). Higher pH conditions (pH > 6) and HA concentrations above 30 mg/L resulted in lower DOC removal efficiencies.

Fig. 1b depicts the variation of UV_{254} removal efficiency with HA concentration for different pH conditions in the presence of a constant TiO_2 loading of 1.0 mg/mL. Complete removal of UV_{254} was attained in the presence of 10 mg/L humic acid. pH dependency in UV_{254} removal could be regarded as insignificant (<10%) for lower initial humic acid concentration conditions displaying $UV_{254,i} = 0.4750\ cm^{-1}$ and $0.6906\ cm^{-1}$ for 20 mg/L and 30 mg/L of HA respectively at pH 7. However, in the presence of higher initial

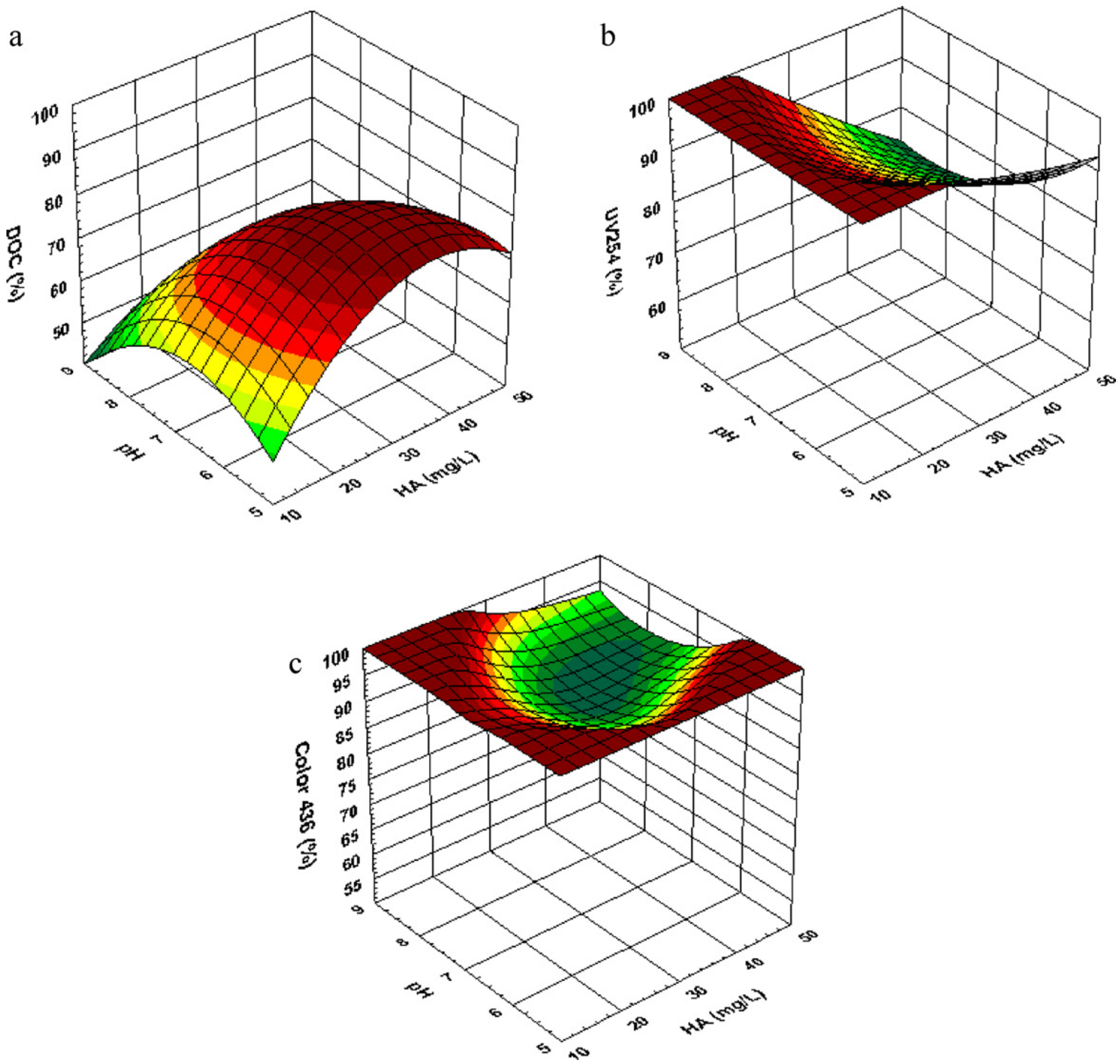

Fig. 1. Variation of DOC, UV_{254} and $Color_{436}$ removal efficiencies as a function of initial humic acid concentration under different pH conditions (5–9) and constant TiO_2 loading of 1.0 mg/mL.

humic acid concentrations, acidic conditions were found to be more favorable for the complete elimination of UV absorbing centers. The reason could be expressed by the TiO_2 surface and humic acid binary interactions expressing UV absorbing centers free for photocatalytic oxidation. The maximum UV_{254} removal efficiency was obtained as 100% at pH 5 and at the maximum HA concentration of 50 mg/L ($UV_{254,i} = 1.141\ cm^{-1}$).

Considerably higher $Color_{436}$ removal efficiencies (>90%) were attained under all pH conditions (Fig. 1c). pH dependent minor differences could be observed in case of initial HA concentrations of $\geq$30 mg/L. Complete removal of $Color_{436}$ was reached in case of 10 mg/L HA under all pH conditions representing a combined effect of pH and a considerably high TiO_2 loading (1.0 mg/L). Photocatalytic degradation of HA (10 mg/L) would certainly result in 100% removal of UV_{254} and $Color_{436}$ due to the presence of considerably higher photocatalyst loading (1.0 mg/mL) (Figs. 2 and 3). The reason could also be explained by the comparatively low DOC contents as 3.33 mg/L expressing 0.2398 cm^{-1} UV_{254} and 0.0452 cm^{-1} $Color_{436}$. The most pronounced pH effect was found to be for the photocatalytic degradation of 40 mg/L HA ($Color_{436,i} = 0.1878\ cm^{-1}$ at pH 6). Initial humic acid concentration of 30 mg/L and at pH 5 could be visualized as optimum conditions for the photocatalytic degradation humic acid in the presence of 1.0 mg/mLTiO_2 loading.

3.3.2. Effect of TiO_2 concentration

The effect of TiO_2 concentration on the removal efficiency of DOC, UV_{254} and $Color_{436}$ at constant pH of 5 for different initial humic acid concentrations were predicted by using response equations with determined coefficients (Eqs. (3)–(5)) as presented in Fig. 2. A general increasing trend was observed in removal efficiency of DOC irrespective of initial humic acid concentration and TiO_2 loading. Maximum DOC removal efficiency (91%) was achieved at an initial HA concentration of 40 mg/L and TiO_2 concentration of 2.0 mg/mL. Increasing the initial HA concentration up to 40 mg/L significantly enhanced the oxidative removal of DOC. Further increase in HA concentration (50 mg/L, $DOC_i = 15.50$ mg/L) did not significantly alter the DOC removal efficiency ($\leq$5%) under all TiO_2 loading conditions (0.1–2.0 mg/mL).

Considerably lower photocatalyst loading affected the UV_{254} removal efficiency ($\sim$30%) for humic acid in the range of 10–50 mg/L. The reason could be explained by the presence of TiO_2 loading related limited surface area available for the adsorption of the increasing amount of humic moieties. Almost complete elimination of UV absorbing centers was attained for the TiO_2 loading of 1.0–1.5 mg/mL irrespective of the humic acid concentration. Further increase in the photocatalyst loading to 2.0 mg/mL displayed

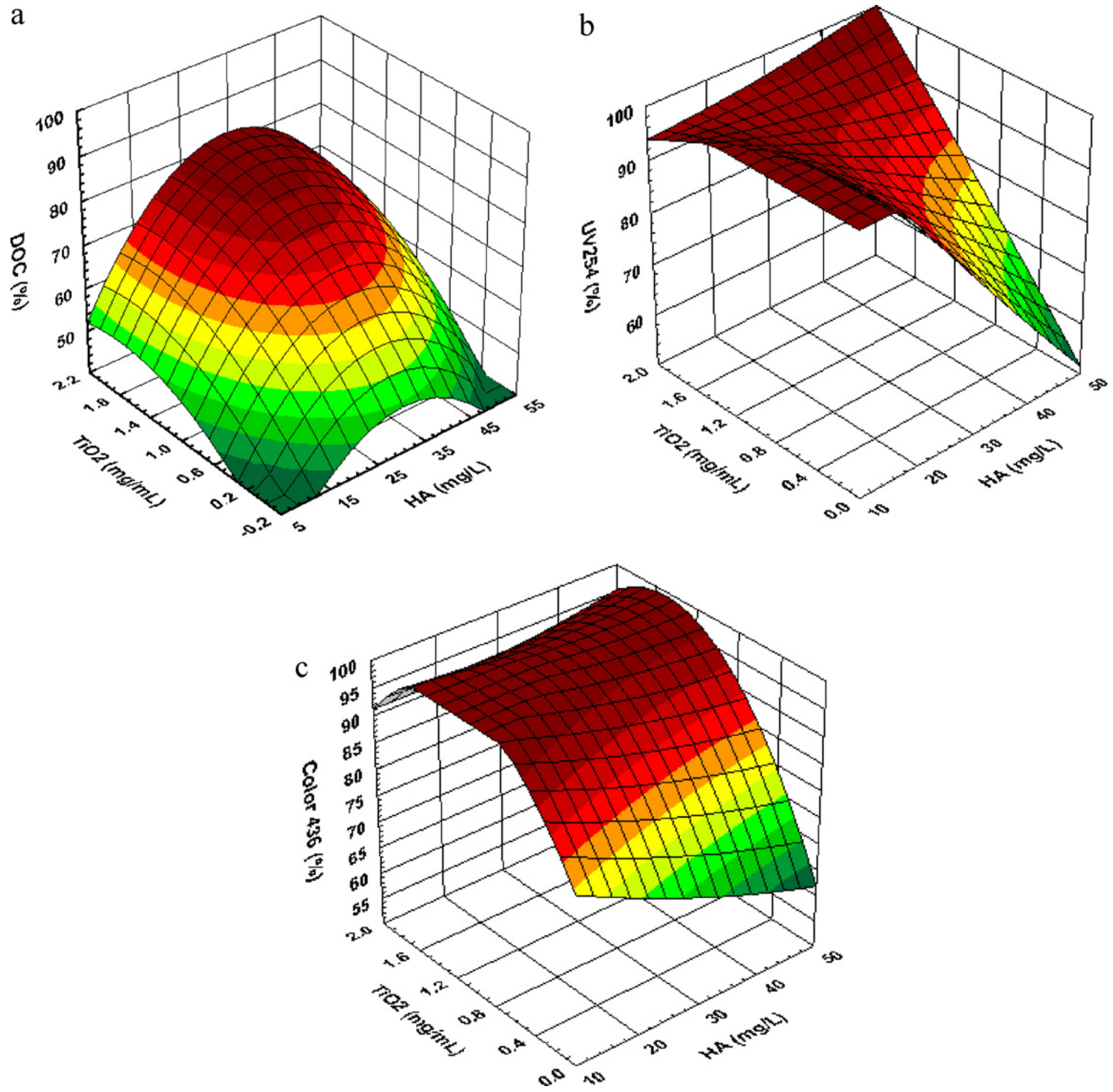

Fig. 2. Variation of DOC, UV_{254} and $Color_{436}$ removal efficiencies as a function of TiO_2 loading at different initial humic acid concentrations (10–50 mg/L) and constant pH 5 condition.

a humic acid concentration dependent UV_{254} removal efficiency probably resulting from the TiO_2 surface blockage by the humic acid moieties. However, for the specified system, TiO_2 concentrations > 1.0 mg/mL would be considered as counterproductive due to photo hindrance caused by the turbidity of the suspensions [3,4]. The optimum UV_{254} removal efficiency (100%) obtained with the addition of 1.0 mg/mLTiO_2 and 30 mg/L HA concentration.

Fig. 2c depicts the variation of $Color_{436}$ removal efficiency with TiO_2 concentration for different HA concentrations at constant pH of 5. Under all conditions ≥80% removal of $Color_{436}$ was attained. Considerably lower TiO_2 loading as 0.1 mg/mLand high TiO_2 loading of 2.0 mg/mL displayed similar reactivity due to the prevailing surface area related adsorption of humic moieties.

The optimum $Color_{436}$ removal efficiency (100%) was achieved at an initial HA concentration of 50 mg/L and TiO_2 concentration of 0.5 mg/mL. It should also be taken into account that the reported HA concentration expresses approximately 50% DOC content with polydisperse properties expressing diverse reactivities towards oxidative decolorization.

3.3.3. *Effect of pH*

The effect of pH on the removal efficiency of DOC, UV_{254} and $Color_{436}$ at constant humic acid concentration of 30 mg/L were predicted by using response equations with determined coefficients (Eqs. (3)–(5)) as presented in Fig. 3.

The most pronounced effect (~40%) with respect to varying loading was predicted under acidic conditions (pH 5). Increasing pH to alkaline conditions resulted in diminished effect of TiO_2 loading probably due to the prevailing negative-negative repulsions. Considerably similar DOC removal was predicted for 30 mg/L humic acid in the presence of 0.1 mg/mL under acidic (pH 5) and alkaline conditions (pH 9). The reason could be attributed to the counter balancing effects of surface charge and the pH dependent deprotonation capacity of humic moieties.

The maximum DOC removal (90%) was obtained after 60 min of oxidation at a TiO_2 concentration of 1.5 mg/mL and the pH of 6. Higher pH (pH > 6) caused decreasing in the removal efficiency. The reason could be attributed to the factors that were presented in the preceding section. pH dependent surface coverage of the oxide surface by the deprotonated and charged humic moieties

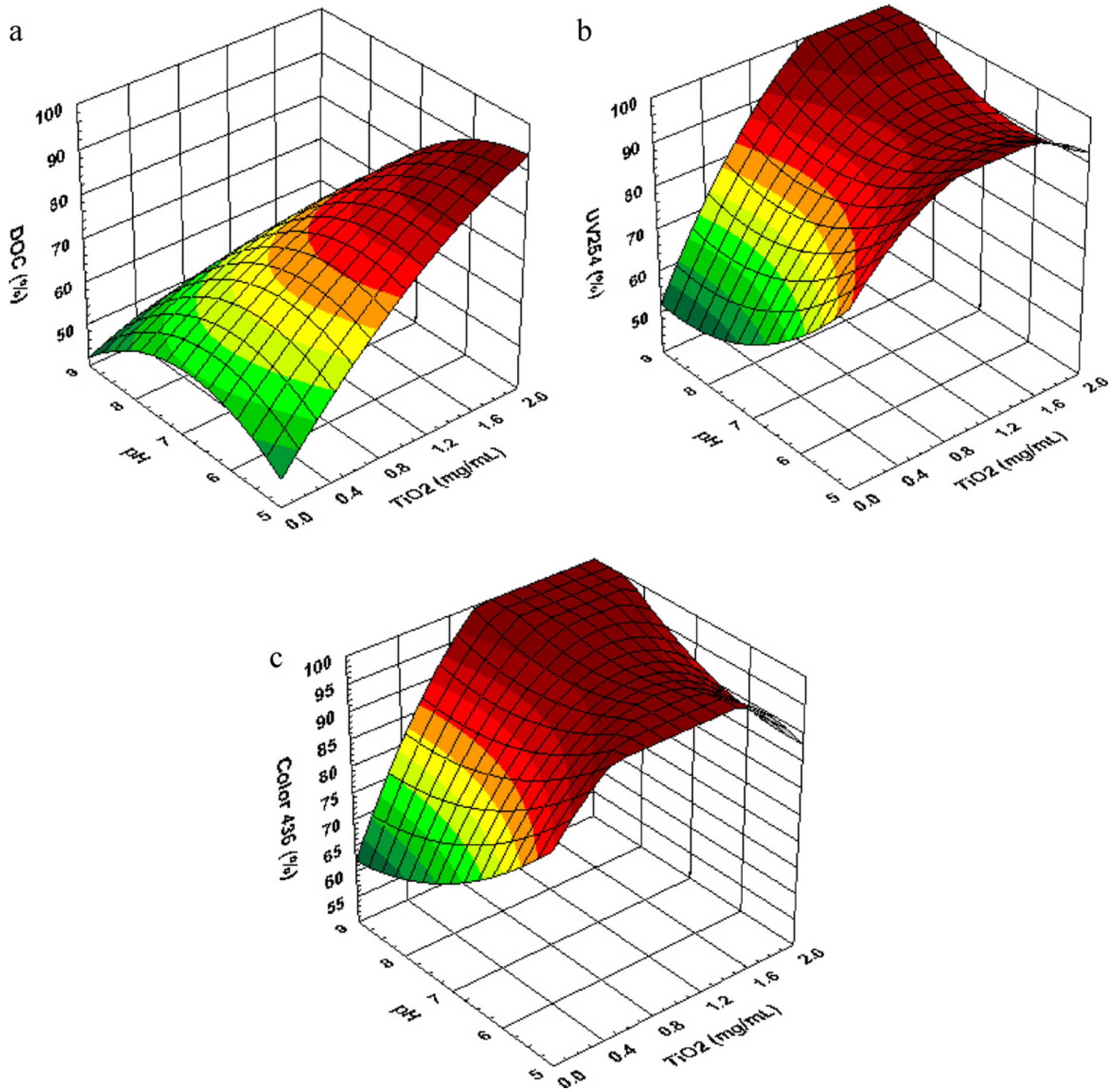

Fig. 3. Variation of DOC, UV_{254} and $Color_{436}$ removal efficiencies as a function of pH at different TiO_2 loadings (0.1–2.0 mg/mL) and constant humic acid concentration of 30 mg/L.

could diminish light penetration thereby hinder the oxidation efficiency. Therefore, slightly acidic conditions could be preferred for the achievement of the higher removal efficiency. The reported results hold prime importance in terms aquatic systems where neutral pH conditions prevail.

Fig. 3b shows the variation of UV_{254} removal efficiency with pH for different TiO_2 concentrations at constant humic acid concentration of 30 mg/L. Noticeably different trends were predicted for the pH dependent effect of TiO_2 loading on the removal of UV_{254} indicating the role of the occupied surface area by the UV absorbing humic moieties. The most pronounced TiO_2 loading effect was predicted at pH 9 that could also be attributed to the role of prevailing electrostatic repulsions under alkaline conditions. Maximum UV_{254} removal efficiency (100%) was achieved at an initial TiO_2 concentration of 1.0 mg/mL and at pH 5.

Under all conditions, considerably higher $Color_{436}$ removal (>70%) was predicted with respect to the removal of UV absorbing centers. The removal efficiency of $Color_{436}$ displayed a lower pH dependency in the presence of different TiO_2 loadings and 30 mg/L humic acid. Considerably similar $Color_{436}$ removal efficiency was predicted under slightly acidic to neutral reaction conditions ($pH \sim\leq pH_{zpc} = 6.3$) expect for the TiO_2 loading of 0.1 mg/mL. The optimum $Color_{436}$ removal efficiency was obtained at pH 5 with the addition of 0.5 mg/mL TiO_2 (Fig. 3c).

3.4. *Effect of irradiation time on the photocatalytic degradation efficiency of humic substances*

Previous studies on photocatalytic oxidation of humic acids revealed pseudo first order kinetic rate constant in the order of $10^{-2}\,min^{-1}$ corresponding to half-life of ≥43 min for humic acid concentration 50 mg/L and TiO_2 loading of 0.25-mg/mL [3–5]. Considering that the rate of humic acid degradation is a function of both initial humic acid concentration and photocatalyst loading under fixed pH conditions, 60 min irradiation period displayed ≥50% removal in terms of the specified UV–vis and DOC parameters. Moreover, 40 min of irradiation period could also reveal a significant degree of removal of humic acid as expressed by DOC, UV_{254} and $Color_{436}$ parameters. The above presented approach was also applied for the assessment of the photocatalytic degradation efficiency using the data attained for 40 min of irradiation period.

Table 4
ANOVA results for response surface quadratic model for 40 min oxidation.

Parameter	Source	Sum of squares	Degrees of freedom	Mean square	*F*-value	Prob > *F*
DOC removal	Model	2126.56	9	236.28	4.05	0.0309
	Residual	467.25	8	58.41		
	Lack of fit	436.98	5	87.40	8.66	0.0528
	Pure error	30.27	3	10.09		
	$R^2 = 0.8199$					
UV_{254} removal	Model	3670.30	9	407.81	4.20	0.0467
	Residual	776.50	8	97.06		
	Lack of fit	729.69	5	145.94	9.35	0.0476
	Pure error	46.81	3	15.60		
	$R^2 = 0.8254$					
$Color_{436}$ removal	Model	1815.21	9	201.69	1.86	0.1977
	Residual	868.53	8	108.57		
	Lack of fit	849.27	5	169.85	26.45	0.0110
	Pure error	19.27	3	6.42		
	$R^2 = 0.6764$					

Below given equations (Eqs. (8)–(10)) represent the DOC, UV_{254} and $Color_{436}$ removals attained for the photocatalytic degradation of humic acid employing the experimental conditions specified as 10–50 mg/L humic acid concentration, 0.1–2.0 mg/mL TiO_2 loading, pH conditions of 5–9 and an irradiation period of 40 min as explained in Section 2.

$$\begin{aligned}\text{DOC removal, \%} = {} & -145.1108 + 3.772\,(\text{HA}) + 81.2967\,(\text{TiO}_2) \\ & + 39.5552\,(\text{pH}) - 0.08295\,(\text{HA} \times \text{TiO}_2) \\ & - 0.2146\,(\text{HA} \times \text{pH}) - 6.4497\,(\text{TiO}_2 \times \text{pH}) \\ & - 0.03417\,(\text{HA})^2 - 9.4106\,(\text{TiO}_2)^2 \\ & - 2.4201\,(\text{pH})^2 \end{aligned} \tag{8}$$

$$\begin{aligned}\text{UV}_{254}\,\text{removal, \%} = {} & 266.8715 - 0.9765\,(\text{HA}) - 23.5975\,(\text{TiO}_2) \\ & - 41.9630\,(\text{pH}) + 0.8192\,(\text{HA} \times \text{TiO}_2) \\ & - 0.1511\,(\text{TiO}_2 \times \text{pH}) + 5.5279\,(\text{HA} \times \text{pH}) \\ & + 0.01017\,(\text{HA})^2 - 11.7299\,(\text{TiO}_2)^2 \\ & + 2.7889\,(\text{pH})^2 \end{aligned} \tag{9}$$

$$\begin{aligned}\text{Color}_{436}\,\text{removal, \%} = {} & 210.0473 + 0.3323\,(\text{HA}) + 34.7154\,(\text{TiO}_2) \\ & - 38.5686\,(\text{pH}) - 0.09809\,(\text{HA} \times \text{TiO}_2) \\ & - 0.3620\,(\text{HA} \times \text{pH}) - 0.3386\,(\text{TiO}_2 \times \text{pH}) \\ & + 0.03035\,(\text{HA})^2 - 9.0472\,(\text{TiO}_2)^2 \\ & + 3.3393\,(\text{pH})^2 \end{aligned} \tag{10}$$

On the basis of the coefficients in Eqs. (8)–(10), it can be concluded that the percent DOC removal or percent mineralization, increases with the HA concentration (X_1), TiO_2 dose (X_2) and pH (X_3). The TiO_2 dose has a more profound effect on the DOC removal as compared to the others. The UV_{254} removal decreases with the HA concentration, TiO_2 dose and pH. The $Color_{436}$ removal, increases with the HA concentration and TiO_2 dose while decreasing with pH. The TiO_2 concentration is more effective than the HA concentration.

The results of ANOVA test for percent DOC, UV_{254} and $Color_{436}$ removals are presented in Table 4. Prob > *F* values of 0.0309 and 0.0277 indicate the employed models are significant for percent DOC and UV_{254} removals, respectively. However, the high Prob > *F* value (0.1977) obtained for percent $Color_{436}$ removals reveal that the model is insignificant for the $Color_{436}$ removal response. This is not unexpected due to the fact that decolorization occurs rapidly under all experimental conditions as expressed by the first order reaction kinetics model parameters [3,4].

The correlation coefficients (R^2) value of the response variables followed the decreasing order of R^2, $UV_{254} > R^2$, DOC $> R^2$, $Color_{436}$. The highest R^2 obtained for UV_{254} removal efficiency indicates that 82.5% of the total variation could be represented by the established model expressing a satisfactory quadratic fit. However, in terms of color removal, only around 68% of the total variation could be explained by the model. Considering the above explained ANOVA test results, the model application explained the reaction quite well and can be employed to navigate the design space at least in terms of DOC and UV_{254} removal efficiencies.

Moreover, correlative interaction was determined for the predicted parameters attained by the use of model equations, i.e. for 60 min of irradiation time (Eqs. (3)–(5)) and for 40 min of irradiation time (Eqs. (8)–(10)). The calculated correlation coefficients were found as $R^2 = 0.847$, 0.691 and 0.700 for DOC, UV_{254} and $Color_{436}$, respectively. These results indicate the importance of the irradiation time period for a successful application of the model to represent the photocatalytic degradation efficiency.

3.5. Model verification on photocatalytic degradation of humic substances

Application of photocatalytic procedures for degradation of humic substances has been mostly studied in terms of determination of reaction kinetics in relation to the operational parameters [5]. These studies were performed considering the traditional one-factor-at-a-time (OFAT) approach, examining the effect of parameters such as initial concentration of target compound, degradation time, catalyst loading and characteristics, pH, UV light source and intensity. According to this approach it was assumed that the factors involved in the process should be independent. However, the result of this univariate analysis could reveal inadequate optimization towards response(s). Sakkas and co-workers [24] reported the importance of these factors in relation to the novel approach of chemometric methods such as response surface methodology (RSM) based on statistical design of experiments (DOEs). Following the application of the RSM methodology, a confirmation study is recommended under the optimized conditions that would enable the comparison of the observed results with the predictions. The developed model would be accepted as applicable irrespective of the changing factors levels provided that the results (response) of confirmation experiments would agree with

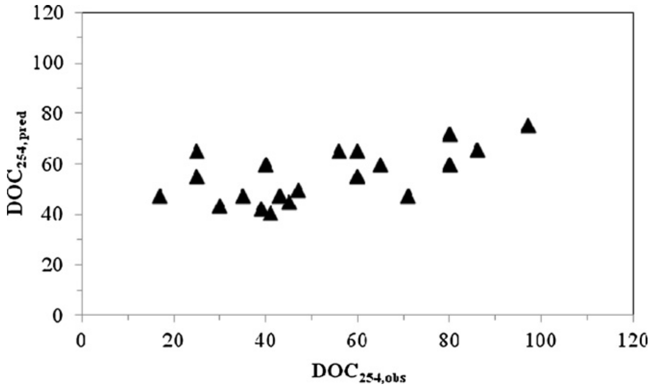

Fig. 4. Correlation between predicted DOC and observed DOC for various humic substances (IHAA HA, IHSS SHA, IHSS FA and RHA) and TiO_2 P-25 specimen.

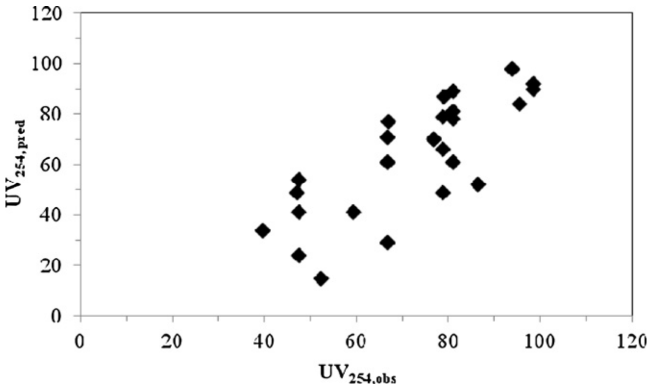

Fig. 5. Correlation between predicted UV_{254} and observed UV_{254} for various humic substances (IHAA HA, IHSS SHA, IHSS FA, and RHA) and TiO_2 P-25 specimen.

the predictions. In a similar approach, considering the above presented results attained by the application of RSM technique, the data achieved so far by Bekbolet and colleagues on the photocatalytic degradation of humic substances under various conditions were reexamined.

Model verification was performed by using the data attained under intra-laboratory standardized experimental conditions [2,37]. Since the characteristics of natural organic matter are known to be site specific, model compounds of different origins displaying diverse properties are generally used for photocatalytic degradation studies. Although humic acid supplied from Aldrich (HA) is widely used as the model compound by several research groups, it could not be completely accepted as the sole source of humic acid representing humic substances and natural organic matter. Therefore, the model compounds of humic substances were selected as Suwannee River humic acid supplied from International Humic Substances Society (IHSS) (IHSS HA), soil humic acid supplied from IHSS (IHSS SHA), humic acid representing terrestrial source from Roth (RHA) and Suwannee River fulvic acid supplied from IHSS (IHSS FA). The selected humic acid concentration range was 10–50 mg/L and photocatalytic oxidation experiments were performed using TiO_2 Degussa P-25 as the photocatalyst and pH was 6–7. For comparison purposes only DOC and UV_{254} parameters were considered since $Color_{436}$ removal displayed considerably higher efficiencies as $\geq$90% for all conditions.

The variations between DOC_{pred} and DOC_{obs} did not display any significant correlative interaction. Roth humic acid of terrestrial origin displayed a non-correlative behavior for DOC < 40 mg/L. Excluding RHA, DOC_{obs} with respect to DOC_{pred} revealed a correlation coefficient of $R^2 = 0.607$. Moreover the UV_{254} data also displayed insignificant relationship for photocatalytic degradation of various humic substances using TiO_2 Degussa P-25 ($R^2 = 0.616$).

Considering that the humic substances display differences with respect to geographic location, origin and climatic conditions from which they arise, elemental compositions of humic substances from all over the world are remarkably similar exhibiting the same general array of functional groups [1]. Therefore, similar reactivities leading to mineralization could be expected from the studied humic substances. However, the presented information (Figs. 4 and 5) displayed different removal efficiencies both with respect to DOC and UV_{254} parameters expressing the importance of the conformational and structural complexity of the humic moieties towards photocatalytic oxidation.

Further insight was devoted to the specific effects of the type of humic substance and TiO_2 specimen. As already mentioned, Aldrich humic acid was widely used as the model humic substance and TiO_2 Degussa P-25 as the photocatalyst specimen, the data were processed to represent the correlation between the predicted and observed DOC and UV_{254} parameters under the above given conditions. The linear regression displayed the following equations (Eqs. (11) and (12)) for Aldrich humic acid and TiO_2 P-25;

$$DOC_{pred} = 0.449\,DOC_{obs} + 29.0 \quad R^2 = 0.771 \tag{11}$$

$$UV_{254,pred} = 0.933\,UV_{254,obs} + 4.42 \quad R^2 = 0.920 \tag{12}$$

Due to the considerably higher correlative interaction UV_{254} could be an indicative parameter for the assessment of the photocatalytic degradation of humic acids. The reactivity of the UV absorbing centers towards reactive oxygen species mainly hydroxyl radicals dominates over the demineralization capacity of the organic carbon content.

4. Conclusive remarks

Based on the application of RSM methodology the effects of the operational parameters, i.e. initial humic acid concentration, TiO_2 loading and initial pH, on the photocatalytic removal efficiency of humic acid as expressed by the DOC, UV_{254}, and $Color_{436}$ removal percentages were presented. Comparative evaluation of the model predictions with respect to the observed results illustrated the optimum conditions that could be regarded as; generally observed humic acid concentration (30 mg/L), slightly acidic conditions (pH 5), and photocatalyst loading of 1.0 mg/mL.

Considering that these results should be stated for a reaction period of 60 min, a comparative approach was also presented for a shorter reaction period (40 min). The reaction period significantly governs the removal efficiency of humic acid in relation to the expressed parameters. From a broader perspective model humic acids could only resemble the natural organic matter to a limited extent, therefore the use of such models should be cautiously interpreted. Although significant results were achieved under the specified conditions, the role of the photocatalyst holds prime importance regarding the specific morphological and physicochemical properties.

In general, UV_{254} parameter could be successfully employed for the elucidation of the humic acid removal under all conditions. On the other hand, decolorization capacity overwhelmingly predominates over demineralization efficiency.

Considering the complex mechanism of humic acid oxidation that remains unresolved, the role of parameters, i.e. specified UV–vis parameters ($Color_{436}$, UV_{254}) and DOC should be reexamined. It is widely known that photocatalytic oxidation proceeds via different mechanistic pathways with respect to the removal of aromatic moieties, color forming centers and organic carbon content. Therefore, the overall resulting effect could be integrated to one indicative parameter (e.g. UV_{254}). Taking into account the prevailing reaction kinetics, reorganizing the dependent variables incorporating the factor of “irradiation time” is also recommended for further studies.

Furthermore, significance of the attained results could be accepted as primarily dependent upon the selected reaction conditions. Considering the heterogeneous nature of photocatalysis, oxidation efficiency is also a function of adsorption process taking place prior to the initiation of the light absorption followed by photo-adsorption and desorption process. Therefore, under the specified conditions, the RSM model could be regarded as applicable for a certain, i.e. user defined conditions and might not indicate a practical and useful approach. Complementary data derived from previous expertise of the authors were also arbitrarily chosen rather than application of the RSM model results to a new set of generic data for the assessment of the RSM model suitability. Final conclusive remark could be that the application of RSM methodology to any photocatalytic degradation system should be very cautiously interpreted especially in case of such complex substrates leading to various complicated interactions.

Acknowledgement

Financial support was provided by the Research fund of Bogazici University Project No: 5196.

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