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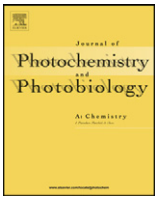

Response surface methodological approach for the assessment of the photocatalytic degradation of NOM

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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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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;

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

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).

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \qquad (2)$$

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