

AQUEOUS PHOTOCATALYSIS, NATURAL ORGANIC MATTER CHARACTERIZATION AND REMOVAL: A CASE STUDY OF THE PHOTACATALYTIC OXIDATION OF FULVIC ACID

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Abstract. Natural organic matter (NOM) is a complex mixture of organic compounds that occurs ubiquitously in both surface and ground waters. Its presence in water supplies not only contributes to aesthetic problems such as taste, odor and color, but also to operational and regulatory issues which include increased chemical usage, increased sludge production and membrane fouling. The variability in the amount and nature of natural organic matter is a significant factor in controlling the reactivity of aquatic humic substances with chlorine during water treatment processes. Hence, the potential for the formation of carcinogenic disinfection byproducts necessitates the removal of organics prior to chlorination stage in search for alternative advanced oxidation technologies to ensure compliance with drinking water quality standards. Humic substances (HS) represent the major fraction of naturally occurring organic substances comprised of carbon rich polydisperse polyelectrolytes. During recent years a significant interest has been devoted to the photocatalytic treatment of HS as model compounds of NOM. This paper addresses some basic issues related to the photocatalytic treatment of a model fulvic acid in relation to the relevant UV-vis and fluorescence spectroscopic properties. The oxidative removal of fulvic acid is evaluated by pseudo first order as well as Langmuir Hinshelwood kinetic models.

Keywords: Natural organic matter, fulvic acid, photocatalytic oxidation, UV-vis spectroscopy, fluorescence spectroscopy

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1. Introduction

Humic substances (HS); mainly humic and fulvic acids are the major fraction of naturally occurring organic substances. They are comprised of highly functionalized carbon rich polydisperse polyelectrolytes. Their ambiguous structures combine both hydrophobic and hydrophilic regions that result in the solubility enhancement modifying the toxic behaviour of various pollutants and impacting the transport of dangerous compounds in the aquatic system. More importantly, HS are well known precursors of carcinogenic and mutagenic trihalomethanes generated in conventional water treatment procedures, including chlorination (Rook, 1974; Singer, 1999). In this respect, it is necessary to remove these organics prior to chlorination stage in search for alternative advanced oxidation technologies to ensure compliance with drinking water quality standards.

During recent years, a significant interest has been devoted to the TiO₂ mediated photocatalytic oxidation of humic acids as model compounds of NOM (Bekbolet, 1996; Uyguner and Bekbolet, 2005a; Uyguner and Bekbolet, 2005b). Owing to the formation of hydroxyl radicals ($\bullet\text{OH}$), photocatalytic oxidation exerts a powerful oxidizing power in the reaction mixture, and thus can mineralize a myriad of undesirable organic matters to CO₂, H₂O and inorganic constituents. Some basic issues related to photocatalytic degradation kinetics of model humic substances supplied from commercial sources and the effect of solution matrix as specified by the presence of some common anions and cations on the photocatalytic removal of a model humic acid was investigated in detail (Bekbolet et al., 1998; Uyguner and Bekbolet, 2005a; Uyguner and Bekbolet, 2005b). However, only a limited number of research has been conducted on the removal of fulvic acids that are the water soluble portion of humic substances (Uyguner and Bekbolet, 2005). One of the recent studies in literature explains the removal of a commercial fulvic acid with an integrated approach incorporating photocatalytic oxidation with ultrafiltration for the effective separation of TiO₂ particles from its aqueous suspension (Fu et al., 2006).

Complementary to previous studies of humic acids and their photocatalytic oxidation properties, the objective of this work is to investigate the photocatalytic degradation of a standard fulvic acid solution focusing on the spectroscopic methods using UV-vis and fluorescence spectroscopy.

2. Materials and Methods

Suwannee River Fulvic Acid (IHSS FA) standard material purchased from the International Humic Substance Society was used as the model humic substance. A stock solution of 1000 mg L⁻¹ was prepared by dissolving fulvic acid in

distilled deionized water and diluting it to a solution of 50 mg L⁻¹ resulting in a dissolved organic carbon (DOC) content of 20.6 mg L⁻¹.

Photocatalytic oxidation of fulvic acid (50 mg L⁻¹) was carried out in the presence of TiO₂ Degussa P-25 (0.25 mg mL⁻¹) in a continuously mixed batch reactor using a 125 W BLF lamp as the light source (Uyguner and Bekbolet, 2005b). Prior to molecular size fractionation, partial oxidation of fulvic acid was carried out up to the extent that UV₂₅₄ absorbance value was removed by approximately 50%.

Molecular size fractionation of raw and photocatalytically treated fulvic acid was performed by Amicon 8050 ultrafiltration stirred cell system through a sequence of membranes which are of 100 kDa, 30 kDa, 10 kDa and 3 kDa nominal molecular size (Uyguner and Bekbolet, 2005b).

2.1. PARAMETERS USED FOR THE CHARACTERISATION OF FULVIC ACID

UV-vis absorbance values of the samples were determined using a Perkin Elmer λ 35 Spectrophotometer. Absorbance values at 436 nm (Color₄₃₆), 400 nm (Color₄₀₀), 365 nm (UV₃₆₅), 300 nm (UV₃₀₀), 280 nm (UV₂₈₀), and 254 nm (UV₂₅₄) were recorded for the evaluation of UV-vis parameters as absorbance ratios such as E₂₅₄/E₃₆₅ (UV₂₅₄/UV₃₆₅), and E₂₅₄/E₄₃₆ (UV₂₅₄/Color₄₃₆). Specific UV absorbance (SUVA₂₅₄, cm⁻¹ mg⁻¹ L) was used to represent DOC (mg L⁻¹) normalized aromatic moieties (UV₂₅₄). Dissolved organic carbon measurements of fulvic acid were performed on a Shimadzu TOCV CSH analyzer.

Fluorescence spectra in synchronous scan mode were recorded on a Perkin Elmer LS 55 luminescence spectrometer in the excitation wavelength range of 300–650 nm using the bandwidth of 18 nm between the excitation and emission monochromators (Senesi, 1990). The emission spectra were scanned over the range of 400–600 nm at a constant excitation wavelength of 350 nm (Senesi, 1990; Hautala et al., 2000).

3. Results and Discussion

3.1. PHOTOCATALYTIC DEGRADATION OF FULVIC ACID

Photocatalytically oxidized fulvic acid displayed the basic UV-vis spectroscopic structural pattern of native fulvic acid irrespective of the irradiation time. In a similar manner, DOC removal also followed an exponential decay as could be modelled by pseudo-first order reaction kinetics:

$$\text{Rate} = -dA/dt = k A \quad (1)$$

where, A is the absorbance of the specified UV-vis parameter of fulvic acid (m^{-1}) or DOC content ($mg L^{-1}$), t is the irradiation time (min), and k is the pseudo-first-order decay rate constant (min^{-1}).

The evaluation of the kinetic data for a variety of humic and fulvic acids from aquatic and terrestrial sources were discussed in a recent study where the half life value for the removal of IHSS FA ($50 mg L^{-1}$) in terms of DOC was reported to be one third of that of UV_{254} (Uyguner and Bekbolet, 2005b). As a complementary approach, confronting the photocatalyst effect, kinetics under different loading conditions were also assessed revealing that both of the rate and rate constants increase with increasing TiO_2 amount.

TABLE 1. Pseudo first order model parameters of photocatalytic removal of $50 mg L^{-1}$ IHSS FA in the presence of different TiO_2 loadings

	0.10 $mg mL^{-1}$ TiO_2		0.25 $mg mL^{-1}$ TiO_2		1.00 $mg mL^{-1}$ TiO_2	
	k min^{-1}	Rate $m^{-1}min^{-1}$	k min^{-1}	Rate $m^{-1}min^{-1}$	k min^{-1}	Rate $m^{-1}min^{-1}$
Color ₄₃₆	3.98×10^{-3}	0.0203	7.22×10^{-3}	0.0368	2.58×10^{-2}	0.132
Color ₄₀₀	3.96×10^{-3}	0.0388	6.71×10^{-3}	0.0658	2.24×10^{-2}	0.219
UV ₃₆₅	4.13×10^{-3}	0.0795	6.46×10^{-3}	0.125	2.00×10^{-2}	0.388
UV ₃₀₀	3.28×10^{-3}	0.176	4.87×10^{-3}	0.259	1.55×10^{-2}	0.825
UV ₂₈₀	2.70×10^{-3}	0.185	4.02×10^{-3}	0.275	1.33×10^{-2}	0.910
UV ₂₅₄	2.65×10^{-3}	0.241	3.76×10^{-3}	0.342	1.22×10^{-2}	1.11

Increasing the TiO_2 loading from $0.1 mg mL^{-1}$ to $1.0 mg mL^{-1}$ by ten fold has the effect of increasing the rate by approximately five fold. In view of the generally presented optimum loading of $1.0 mg mL^{-1}$ of TiO_2 , the pseudo first order degradation rate constants for the specified UV-vis parameters range from $1.22 \times 10^{-2} min^{-1}$ to $2.58 \times 10^{-2} min^{-1}$. However, different results were reported in literature, as depicted by Fu et al., (2006), $0.50 g L^{-1}$ of a nanostructured $TiO_2/silica$ gel photocatalyst was found to be the optimum concentration for the photocatalytic removal of a fulvic acid. It was explained that increasing the catalyst concentration had the effect of decreasing the degradation rate of fulvic acid. Considering the use of different photocatalyst, reactor, and fulvic acid of various origins, it is plausible to achieve diverse results. Taking into account the comprehensive network of reactions occurring during the photocatalytic process, a complex kinetic model comprising all the dependent parameters on the degradation rate was developed (Minero, 1999). However, the most widely applied kinetic models of photocatalytic decomposition of organic compounds are based on Langmuir-Hinshelwood (L-H) equation which is a modified form of pseudo first order reaction kinetics (Equation 2). According to

L-H mechanism, the reaction rate is proportional to the surface coverage assigned for the reactant.

$$R_{LH} = k_{LH} K_{LH} A / (1 + K_{LH} A) \quad (2)$$

where R_{LH} ($\text{m}^{-1} \text{min}^{-1}$) is the rate of the reaction, k_{LH} (min^{-1}) is the reaction rate constant, K_{LH} (m), the adsorption coefficient of the reactant onto TiO_2 under irradiation conditions and A (m^{-1}) the initial value of the specified UV-vis parameters or DOC content (mg L^{-1}) of fulvic acid. The linear transformation of the L-H type relationship, by plotting the reciprocal of the initial rate against the reciprocal of the initial substrate concentration allows the values of the kinetic parameters k_{LH} and K_{LH} to be determined from the intercept and the slope of the straight line as presented in Table 2.

TABLE 2. Langmuir Hinshelwood kinetic parameters of fulvic acid (IHSS FA: 20–50 mg L^{-1} , TiO_2 : 0.25 mg mL^{-1})

Kinetic parameters	Color ₄₃₆	Color ₄₀₀	UV ₃₆₅	UV ₃₀₀	UV ₂₈₀	UV ₂₅₄
k_{LH}, min^{-1}	0.0089	0.0209	0.0513	0.0991	0.131	0.189
K_{LH}, m	0.822	0.487	0.470	0.102	0.0701	0.0523
$R_{LH}, \text{m}^{-1}\text{min}^{-1}$	0.00742	0.0178	0.0469	0.0857	0.112	0.161

The effect of the model parameters on the overall rate equation is expressed by the L-H rates following the same increasing trend of the L-H rate constants. Both of the constants increase in the order of Color₄₃₆, Color₄₀₀, UV₃₆₅, UV₃₀₀, UV₂₈₀ and UV₂₅₄ revealing that UV absorbing centers may be removed more selectively than the color forming moieties. On the other hand, the adsorption coefficients, K_{LH} , in the range of 0.822 to 0.0523 display a decreasing trend with respect to decreasing absorbance values. The respective removal rates of fulvic acid are found to be relatively lower than the removal rates of humic acids that have longer chain fatty acid moieties and higher hydrophobicity (Uyguner and Bekbolet, 2005a).

3.2. UV-VIS SPECTROSCOPIC ANALYSIS

UV-vis spectroscopy was utilized as an effective tool for the characterization of humic substances either in terms of spectral changes in a defined wavelength domain or by specific absorbance values measured at certain wavelengths.

It was reported by several researchers that the quotient E_{250}/E_{365} , which is a property of aquatic humic substances, increases as the aromaticity and molecular size decreases (Peuravuori and Pihlaja, 1997). The higher E_{250}/E_{365} ratio of IHSS FA is in agreement with its lower aromatic content and lower

molecular size as opposed to other humic substances recently studied (Uyguner, 2005). The ratio of E_{254}/E_{436} gives a good impression about the intensity of the UV absorbing functional groups compared to the colored ones. E_{254}/E_{436} values in the range of 4–11 were reported for terrestrial dissolved organic matter which has a greater organic matter content associated with the presence of tannin like or humic like substances derived from plants and soil organic matter (Battin, 1998). In all cases, the highest ratio was achieved for IHSS FA compared to the other humic acids. Accordingly the UV-vis parameters of treated fulvic acid as a function of irradiation time were presented in Table 3.

TABLE 3. UV-vis parameters of fulvic acid as a function of photocatalytic irradiation time (IHSS FA: 50 mg L⁻¹, TiO₂: 0.25 mg mL⁻¹)

time, min	E_{254}/E_{365}	E_{254}/E_{436}	SUVA ₂₅₄
0	4.80	18.17	4.42
30	5.07	18.88	5.96
60	5.59	21.63	5.94
90	5.99	23.96	3.94
IHSS FA raw	4.70	17.86	4.42

Changes in the spectroscopic ratios and SUVA₂₅₄ values were reported for fulvic acid after 0, 30, 60 and 90 min of irradiation time which approximately correspond to 6%, 38%, 47% and 52% removal of DOC, respectively (Table 3). Prior to photocatalysis, preadsorption of fulvic acid could be assessed by the initial introduction of titanium dioxide to the solution ($t = 0$ min) in the absence of light. However, this process does not indicate any significant difference in the respective absorbance ratio values as presented in Table 3. Dahlen et al. (1996) reported that E_{254}/E_{365} ratio increased from 4.5 to 4.9 while the dissolved organic carbon content of fulvic acid decreased by 20% after UV-vis irradiation. In a recent study related to the photocatalytic degradation of humic acid the specified absorbance ratio increased from 2.7 to 3.4 after 30 min with a subsequent reduction of DOC by 48% (Uyguner and Bekbolet, 2005b). Similarly, the photocatalytic oxidation of fulvic acid after 30 min resulted in a 8% increase of E_{254}/E_{365} ratio.

Initial work on the characterization of different humic substances of different origins revealed SUVA₂₅₄ results ranging from 7.0 to 9.5 m⁻¹ mg⁻¹ L for humic acids (Uyguner, 2005). These values are much higher than SUVA₂₅₄ value obtained for fulvic acid (4.4 m⁻¹ mg⁻¹ L). Considerably lower values attained for fulvic acid clearly indicate more hydrophilic character with respect to humic acids. Taking into account the chemical interpretation of the absorbance values, the use of some spectroscopic ratios was also launched in literature for

the assessment of the structural diversity of the complex humic moieties (Hautala et al. 2000). On the other hand, the interpretation of the UV-vis absorption intensities during photocatalytic oxidation in correlation to the removal of organic carbon revealed a substantial increase of $SUVA_{254}$ value by 35% after 30 min and a relevant decrease of 11% after 90 min of irradiation.

3.3. MOLECULAR SIZE DISTRIBUTION PROFILES OF FULVIC ACID

Aiming at focusing on a comparative basis, the parameters linked to molecular size of fulvic acid were measured by UV-vis spectroscopy after molecular size fractionation in the range of 0.45 μm to 3 kDa for both raw and partially oxidized fulvic acid (Figure 1 and Figure 2).

The fast removal of both of the UV-absorbing moieties and color forming groups during photocatalytic oxidation as evaluated in terms of molecular size fractions via ultrafiltration process is noticeable.

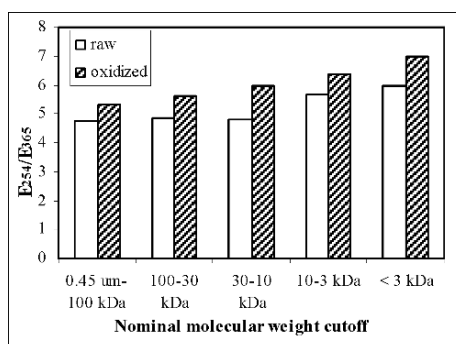


Figure 1. Comparison of E_{254}/E_{365} ratio of raw and treated fulvic acid

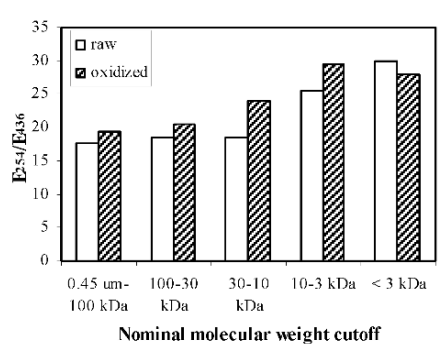


Figure 2. Comparison of E_{254}/E_{436} ratio of raw and treated fulvic acid

As previously reported, the UV-vis spectra of the molecular size fractions of humic substances exhibit a similar declining pattern, the absorbance values of which also gradually decrease with the molecular size fractions (Uyguner and Bekbolet, 2005a, Alberts et al., 2002). The differences of the absorbance ratios of each size fraction indicate diverse reactivities. As a general trend, the absorbance ratios of the fractionated fulvic acids also increase with decreasing molecular size. Such a pattern suggests a shift in the UV-vis absorbance towards higher wavelengths with increasing molecular sizes as reported by Duarte et al. (2003).

3.4. FLUORESCENCE SPECTROSCOPIC ANALYSIS

The synchronous scan fluorescence spectra of raw and partially oxidized fulvic acid with respect to their decreasing size fractions are presented in Figure 3 and Figure 4.

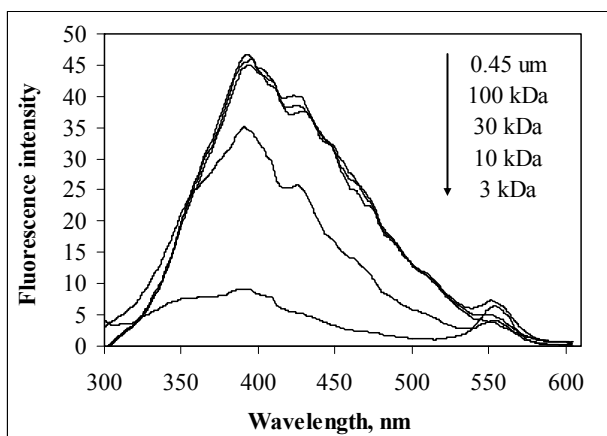


Figure 3. Synchronous scan spectra of the molecular size fractions of raw IHSS FA

As could be seen from Figure 3, raw IHSS FA has a sharp peak around 395 nm. The fluorescence intensity exhibits the same emission maxima and the same fluorescence intensity up to 30 kDa fraction. For the lower size fractions of 10 kDa and 3 kDa, a rapid decline of the fluorescence intensity is observed.

As a general trend, oxidation leads to a shift of the fluorescence intensity to lower wavelengths (Figure 4). After partial oxidation, in addition to the

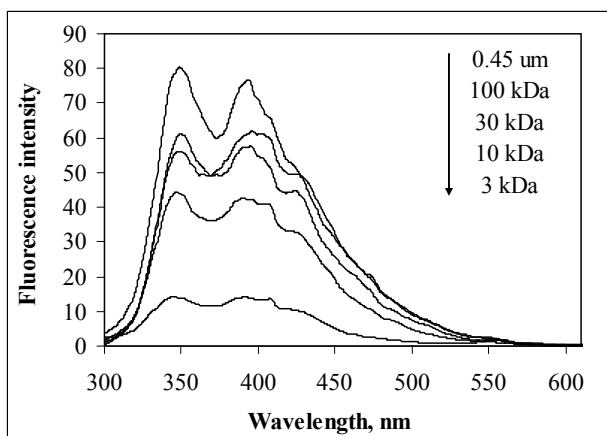


Figure 4. Synchronous scan spectra of the molecular size fractions of oxidized IHSS FA

presence of peak maxima at 400 nm, the formation of another peak around 350 nm is observed. The fluorescence intensity decreases up to 10 kDa keeping the twin peak shape of the spectra.

The comparison of the two spectra shows that the fluorescence intensities of each size fraction significantly increase after photocatalytic oxidation with a blue shift of the spectra. It is noted that all fractions of fulvic acid play a significant role in the radical initiated photocatalytic oxidation process.

4. Conclusions

The photocatalytic degradation of fulvic acid was investigated focusing on the kinetics of degradation based on the use of model equations. The spectroscopic changes induced during the photocatalytic oxidation process were evaluated by UV-vis and fluorescence spectroscopy. The declining trend of the specified UV-vis parameters, the related changes in the fluorescence spectra, decrease of TOC content during degradation, indicated the oxidative degradation of fulvic acid by photocatalytic oxidation.

Moreover, based on the comparison between the synchronous scan fluorescence spectra of the molecular size fractions of raw and oxidized fulvic acid, it could be concluded that oxidative cleavage of the molecule leads to a blue shift of the spectra which is indicative to the formation of new fluorophores. Hence, molecular size specific distribution of the absorbance ratios could be assessed for the oxidized fractions of aquatic humic substances.

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