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Evaluation of humic acid photocatalytic degradation by UV–vis and fluorescence spectroscopy

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Abstract

Photodegradation of humic substances causes drastic changes in the UV–vis absorption and fluorescence properties of humic acids. In this study it is intended to fulfill the lack of knowledge about the spectral changes of humic acids during photocatalytic oxidation processes and elucidate the effects observed on the molecular size distribution of humic acid focusing on their analysis by UV–vis and fluorescence spectroscopy.

As confirmed by the spectroscopic evaluation of the molecular size distribution data, photocatalytic degradation of humic acid leads to the formation of lower molecular size (small fractions) and higher UV absorbing compounds. For fractions less than 10 kDa, UV_{254} absorbing moieties in treated humic acid samples become higher than that of raw humic acid designating the generation of new species during photocatalysis. UV–vis spectroscopic changes were also evaluated by the parameters relating to the concomitant removal of the total organic carbon as well as by the ratios using absorption values at discrete wavelengths. Moreover, the fluorescence spectra of treated humic acid samples show decreasing intensity profiles with increasing photocatalytic irradiation time.

Keywords: Photocatalytic degradation; Humic acid; Molecular size distribution; Fluorescence spectroscopy

1. Introduction

Humic substances mainly humic acids represent a major fraction of natural organic matter in ground and surface waters that are known to be a complex class of biogenic polyanionic weak electrolytes with varying molecular sizes. Macromolecules of humic acid contain conjugated olefinic, aromatic, phenolic–semiquinone–quinone structures of a wide spectrum with functional groups (–C=O, –COOH, –OH, –NH–, $-NH_2$, –N=) and chromophores that are capable of absorbing electromagnetic radiation up to about $\lambda = 1.5\ \mu m$.

In recent years, TiO_2 based photocatalysis of humic acids (HA) has been extensively investigated [1,2]. The research efforts in this area are mainly based on assessing the factors that describe the kinetics and mechanistic pathways of photocatalytic removal of humic acids. The inhibition and competition effects on the TiO_2/UV system in the presence of humic acid, different TiO_2 brands, various metal ions, anions and oxyanions have also been studied to understand the limitations of the photocatalysis [1–3]. As a serial study of this subject, a further attempt is made to investigate the properties of photocatalytically oxidized humic acids focusing on their spectroscopic characterization by UV–vis and fluorescence spectra. The structural and conformational characterization of humic acids is extremely challenging because of their highly heterogeneous nature in relation to their photophysical, photochemical and photobiological roles in natural waters. Hence, it is intended to fulfill the lack of knowledge about the spectral changes of humic acids during oxidation processes and elucidate the effects of the molecular size distribution of photocatalytically treated humic acid samples.

2. Experimental

2.1. Photocatalytic degradation

Humic acid purchased from Aldrich as sodium salt was used to simulate the organic matter in natural waters.

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Photocatalytic degradation of humic acid (20 mg L^{-1}) was carried out in a 50 mL cylindrical Pyrex reaction vessel using titanium dioxide Degussa P-25 as the photocatalyst (0.10 mg mL^{-1}) at the natural pH of the solution (pH 6.5) as described elsewhere [1,4]. The reaction vessel was illuminated from the top and continuous stirring of the suspension was provided by means of a magnetic stirrer. A 125 W black light fluorescent lamp (BLF) emitting radiation between 300 and 420 nm with a maximum at 350 nm was used as the light source. Prior to analysis, TiO_2 was removed from the reaction medium by filtration through 0.45 μm Millipore membrane filters.

2.2. Fractionation of humic acid by sequential-ultrafiltration system

Following filtration through 0.45 μm Millipore membrane filters humic acid samples were fractioned into different nominal molecular size ranges using ultrafiltration stirred cell system (Amicon Corp. Model 8010) [5]. The nominal molecular sizes were 100, 30, 10 and 3 kDa, respectively. The validity of the ultrafiltration system was checked by controlling the recovery of raw humic acid in terms of UV_{254} (95%) and $Color_{436}$ (99%).

2.3. Instrumental analysis

UV–vis spectroscopic measurements of the samples were performed on a Shimadzu UV160A double beam spectrophotometer using 1 cm quartz cells. Fluorescence spectra in synchronous scan mode were recorded on a Perkin Elmer LS 55 luminescence spectrometer equipped with a 150 W xenon arc lamp and a red sensitive photomultiplier tube. A scan speed of 400 nm min^{-1} was used with a slit width opening of 10 nm. Synchronous scan spectra were acquired in the excitation wavelength range of 300–650 nm using the bandwidth of $\Delta\lambda = 18$ nm between the excitation and emission monochromators [6]. Fluorescence spectra for water blanks were also obtained to correct for Raman spectral overlap. Since all the spectra were recorded on the same instrument using the same experimental parameters, a comparative discussion of the spectra is acceptable although, no corrections for fluctuation of instrumental factors and for scattering effects (e.g. primary and secondary inner filter effects) were applied to the data [6,7]. Total organic carbon contents of the samples were measured on a Shimadzu TOC-V CSH total organic carbon analyzer.

2.4. Parameter specification

UV–vis parameters were described in terms of the absorbance values measured at the selected wavelengths as follows: absorbance values at 436 nm as $Color_{436}$, 400 nm as $Color_{400}$, 365 nm as UV_{365}, 300 nm as UV_{300}, 280 nm as UV_{280} and 254 nm as UV_{254}. These UV and Color designated terms were used to signify the previous data [8,9]. The related absorbance ratios were described as E_{254}/E_{365} (UV_{254}/UV_{365}), E_{280}/E_{365} (UV_{280}/UV_{365}), E_{254}/E_{436} ($UV_{254}/Color_{436}$), E_{280}/E_{436} ($UV_{280}/Color_{436}$), and E_{300}/E_{436} (UV_{300}/UV_{365}). The E term was selected to simplify the notation as well as to refer to the relevant literature data [10,11].

Specific UV absorbance ($SUVA_{254}$, $cm^{-1}\,mg^{-1}\,L$) was used to represent TOC normalized aromatic moieties (UV_{254}) whereas specific color absorbance ($SCOA_{436}$, $cm^{-1}\,mg^{-1}\,L$) was defined as $Color_{436}$/TOC to signify organic carbon normalized color forming moieties. $SUVA_{365}$ was also calculated in a similar fashion as the ratio of the UV_{365} absorbing species to TOC.

3. Results and discussion

3.1. Photocatalytic degradation kinetics of humic acid

Photocatalytic degradation of humic acid in terms of UV–vis parameters as well as TOC removal follows first order kinetics as previously reported in literature [1,4].

In the present study, the related pseudo first order model reaction rate constants, k (min^{-1}) for humic acid removal were found to be decreasing in the range of 2.98×10^{-2}, 2.93×10^{-2}, 2.71×10^{-2}, 2.40×10^{-2}, 2.15×10^{-2}, 2.01×10^{-2} and $1.23 \times 10^{-2}\,min^{-1}$ for the specified UV–vis parameters of $Color_{436}$, $Color_{400}$, UV_{365}, UV_{300}, UV_{280}, UV_{254} and TOC, respectively. The corresponding half life ($t_{1/2}$, min) values were calculated as 23, 24, 26, 29, 32, 35 and 56 min, respectively. The rate constant for TOC removal was considerably slower than the rate constant values obtained from the UV–vis parameters. Although the removal of color forming moieties was comparatively faster than the removal of UV absorbing centers, an approximation was set forward to assess 50% degradation of humic acid with respect to all the specified parameters. As an average of the half life values calculated for UV–vis parameters, 30 min was chosen to represent partial degradation of humic acid. At this stage almost 40% of $Color_{436}$ would still be present leading to a significant and meaningful evaluation of the studied parameters after molecular size distribution.

3.2. Evaluation of spectroscopic properties in relation to photocatalytic degradation

3.2.1. UV–vis spectroscopic analysis

It is well known that the UV–vis spectra of humic acids are broad, featureless and monotonously decrease with increasing wavelength. Displaying the same basic pattern of declining trend, a decrease in the absorbance values was observed with the increasing irradiation time after photocatalytic oxidation [2,5].

The absorption properties are conventional and versatile for the characterization of dissolved organic matter in natural waters. Various absorption wavelengths at 250, 254, 270, 280, 300, 365, 400, 436 and 465 nm as well as ratios like Abs_{250}/Abs_{365}, Abs_{465}/Abs_{665} have been cited in literature for the spectral differentiation of humic substances [10,12–16]. Amongst them, UV absorbance at 254 nm (UV_{254}) was interchangeably measured with total organic carbon (TOC) as a surrogate parameter to represent the natural organic matter content in natural waters [17]. The UV absorptivity at 280 nm was also introduced to represent total aromaticity, because, π–π^* electron transition occurs in this UV region (ca. 270–280 nm) for phenolic arenes, benzoic acids, aniline derivatives, polyenes and polycyclic aromatic hydrocarbons with two or more rings [14,15]. Many of these compounds are thought to be common structural subunits in humic matter and the quotient E_2/E_3 as absorbance ratios measured at 250 and 365 nm has been reported to correlate with the molecular size and aromaticity [10]. Lipski et al. defined a color coefficient as $Q_{270/400}$ (the ratio of absorbances at 270 and 400 nm) to characterize the degradation of phenolic/quinoid core of humic acid to simpler carboxylic aromatic compounds [18]. UV–vis parameters of treated humic acid as a function of irradiation time during the oxidation process are presented in Fig. 1.

Irradiation time dependent changes are observed in spectroscopic properties during each stage of humic acid photocatalytic degradation starting with $t = 0$ min which is the initial titanium dioxide introduction to humic acid solution in the absence of irradiation. No preadsorption equilibrium was attained prior to photocatalysis and the absorbance ratios were instantaneously measured after TiO_2 addition. This point represents the initial adsorption effect prior to photocatalysis. The values of the absorbance ratios during photocatalytic oxidation are higher than that of raw humic acid gradually increasing as irradiation time increases.

Although the absorbance measurements at wavelengths 254 and 280 nm were interchangeably used in literature to represent aromatic content of humic acids, the values for E_{254}/E_{365} deviate from E_{280}/E_{365} ratios with increasing irradiation time by 14–20% difference denoting the significance of 280 nm as a discrete wavelength. Dahlen et al. reported that E_{254}/E_{365} ratio increased from 4.5 to 4.9 and TOC of fulvic acid decreased by 20% after UV–vis irradiation [20]. Accordingly, in this study E_{254}/E_{365} value for humic acid increased from 2.7 to 3.4 after 30 min of photocatalysis with a subsequent 48% reduction of TOC. The spectroscopic changes during photocatalysis could be better visualized in terms of quotients calculated with respect to $Color_{436}$ rather than with UV_{365}. The reason may be attributed to the higher removal rate of color forming moieties revealing the quantitative assessment more reliable. Consequently, the ratio of UV_{254} to $Color_{436}$ may represent an alternative indicative parameter for the elucidation of the photocatalytic degradation efficiency.

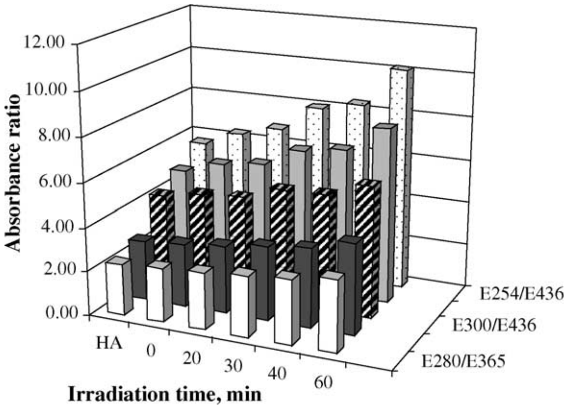


Fig. 1. UV–vis parameters of humic acid as a function of the irradiation time.

Concomitantly, the use of similar absorbance ratios was also introduced by several researchers. Eggins et al. reported that during photocatalytic degradation of humic acid the absorbance ratio 254 nm/400 nm and color in Hazen units was reduced by 50% after irradiation for 12 min [19]. However, in their study the possible adsorption of humic acid onto TiO_2 was increased with the equilibration period (30 min) that was applied before irradiation. Additionally, instead of 0.45 μm Millipore membrane filters, humic acid was filtered through 0.22 μm filters that would possibly lead to the alteration of the preadsorption and molecular size distribution of the humic acid sample.

Lipski et al. attributed the increase of $Q_{270/400}$ ratio of humic acids during UV irradiation to the degradation of long-wavelength absorbing chromophores such as quinoid and semiquinoid arrangements, and aromatic and/or heterocyclic zwitteranions i.e. aminochromes [18].

Since the removal of organic carbon content was apparently accomplished by the diminishing of UV–vis absorption intensities during the course of the photocatalysis, the interpretation of the specific absorbance parameters such as $SUVA_{254}$, $SUVA_{365}$ and $SCOA_{436}$ was presented in Table 1. The initial $SUVA_{254}$, $SUVA_{365}$ and $SCOA_{436}$ were found to be 0.0075, 0.0027 and 0.0013, respectively. Considerably insignificant decrease ($\leq 10\%$) was observed for all the specific absorbance parameters after the introduction of TiO_2. On the other hand, after 30 min of irradiation and in the presence of abundant source of organic carbon in the reaction medium, substantial decreases as 21% $SUVA_{254}$, 33% $SUVA_{365}$ and 46% $SCOA_{436}$ were attained.

$SUVA_{254}$ has been reported to be proportional to both the apparent molecular weight and the aromaticity of humic substances [21]. Compared to that of raw humic acid approximately 37% decrease of $SUVA_{254}$ and 59% decrease of $SUVA_{365}$ were achieved after 60 min of photocatalytic

Table 1
Specific absorbance parameters of humic acid as a function of irradiation time during photocatalysis

	$SUVA_{254}$	$SUVA_{365}$	$SCOA_{436}$
HA	0.075	0.027	0.013
0 min	0.071	0.027	0.012
30 min	0.059	0.018	0.007
60 min	0.047	0.011	0.005

degradation revealing lessened degree of aromaticity in relation to the removal of organic carbon. At this stage the reaction medium was composed of unreacted humic acids and the degradation products expressing almost 50% removal of TOC. Considering relatively higher removal rate of Color_{436} with respect to the removal rates of UV_{254} and UV_{365} the importance of the changes observed in SCOA_{436} would be limited by the irradiation time. Therefore, SCOA_{436} parameter probably would not display a discriminative significance due the lower Color_{436} attained during extended periods of photodegradation. As verified by the decrease in the specific absorbance values, humic substances are degraded to less UV–vis absorbing compounds through the formation of a series of intermediates and their consequent reactions. The decreasing trend of TOC and the relevant parameters also indicate the mineralization of humic acid to carbon dioxide and water.

3.2.2. Fluorescence spectroscopic analysis

Synchronous scan excitation spectra not only offer a potential use to reduce overlapping interferences but also provide a possibility for each fluorescent component to be identified in a spectral range.

The fluorescence spectra of all treated humic acid samples are characterized by broad peaks the intensities of which relatively decrease with increasing photocatalytic irradiation time (Fig. 2). Raw humic acid has a sharp peak around 473 nm with a relative fluorescence intensity of 44.7 and a moderate peak around 400 nm. Peuravuori et al. ascribe the maximum around 460 nm to polycyclic aromatics consisting of seven fused benzene rings [7]. It is noteworthy that the characteristic peak of humic acid is significantly quenched even with the sole action of TiO_2 prior to irradiation. This indicates the importance of initial adsorption of humic acid onto TiO_2. After 60 min of irradiation, the characteristic sharp peak of raw humic acid completely disappears; the moderate peak around 400 nm decays in intensity and another peak of low intensity around 350 nm emerges.

The train-loops attachment and folding of humic acid on TiO_2 might lead to the masking of the fluorescent moieties in humic acid structure [22]. On the other hand, the carboxylic functional groups of humic acids are known to attach to the TiO_2 surface [23]. The significant decrease of the sharp peak of humic acid at $t = 0$ min is accompanied by approximately 44% TOC removal. Furthermore, disappearance of the characteristic peak of humic acid after photocatalysis was observed and this could be attributed to the removal of carboxylic functional groups. Similar results were presented in literature and the rapid extinction of the fluorescence intensity of humic acid during photocatalysis was ascribed to the destruction of aromatic structures of humic acid [24]. Conversely, increasing relative fluorescence intensity after chlorination, ozonation and UV treatment of humic substances has also been reported [25,26]. Moreover, Eggins et al. reported that humic acids are photocatalytically degraded to lower molecular weight compounds and the intermediates of the reaction can be highly fluorescent [19]. However, considering the diverse reaction mechanisms and different experimental conditions, contrary results would also be plausible.

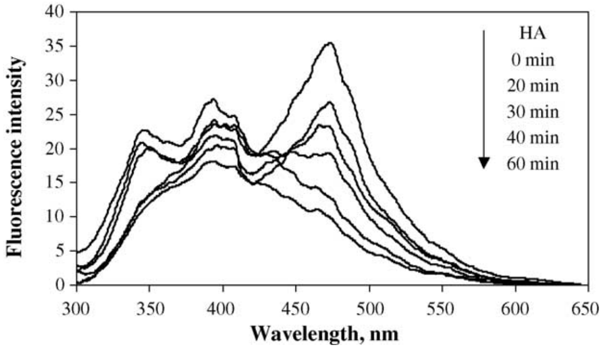


Fig. 2. Synchronous scan excitation spectra of photocatalytically oxidized humic acid in relation to the irradiation time. HA represents raw humic acid.

3.3. Evaluation of spectroscopic properties in relation to molecular size distribution

3.3.1. UV–vis spectroscopic analysis

Ultrafiltration is a common method to fractionate humic substances into different molecular size ranges. In order to understand more about the spectroscopic characteristics of photocatalytically oxidized humic acid samples, raw and treated humic acids have been ultrafiltered into size fractions using membranes in the range of 100–3 kDa and compared with respect to the specified parameters (Fig. 3A and B).

The molecular size distribution of the samples were classified into three fractions: "large" (L) <0.45 μm, >100 kDa; "medium" (M_1, M_2) <100 kDa, >10 kDa; "small" (S_1, S_2) <10 kDa. Molecular size distribution of raw humic acid exhibited a decreasing trend in all the fractions for Color_{436} and UV_{254}. On the other hand, the effect of photocatalytic oxidation of humic acid was represented by an inconsistent manner for both Color_{436} and UV_{254} parameters with respect to the molecular size distribution profile. Primary effect was observed mainly on the removal of L fraction followed by M_1 and to a lesser extent on M_2 fraction. Both large (L) and medium fractions (M_1 and M_2) were not found to be different from each other for the specified parameters. However, small fractions (S_1 and S_2) displayed quite low UV–vis absorbing properties compared to the higher molecular size fractions.

The decrease in UV_{254} of humic acid fractions suggested that the hydroxyl radical attack proceeded mainly on the aromatic moieties of the molecules. Although alterations are observed on molecular size distribution data, an increase of UV_{254} is prominent in "small" fractions. This might indicate the formation of new species exhibiting a significant absorption at 254 nm during oxidative degradation.

The polydisperse nature of humic acid unifying components of dissimilar molecular weights is clearly observed from the presented absorbance ratios of the

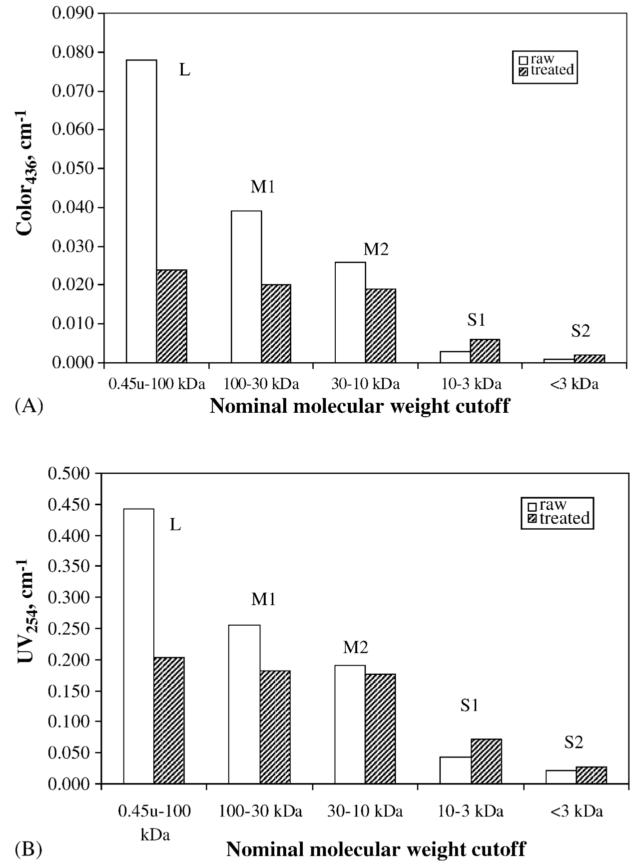


Fig. 3. (A) Molecular size distribution data in terms of Color_{436}; (B) molecular size distribution data in terms of UV_{254}.

molecular size distribution data (Fig. 4A and B). When ultrafiltration is applied, it does not involve explicit size or functional group separation however, it produces humic acid fractions of a certain size distribution that show spectroscopic evidence of distinct structural differences. The ratios of E_{254}/E_{365} and E_{280}/E_{365} are found to be very close to each other resembling similar molecular size composition with a discriminative S_2 fraction after which the ratio of raw humic acid becomes significantly higher than that of treated humic acid. On the other hand, the ratios for E_{254}/E_{436}, E_{280}/E_{436} and E_{300}/E_{436} exhibit similar trends with discriminative absorbance ratios, which are considerably high for the small fractions of raw humic acid. Hence, the ratios of E_{280}/E_{365} and E_{254}/E_{436} were presented in Fig. 4A and B as representative absorbance ratios. An inverse relationship was observed between the molecular size distribution of treated humic acid samples and their respective absorbance ratios. Similar results have been reported in literature for humic substances [10]. Substantial differences among the humic acid fractions of different molecular sizes point out the importance of characterizing the size fractions properly to better understand the spectroscopic properties of photocatalytically oxidized humic acids.

As confirmed by the decrease of Color_{436}, the photocatalytically treated humic acid samples are known to decolorize quite rapidly with a half life of 23 min [1].

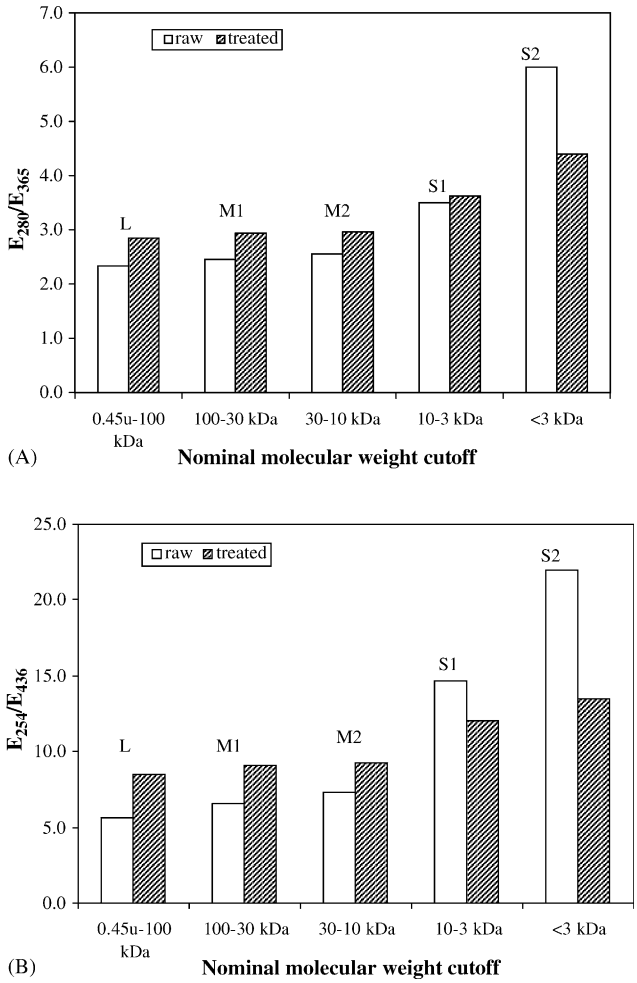
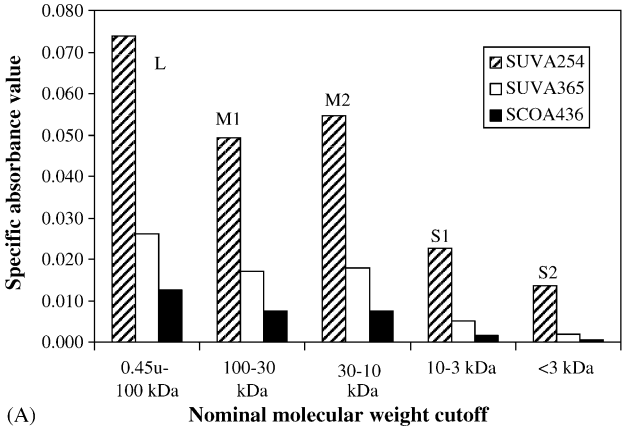


Fig. 4. (A) Comparison of E_{280}/E_{365} absorbance ratio for raw and treated humic acid; (B) comparison of E_{254}/E_{436} absorbance ratio for raw and treated humic acid.

Moreover, photodegradation of relatively resistant humic acid to compounds of lower molecular weight during irradiation is likely [5,19]. The removal efficiencies of UV absorbing centers could be ascribed as relatively slower with respect to the color forming moieties ($t_{1/2} \approx 35$–32 min for UV_{254} and UV_{280}). Hence, the decrease in Color_{436} and the increase in UV_{254} values during the photocatalytic degradation time course cannot compensate for the generally increasing trend of E_{254}/E_{436} and E_{300}/E_{436} ratios. Such a pattern suggests a higher degree of aromaticity of the highest size fractions of humic acids [10,11].

Further elucidation of molecular size distribution characteristics of raw and treated humic acid samples are presented by SUVA_{254}, SUVA_{365} and SCOA_{436} parameters (Fig. 5A and B).

The calculated SUVA_{365} and SCOA_{436} parameters for both raw and treated humic acid samples show a generally decreasing trend directly proportional to the size fractions. However, a fluctuation in medium size fractions with a slight increase of M_2 fraction is observed for SUVA_{254} values. The general decline in specific absorbance values



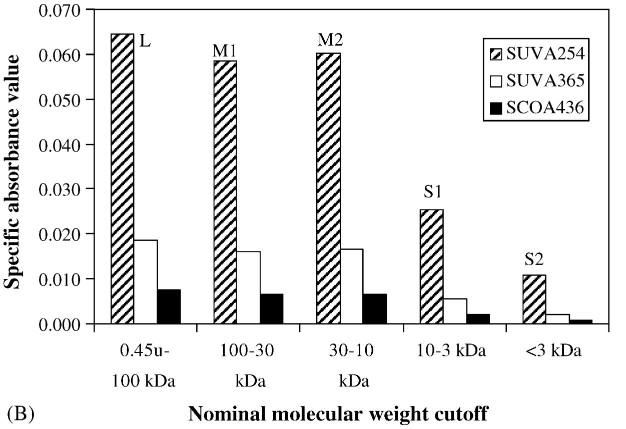


Fig. 5. (A) Specific absorbance ratios for raw humic acid; (B) specific absorbance ratios for treated humic acid.

towards smaller size fractions is consistent with the findings of Alberts et al. who have studied the size fractions of fresh water natural organic matter [27].

The decrease of the UV absorbing properties of each humic acid fraction may be a consequence of the decomposition of the humic material to smaller molecular size fractions. The photocatalytically treated humic acid samples revealed size fractions smaller than 10 kDa (S_1, S_2 fractions) exhibiting higher amount of aromaticity than S_1 and S_2 fractions of raw humic acid as confirmed by their UV_{254} absorbance values. Furthermore, for the small fractions, TOC value for raw humic acid is 32–35% lower than that of the corresponding treated humic acid fractions. This indicates the degradation of the high molecular size fractions of humic acid to lower molecular weight compounds. Considering the polydisperse nature and the micelle like structure of humic acid, the physical entrapment of small fractions of humic acids by larger molecules (host–guest interactions) is possible. As suggested by Smeulders et al., due to the conformational changes, voids can be formed in humic material, which could occlude other molecules [28]. Similarly, an increase in the percentage of the smallest molecules (500–300 Da) of natural organic matter fractions after ozonation and oxidation with chlorine dioxide was reported [29]. Breaking up of the large molecules alters molecular size distribution data towards smaller molecules. Differing trends depending on the oxidation reaction mechanism would result in diverse molecular size distribution patterns.

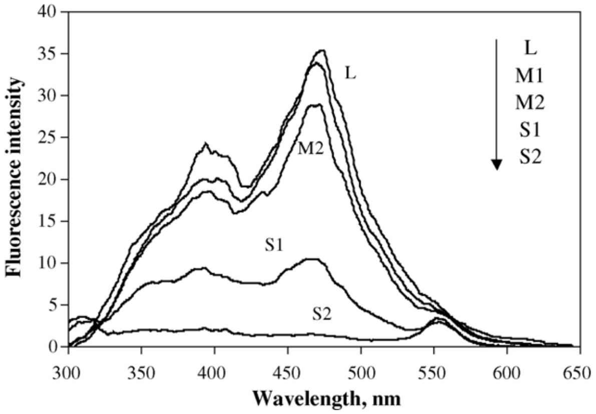


Fig. 6. Synchronous scan excitation spectra of molecular size fractions of humic acid.

3.3.2. Fluorescence spectroscopic analysis

In a comparative approach, the fluorescence spectra of molecular size fractions of raw humic acid were presented in Fig. 6.

The synchronous scan spectra of each size fraction exhibit a decreasing trend in terms of fluorescence intensity. The spectral difference between raw humic acid and M_2 fraction becomes evident as the characteristic peak at 473 nm decays in intensity and completely disappears for humic acid fractions <3 kDa. As illustrated in Fig. 2, the synchronous scan spectra of humic acid photodegradation also leads to the gradual decrease of fluorescence intensity in the 450–600 nm region. This might indicate the degradation of the high molecular weight components of humic acid and formation of lower molecular size fractions of humic acid during photocatalysis. In general, electron withdrawing groups (e.g., –COOH) decrease and electron donating groups (such as –OH, $-NH_2$) increase the intensity of fluorescence in aromatic compounds [6]. The decrease in the fluorescence intensity of lower molecular weight fractions of humic acid and the formation of a minor intensity peak around 550 nm could be due to the depletion of the aromatic and/or polyphenolic contents which are mostly of high molecular weight and also due to the enrichment of its carbohydrate materials which do not give fluorescence. Additionally, the presence of carbonyl containing substituents, hydroxyl, alkoxyl and amino groups cause a shift in fluorescence to longer wavelengths [6].

The molecular size fractions of treated humic acid samples are distinguished by the presence of two moderate peaks around 400 and 350 nm that decrease in intensity with the decreasing size fractions (Fig. 7). When compared to the profiles of raw humic acid fractions, the fluorescence spectra of all the fractions of treated humic acid shift to lower

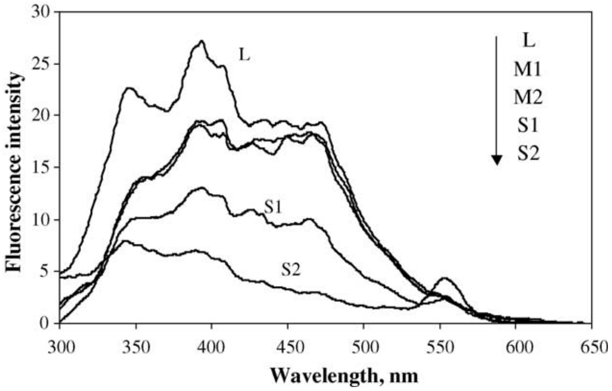


Fig. 7. Synchronous scan excitation spectra of molecular size fractions of treated humic acid.

wavelengths. The reason could be related to the probable formation of partial oxidation products such as alcohols, aldehydes, ketones and carboxylic acids. For both raw and treated humic acid samples, the formation of a peak around 550 nm is observed for the small size fractions. A broad band is observed for the S_1 size fractions of both of the raw and treated humic acid. S_2 size fraction of the treated humic acid exhibits a higher intensity peak that has shifted to blue region with a broader band than the corresponding size fraction of raw humic acid.

4. Conclusions

In this manuscript the potential use of several absorbance ratios that have frequently been cited in literature for the spectroscopic characterization of natural organic matter has been emphasized by examining their trends in photocatalytic oxidation of humic acid.

During photocatalytic degradation drastic changes were assessed in the absorption and fluorescence properties of humic acids relevant to the molecular size distribution profiles. The values of the specified absorbance ratios expressed an increasing trend during the time course of the photocatalytic oxidation. Although the absorbance wavelengths at 254 and 280 nm were interchangeably used in literature to represent aromaticity of humic acids, the values for E_{280}/E_{365} deviated from E_{254}/E_{365} ratios with increasing irradiation time by approximately 20% difference denoting the significance of 280 nm as a discrete wavelength. Furthermore, the ratio of UV_{254} to $Color_{436}$ might be used as an indicative parameter of photocatalytic degradation efficiency. On the other hand, the fluorescence spectra of treated humic acid samples were characterized by broad peaks the intensities of which relatively decreased with increasing photocatalytic irradiation time. The train-loops attachment and folding of humic acid on TiO_2 during photocatalysis might constitute an explanation to the masking of the fluorescent moieties in humic acid structure as observed by the decrease in fluorescence intensity during photocatalysis.

As confirmed by the spectroscopic evaluation of the molecular size distribution data, photocatalytic degradation of humic acid revealed the formation of lower molecular size (small fractions) and higher UV absorbing compounds. For molecular size fractions smaller than 10 kDa, UV_{254} absorbing moieties in treated humic acid samples become higher than that of raw humic acid designating the generation of new species during photocatalysis.

Moreover, the effective operational parameters such as the type of catalyst, light intensity, solution matrix, degradation profile of the parent compound, formation of the intermediates, their possible interaction with each other and humic acid might induce structural changes which could not be well defined with UV–vis and fluorescence spectroscopy. The elucidation of these remarks requiring further sophisticated instrumental analysis may constitute the scope of a future study.

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