Effect of partial oxidation by ozonation on the photocatalytic degradation of humic acids

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ABSTRACT. In this study humic acids, which are known to be a heterogeneous group of organic macromolecules found in natural waters, were oxidized using ozonation and photocatalysis in a sequential system. Ozonation was employed for achieving partial oxidation of humic acids prior to photocatalytic oxidation. Degradation of humic acid was explained by using pseudo first order reaction rate model based on UV-vis measurements. An improvement was achieved in the photocatalytic degradation rates with respect to the degree of pre-oxidation by ozonation. Due to the surface oriented nature of photocatalysis, adsorption characteristics of partially oxidized humic acid samples on TiO_2 photocatalyst were evaluated by the application of the Freundlich adsorption model. The photocatalytic degradation rates did not correlate well with the dark adsorption characteristics of the pre-ozonated as well as untreated humic acid samples.

1. INTRODUCTION

Removal of humic substances has long been of concern in water treatment due to their diverse reactivity and abundance in natural waters. The acid insoluble humic acid fraction of humic substances in water is the main precursor of Disinfection by Products (DBP's) especially Trihalomethanes (THM's) forming upon chlorination. Presence of humic acids in the distribution system favors the bacterial regrowth in the network, which may lead to serious sanitary problems in drinking water quality. Humic acids also act as natural photosensitizers in heterogeneous as well as homogeneous solutions yielding active oxygen species such as $^1O_2$, $HO^\bullet$, $HO_2{}^\bullet$ and $O_2{}^{\bullet-}$ [1, 2]. They impart yellow color, exhibit acidic character, are chemically complex in nature and behave like polyelectrolytes in aqueous medium, therefore they may initiate detrimental reactions. Consequently, the removal of humic acids constitutes one of the prevailing tasks in drinking water treatment.

Naturally occurring humic acids (HA's) possess partially aromatic structure with significant amounts of unsaturated sp^2 hybridized carbon (e.g. aromatic carbon). They also contain volatile organic compounds that have become entrapped in polymeric network. Therefore, humic acids are considered to be polydisperse and heterogeneous with respect to size and shape as well as charge.

Ozone treatment reduces or eliminates the need for chlorination and decreases formation of DBP's as well as THM's [3]. Ozonation of humic acids leads to a fast color removal and a steady decrease in UV-absorbance [4]. An improvement in biodegradability is also observed upon ozonation of natural waters due to the cleavage of aromatic rings [5]. Although the opportunity of enhancing further treatments such as coagulation-flocculation or activated carbon adsorption is offered by ozonation, one major disadvantage of this process is the observed inefficiency in abatement of the total organic matter TOC [6].

It has been shown previously that heterogeneous photocatalysis is a promising route for the degradation of humic acids under various experimental conditions simulating natural water systems [7–9]. Photocatalytic inactivation of *E. coli* and the reactivity of humic acid with hypochlorite ion via photolytic and photocatalytic pathways were evaluated in relation to the elimination of THM's surrogates and for the assessment of the disinfection capacity of TiO_2 [10, 11]. Recently, the photocatalytic efficiencies of TiO_2 powders were also investigated on the decolorization of humic acids [12].

Due to the inefficacy of ozonation in attaining complete TOC abatement and the advantage of photocatalysis in achieving total mineralization, a sequential oxidation system was considered. This research has addressed the effect of partial oxidation by ozonation on the photocatalytic degradation of humic acids.

2. METHODOLOGY

2.1. Materials and methods.

Humic acid was supplied from Aldrich and working humic acid solutions ($20\,\mathrm{mgL^{-1}}$) were prepared upon dilution of a $1000\,\mathrm{mgL^{-1}}$ stock solution that was prepared by using distilled-deionized water.
Selected properties of humic acid used in this study:
Carbon content, wt % 34.4.

Specific ultraviolet absorbance at 254 nm: 0.070 cm^{-1} $(\text{mg C/L})^{-1}$

The photocatalyst, TiO_2 (loading: 0.5 mgmL^{-1}) used in photocatalytic degradation experiments was supplied from Degussa as P-25.

Selected properties of Degussa P-25 TiO_2 used in this study:
Specific surface area: 55 $\text{m}^2\ \text{g}^{-1}$.
Crystal form: 80% anatase and 20% rutile.
Average particle size: 30 nm.

Parameters studied: Humic acid degradation was followed by spectroscopic measurements in UV-vis region by using Shimadzu 160A spectrophotometer. All absorbance measurements were performed at wavelengths of 254 nm (UV_{254}), 280 nm (UV_{280}) and 436 nm ($Color_{436}$) using a 1 cm path length quartz cell.

Orion pH meter was used to follow the changes in pH.

Ozonation experiments were carried out according to the procedure outlined previously by Kerc, *et al.*, 2000 [13]. Photocatalytic degradation and batch adsorption experiments were performed according to Bekbolet, *et al.*, 2002 [12].

2.2. Degradation kinetics. The global degradation of humic acids by ozone application or by photocatalysis can be represented by the following simple reaction:

$$HA + Ox(O_3/{}^\bullet OH) \longrightarrow HA_{ox},$$

where Ox implies oxidizing species and HA_{ox} denotes oxidized humic acid.

The humic acid concentration versus reaction time curves suggest that the degradation reaction can be described by pseudo-first-order kinetic model with respect to humic acid concentration. According to this kinetic approach; the rate equation can be given as:

$$-d[HA]/dt = k[HA],$$

where, k represents the apparent pseudo-first-order rate constant for the degradation process.

Upon integration with the boundary conditions;

$$[HA] = [HA]_0 \quad \text{for } t = 0,$$
$$[HA] = [HA] \quad \text{for } t = t.$$

The above given equation transforms into;

$$\ln[HA]/[HA]_0 = -k \cdot t.$$

Thus, a curve of $\ln[HA]/[HA]_0$ versus t should give straight line with a slope equal to apparent reaction rate constant, k (time^{-1}).

The half-life, $t_{1/2}$ (time) of a reactant is the time required for its concentration to reach 50% of its initial value. Then, $t_{1/2}$ is expressed as;

$$t_{1/2} = \ln(1/2)/k.$$

3. RESULTS AND DISCUSSION

The use of ultraviolet absorbance at 254 nm (UV_{254}) is widely accepted to represent the concentration of humic acid in aqueous solutions [14]. The parameters represented by UV_{254} and UV_{280} exhibit the potential of reactions of aromatic functional groups. Therefore, the changes in UV_{254} and UV_{280} as well as the changes in visible absorbance values measured at 436 nm ($Color_{436}$) indicate preferably the structural changes due to degradation [15].

3.1. Partial oxidation of humic acid by pre-ozonation. Ozonation was applied to humic acid solutions under the specified experimental conditions to achieve partially oxidized humic acid samples prior to photocatalytic oxidation. The applied ozone dosages were presented in Table 1 both as input dosage form (mgL^{-1}) and as volume corrected normalized to the organic carbon content form. The extent of oxidative degradation was determined by the changes in the parameters (Table 1) and presented in the normalized forms as $[HA]/[HA]_0$ based on UV_{254} and $Color_{436}$ and percent UV_{280} removal (Figure 1).

The applied ozone doses for the preparation of partially oxidized humic acid samples could be considered as equivalent to pre-ozonation ozone dosages for an effective $Color_{436}$ and UV_{254} removal [5].

Table 1. *Characterization of pre-ozonated humic acid samples.*

Sample	Ozone dosage		UV_{254}	$Color_{436}$	pH
	mgL^{-1}	mg O_3/mg C	m^{-1}	m^{-1}	
Humic acid	–	–	44.8	9.2	6.2
Sample 1, S1	1.47	0.20	40.3	7.3	6.4
Sample 2, S2	2.45	0.34	36.3	5.3	6.2
Sample 3, S3	4.41	0.61	29.7	3.8	5.8
Sample 4, S4	7.35	1.0	19.9	1.8	5.8

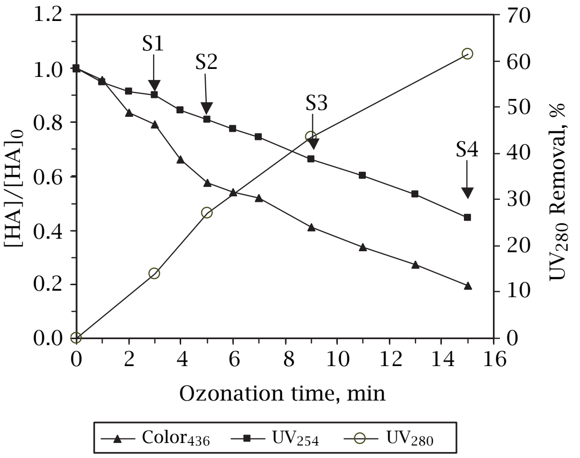


Figure 1. *Pre-ozonated humic acid properties.*

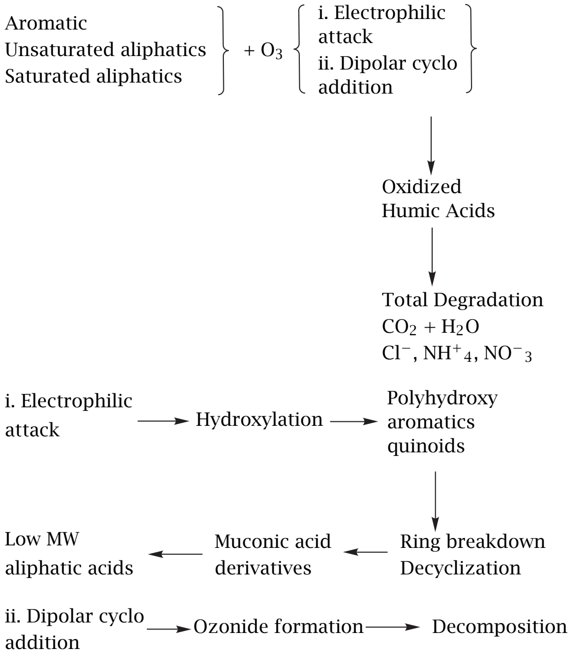
The samples as represented by S1–S4 exhibited changes in $Color_{436}$ as 20%–80% and in UV_{254} as 10%–55% in relation to the properties of humic acid solution.

Based on the previous findings, dissolved ozone was rapidly consumed by humic acid during the experiments resulting in partially oxidized humic acid fragments [13]. The rate of reaction between ozone and organic carbon compounds is known to be a function of carbon bonding, functional group content with aromatic compounds or compounds with e^- donating functional groups [16]. Therefore the effect of pre-ozonation degree could be ascribed to the changes in UV_{254} and $Color_{436}$ as well as changes in UV_{280} (Figure 1). UV_{280} removal rates were found to be ~ 8% faster than UV_{254} and ~ 16% slower than the $Color_{436}$ removal rates for samples 2–4. For the slightly oxidized sample S1, the comparative results showed merely 5% changes for both of the parameters, UV_{254} and $Color_{436}$.

Ozone is widely accepted as a powerful pre-oxidant ($E = 2.07\,V$) that is capable of reducing humic acid content of a water sample to a certain extent. The pH of the reaction medium determines the differential effects between the highly specific-direct molecular O_3 attack and the rapid/nonspecific-secondary free radical species attack (e.g., $^{\bullet}OH$). Since all of the ozonation experiments are carried out under neutral pH conditions, the direct action of O_3 on humic acid is assumed to be the main route of oxidation.

Ozone action on humic acid can be presented by the following reaction scheme;

Humic Acid Moieties



where MW denotes molecular weight.

Attacking as an electrophile, ozone preferentially reacts with electron rich humic acid moieties. The major source of electron rich moieties is sp^2-hybridized carbon, such as those contained in unsaturated carbon structures, eg: aromatic, olefinic etc. Functional groups, such as hydroxyls ($-OH$) and amines ($-NH_2$) are electron donating and enhance the reactivity of adjacent carbon bonds. On the other hand; functional groups such as carboxyl groups ($-COOH$) are electron withdrawing and may have tended to decrease the reactivity of adjacent bonded carbon. Therefore, the initial carbon structure and functionality have affected the reaction rate of ozone with humic acid [16, 17].

In practice, oxidation by pre-ozonation leads to rapid elimination of color and this step partly causes the degradation of the aromatic structure. For an efficient removal of natural organic matter as well as humic acids, intermediate ozonation is recommended [5]. Ozonation of humic acid solutions leads to a quick decolorization and a substantial decrease in UV absorbance as presented in Table 1. in terms of UV spectroscopic properties as UV_{280} and UV_{254}. This is mainly attributed to a loss of aromaticity by decyclization of the humic acid macromolecule. Under extended ozone application conditions, the resultant products are basically aldehydes and carboxylic acids that accumulate in the medium due to their resistance towards O_3 reactivity [18].

The changes in $Color_{436}$ reflected the removal of color forming chromophoric moieties of humic acid. The electrophilic attack of O_3 on phenolic groups of humic acid results in the formation of pseudo-quinoic groups and at higher O_3 doses a decrease of the quinoic groups corresponding to the break down of the aromatic cycle leads to the generation of carboxylic acids. The main contributing factor to the explanation of this complex mechanism was reported as O_3/humic acid ratio [5, 16]. It is also reported that both the aromaticity and size of the organic acids are reduced after ozonation and as a consequence although the addition of acidic functional groups increases the polarity of the partially oxidized molecules, the charge density of the compounds remains relatively low and the solubility of the compounds is not increased substantially [19]. The acid formation should be the major indication of the release of the acidic products and this effect on pH could be followed during sample preparation due to the differences in ozonation dosages. The recorded pH changes in between the samples can be accepted as insignificant under the specified experimental conditions. The highly oxidized humic acid sample exhibited only 9.5×10^{-7} moles $H^+ L^{-1}$ (Table 1).

3.2. Photocatalytic degradation of pre-ozonated humic acid solutions.

The pre-ozonated samples were subjected to photocatalytic degradation and the removal efficiencies were presented in terms of UV_{254}.

Table 2. *Kinetic parameters for* UV_{254} *reduction by photocatalysis.*

Sample	Rate constant, k (min^{-1})	Half-life, $t_{1/2}$ (min)	Initial rate, R ($m^{-1}min^{-1}$)
Untreated humic acid	2.64×10^{-2}	26	1.18
Sample 1, S1	2.55×10^{-2}	27	1.03
Sample 2, S2	2.75×10^{-2}	25	0.998
Sample 3, S3	3.36×10^{-2}	20	0.998
Sample 4, S4	3.99×10^{-2}	17	0.794

The degradation profiles of the pre-ozonated samples are given in Figure 2. The data were fitted to the pseudo first order reaction rate model and the kinetic parameters are shown in the Table 2.

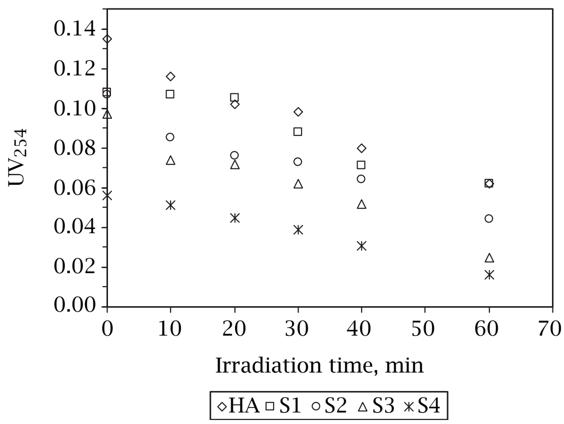


Figure 2. *Photocatalytic degradation profiles of the humic acid and the pre-ozonated humic acid samples.*

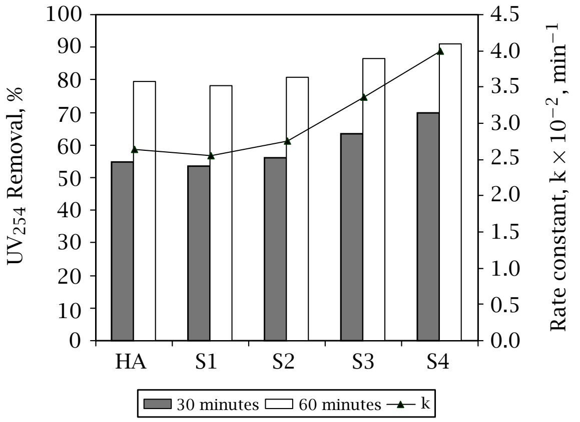


Figure 3. *Time-dependent comparison of photocatalytic degradation of humic acid and pre-ozonated humic acid samples.*

From a general point of view, the pseudo first order rate constants differed by 50% in relation to a pre-oxidation degree of 55% for UV_{254} and 80% for $Color_{436}$. One striking feature of the degradation data is that no significant effect (< 5%) is observed in photocatalytic rate constants for pre-ozonation removal degrees up to 35% for UV_{254} and 55% for $Color_{436}$. Further changes in humic acid structure due to the ozonation significantly altered the photocatalytic rate constants by 27% and 50% for the samples 3 and 4, respectively.

The most pronounced effect was observed in 30 minutes of irradiation time, at which 55% of untreated humic acid was degraded whereas 70% removal was calculated for sample 4 that was already oxidized to a high level. For 60 minutes of irradiation time, the degradation rates increased by approximately 45% as presented in Figure 3. The kinetics of the photocatalytic oxidation of the pre-ozonated humic acid samples revealed half-life values < 30 min for all of the samples. For longer irradiation periods no distinct behavioral difference was observed between the samples towards OH radical/h^+ induced pre-oxidation of humic acid.

TiO_2 *Mechanism:* Photocatalytic degradation process basically relies on the nonselective reactivity of the oxidizing species namely $^\bullet OH$ radical possessing a high oxidation potential.

When TiO_2 is irradiated with photons of less than 385 nm, the band-gap energy (E_{bg}) is exceeded and an electron is promoted from the valance band to the conduction band. The resultant electron-hole pair (e_{CB}^-/h_{VB}^+) has a lifetime in the space-charge region that enables its participation in chemical reactions. The most widely postulated reactions are shown below:

Initiation reaction:

$$TiO_2 + h\nu(\lambda < 385\,nm) \longrightarrow h_{VB}^+ + e_{CB}^-,$$
$$h_{VB}^+ + e_{CB}^- \longrightarrow \text{heat} \longrightarrow \text{recombination reaction.}$$

Oxidation reactions induced by h_{VB}^+:

$$h_{VB}^+ + H_2O_{ads} \longrightarrow {}^\bullet OH + H^+,$$
$$h_{VB}^+ + OH^-_{\ ads} \longrightarrow {}^\bullet OH.$$

Reduction reactions induced by e_{CB}^-:

$$e_{CB}^- + O_{2,ads} \longrightarrow O_2^{\bullet -},$$
$$2e_{CB}^- + O_{2,ads} + 2H^+ \longrightarrow H_2O_2,$$
$$H_2O_{2,ads} + e_{CB}^- \longrightarrow {}^\bullet OH + OH^-.$$

The OH radical bound to the semiconductor surface is a chemical equivalent to the surface trapped hole. The hydroxyl radical is able to react with almost all organic

Table 3. *Adsorption properties of humic acid onto* TiO_2.

	K_F	1/n	q_A, $m^{-1}g^{-1}$
Humic acid	1102	0.39	2632
Sample 1, S1	442	0.96	2664
Sample 2, S2	256	1.17	2368
Sample 3, S3	512	0.64	1696
Sample 4, S4	–	–	880

molecules thus initiate the oxidative degradation. On the other hand, since the photocatalytic oxidation reactions take place on the surface of the photocatalyst, the elementary reaction steps of humic acid (HA) on the TiO_2/water interface can be represented by the following equations:

$$O_2 + TiO_2 \longrightarrow O_{2,\mathrm{ads}},$$
$$H_2O + TiO_2 \longrightarrow H_2O_{\mathrm{ads}},$$
$$HA_{\mathrm{aq}} + TiO_2 \longrightarrow HA_{\mathrm{ads}},$$

where, subscripts aq and ads denote aqueous and adsorbed species, respectively.

In case of irradiation with light in visible region:

$$HA + h\nu(\lambda > 400\,\mathrm{nm}) \longrightarrow HA^{*}{}_{\mathrm{ads}} \longrightarrow \text{sensitized reactions}.$$

Hydroxyl radical is an extremely powerful oxizing agent with a redox potential of + 2.8 V. The attack of the produced oxidants as $^{\bullet}OH$/ $^{\bullet}HO_2$ radicals may result in structural changes via hydroxylation, decarboxylation and decyclization in humic acid molecule producing less hydrophobic and less adsorbing aromatic moieties.

$^{\bullet}OH$ radical reactions:

$$^{\bullet}OH + H_2O_2 \longrightarrow {}^{\bullet}HO_2 + H_2O,$$
$$^{\bullet}OH + HA_{\mathrm{ads}} \longrightarrow {}^{\bullet}A + H_2O \longrightarrow \text{via radical reactions} \longrightarrow \cdots HA_{\mathrm{ox}} \longrightarrow \cdots CO_2 + H_2O.$$

Therefore, upon direct action of the oxidants, humic acid is expected to be degraded by far to the formation of CO_2 and H_2O. For prolonged irradiation periods ($t > 3$ h) photocatalysis transforms to photomineralization as followed for sample 4 revealing almost 95% TOC removal.

3.3. Adsorption properties of pre-ozonated humic acid solutions onto TiO_2.

It has been shown extensively that adsorption plays a prominent role in the course of photocatalytic degradation of organic pollutants. Therefore, the adsorption characteristics of untreated as well as treated humic acid samples on TiO_2 have been investigated. The data obtained by batch adsorption experiments were fitted to the Freundlich adsorption model as given below:

$$q_A = K_F C_e{}^{1/n},$$

q_A: adsorbed amount of adsorbate per mass of adsorbent ($m^{-1}g^{-1}$),
C_e: equilibrium concentration of the adsorbate (m^{-1}),
K_F and 1/n: empirical constants.

The isotherms revealed perfect fits to the Freundlich model especially for the untreated humic acid molecule. Degree of pre-ozonation significantly altered the adsorption profile of humic acid on TiO_2. As compiled in Table 3, K_F values were in between 256 and 512 and 1/n values reflected an adsorption intensity trend towards linearity. On the other hand, for Sample 4, adsorption profile showed a cluster type accumulation in a C_e region of 5.4–17.5 m^{-1} and a q_A region of 484–3120 $m^{-1}g^{-1}$. Therefore for comparison purposes the q_A values corresponding to 0.5 $mgmL^{-1}$ photocatalytst loading that was used during photocatalytic degradation experiments were selected. The adsorption trend of q_A calculated as 2664, 2368, 1969 and 880 $m^{-1}g^{-1}$ for samples 1–4 respectively clearly explains the tendency of decreasing adsorption capacity of treated humic acid solutions on TiO_2. These results may suggest that the preozonation transformed humic acid molecule into more desorbable compounds that might migrate to the bulk solution. Bearing in mind that the structure of humic acid molecule was strongly altered due to partial oxidation, the decreasing trend in q_A can be explained by the changes in size and the degree of the functional groups taking part in surface reactions.

Untreated humic acid molecule contained more functional groups as deprotonated carboxylic groups leading to a strong attraction with the positively sites of TiO_2 through carboxylate linkages as well as hydrogen bonding [20]. The effect of ozonation on humic acid structure is mainly expressed by the decrease in size and loss of aromaticity as well as increased hydrophilicity thereby increased charge attraction. Humic acid/TiO_2 binary system is mainly governed by the binding capability of humic acid onto TiO_2 primarily due to the presence of oxygenated functional groups.

Most of the formed new groups on ozonation are strongly acidic and hydrophilic and would undergo charge attraction when brought into close proximity with the positively charged sites of TiO_2 and repulsion due to the negatively charged centers. Therefore, pH dependent deprotonation of the functional groups of humic acid and the characteristics of the titanium dioxide surface should govern the adsorption characteristics of humic acid samples.

Since humic acid is considered as negatively charged at the pH of zero proton condition, $pH_{zpc} = 6.3$ due to the deprotonation of the carboxylic groups, the electrostatic interaction between charged humic acid segments and TiO_2 should be attractive at $pH < 6.3$ and impulsive at $pH > 6.3$.

$$TiOH + H^+ \longrightarrow TiOH_2{}^+ \qquad K_{a1},$$
$$TiOH + OH^- \longrightarrow TiO^- + H_2O \qquad K_{a2},$$
$$pH_{ZPC} = (pK_{a1} + pK_{a2})/2.$$

Besides Coulomb forces of attraction, favorable energetic compensation must exist; nonelectrostatic specific interactions between humic acid functional groups and TiO_2 surface should be involved for adsorption to occur. Contribution of the hydrophobic properties of humic acids may also be considered.

Under the presented experimental conditions, photocatalytic degradation rates revealed no distinct correlation with the adsorption characteristics of the partially oxidized humic acid samples. The reason may be explained by the complex nature of the reaction mechanism. Dark adsorption coefficients are not sufficiently indicative of the photo adsorption/photo desorption processes taking place during the early stages of irradiation.

For a better understanding of the kinetics of the photocatalytic oxidation of the pre-ozonated humic acid samples, the application of the Langmuir-Hinshelwood kinetic model is recommended.

4. CONCLUSIVE REMARKS AND RECOMMENDATIONS

Oxidation by pre-ozonation alters the spectroscopic properties of humic acid as explained by UV_{254}, UV_{280} and $Color_{436}$. On the other hand, the complex nature of the ozonated humic acid medium could not be specifically expressed by only UV-vis properties.

Photocatalytic oxidation rates as explained by pseudo-first order kinetic model, were significantly affected by the degree of pre-oxidation by ozonation. The initial rate of UV_{254} removal differed by 35% in relation to the preozonation effect. On the other hand, preozonation followed by photocatalytic oxidation resulted in 80% color removal of humic acid.

No significant correlation could be attained between the photocatalytic oxidation rates and the dark adsorption properties of the ozonated as well as untreated humic acid samples.

Further experimental study on the sample characterization and the application of the Langmuir-Hinshelwood kinetic model is recommended to elucidate the sequential oxidation of humic acids via ozonation followed by photocatalytic oxidation as well as the application of the filtration technique to express the molecular size distribution of the samples.

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