

Research Article

Contribution of Metal Species to the Heterogeneous Photocatalytic Degradation of Natural Organic Matter

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The role of organic matters which are high molecular weight macromolecules in natural water supplies and their subsequent removal by advanced oxidation technologies has gained importance because they possess a substantial capacity to complex dissolved metal species. The present study was conducted to evaluate the impact of aqueous Cr(VI) and Mn(II) species on the photocatalytic oxidation of humic acids as a major component of natural organic matter in aquatic systems. The photocatalytic decolorization rate of humic acid was followed by pseudo-first-order and Langmuir-Hinshelwood kinetic models. The presence of aqueous Cr(VI) and Mn(II) species did not significantly alter the degradation efficiency ($\leq 20\%$) in terms of first-order kinetic model. Although the impact of manganese species could be considered as insignificant, a substantial adsorption effect could be assessed as reflected by respective Langmuir-Hinshelwood kinetic model parameters.

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1. INTRODUCTION

Natural organic matter, namely humic substances are composed of heterogeneous macromolecules consisting of multiple functional groups randomly arranged. They possess a substantial capacity to complex dissolved species such as metal ions and they can interact with mineral surfaces. Their role in natural waters has gained importance because of these interactions which control the behavior and mobility of metals in the aquatic environment. Although the chemistry of humic substances in aqueous environments has been thoroughly investigated, uncertainties still exist on their behavior in conditions comparable to those of natural aquatic systems. Trace metals are the major constituents of most of the aquatic systems. They originate from the natural interactions of water, sediments, and the atmosphere and their impact on aquatic life as well as reactivity depends on the species formed due to association with other dissolved or suspended components of the system [1].

Chromium(VI) is a frequent contaminant in wastewaters arising from industrial processes such as electroplating, leather tanning, or paint manufacture. On account of its carcinogenic properties, its concentration in drinking waters has been regulated in many countries and the

maximum limit in drinking waters is 0.10 mg L^{-1} . Manganese is one of the trace elements in the earth's crust. The quantity of manganese ions has great importance for drinking and process waters. It causes undesirable taste and aesthetic problems in drinking waters. For this reason, the presence of manganese content is limited by 0.05 mg L^{-1} in drinking waters and by 0.2 mg L^{-1} or less in industrial waters [2].

In pursuit of more efficient water treatment procedures, the study of light induced oxidation reactions catalyzed by titanium dioxide has received increased attention during the past decade. Hence, the photodegradation of dissolved organic contaminants on TiO_2 slurries has become a promising procedure for water purification. Many studies on photocatalytic degradation concern only the single component systems whereas there are a limited number of papers revealing decontamination of complex systems. Previous studies cover the results of oxidation and reduction of various metals (e.g., Mn^{2+} , CrO_4^{2-} ...) by UV irradiated TiO_2 particles in aqueous solutions and the photocatalytic oxidation of organic compounds in the presence of trace metals [3–10]. As recently reported in the review of Litter, the presence of dissolved metal ions can induce various effects on the rate and efficiency of photocatalytic

reactions [11]. The effect is strongly dependent on the type and concentration of the metal ion resulting in either an increase in the photocatalytic rate or in an inhibitory effect [11].

Over the last several years, the photocatalytic oxidation of humic acids in natural waters has been studied extensively [12–14]. However, much less is known about how the photocatalytic degradation of humic acid at TiO_2 /solution interface is influenced by the presence of metal ions. There exist few studies that have been carried out concerning complex systems which are the actual situations of the environmental pollution. Therefore, the present study was conducted to assess the effect of chromium as Cr(VI) and manganese ions as Mn(II) on the TiO_2 mediated photocatalytic degradation of humic acid.

Considering humic macromolecule as a model for natural organic matter and trace metal ions such as chromium and manganese as pollutants introduced into the aquatic system, the modeling of the photocatalytic degradation processes in natural water supplies was investigated based on the interactions of TiO_2 , humic acid, chromium, and/or manganese system.

2. EXPERIMENTAL DETAILS

2.1. Materials

Commercial humic acid was supplied from Roth and stock humic acid solution (1000 mg L^{-1}) was prepared according to a previously outlined procedure [15]. Appropriate dilutions were made with distilled deionized water. The most common form of TiO_2 Degussa P-25 was used as the photocatalyst. It is composed of 80% anatase and 20% rutile. Chromium(VI) and manganese(II) solutions were prepared according to *Standard Methods* [16].

2.2. Photoreactor

Photocatalytic oxidation experiments were performed in a 50 mL cylindrical pyrex reaction vessel. A 125 W black light fluorescent lamp emitting radiation between 300 and 420 nm with a maximum at 350 nm was used as the light source. The intensity of the incident light, measured by ferrioxalate actinometry, was $2.84 \mu\text{E min}^{-1}$ [17]. The reaction vessel was illuminated from the top and continuous stirring of the suspension was provided by means of a magnetic stirrer.

2.3. Procedure

Bench scale experiments were performed at neutral pH conditions ($\text{pH} = 6.7$). Ten mg L^{-1} of humic acid solution containing chromium ion concentrations ranging from 0.05 mg L^{-1} to 0.20 mg L^{-1} or manganese concentration of 0.05 mg L^{-1} was added directly to the reaction vessel containing 0.25 mg mL^{-1} TiO_2 . The photocatalytic degradation was carried out for certain reaction periods ranging from 0 to

60 minutes. Prior to spectrophotometric analysis, TiO_2 was removed from the suspension by filtration through a $0.45 \mu\text{m}$ Millipore membrane filter. The clear solution was analyzed with a Perkin Elmer Lambda 35 UV-vis spectrophotometer for absorbance of humic acid at 436 nm as represented by the removal of color forming moieties (Color_{436} , m^{-1}) and 254 nm with respect to the removal of aromatic groups (UV_{254} , m^{-1}).

3. RESULTS AND DISCUSSIONS

3.1. Preliminary experiments

Preliminary studies were conducted to study the interactions of humic acid and metal ions as a binary system. Previously reported results of chromium and humic acid interactions revealed that even after 24 hours of continuous mixing, the change observed for Color_{436} and UV_{254} parameters of humic acid was found to be insignificant ($< 5\%$) and independent of the added chromium ion concentration [18]. As presented in Figure 1, no significant deviation was observed in the spectra of humic acids in the presence of metal ions however, a slight increase in 350–400 nm is noticeable. It was reported that chromate esters show characteristic absorption bands around 350–400 nm region of the spectrum and the most drastic band at 365 nm wavelength was ascribed to Cr(VI) oxy esters in the literature [19, 20]. This distinct absorption band is similar to that reported by Lu et al., in the reaction of dichromate with humic substances which is known to be associated with the formation of Cr(VI) complex with diol, carboxylic acid, and polyphenol groups in humic substances [21].

Experiments were also carried out to investigate the binary interactions of humic acid and manganese ions in the absence of TiO_2 . The initial absorbance difference between humic acid and humic acid in the presence of manganese was negligible ($\Delta\text{Abs} \leq 0.005$) for $\lambda > 240 \text{ nm}$ indicating that no reaction occurred between humic acid and the specified metal. However, spectra of humic acid in the presence of manganese ions reveal relatively higher absorbance in the wavelength region of 200 nm–240 nm (Figure 1). Even under conditions of irradiation, no significant removal of humic acid or humic acid in the presence of manganese was observed. As reported by Gamble et al., hydrated manganese(II) ions and humic substances might form outer-sphere complexes in which manganese(II) ions remain partly hydrated at binding sites of humic acid [22]. It was also reported that manganese(II) interacts directly with carboxylate anionic groups in humic substances forming a weak complex with a $\log K$ value of $2.0 (\pm 0.1)$ [21]. However, the complexation of manganese with humic acid could not be observed with UV-vis spectroscopy under the specified experimental conditions.

In the ternary system comprising the dark interactions of humic acid, chromium, and TiO_2 , the interference of humic acid on the adsorption of chromium species onto TiO_2 was observed as reported in a recently published paper

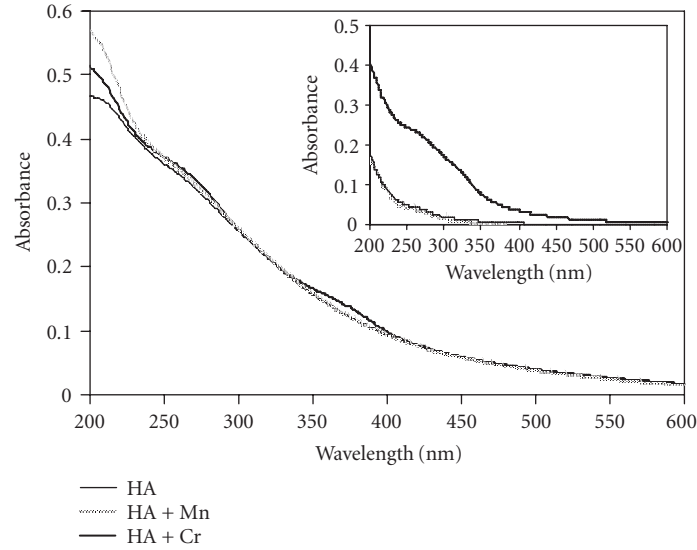


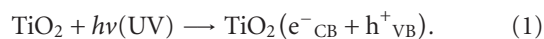
FIGURE 1: UV-vis spectra of humic acid in the presence of metal ions. (Inserted figure: the absorbance change after photocatalytic irradiation for 60 minutes.)

[18]. The presence of humic acid would decrease the adsorption efficiency of chromium ions because of the competitive adsorption on the active sites of TiO_2 [18]. In adsorbed state, the coordination of metals by ligands such as carboxyl, phenolic or sulfhydryl groups is consequently similar to the equivalent process taking place in solution. However, bearing in mind that chromium ion is mainly in the form of an oxyanion, the reactions of which can be explained by interactions of an electrostatic or covalent nature or both. Control reactions of humic acid and manganese without irradiation (dark reactions) in the presence of catalyst revealed an initial adsorptive removal of approximately 35% with respect to UV_{254} removal of humic acid. This could also be explained by a surface complexation model.

3.2. Photocatalytic degradation

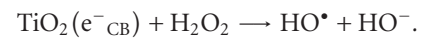
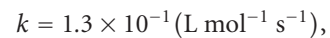
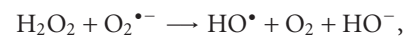
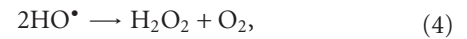
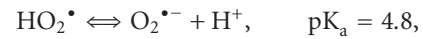
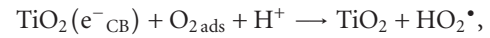
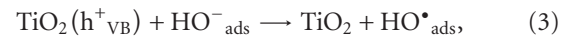
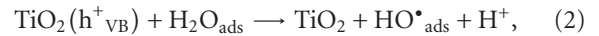
3.2.1. Mechanistic explanation of primary events in photocatalytic degradation

Continuous band-gap irradiation (E_{bg} is 3.2 eV (390 nm) in anatase and 3.05 eV (420 nm) in rutile) of an aqueous semiconductor dispersion excites an electron from the valence band (VB) to the conduction band (CB), creating an electron-hole pair. The heterogeneous photocatalytic process takes place through a complex sequence of reactions that can be expressed by the following set of equations:



The formation of redox pair could either be followed by respective reactions or a recombination reaction resulting in

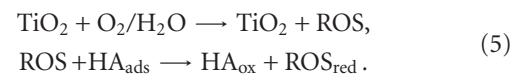
the dissipation of the reactive species:



In relation to the possible binary and ternary interactions, the photocatalytic degradation mechanism of humic acid in the presence of metal ions might proceed through the outlined pathways as the following.

Pathway 1

The degradation of humic acid might take place via direct photocatalytic reaction and metal species remain in solution and interact separately:



Pathway 2

The binary system composed of metal humate adsorbs onto the photocatalyst and degradation takes place by the action

TABLE 1: Pseudo-first-order model parameters for the photocatalytic degradation of humic acid in the presence of metal ions.

Color ₄₃₆	k (min ⁻¹)	t _{1/2} (min)	Intrinsic photocatalytic activity (m ⁻¹ min ⁻¹ m ⁻²)
Humic acid	3.86 × 10 ⁻²	18	0.404
Humic acid + Cr(VI)	3.13 × 10 ⁻²	22	0.337
Humic acid + Mn(II)	3.37 × 10 ⁻²	20	0.343
UV ₂₅₄	—	—	—
Humic acid	2.73 × 10 ⁻²	25	1.446
Humic acid + Cr(VI)	2.06 × 10 ⁻²	34	1.073
Humic acid + Mn(II)	2.31 × 10 ⁻²	30	1.226

of the reactive oxygen species:



where D denotes the electron donor, ROS denote reactive oxygen species such as $\cdot\text{OH}$, H_2O_2 , $\text{O}_2^{\cdot-}$, ads denote adsorbed species, ox denote oxidized species, and red denote reduced species.

3.2.2. Kinetic approach to photocatalytic degradation

In general, photocatalytic oxidation rate is explained in terms of pseudo-first-order reaction model. On the other hand, the rate of photocatalytic oxidation of an electron donor at the TiO_2 surface varies as a function of the dissolved concentration of the electron donor according to a Langmuir-type isotherm. The rate of the photocatalytic reduction of a dissolved electron acceptor has also been reported to be a Langmuir-type function of the concentration of the electron donor in the presence of TiO_2 . These findings are in agreement with the assumption of an inner spherically bound electron donor since a Langmuir-type adsorption is consistent with the formation of a surface complex by surface-ligand exchange. Therefore, the photocatalytic degradation of humic acid in the presence of metal ions was modeled based on Langmuir Hinshelwood (L-H) as well as simple pseudo-first-order kinetic model [23, 24].

The UV-vis spectra of humic substances monotonously decrease with increasing wavelength [14, 25]. The photocatalytic degradation profile of humic acid in the presence of metal ions also displayed the same basic, featureless pattern of monotonous decline as a function of wavelength and a decrease in the absorbance values was observed with the increasing irradiation time during photocatalytic oxidation. The inset in Figure 1 shows the UV-vis spectra of humic acid, humic acid/manganese, and humic acid/chromium solutions after 60 minutes of photocatalysis.

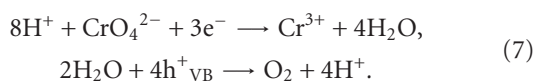
The related absorbance data were followed with respect to Color₄₃₆ and UV₂₅₄ and applied to the pseudo-first-order kinetic model. Considering the surface oriented nature of photocatalytic degradation kinetics, the photocatalytic removal rates were normalized with respect to the surface area of the photocatalyst and presented as intrinsic photocatalytic activities (Table 1).

The removal of color forming groups (Color₄₃₆) revealed considerably higher pseudo-first-order kinetic constant with respect to the UV absorbing centers (UV₂₅₄). Following the contribution of trace metals, the intrinsic photocatalytic degradation rate of humic acid decreased by 17% for Color₄₃₆ and 26% for UV₂₅₄ in the presence of chromium ion. In contrast, in a study by Xu et al. in 2005 the degradation of methyl tert-butyl ether (MTBE) in the presence of Cr(VI) was reported to be significantly quicker than the MTBE single system by UV/ TiO_2 process [26]. The slight decrease in the photocatalytic oxidation rate of humic acid in the presence of Cr(VI) might be explained by the possible competitive complexation and oxidation-reduction reactions taking place in the medium between humic acid and the metal ion, which might have affected the adsorption properties on the active sites on the TiO_2 surface. According to Stumm and Morgan, a metal must bind to the surface through its coordinate sphere by filling all of its available coordination sites with ligands so that it becomes nonadsorbable [27]. Chromium(VI) in the form of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) does not express any available sites for chelate formation. Therefore, possible reduction of chromium(VI) could be expected either directly by the humic acid or by the use of the photogenerated electrons in the presence of irradiated titanium dioxide powders.

Considering the stepwise reaction of chromium(VI) with humic acid, the first step constitutes the formation of chromium(VI) complex with diol, carboxylic acid, and polyphenol groups in humic substances [21]. The next step is a redox process occurring under acidic conditions, in which humic substances are detected to reduce chromium(VI) to chromium(V) as an intermediate, and then to chromium(III) which is complexed by humic substances [28]. Under neutral pH conditions ($\text{pH} \cong 6.7$) at which our study was conducted, reduction to chromium(III) is not expected to be the major pathway of photocatalytic degradation process.

On the other hand, the ultraviolet illumination of Cr(VI) solutions containing TiO_2 in suspension was found to reduce Cr(VI) to Cr(III) at neutral pH [3, 29]. From simulation of Cr(VI) speciation with using MINTQA2 program, CrO_4^{2-} is known to be a major species above pH 7 [30]. Hence, the reaction mechanism could be explained as the reduction of Cr(VI) to Cr(III) by electrons followed by the oxidation of

water through hole reactions as given in (7). Hence, the reaction mechanism could be explained as the reduction of Cr(VI) to Cr(III) by electrons followed by the oxidation of water through hole reactions. The presence of oxygen competed with Cr(VI) for the photogenerated TiO₂ electrons and therefore resulted in a decrease of the photoreduction yield according to the presented equations:



Accordingly, the photoreduction process might be expected to take place by electron transfer from illuminated TiO₂ to anionic Cr(VI) species. CrO₄²⁻ is expected to form outer sphere complexes whereas Cr(III) can form inner sphere complexes with TiO₂ either as a monodentate linkage or by a bidentate chelation mechanism [2]. Due to the reduction of the number of active sites on the TiO₂ surface, the reaction rate might also be expected to decrease. The retardation effect of chromium ion on the photocatalytic degradation rate of humic acid might be related to the use of the photogenerated titanium dioxide electrons for the possible reduction of Cr(VI), therefore leading to the decreased generation of hydroxyl radical and possible inhibition on the removal rate of humic acid. Cr(VI) ions in solution alter the redox mechanism and affect the adsorptive properties of the photocatalyst and hence the photocatalytic oxidation rate of humic acids in the aqueous phase, through Cr(VI) reduction to Cr(III) in the presence of irradiated TiO₂ and possible complexation of Cr(III) by humic acid at water-mineral oxide surface [3, 28, 29]. Moreover, the slight retardation observed in the oxidation rate of humic acid could also be attributed to a probable adsorption mechanism of oxyspecies of chromium(VI) on the positively charged TiO₂ surface [31].

Three component adsorption systems allow the formation of different surface adsorbate configurations resulting in a “metal-like,” “ligand-like” or both “metal-like and ligand-like” adsorptive behaviors [32]. Accordingly, in this study a ligand-like adsorption behavior might be expected for the humic acid and chromium system. As verified by Stumm and Morgan, available coordination sites of chromium would be filled by the ligands of humic acid and thereby adsorption of humic acid instead of the metal ion onto the surface of the photocatalyst would be favored [27]. In the presence of metal ions, due to the possible complex formation between humic acid and the metal ions, rearrangement of the electrostatic forces takes place, and formation of a micelle-like cage structure by metal ion-bridging interactions might be expected [33].

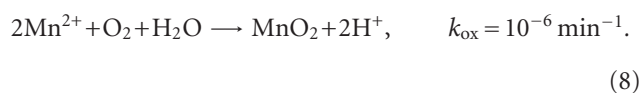
The photocatalytic reduction of Cr(VI) to Cr(III) at different pH values using TiO₂ as the photocatalyst and a variety of organics such as methanol, formic acid, salicylic acid, EDTA, phenol, and nitrobenzene was investigated in several studies [26, 30, 34, 35]. It was reported that the photocatalytic conversion of Cr(VI) to Cr(III) in the presence of salicylic acid at different pH values (pH 1 to pH 6) followed

first-order reaction kinetics [34]. Rapid reduction of Cr(VI) was also observed with EDTA, mandelic acid, and citric acid. Since humic acids contain a variety of functional groups similar to those model compounds, reduction of Cr(VI) in the presence of humic acid could also be expected but unfortunately could not be verified under the specified conditions.

The effect of different chromium ion concentrations in the range of 0.005 mg L⁻¹ to 0.20 mg L⁻¹ on the removal rate of humic acid was also investigated. The related pseudo first-order rate constants revealed higher removal rates in terms of Color₄₃₆ with respect to UV₂₅₄. The results indicated that chromium ions in the range of 0.05–0.20 mg L⁻¹ induced a retardation effect on humic acid degradation with rate constants of the same order of magnitude. Compared to humic acid degradation, a significant decrease in the reaction rate was detected in the presence of 0.05 mg L⁻¹ chromium. The reaction rate constant in the presence of 0.05 mg L⁻¹ chromium was 2.51 × 10⁻² min⁻¹ and 2.02 × 10⁻² min⁻¹ in terms of Color₄₃₆ and UV₂₅₄, respectively. Doubling chromium ion concentration had an effect of increasing the rate constant for Color₄₃₆ by 20% whereas no significant change was observed for the corresponding rate constant of UV₂₅₄. Further increase in the chromium ion concentration did not cause any change in the reaction rates for the parameters studied (reaction rate difference < 1%).

The effect of manganese ions on the photocatalytic degradation of humic acid in terms of Color₄₃₆ and UV₂₅₄ was assessed through the rate constants as 3.37 × 10⁻² m⁻¹ min⁻¹ and 2.31 × 10⁻² m⁻¹ min⁻¹, respectively (Table 1). In the presence of manganese ion, almost 15% retardation was detected in the photocatalytic degradation rate of humic acid for the color forming centers. The removal rate of UV₂₅₄ for humic acid in the presence of manganese ions was calculated to be 0.843 m⁻¹ min⁻¹. Compared to the photocatalytic degradation rate of humic acid in the presence of 0.10 mg L⁻¹ chromium ion, almost 11% decrease was detected for UV₂₅₄. In the absence of metal ions, the photocatalytic degradation of humic acid alone was found to be the fastest with a reaction rate of 0.994 m⁻¹ min⁻¹.

The visual examination of the reaction medium did not reveal any precipitate formation due to the oxidation of Mn(II) to MnO₂:



It is known that the photocatalytic oxidation of manganese(II) to insoluble MnO₂ is thermodynamically possible ($k_{\text{ox}} = 10^{-6} \text{ min}^{-1}$) in neutral to acidic aqueous medium, followed by a pH decrease during the reaction ($\Delta\text{pH} = 0.40$) [5]. Under the specified experimental conditions, a pH drop ($\Delta\text{pH} = 0.65$) was observed which might be either an indication of MnO₂ formation or be related with the possible degradation of humic acid to organic acids and/or CO₂. On the other hand, k_{ox} constant of the reaction ($k_{\text{ox}} = 10^{-6} \text{ min}^{-1}$) is very slow compared to the photocatalytic degradation rate of humic acid ($k = 3.86 \times 10^{-2} \text{ min}^{-1}$). Therefore, the photocatalytic oxidation of humic acid in the

TABLE 2: Pseudo first-order and Langmuir-Hinshelwood rate constants.

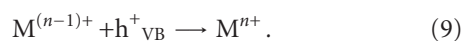
Color ₄₃₆	First-order rate (m ⁻¹ min ⁻¹)	Langmuir-Hinshelwood			
		k _{LH} (m ⁻¹ min ⁻¹)	K (m)	t _{1/2} (min)	Rate* (m ⁻¹ min ⁻¹)
Humic acid	0.278	0.124	0.600	38	0.101
Humic acid + Cr(VI)	0.225	0.0625	0.401	87	0.0461
Humic acid + Mn(II)	0.242	0.148	0.580	32	0.119
UV ₂₅₄	—	—	—	—	—
Humic acid	0.994	0.468	0.141	49	0.392
Humic acid + Cr(VI)	0.738	0.250	0.0958	101	0.195
Humic acid + Mn(II)	0.843	0.486	0.0965	52	0.379

*Rate was calculated for 10 mg L⁻¹ humic acid, Cr(VI): 0.10 mg L⁻¹, Mn(II): 0.05 mg L⁻¹.

presence of manganese ion might be more favorable than the direct oxidation of Mn(II) to MnO₂. According to Ghosh and Schnitzer, in the presence of metal ions, due to a possible complex formation with humic acid, rearrangement of the electrostatic forces takes place [1]. The formation of a micelle-like cage structure by metal ion-bridging interactions might also be expected as explained for the interactions of chromium species [33].

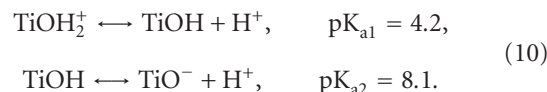
Aqueous manganese ion speciation studies indicate that Mn(II) ion is in the form of hydrated aqua complex, Mn(H₂O)₆²⁺ at pH ≈ 7. As reported by Gamble et al., hydrated manganese(II) ions and humic substances might form outer-sphere complexes in which manganese(II) ions remain partly hydrated at binding sites of humic acid [22]. It was also shown that manganese(II) interacts directly with carboxylate anionic groups in humic substances forming a weak complex with a log *K* value of 2.0 (±0.1) [21]. The slightly lower value of the reaction rate constant in the presence of manganese ion, (*k* ≤ 13% for Color₄₃₆, *k* ≤ 15% for UV₂₅₄) compared to the rate constant *k* of humic acid, might be explained by the possible complex formation with humic acid. The weak formed complex might block the active sites on the TiO₂ surface and hence lead to a slight reduction in the photocatalytic removal rate of humic acid. In accordance with this, in the presence of manganese ions, high adsorption constants were obtained from the adsorption experiments for the UV-absorbing centers [36]. This reveals that the adsorption process is being favored by the aromatic moieties rather than the color forming centers where adsorption constants of humic acid and humic acid/manganese binary systems were not significantly different. However, the observed phenomenon could not be explained clearly due to the lack of the available literature knowledge.

The photocatalytic oxidation of toluene, using TiO₂ as the photocatalyst, was carried out in the presence of 10⁻⁵ M manganese(II) at pH 3 and a significant increase in the reaction rate was observed contrary to the findings of this study [10]. The increase in the reaction rate was explained by the oxidation of metal ions by the photogenerated holes, proceeding in competition with reaction (9):



The consumption of holes (h⁺_{VB}) by the metal ion results in an increased rate of •OH radical formation through the reactions as presented in (2) and (3).

On the other hand, the point of zero charge (PZC) for TiO₂ Degussa P-25 was reported as pH_{pzc} ≈ 6.3 [37]. In acidic medium (pH < pH_{pzc}) the particle surface is positively charged and the adsorption of anionic and polar substrates is enhanced; in basic medium (pH > pH_{pzc}) the surface charge is negative and the adsorption of cationic species is favored:



According to these reactions under neutral pH conditions, the TiO₂ surface comprises of an equal number of positive and negative charges. As a result of this, repulsive and attractive electrostatic forces of the same strength are generated on the surface. Due to electrostatic interactions, the negatively charged sites on TiO₂ might be expected to interact with the cationic manganese ions found in solution as Mn(H₂O)₆²⁺. Finally, as a result of the competitive reactions between metal ion, ligands of humic acid, and the photocatalyst; the photocatalytic removal efficiency of humic acid in the presence of manganese ions might be altered with no significant change in oxidation rates irrespective of the reaction pathways as explained by expressions (5)-(6).

The impact of metal ions on the photocatalytic oxidation of humic acid could be better explained in terms of Langmuir-Hinshelwood kinetic model where the role of adsorption effects was also considered. Therefore, photocatalytic degradation experiments were performed for humic acid in the concentration range of 5 mg L⁻¹ to 20 mg L⁻¹ considering the highest probable concentration of humic acid in natural waters. By the modeling of the kinetic data the following *k*_{LH} (reaction rate constant) and *K* (adsorption constant) values were calculated. The L-H kinetic parameters as well as pseudo first-order rates (compiled from Table 1) were presented in Table 2.

Irrespective of the systems, as a general trend, *k*_{LH} values calculated for Color₄₃₆ are lower than the values calculated with respect to UV₂₅₄. However, the calculated adsorption constants, (*K*), for Color₄₃₆ exhibit a comparatively opposite

trend, displaying values that are four- to five-fold higher than the adsorption constants of UV₂₅₄ absorbing moieties. In accordance with the ordering of k_{LH} , the L-H rates also exhibit similar trend.

The presence of chromium ions resulted in decreased removal rates on the photocatalytic degradation of humic acid compared to the baseline rate that is the rate obtained in the absence of the metal ions. Approximately, 54% and 50% decrease in the L-H reaction rate was attained for Color₄₃₆ and UV₂₅₄, respectively. Accordingly, the reaction rate constant k_{LH} and adsorption constant K of humic acid were significantly lower in the presence of chromium. The decrease in the rate constant might be due to absorption of UV illumination by a complex between chromium and humic acid oxidation intermediates. The inhibition effect could be related to strong adsorption effects which could be explained by Freundlich adsorption constants [18].

Examination of the constants for humic acid and humic acid in the presence of manganese indicated that the values of k_{LH} were slightly higher in the presence of the metal ion. For Color₄₃₆, the reaction rate for 10 mg L⁻¹ humic acid was calculated to be 0.101 m⁻¹ min⁻¹. In the presence of manganese ion, the reaction rate was detected to be the fastest with a value of 0.119 m⁻¹ min⁻¹ and the slowest reaction rate was achieved in the presence of chromium ion with a value of 0.0461 m⁻¹ min⁻¹.

Pseudo first-order rates were found to be comparatively higher than the L-H rates. Considering the overall effect of the adsorptive interactions, the related K values could be an indicator parameter for both of the removal rates as explained by both of the kinetic models.

4. CONCLUSION

Decolorization rate (Color₄₃₆, m⁻¹) as well as the removal of aromatic moieties (UV₂₅₄) of humic acid by photocatalytic oxidation was followed by pseudo first-order and Langmuir-Hinshelwood kinetics. The presence of 0.10 mg L⁻¹ chromium ion, which is the maximum allowable limit in natural waters, retarded the removal rates for all of the parameters when compared with the baseline rate of humic acid (for Color₄₃₆, $k \leq 17\%$; and for UV₂₅₄, $k \leq 26\%$). The reduction in degradation rate of humic acid could be explained by the possible competitive complexation and oxidation-reduction reactions taking place in the medium. On the other hand, the magnitude of the effect of degradation is irrespective of the concentration of Cr(VI) species.

In the presence of manganese (0.05 mg L⁻¹) ion, slight decrease in the pseudo-first-order rate constants of humic acid was observed both for Color₄₃₆, and UV₂₅₄ as $k \leq 15\%$. The reason for this might be explained by the formation of a weak complex with humic acid which might have blocked the active sites on the TiO₂ surface and hence, reducing the photocatalytic removal of humic acid.

The pseudo-first-order rate constant simply explains the overall removal tendency covering all competitive and consecutive reactions, therefore the use of Langmuir-Hinshelwood equation is recommended to explain the pho-

tocatalytic oxidation rate of humic acid in the presence of metal ions. The evaluation of the results in terms of Langmuir-Hinshelwood rate with respect to Color₄₃₆ suggests 54% decrease in the presence of chromium. On the other hand, 15% increase was observed in the presence of manganese with respect to Color₄₃₆. Cr(VI) and Mn(II) ions in solution alter the redox mechanism and affect the adsorptive properties of the photocatalyst and hence the photocatalytic oxidation rate of humic acids. The impact of manganese ion on the photocatalytic oxidation could be better explained in terms of L-H kinetics where the adsorption effects were also considered.

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