Photocatalytic mineralization of humic acids with TiO₂: Effect of pH, sulfate and chloride anions

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ABSTRACT. Aims of the present work are to investigate the photomineralization of commercial humic acid in water solution. The effect of initial pH of solution and different anions (chloride, sulfate and mixture) on the photocatalytic degradation of HA with titanium dioxide in aqueous solution has been examined. The photocatalytic mineralization rate in alkaline solution is lower than in neutral and acidic solution. In our conditions no effect of chloride ions on the degradation rate is observed. The influence of the sulfate depends on its concentration in the solution. For a large concentration, we note a decrease of the mineralization rate.

1. INTRODUCTION

The heterogeneous photocatalysis for total oxidation of organic and inorganic water and air pollutants has been studied extensively during the last twenty years [1–6]. Irradiation of semi-conductors like TiO₂ in suspension or fixed to various supports, in aqueous solutions containing organic pollutants, creates a redox environment which is able to destroy these compounds. Many researchers [1–4] have shown that most organochloride compounds as well as many pesticides, herbicides, surfactants and colourings are completely oxidized into mineralized products like carbon dioxide, hydrochloric acid and water.

The humic acids (HA) have a significant role in the aquatic systems. They can complex heavy metals and organic pollutants such as pesticides, insecticides and herbicides [7]. But they are especially precursors of mutagenic products [7, 8]. Indeed they will react with the chlorine used for the disinfection of water, to give organochloride compounds which are well-known to be carcinogenic products [9]. The heterogeneous photocatalysis can be an effective alternative solution for the elimination of the HA from aqueous solution [2–5]. According to Corin [10] the direct photolysis of the HA leads to formation of low-molecular-weight carboxylic acids (oxalic, succinic, formic, acetic ...).

Aims of the present work are to investigate the photomineralization of commercial humic acid in water solution. The mineralization kinetics was controlled by Total Organic Carbon (TOC). The effect of initial pH of solution and different anions (chloride, sulfate and mixture) on the photocatalytic degradation of HA with titanium dioxide in aqueous solution has been examined.

2. EXPERIMENTAL PART

2.1. Reagents and analytical procedures. Humic acid sodium salts were supplied by Sigma-Aldrich Company and the titanium dioxide P25 from Degussa Corporation (70% anatase, 99.8% purity, average particle size 30 nm and specific surface of 50 m²/g) was used as received. All chemicals were reagent grade and were used without further purification. The TOC values at different irradiation times were determined with Shimadzu TOC Analyzer (TOC-5050-A). The samples taken for analyses contain no filtrated TiO₂. The pH of the solution was adjusted with NaOH or HCl solution at 3.4, 7.8 and 11.5.

2.2. Photocatalysis experiments. Photocatalysis experiments were carried out in a Solar box ATLAS SUNTEST CPS+ simulating natural radiation. The light source was a vapour xenon lamp (300 nm < λ < 800 nm). In order to determine the photocatalytic mineralization kinetic, the initial concentration of humic acids amounted 100 mg/l. Homogeneous mixing was provided by sonication of the slurry for 5 minutes with titanium dioxide. The mixture was mixed by magnetic stirrer in the dark for 30 minutes in order to obtain equilibrium state. The time zero was the beginning of irradiation. For all experiments the photocatalyst concentration was 1 g/l except the experiment where the influence of TiO₂ loading (from 0.1 to 2 g/l) was studied. The volume of the reaction solution was 300 mL and illuminated surface 80 cm². The process was conducted at 20 °C. The mineralization of HA were analyzed without filtration by direct injection in the TOC analyser.

3. RESULTS AND DISCUSSION

3.1. Preliminary studies. In a previous work [11], we have investigated the adsorption of HA at TiO_2 surface, because adsorption could play a prominent role in catalytic photodegradation of organic molecules [12–14]. In this study, the measurements of HA adsorption were carried out by UV-light adsorption and by TOC analysis. In all cases, the adsorption kinetics were fast and equilibrium is reached within 30 minutes. We observed that the Langmuir model [15] can not be used, as others authors have been observed for hydroxybenzoic acids [16]. We have verified that the direct photolysis (without TiO_2) of HA is very weak (Figure 1).

Figure 1. Photolysis and photomineralization of HA with $[\text{TiO}_2] = 0.5$ and 1 g/l .

No obvious degradation of HA in this condition, occurred within 6 h [11, 17, 18]. The low increase of the TOC is induced by the slow evaporation of the mixture during the experiment. The evolution of TOC demonstrates the ability of TiO_2 to act as an efficient catalyst in the photodegradation of humic acid. The global evolution of the degradation shows two distinct domains.

At the beginning of the reaction, the TOC value decreases slowly (domain I) and then pseudo first order is observed for the TOC decrease (domain II). The initial decrease is connected with the amount of TiO_2 in suspension: the lower TiO_2 amount, the longer is the duration of this initial step [11]. The classical saturation phenomenon is noted for TiO_2 amount higher than 1 g/l [2] and will be also discussed later.

The fair evolution of TOC means that the mineralization of humic acid is rather limited in the domain I. The evolution of the reaction is certainly due to a surface degradation of carboxylate leading to shorter chain of HA followed by the re-adsorption of macromolecule. It was proven that photodegradation can proceed in surface via oxidation by hole and this mechanism is favored in case of adsorbed molecules [1–5] and sometime it is only mechanism found. All these observations suggest that the surface degradation of adsorbed HA via the carboxylate or phenolate surface groups leads to photodepolymerization. HA is progressively degraded by surface oxidative mechanism and so long as some macromolecules issued from HA remain in solution this

mechanism predominates. The slow decrease of TOC is certainly to be attributed to the CO_2 evolution from surface oxidation of adsorbed carboxylate.

The influence of the photocatalyst concentration on the mineralization kinetics of HA has been investigated employing different concentrations of Degussa P25 varying from 0.1 to 2 g/l (Figure 2 and ref. [11]).

Figure 2. Influence of the catalyst concentration on the photomineralization of humic acids.

For higher concentrations of TiO_2 , the removal efficiencies decreased with increasing amount of TiO_2 . These results show that there is an optimum amount of TiO_2 . Above this concentration level (between 0.5 and 1 g/l), the suspended particles of TiO_2 block UV-light passage and reduce the formation of electron/hole pairs and active sites. Most likely, the turbidity and color of treated solution, along with the effect of TiO_2 blocking in solution, made the decomposition less effective.

3.2. Influence of the initial pH on the photomineralization of humic acids.

The photocatalytic mineralisation of HA adjusted to various initial pH values by HCl or NaOH is shown in Figure 3, as the decrease of the relative concentration C/C_0 of TOC with the time of irradiation (where C is the running concentration and

Figure 3. Evolution of TOC during illumination of humic acids solution ($[\text{HA}] = 100 \text{ ppm}$) containing TiO_2 (1 g/l) at different initial pH values (3.4 , 7.8 and 11.5).

Table 1. Adsorption of HA at TiO₂ according to the pH.

Initial pH	TOC of initial HA solution (mg/l)	TOC of HA solution after addition of TiO ₂ and filtration (mg/l)	Percentage of adsorption
3.4	32.17	4.67	85.4%
7.8	35.62	26.82	26.2%
11.5	37.10	35.23	5.0%

Scheme 1. Repulsive effect of negative TiO₂ surface in alkaline conditions.

Co is the concentration at the beginning of the irradiation). The change of pH during photodegradation tests was found to be not significant (0.5 units).

As shown in Figure 3, the photocatalytic mineralization rate in alkaline solution (pH: 11.5) is lower than in neutral and acidic solution. The photocatalytic oxidation rate is largely dependent upon the amount of surface-adsorbed hydroxyle groups. It is well known that the surface of TiO₂ is amphoteric and consequently, the charge of surface is pH-dependant [19]. The pH_{pzc} (the point of zero charge) is close to 6.3. The behavior of HA can be explained both by the evolution of adsorption (versus pH, see Table 1) and the change of the molecular form (according to the pH [7]).

At higher pH, more functional groups were ionized to yield a larger negative charge. Humic acids contain both hydrophobic and hydrophilic functional groups mainly in the carboxyl, phenolic hydroxyl, alcoholic hydroxyl and carbonyl forms (Scheme 1). At pH 11.5, there is a high repulsion of carboxylate ions by the negative TiO₂ surface and the adsorption of HA at the catalyst surface is very weak (5%) . At pH close to pH_{pzc} (7.8) this effect is lower.

3.3. Effect of the anions in solution during the photodegradation of HA. The real wastewater contain variable concentrations of inorganic ions in particular chloride and sulfate. For this reason we have determined the effect of the Cl⁻, SO₄²⁻ concentration and

the mixture of both on the photocatalytic rate of humic acids degradation.

Effect of chloride ions: Figure 4 showed the effect of chloride on the photomineralization of HA at natural pH (7.8). The NaCl (4.1 g/l) addition showed no effect on the reaction. However, it is known that the addition of chloride ions induces an inhibitive effect on the photocatalytic reaction [21, 22], but this effect is dependent on the pH of the aqueous solution. The study by Wang, *et al.* [21] indicated that at low pH, the chloride ions are strongly adsorbed on the TiO₂ surface and reduce the photodegradation rate. In neutral or alkaline conditions, the addition of chloride ions did not influence the reaction. The authors report that the main explanation is the acid/base properties of TiO₂-P25 surface

Figure 4. Chloride effect on the photomineralization of HA in aqueous solution of TiO₂ = 1 g/l.

Scheme 2. Procedures for the evaluation of Cl^- effect.

(adsorption with TiOH_2^+ at low pH and repulsion of Cl^- by TiO^- at basic pH). In our study, the pH was in the range 7.5–8 ($\text{pH} > \text{pH}_{\text{zpc}}$), and the TiO_2 -P25 surface is weakly negative, due to predominant species TiO^- .

We have already shown that the humic acids had a much more significant affinity for the surface of TiO_2 than the chloride ions. For that we used two distinct procedures (Scheme 2):

The results of the Figure 4 show that HA made a screen between the catalyst and chloride. Because for test 1, they are added in the solution after the humic acid and in the second procedure (test 2), if we added the HA after the Cl^- , HA induces a desorption of the ions chlorides present on the TiO_2 . These experiments show well the chelating effect of the humic acids. On the other hand these results are not in accordance with those obtained by Bekbolet *et al.* [22]. This author observed that the presence of chloride ions caused relevant reduction in the reaction rate (about 25%). However in this case, the rate constants have been determined by the decrease of the colour at 400 cm^{-1} and not by TOC analysis. We can conclude that the effect of chloride ions is not the same for mineralization and for decolourization.

Effect of sulfate: Some real wastewaters contain a large concentration of sulfate ions. For example in

the leachate of municipal landfills in Poland, $[\text{SO}_4^{2-}]$ concentration is comprised between 0.5 and 10 g/l. To evaluate the influence of these anions, we used two concentrations: 1 g/l and 7.75 g/l. On the Figure 5, we can show that the concentration of 1 g/l unmodified the kinetic of mineralization. However for $[\text{SO}_4^{2-}] = 7.75\text{ g/l}$ the mineralization rate is reduced during the three first hours (after 180 min of irradiation only 30% of the

Figure 5. Sulfate effect on the photomineralization of HA in aqueous solution of $\text{TiO}_2 = 1\text{ g/l}$.

solution has been mineralized) when for $[\text{SO}_4^{2-}] = 1 \text{ g/l}$, there is 70% of mineralization.

We have already found in the previous study [11] that the photomineralization of Aldrich humic acids was achieved in two steps. Firstly, there is a fragmentation of the macromolecules in more little molecules with a slowly transformation of organic carbon in mineral carbon. In the second step, these little molecules will re-adsorb at the TiO_2 surface and mineralize fastly. On the Figure 5, we can see that this second step is not influenced by the presence of the sulfate ions. After 300 min of irradiation, the mineralization is the same that for the other tests. The presence of the sulfate ions modifies the first step and favours the second one. The reason may be the enhanced rate of oxidation due to the sulfate radicals formed by the reaction of the sulfate ions with OH radicals [23]. As a strong oxidizing agent, the sulfate radicals could accelerate the reaction. Zhu Hua, *et al.* reported that the photocatalytic oxidation rate of monocrotophos was increased by increasing the sulfate ions concentration [24].

Effect of mixture: To evaluate the influence of the sulfate and chloride mixture on the photomineralization rate of HA, the employed concentrations are as follows: $[\text{Cl}^-] = 2.5 \text{ g/l}$ and $[\text{SO}_4^{2-}] = 7.75 \text{ g/l}$. The presence of both anions induced relevant reduction in the reaction rate. The rate constant decreased during the irradiation (Figure 6). We have a drawing effect of sulfate and chloride on the reaction. This observation is important because the real wastewaters contain different anions in different concentrations.

Figure 6. Mixture effect of anions on the photomineralization of HA in aqueous solution of $\text{TiO}_2 = 1 \text{ g/l}$.

4. CONCLUSION

In the present study, the influence of some parameters on the photocatalytic mineralization of humic acids in presence of titanium dioxide has been brought to the fore. It is necessary to take into account the composition of real wastewaters for their photocatalytic treatment. The effect of solution matrix can be reported as follows:

- The pH has an important effect on the photomineralization of HA. It is necessary to work at acidic (or neutral) pH, because at alkaline pH there is much repulsion of HA by negative TiO_2 surface.
- In our conditions no effect of chloride on the degradation rate are observed.
- The influence of the sulfate depends on its concentration in the solution. For a great concentration, we note a decrease of the rate for the first step of the reaction.

The presence of anions induces a decrease of the rate for the first step of the reaction, but finally the TOC values are the same at the end of the experiments.

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