

Short communication

Photocatalytic decomposition of humic acids on TiO₂ Part I: Discussion of adsorption and mechanism

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Abstract

In this paper we present the results of the photocatalytic degradation of humic acids (HAs) in aqueous solution. Bench scale experiments were carried out using titanium oxide as photocatalyst. We studied the adsorption of HAs on TiO₂ surface and we describe the kinetics of their photocatalytic degradation. The adsorption study of HA at three pH solution (1.9/7.5/11) by FT-IR DRIFT technique indicated that at acidic pH, HA are adsorbed on TiO₂ mainly by carboxylate groups. We determined the isotherms of HA and it was shown that Langmuir model cannot be applied in this case. However, if the asymptotic values of the isotherms were assumed for these analytical methods the close values were obtained. The kinetics of degradation was followed with TOC and pH. There are no important pH evolutions. It was obtained 88% of TOC removal after 6 h of irradiation with optimum TiO₂ loading 1.0 g/l. We observed the presence of two domains of HA degradation kinetics. In the first step, slight TOC decreased possibly due to the photodepolymerization of adsorbed HA on TiO₂. In the second one, the photodegradation followed pseudo-first-order kinetics. Organic intermediates were determined by high performance liquid chromatography (HPLC) (PDA-detector) analysis as well as biological oxygen demand (BOD₅). It was shown that photocatalysis process improved the biodegradability of HA nevertheless mineralization process mainly occurred and there was no large amount of easy biodegradable species present in the reaction solution.

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Keywords: Photocatalysis; Titanium dioxide; Humic acids; TOC; BOD₅; Adsorption

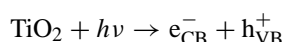
1. Introduction

The humic acids (HAs) have a significant role in the aquatic systems. They can complex heavy metals and organic pollutants such as pesticides, insecticides and herbicides [1]. But they are especially precursors of mutagenic products [1,2]. 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 [3]. The HA generally form the major fraction of the dissolved organic matter in surface water that represents 90% of dissolved organic carbon [4]. They are formed during the decomposition of plants and dead animals. The HA have structures which are not yet well identified. Usually they contain carboxylic, carbonyl, methoxyl, hydroxyl and phenolic function groups [4].

In many countries, the HA is eliminated from water before chlorination by coagulation with aluminium sulphate

and filtration. However, coagulation process brings two main disadvantages. Firstly, is the maintenance of residual sludge with high aluminium concentration. Secondly, treated water needs high quality monitoring of aluminium concentration. While the water contains more than 0.2 g/l it is not recommended for drinking [3]. Moreover, it needs to be mentioned that during this conventional treatment process only 10–50% of the TOC are eliminated [5].

The heterogeneous photocatalysis can be an effective alternative solution for the elimination of the HA from aqueous solution [6–9]. With this process it is possible to degrade the majority of the organic molecules, without adding of additional chemicals except the photocatalyst (e.g. titanium dioxide). The basic process of photocatalysis consists of ejecting an electron from the valence band (VB) to the conduction band (CB) of the TiO₂ semiconductor creating a h⁺ hole in the VB. This is due to the UV irradiation of TiO₂ with an energy equal or superior to the band gap (>3.2 eV):



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This is followed by the formation of extremely reactive radicals (like OH^\bullet) at the semiconductor surface and/or a direct oxidation of the polluting species. According to Corin et al. [4] direct photolysis of the HA leads to the formation of low-molecular-weight carboxylic acids (oxalic, succinic, formic, acetic, etc.).

During this work the photomineralization and photodecomposition of commercial HA in water solution have been studied. The mineralization kinetics was controlled by total organic carbon (TOC) and pH changes determination. Organic intermediates were studied with high performance liquid chromatography (HPLC) analysis, as well biodegradability (measuring biological oxygen demand, BOD_5) evolution was determinate. In order to investigate the HA degradation mechanisms, we have studied the adsorption of these compounds on TiO_2 in aqueous solution by diffuse reflectance infrared spectroscopy (DRIFT) of the solids and by determination of kinetic and adsorption isotherms. The DRIFT is perhaps one of the most valuable and informative methods among the different IR analysis techniques [10–13].

2. Experimental part

2.1. Products and analysis

HAs sodium salts was supplied by Sigma–Aldrich company and titanium dioxide P25 from Degussa (70% anatase, 99.8% purity, average particle size 30 nm and specific surface of $50\text{ m}^2/\text{g}$) was used as received. The chemicals purchased to assist in HPLC analysis were obtained from Fluka. Milli-Q water was used throughout for the preparation of aqueous solutions or as a component of the mixed water–acetonitrile–phosphoric acid mobile phase.

The degradation of HA as well as formation and disappearance of the oxidation products were analysed after filtration ($0.45\ \mu\text{m}$) by high performance liquid chromatography (HPLC Waters 600 pump and 996 photodiode array detector, SUPELCOGEL Carbohydrate column and acetonitrile (15%), water (84%) and phosphoric acid (1%) mixture as mobile phase). The TOC values at different irradiation times were determined with Shimadzu TOC Analyser, TOC-5050-A. The samples taken for analyses contained TiO_2 and were filtrated by $0.45\ \mu\text{m}$ Whatman cellulose nitrate membrane filters. The pH of the solution was not adjusted and at the beginning of experiments was in the range 7–7.5. Biodegradation studies were carried out in Aqualitic thermostated 20°C system with BOD sensors. All the BOD_5 samples were inoculated by 2 ml of effluent from biological reactor. Samples were taken at different degradation times without TiO_2 separation.

2.2. Adsorption experiments

The affinity of HA to TiO_2 was determined by the batch equilibrium experiments in the dark. Research was carried

out on suspension prepared by mixing 100 ml solution of various HA concentration at natural pH (7.3–7.6) and fixed amount of catalyst P-25 Degussa (1 g/l). To determine isotherms of adsorption each solution was mixed using magnetic stirrer. Preliminary investigation proved that HA was adsorbed quickly on the TiO_2 particles from aqueous solution. After 2 h of mixture the samples were taken and filtrated. It has been checked that about 15% of HAs remained on $0.45\ \mu\text{m}$ filters from raw (without TiO_2) solution. Therefore, the blank samples were prepared. The raw solution of known HAs concentration was filtered ($0.45\ \mu\text{m}$ filters). Obtained in this way blank samples were used for further calculation of HA adsorption. The concentrations were measured by UV–visible absorption spectroscopy analysis using Shimadzu spectrophotometer at 245 and 400 nm as well as TOC analyser.

2.3. DRIFT experiments

The solutions of HA (100 ppm) were preliminary filtered through Millipore filters ($45\ \mu\text{m}$ diameter). The pH of HA solution was adjusted, before TiO_2 addition, to pH ranged from 1.9 to 11 with appropriate quantity of 0.1 mol/l of NaOH or HCl solutions. The suspension of TiO_2 , after 2 h of mixing by magnetic stirrer in the dark, was separated from liquid by filtration on $0.45\ \mu\text{m}$ cellulose nitrate membrane Whatman filters. Next TiO_2 samples were dried in the open air for 24 h (at 25°C) and for 5 h under vacuum (at 40°C), still in the dark. Simultaneously, a blank sample (TiO_2 treated with distilled water) was prepared.

Samples were loaded stress into 10 mm diameter stainless cups and the top surfaces of powders were levelled. Spectra were recorded for infrared measurements from 4000 to 700 cm^{-1} and resolution of 4 cm^{-1} as single beam spectra. The measurements were carried out on a Digilab FTS-185 Fourier transform spectrometer by a liquid nitrogen cooled narrow-band mercury–cadmium–telluride (MCT) detector. The infrared spectra were recorded by DRIFT technique using Graseby–Specac accessory. A KBr single-beam spectrum was registered and used as a reference for reconstruction of absorbance like working spectra.

2.4. 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 ($300\text{ nm} < \lambda < 800\text{ nm}$). In order to determine the photocatalytic mineralization kinetic, the initial concentration of HAs amounted 100 mg/l. Homogeneous mixing was provided by sonication of the slurry for 5 min with titanium dioxide. The mixture was mixed by magnetic stirrer in the dark for 30 min 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 TiO_2 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 degradation of HA as well as formation and disappearance of the oxidation products were analysed after filtration by HPLC and the degradation kinetic by TOC.

3. Results and discussion

3.1. HA adsorption studied by DRIFT spectroscopy, UV-light absorption and by TOC analysis

Adsorption could play a prominent role in catalytic photodegradation of organic molecules [11,14,15] and, e.g. can explain selective oxidation in the case of mixtures treatment [16]. In this part, the measurements of HA adsorption were carried out by UV-light adsorption at two wavelengths (254 and 400 nm) and in parallel by TOC analysis. Some saturated TiO₂ were characterised by IR spectroscopy in mode DRIFT. In all cases, the adsorption kinetics were fast and equilibrium is reached within 30 min. The adsorption isotherms are given in Fig. 1. ([HA]_{ads} is the amount of HA in mg adsorbed per gram of TiO₂ and [HA]_{eq} the equilibrium concentration in mg per litre.) We observe that the [HA]_{max} values determined by the UV method at the different wavelengths are similar and lower than the values given by the TOC analysis. In our case, it is clear that the Langmuir model [17] cannot be used. Some reasons can be given to explain this observation: (1) the Langmuir model rules a physisorption and not a chemisorption, and we observe in all the studied pH range (1.9–11) the formation of surface carboxylate by DRIFT spectroscopy (strong bands at 1580 and 1390 cm⁻¹ attributed to asymmetric and symmetric stretching vibration [18]); (2) as received HA samples are heterogeneous and the reproducibility of the experiments is rather limited; (3) the configuration of adsorbate (HA) strongly depends on the concentration of HA in solution

and consequently strongly influences the adsorbed amount at equilibrium [19]. Nevertheless, if we consider only the asymptotic maximum values of the isotherms (maximum adsorption capacity) we find close results. These values are also coherent with those reported by Enriquez and Pichat [20] for the same solid and HAs.

3.2. Direct photolysis and photomineralization of HA

Fig. 2 displays the direct photolysis (without TiO₂) of HA. No obvious degradation of HA in this condition occurred within 6 h [21,22]. 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 TiO₂ to act as an efficient catalyst in the photodegradation of HA. 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 TiO₂ in suspension: the lower TiO₂ amount, the longer is the duration of this initial step (domain I, Fig. 3). The classical saturation phenomenon is noted for TiO₂ amount higher than 1 g/l [7] and will be also discussed later.

The fair evolution of TOC means that the mineralization of HA 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 favoured in case of adsorbed molecules [6–9]. All these observations suggest the surface degradation of adsorbed HA via the carboxylate or phenolate surface groups leads to the photodepolymerization. HA is progressively degraded by surface oxidative mechanism and so long as some macromolecules issued from HA

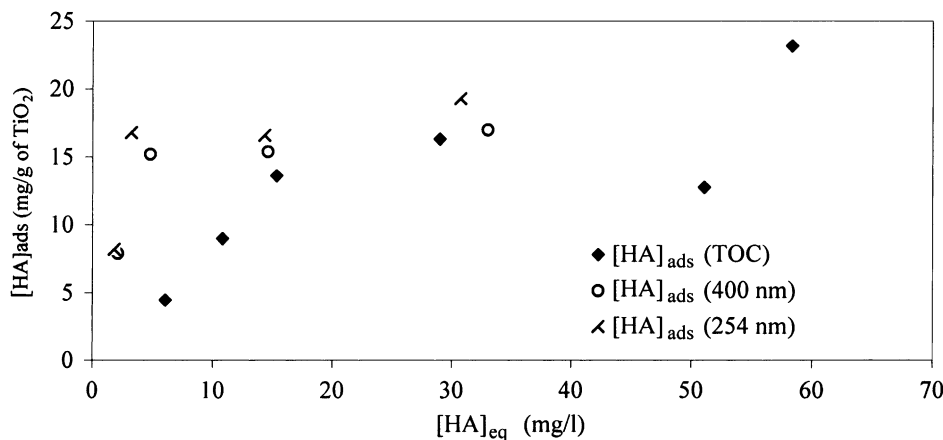


Fig. 1. Adsorption isotherm of HA on TiO₂; [HA]_{ads} is the concentration of HA adsorbed per gram of TiO₂ determined by TOC and UV-visible spectroscopy at 254 and 400 nm; [HA]_{eq} is HA mass concentration at the equilibrium.

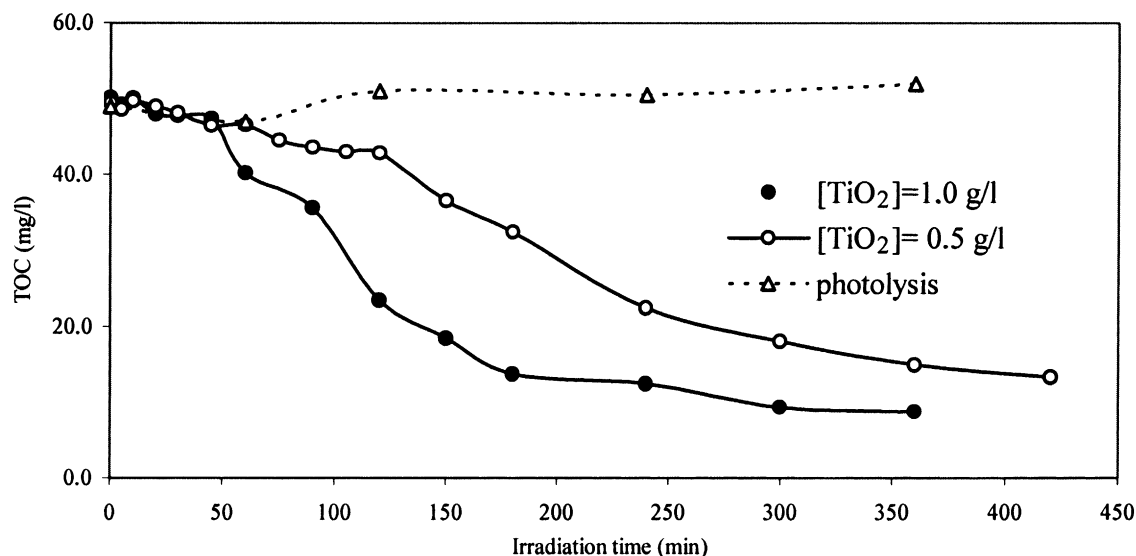


Fig. 2. Photolysis and photomineralization of HA with $[\text{TiO}_2] = 0.5$ and 1 g/l .

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.

3.3. HPLC analysis of the formation and disappearance of by-products

The photocatalytic degradation of HA as well as the formation and disappearance of the by-products were followed by HPLC [23]. The UV spectra were measured from 200 to 400 nm. It needs to be mentioned that none of separated products on the column showed a maximum of absorbance. In order to illustrate in the best way the evolution of forming products the wavelength of 206 nm was selected.

Fig. 4 depicts the chromatograms obtained for different photocatalytic degradation times with $\text{TiO}_2 = 0.5 \text{ g/l}$. Very similar chromatograms were received employing 1.0 and 2.0 g/l TiO_2 concentrations. It was found that HA solution (100 ppm) at $t = 0$ presents only one peak (P1) with retention time of 3.0 min. Along with irradiation time two

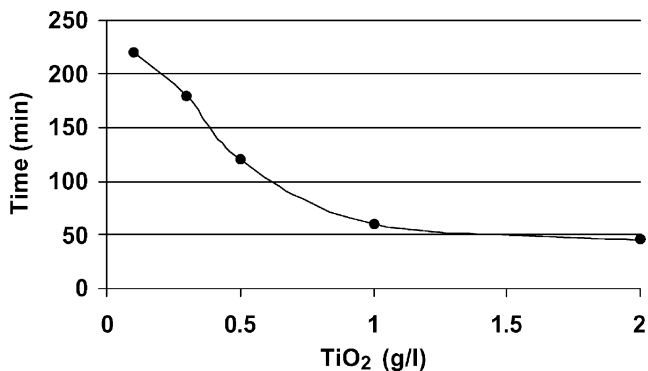


Fig. 3. Evolution of the initial step according to the TiO_2 amount.

supplementary peaks appeared. There were peaks (P2) and (P3) at retention times 3.7 and 5.3 min, respectively. Moreover, the increase of the intensity of the first peak after 120 min of process indicates that molar structures of HAs were rearranged. This time corresponds to the end of the domain I.

It could be explained by the formation of by-products. During the photocatalytic reaction the decrease of P2 and increase of P3 was observed simultaneously. Peak 3 seems to be associated with photoresistant products or nonadsorbed products. These products explain the level of the TOC after 6 h of irradiation. Fig. 5 shows area peak for the different reaction times.

The UV spectra of oxidation compounds were compared with some registered standard model spectra of low-molecular-weight organic carboxylic acids (4-hydroxybenzoic acid, oxalic, succinic, malonic acids) known as possible degradation products of HA [4]. Unfortunately, HPLC analysis did not allow identifying individual oxidation intermediates of HA. However gave an idea about the mechanic evolution of this complex compounds during photocatalytic process.

Resuming these results it should be indicated that the photodegradation of HA leads to smaller molecules. Two kinds of molecules are produced: easily photodegraded one (peak 2) and photoresistant one (peak 3). We can estimate the last molecules as about 10% in weight of the starting material considering the TOC level.

3.4. Influence of the TiO_2 concentration on the photomineralization kinetic of AH

The influence of the photocatalyst concentration on the mineralization kinetics of HA has been investigated employing different concentrations of P-25 Degussa varying from

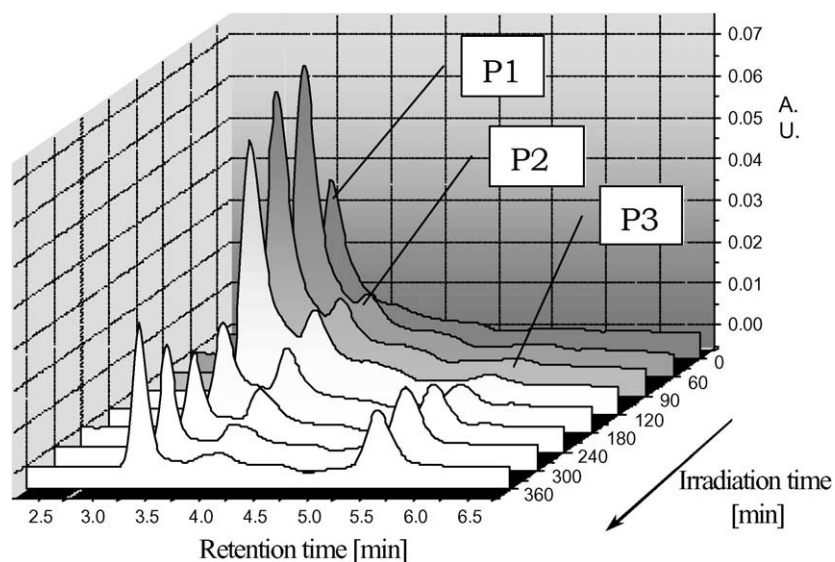


Fig. 4. Chromatograms of products of photocatalytic degradation HAs with $[\text{TiO}_2] = 0.5 \text{ g/l}$.

0.1 to 2 g/l (Fig. 6). 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 [22]. Most likely, the turbidity and colour of treated solution, along with the effect of TiO_2 blocking in solution, made the decomposition less effective.

3.5. The biodegradability changes during photocatalytic decomposition of HAs

BOD measurement allows to follow the biodegradability of organic HA intermediates products during irradiation time. Fig. 7 depicts that the raw HA are refractory com-

pounds (BOD_5 of 100 ppm HA solution is 1 mg/l). However, it was found that biodegradability (understand as amount of BOD_5 in the relation to TOC contents in the sample) of HA increased with irradiation time. The BOD_5/TOC ratio raised from 0.02 at $t = 0$ to 0.53 after 3.5 h of photocatalysis.

This indicates that photocatalysis process can break down or rearrange molecular structures of HA and convert the nonbiodegradable organics to more biodegradable forms. It is of great importance in the case of the application of a physicochemical–biological coupled system to wastewater treatment [24]. If the wastewater contains a big amount of recalcitrant compounds the preliminary photocatalytic treatment can transform these organic compounds into easily biodegradable by-products. Finally allows improving of biological step efficiency and achieving reduction of the cost of the treatment.

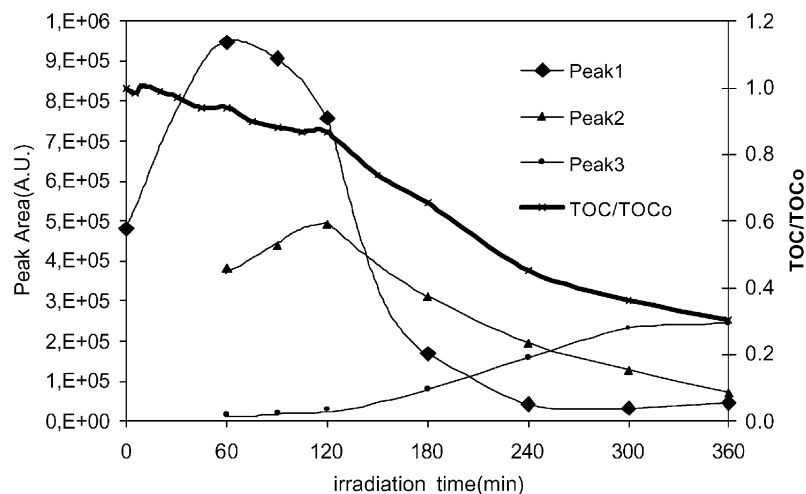


Fig. 5. Area peak (P1, P2 and P3) dependence on irradiation time of 100 ppm HA solution and TOC evolution of HA.

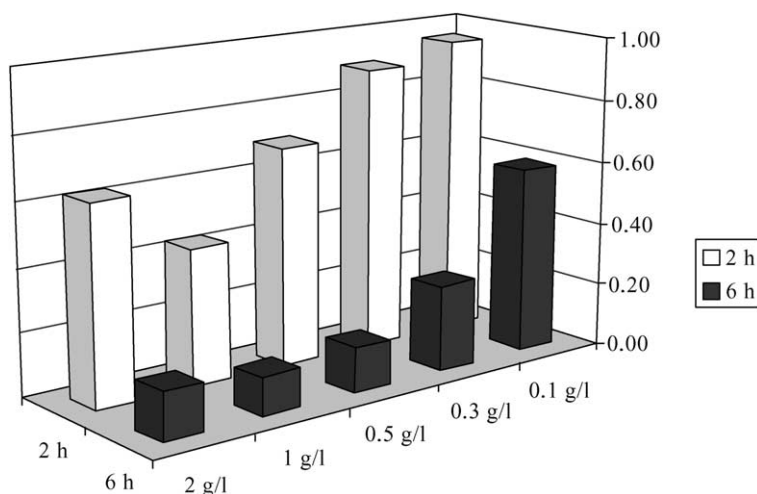


Fig. 6. Influence of the catalyst concentration on the photomineralization of HAs.

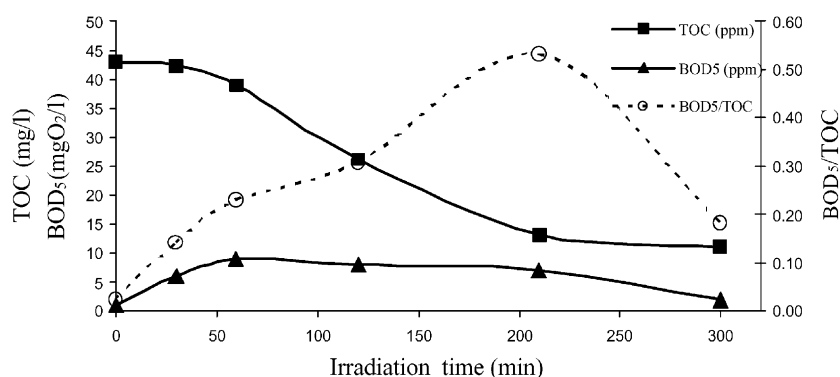


Fig. 7. BOD₅ measurements and TOC analysis during the irradiation of [HA] = 100 ppm with [TiO₂] = 1.0 g/l.

In our batch experiments only slight increase in the BOD₅ (maximum 9 mg/l) was observed. It can be suggested that during photocatalysis process the HA were mainly mineralised (converted to CO₂, especially during the second domain) without forming large amounts of biodegradable species and in other words macromolecules of HA, which were broken down to less aromatic, simpler compounds were transformed and removed immediately in form of CO₂. More supplementary investigation should be done to explain the behaviour of HA during photocatalytic treatment.

4. Conclusion

The results obtained in a bench scale experiments were encouraging and photocatalytic treatment of HAs solution appears as an efficient process.

We found that adsorption play a prominent role in photocatalytic degradation HA. Study of the HA adsorption on the TiO₂ surface by DRIFT spectroscopy indicates that at the acidic pH, HA were adsorbed on TiO₂ mainly as

carboxylate surface groups. DRIFT spectra show also presence of free carboxylic groups. It was shown that Langmuir model of adsorption cannot be applied in the case of HA.

The global evolution of the photocatalytic degradation has shown two distinct domains. For the first step, we observe a slow decrease of TOC probably due to photodepolymerization of adsorbed HA on TiO₂ surface. After photodegradation follows pseudo-first-order kinetic and this behaviour is connected with mineralization of HA to by-products. It was received 88% of TOC removal with optimum TiO₂ loading of 1.0 g/l after 6 h of irradiation.

It was found that biodegradability of refractory organic substances such as HA increase with irradiation time. It is of great importance in the case of the application of physicochemical–biological coupled system to wastewater treatment. Photocatalysis process can break long organic molecules into smaller biodegradable compounds and can make their biological treatment eligible. It may at the end reduce the cost of process. However, it was indicated that during photocatalysis of HA mineralization process was dominating without forming large amounts of easy biodegradable species in our conditions.

References

- [1] E. Lichtfouse, J. Leveque, *Analysis* 7 (1999) 383–442.
- [2] G.S. Wang, C.H. Liao, F.J. Wu, *Chemosphere* 42 (2001) 379–387.
- [3] B.R. Eggins, F. Palmer, A. Byrne, *Wat. Res.* 31 (1997) 1223–1226.
- [4] N. Corin, P. Backlund, M. Kulovaara, *Chemosphere* 33 (1996) 245–255.
- [5] G.S. Wang, S.T. Hsieh, C.S. Hong, *Wat. Res.* 34 (2000) 3882–3887.
- [6] M. Schiavello (Ed.), *Heterogeneous Photocatalysis*, Wiley, New York, 1997.
- [7] D. Bahnemann, in: P. Boule (Ed.), *Handbook of Environmental Photochemistry*, Springer, Berlin, 1999, p. 285.
- [8] D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat, N. Serpone, in: G.R. Helz, R.G. Zepp, D.G. Crosby (Eds.), *Aquatic and Surface Photochemistry*, Lewis, Boca Raton, FL, 1994, p. 261.
- [9] P. Pichat, in: G. Ert, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Photocatalysis*, VCH/Wiley, Weinheim/New York, 1997, p. 2111.
- [10] M.T. McKenzie, S.R. Culler, J.L. Koenig, *Appl. Spectr.* 6 (1984) 787–791.
- [11] D. Robert, S. Parra, C. Pulgarin, A. Krzton, J.V. Weber, *Appl. Surf. Sci.* 167 (2000) 51–58.
- [12] L. Palmisano, *New. J. Chem.* 12 (1988) 847–854.
- [13] K.D. Dobson, A.J. McQuillan, *Spectrochim. Acta A* 55 (1999) 1395–1402.
- [14] H.Y. Chen, O. Zahraa, M. Bouchy, *J. Photochem. Photobiol. A* 108 (1997) 37–45.
- [15] J.M. Herrmann, P. Pichat, *J. Chem. Soc., Faraday Trans. I* 76 (1980) 1138–1152.
- [16] A. Piscopo, D. Robert, J.V. Weber, *Entropie* 228 (2000) 27–30.
- [17] I. Langmuir, *J. Am. Chem. Soc.* 37 (1915) 1139.
- [18] C.H. Giles, A.P. DaSilva, I.A. Easton, *J. Colloid Interf. Sci.* 47 (1974) 766.
- [19] K.K. Au, A.C. Penisson, S. Yang, C.R. O'Melia, *Geochim. Cosmochim. Acta* 63 (1995) 2903–2917.
- [20] R. Enriquez, P. Pichat, *Langmuir* 17 (2001) 6132–6137.
- [21] M. Bekbolet, G. Ozkosemen, *Wat. Sci. Technol.* 33 (1996) 189–194.
- [22] M. Bekbolet, *J. Environ. Sci. Health A* 31 (1996) 845–858.
- [23] A.J. Motheo, L. Pinhedo, *Sci. Total Environ.* 256 (2000) 67–76.
- [24] C. Pulgarin, M. Invernizzi, S. Parra, V. Sarria, R. Polania, P. Peringer, *Catal. Today* 54 (1999) 341–352.