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PHOTOCATALYTIC DEGRADATION OF THE HUMIC SPECIES AS A METHOD OF THEIR REMOVAL FROM WATER – COMPARISON OF UV AND ARTIFICIAL SUNLIGHT IRRADIATION

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The possibility of application of the process of photocatalytic decomposition of humic substances (humic acid – HA) to their removal from water was investigated. Commercial TiO_2 (Evonic-Degussa P-25) and the periodic reactor were used in the experiments. The decomposition under artificial sunlight (ASL) and UV irradiation was tested. It was stated that ASL irradiation is not sufficient to cause significant decomposition of HA whereas TiO_2 appeared to be very effective under the UV irradiation. Strong adsorption of HA on the surface of TiO_2 was observed.

keywords: humic substances, photocatalysis, photodegradation, TiO_2*, water purification*

1. INTRODUCTION

Severe requirements regarding the quality of drinking water result in the necessity to elaborate the innovative methods of water treatment. So far applicable disinfection methods secured only neutralization of microorganisms but remaining problem are

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hardly – degradable organic compounds present in water which cannot be remove by simple filtration or coagulation processes.

Humic substances represent a major fraction of natural organic matter (NOM) in ground and surface waters that are known to be a complex class of biogenic polyanionic weak electrolytes with varying molecular sizes [1]. These substances have not as yet been properly chemically defined. Only average molecular weight can be determined [2] in the case of humic substances. They are formed during the degradation of plants and animal material, and both microbiological and abiotic processes contribute to their production [3]. Humic substances (HS) can be further separated into three classes, according to solubility, as humic acids, fulvic acids and humins [2]. Macromolecules of humic acid contain conjugated olefinic, aromatic, phenolic–semiquinone–quinone structures of a wide spectrum with different functional groups (–CO, –COOH, –OH, –NH–, $–NH_2$, –N) and chromophores [1]. They are capable of absorbing UV radiation. In many publications authors stated that the short – wave UV range of solar radiation (UV – B, $\lambda < 320$ nm) is the most important mineralizer of humic species [4]. What else, humic substances react with chlorine species (OCl^-/HOCl) and produce trihalomethanes (THMs), haloacetic acids (HAAs) and other halogenated disinfection byproducts (DBPs) in chlorinated water [5]. Trihalomethanes have been known to cause cancer and other toxic effects in human beings [6]. In addition, humic substances can form strong complexes with both inorganic and organic contaminants and mineral surfaces and they have been known as photoreactive contaminants. [7] From these reasons HAs are considered as highly reactive species in the environment and their removal from water during the water treatment is necessary.

Recently TiO_2 based photocatalysis of humic acids (HAs) has been extensively investigated [9–17]. It has been known that solar radiation alone has not enough energy for sufficient degradation of humic substances, but in combination with heterogeneous photocatalyst - titanium dioxide (TiO_2), with or without other chemicals, the degradation rate could increase [8].

The main photochemical phenomenon in the UV/TiO_2 process is the formation of an electron/hole pair through the absorption of light with the energy equal or greater than the band gap of TiO_2 ($E_{bg} = 3.2$ eV). Energized electrons and holes can either recombine, dissipating energy or be available for redox reactions with electron donor or electron acceptor species adsorbed on the semiconductor surface [18]. In aqueous environment at the presence of oxygen highly reactive oxygen species ($OH^\bullet$, $O_2^{\bullet -}$) are formed in the photocatalytic process. The oxidation/reduction processes involving those species may lead to complete degradation of organic compounds to CO_2 and to the formation of low-molecular-weight carboxylic acids (oxalic, succinic, formic, acetic, etc.) [3].

The aim of this study was to test the applicability of the photocatalytic process with the use of titanium dioxide to the removal of humic acids from water and to establish the optimum conditions for the application of this process. In this work the photocatalytic removal of humic acid (HA) under UV and artificial sunlight (ASL) irradiation was examined by monitoring changes in the UV absorbance at the wavelength of 254 nm (A_{254}). The absorbance value measured at 254 nm is widely accepted as a parameter which shows the degradation rate of humic acids and a parameter replacing total organic carbon (TOC) – usually used to measure photodegradation rate of HAs [18]. TiO_2 Degussa P – 25 is commercially available form of TiO_2 and has been used in many studies because of its chemical stability, availability and photocatalytic activity for oxidative destruction of organics [9,16,17].

2. EXPERIMENTAL

2.1. Materials

Deionized water for the preparation of the solutions was obtained from the Millipore Direct Q UV apparatus. TiO_2 powder Degussa P – 25 Aeroxide (SPECIFIC surface area - 50 m^2 g^{-1}) was kindly supplied by Evonic-Degussa and used as a photocatalyst for the degradation of humic acid without any modification. Humic acid sodium salt (technical grade) was supplied by Sigma – Aldrich. HA working solution of 40 mg dm^{-3} for photocatalytic degradation experiments was always freshly prepared by dilution of the stock solution (500 mg l^{-1}) with water. Stock solution was prepared in a following way. 500 mg of the HA sodium salt was dispersed in deionized water and sonificated 60 minutes in order to accelerate the dissolution of the HA. Then, the suspension was filtered through the 0.45 μm filter (Sartorius Membrane Filters) with the use of Sartorius filtration apparatus. Next, filtered solution was centrifugated at the rate of 15000 rpm for 60 minutes. Such prepared solution was stable for weeks.

2.2. Photodegradation experiments

The photooxidation experiments were performed in two quartz flat bottomed batch reactors of the volume 40 ml. In one of the reactors halogen lamp (150 W, Philips) was used as the artificial sunlight (ASL) source, in the other one, dedicated for ultraviolet (UV) region, the high pressure xenon arc lamp (250 W, Optel) was applied. Both lamps were used without any cut-off filters, except the layer of cooling water flowing below the bottom of the cell. The cell illumination was monitored by the radiometer Radiometer RD 0.2/2/100 (Optel). In those measurements sensor was placed at the top of the empty reactor. The distance between the source and the sensor was about 25 cm for ASL and 15 cm for UV light and the illumination area was 16.3 cm^2. The irradiation intensity was 68.8 mW cm^{-2} for ASL and 48.8 mW cm^{-2} for UV source. The photocatalyst suspension was stirred during the experiments in both reactors with a mechanical stirrer at a constant rate of 300 rpm. Mechanical stirrer, with the stirring rod positioned a few millimeters above the bottom of the cell was used instead of a magnetic stirrer to avoid "milling" of the TiO_2 grains during the experiment. The temperature was stabilized at 25±0.5°C (Fig. 1). Together with the sample used in a photocatalytic experiment an identical reference sample was always prepared and kept in the dark during the same period of time. After the experiment three portions of both suspension and reference samples were taken, subjected to 25 min of centrifugation at 15000 rpm to separate TiO_2 and then analyzed for the contaminant concentration. In that way the influence of adsorption on the TiO_2 surface on the uptake of the contaminant from the solution was eliminated.

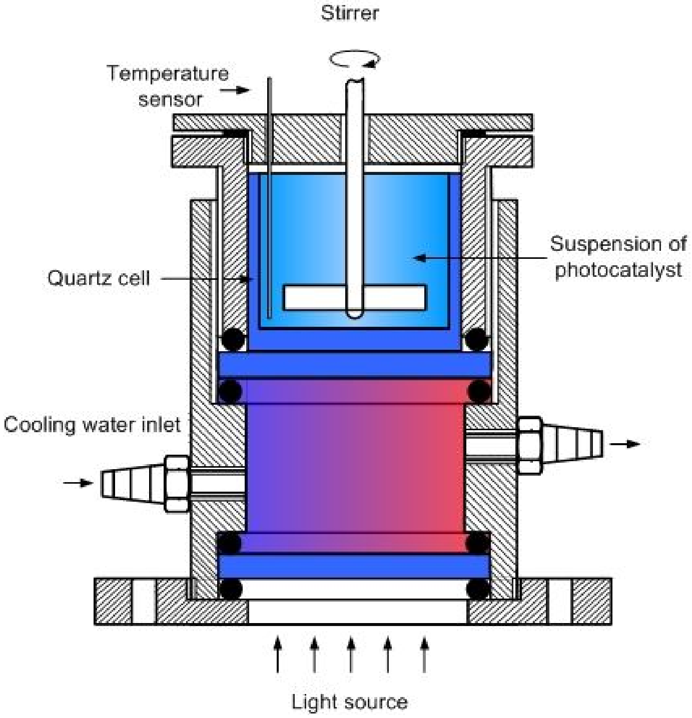

Fig. 1. The scheme of the quartz flat bottomed photoreactor

Samples were irradiated with halogen or xenon lamp for the time period from 10 min to 9 hours depending on the aim of the experiment. After irradiation the investigated solution was transferred to the Eppendorf vessel of the 2 ml volume and centrifugated at the rate of 15000 rpm for 25 minutes before spectrophotometric analysis. The absorption of the supernatant at the wavelength of 254 nm was measured using Specord

40 (Analytic Jena) single beam spectrophotometer.

The photooxidation experiment in this study included a few sets of tests for different objectives. The first set of experiments was carried in order to determine the degree of HA degradation under UV and ASL irradiation in the absence of photocatalyst. Initial HA concentration in that series of experiments was always 40 mg dm^{-3}, the duration of the experiment was extended to 9 h. The next step was the investigation of adsorption and desorption processes of humic acid on TiO_2 surface. Again the same initial HA concentration of 40 mg dm^{-3} was used. The third set of tests was performed with different experimental conditions including UV/ASL irradiation and TiO_2 catalyst in order to determine the best experimental conditions. The fourth set of tests was carried out with different TiO_2 loadings (100, 200, 500, 1000, 2000 mg dm^{-3}) to determine the effects of TiO_2 loading during the photodegradation reaction of HA. Finally the set of tests was carried out to determine the photodegradation rate of humic acid as a function of initial concentrations of HA (20, 40, 60 and 80 mg dm^{-3}).

3. RESULTS AND DISCUSSION

3.1. Decomposition of HA during UV/ASL irradiation in the absence of a photocatalyst

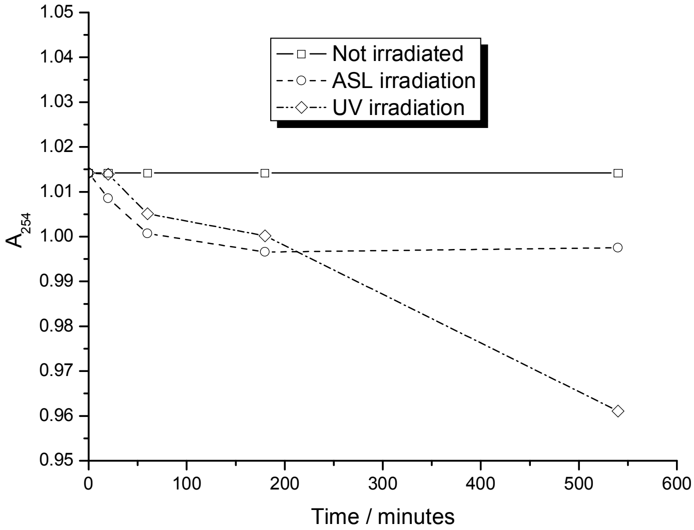

Fig. 2. Change of absorbance of the solution of humic acid (concentration 40 mg dm^{-3}) at the wavelength 254 nm under UV and ASL irradiation.

In the preliminary investigations humic acid degradation in the absence of photocatalyst was followed. Parallel blank experiment (without the irradiation of the samples) was performed too. The changes in the absorbance at 254 nm during the 9 h of reaction are showed in Fig. 2.

The changes in A_{254} even during the prolonged reaction periods were found to be negligible. Absorbance decreased only by 5.3 % after 9 h of irradiation by UV lamp, the decrease in absorbance caused by ASL was of the order of 2% only. It means that the irradiation by either ASL or ultraviolet light is not enough to attain significant degradation of humic acid without a photocatalyst. So the simultaneous action of irradiation and the photocatalyst – TiO_2 - was investigated in further work.

3.2. Adsorption of humic acid on TiO_2 surface

In order to investigate the effectiveness of the HAs removal in a photocatalytic process the influence of the adsorption of HAs on titania surface on the abstraction of HA from the solution should be determined. Tested catalyst – titanium dioxide Degussa P – 25 has high specific surface area (50 $m^2 g^{-1}$) and can adsorb quite a lot of HA. So, the experiment was performed to test adsorption of HA on TiO_2 in order to conclude which portion of HA, that disappeared from the solution, was degraded in a photocatalytic reaction and which part was simply adsorbed on the surface.

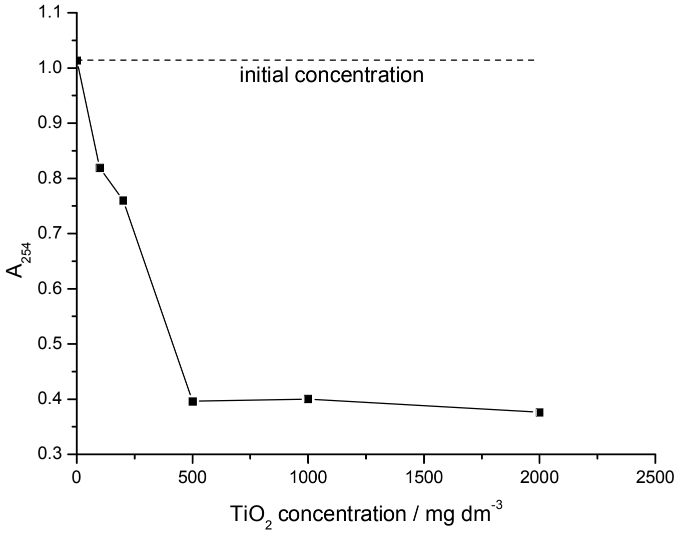

Fig. 3. Changes of absorbance of the HA solution (concentration 40 mg dm^{-3}) at the wavelength 254 nm in the dark due to the adsorption of humic acid on TiO_2 surface.

The suspensions of P – 25 TiO_2 (100, 200, 500, 1000, 2000 mg dm^{-3}) in solution of HA sodium salt (40 mg dm^{-3}) were prepared and kept in the dark for 1 hour, then the absorbance value of the samples was measured. The results are presented in Fig. 3.

The results presented in Fig. 3 indicate that TiO_2 adsorbs strongly HA – more than 60% of HA was adsorbed on TiO_2 surface for the suspension concentration higher than 500 mg dm^{-3}. For that reason rather low concentration of TiO_2 was used in the experiments (usually 100 mg dm^{-3}) and the results of the experiments were always compared with the results obtained for samples of the same composition, kept in dark during the same time. Another conclusion which may be drawn from the experiment presented in Fig. 3 is that HA is composed of at least two components, one adsorbing easily at the TiO_2 surface, the other one that does not adsorb at all or adsorbs to a very limited extent.

Photodegradation reaction of such complicated compounds, as undoubtedly humic substances are, is not possible to occur in one stage. Intermediate species formed during degradation may desorb from the surface with some delay. So, the experiment to verify the occurrence of desorption of HA decomposition byproducts was performed. A HA solution of the concentration 40 mg dm^{-3} with the addition of TiO_2 (100 mg dm^{-3}) was UV and ASL irradiated through the 60 min, then for the next 3 hours stirred at the absence of light. Absorbance of the solution was measured just after the irradiation period and after 1, 2 and 3 hours of stirring. Results of experiments are showed in Figs 4 and 5.

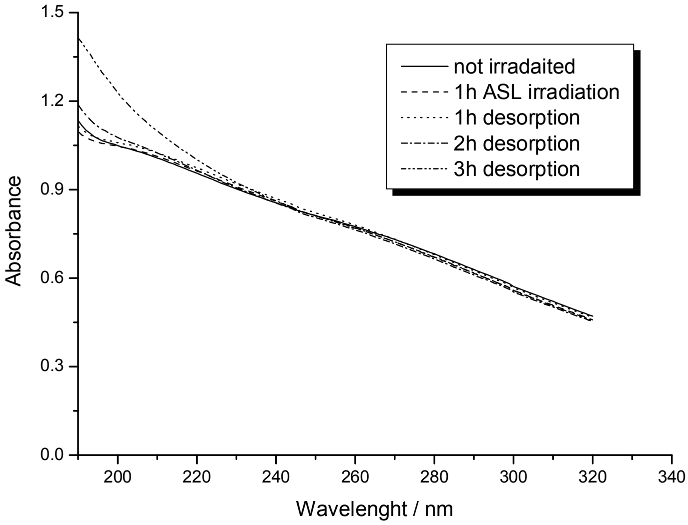

Fig. 4. UV spectra of humic acid solution (initial concentration 40 mg dm^{-3}) after 1 h of ASL irradiation and subsequent 3 hours in the dark.

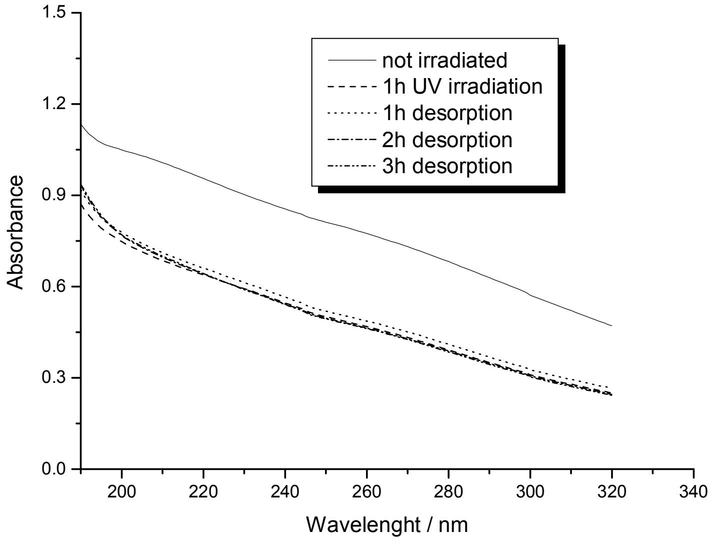

Fig. 5. UV spectra of humic acid solution (initial concentration 40 mg dm^{-3}) after 1 h of UV irradiation and subsequent 3 hours in the dark.

Fig. 4 and 5 showed that desorption of probable intermediate products of HA degradation from TiO_2 occurred to a very low degree. After ASL irradiation the spectra differed from each other to some extent in the wavelength range of 190 – 220 nm, however in the case of UV irradiation no desorption might have been observed. Note that in both cases (UV and ASL) no changes in the absorption at the wavelength 254 nm were observed.

3.3. Degradation of HA at the TiO_2 surface

The suspension consisting of 40 mg dm^{-3} of HA sodium salt and 100 mg dm^{-3} of TiO_2 was UV and ASL irradiated. The parallel blank test was conducted too. The samples were irradiated 10 min, 20 min, 40 min, 60 min, 120 min and 180 min. Fig 6 shows the results of photocatalytic experiment.

After 20 min of UV irradiation 15 % decrease of A_{254} was observed whereas 1 – hour UV irradiation of HA in TiO_2 suspension caused nearly 50 % drop of HA concentration. So 60 min irradiation time was selected as optimal to investigate the degradation rate of humic acid during the photocatalytic process. The results of ASL irradiation of the samples showed much lower decrease of absorbance - only about 18 % after 3 hour exposure to ASL. Note that almost linear dependence of absorbance on time was observed in the initial period of reaction. It may suggest that the rate of decomposition reaction was controlled by the rate of the generation of reactive radicals, not by the rate of humic acid reaction with these radicals.

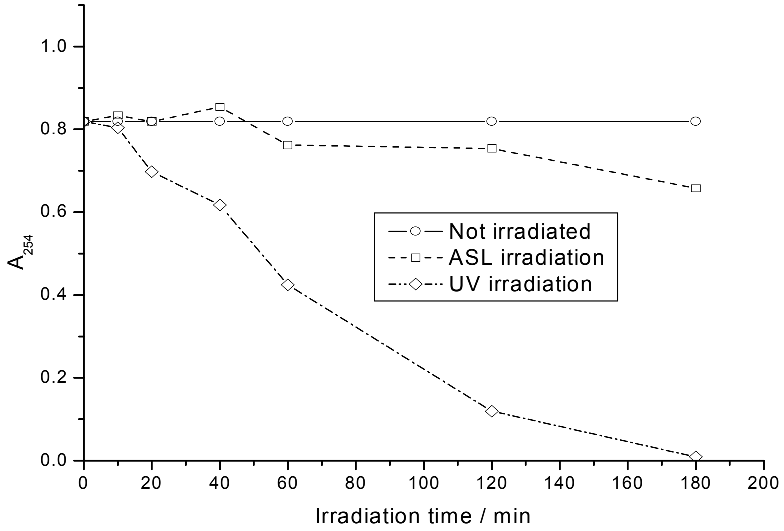

Fig. 6. Changes of absorbance at 254 nm of humic acid solution under UV and ASL irradiation at the presence of TiO_2. Concentration of photocatalyst: 100 mg dm^{-3}, concentration of HA: 40 mg dm^{-3}.

3.4. The effect of TiO_2 loading on the photodegradation of HA.

To begin with the study of optimal TiO_2 dosage it is necessary to remember that the decrease of HA concentration in solution might be caused not only by photodegradation reaction but also by the adsorption of HA on TiO_2 surface. Further, the presence of TiO_2 particles in suspension causes the dispersion of radiation. At the high TiO_2 concentration the penetration depth of radiation into the layer of suspension may be limited, leaving part of the solution not irradiated. The last effect undoubtedly depends on the cell geometry. Te decrease of the radiation intensity due to (mainly) dispersion of light on TiO_2 particles is presented in table 1. So, the growth of TiO_2 concentration in suspension caused not only the enhancement of degradation rate due to the increase of the available catalyst surface area but also the increase of the HA amount adsorbed at the TiO_2 surface as well as the decrease in degradation rate due to the increase in light dispersion.

The effect of TiO_2 dosage on the degradation of HA was investigated for the same initial HA concentration (40 mg dm^{-3}) and different TiO_2 concentrations (100, 200, 500, 1000 and 2000 mg dm^{-3}). The time of the experiment was 1 h. The results were compared with the absorbance values of the samples kept in the dark for 1 h and are depicted in Fig. 7.

Table 1. Impact of TiO_2 presence in the cell on radiation intensity.

Conditions of the experiment	Radiation	
	ASL	UV
Empty cell, measurement above the top of the cell	68.8 mW cm^{-2}	48.8 mW cm^{-2}
1000 mg dm^{-3} TiO_2, 40 ml of solution, measurement above the surface of reaction suspension	10 mW cm^{-2}	4 mW cm^{-2}

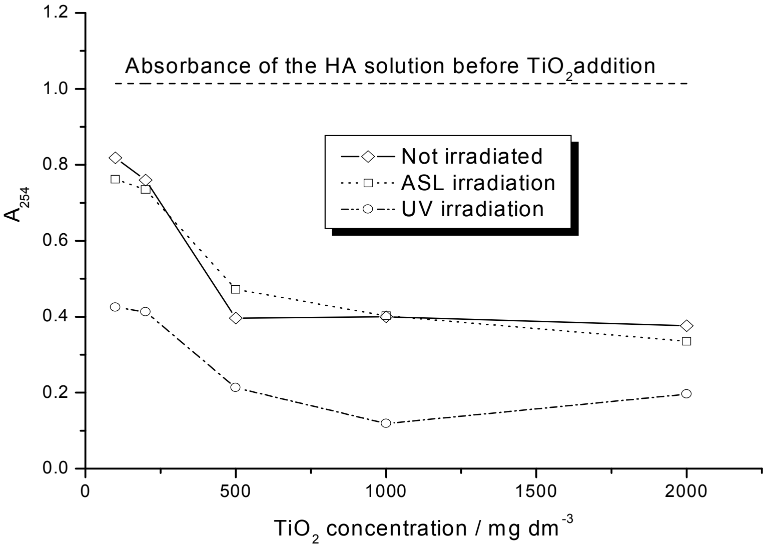

Fig. 7. Decrease of the absorbance of HA solution at 254 nm under the influence of UV and ASL irradiation, depending on TiO_2 concentration in investigated suspension. Irradiation time 60 min, initial HA concentration 40 mg dm^{-3}.

From the course of the curve recorded for UV irradiated samples it have to be concluded that 100 and 200 mg dm^{-3} TiO_2 additions gave similar results (about 45 % conversion of HA). Dramatic increase in absorbance was noticed when the dosage of TiO_2 was increased to 500 mg dm^{-3}. Significant differences were also recorded between 500 mg dm^{-3} and 1000 mg dm^{-3} TiO_2 dosages however no further decrease of absorbance value was observed when the TiO_2 dosage was increased from 1000 mg dm^{-3} to 2000 mg dm^{-3}, contrary some increase of absorbance was noticed. As the difference between 200 mg dm^{-3} and 500 mg dm^{-3} may be ascribed to the increased adsorption, the increase in absorbance observed for the loading 2000 mg dm^{-3} may probably be ascribed to very strong dispersion of radiation by the suspension of high concentration.

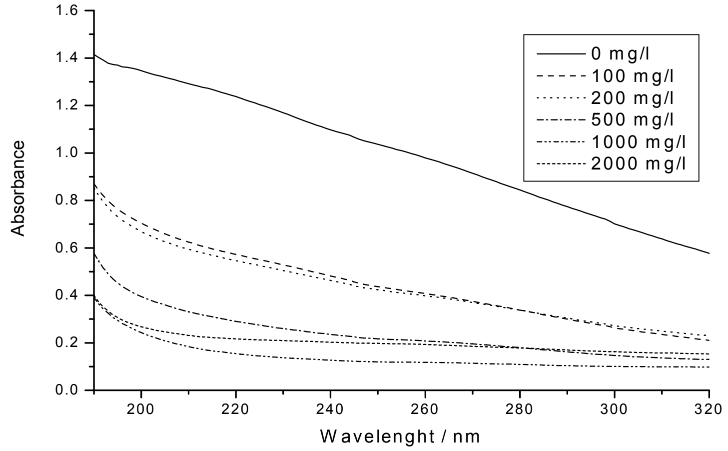

Fig. 8. UV spectra of the reaction mixture after 60 min of irradiation by UV light for different TiO_2 concentrations (marked in the figure). Initial concentration of HA 40 mg dm^{-3}.

The UV spectra of the reaction mixture after 1 hour of UV irradiation are presented in Fig. 8. The character of the spectrum changes, depending on the dosage of TiO_2, however it is impossible to draw clear conclusions because of the mutual influence of adsorption and degradation reaction on the spectrum.

3.5. The influence of the initial HA concentration on the photodegradation rate of HA

The series of solution consisted of 20, 40, 60 and 80 mg dm^{-3} of HA and 100 mg dm^{-3}_of TiO_2 was prepared. Samples were UV and ASL irradiated for 60 min. The results are depicted in Fig. 9 and 10. The experimental results, presented in Figs 9 and 10 again suggest that the reaction rate is limited by the rate of reactive oxygen radicals, not by the process of their reaction with HA. Note that the amount of HA removed from the solution was almost independent on initial concentration of HA, except the first point, for the initial concentration of 20 mg dm^{-3} where the absorbance after reaction dropped down to zero. So, it may be stated that the reaction of the decomposition of humic acid in our case did not followed the Langmuir – Hinshelwood

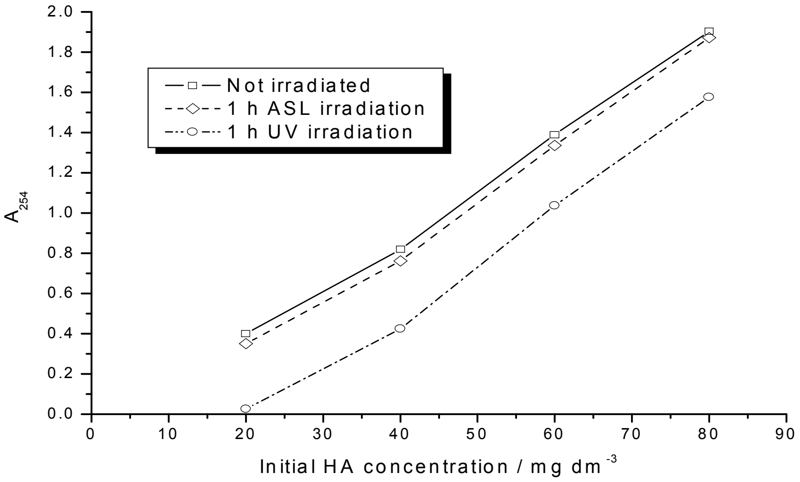

Fig. 9. Influence of initial concentration of HA on the absorbance at 254 of HA solution, depending on TiO_2 concentration in suspension. Irradiation time: 60 min.

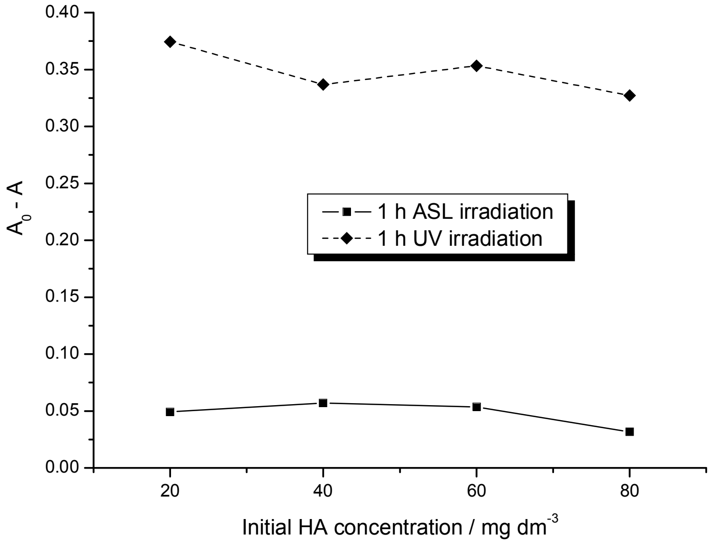

Fig. 10. Decreases of absorbance values of HA at 254 nm in TiO_2 suspension under the influence of ASL and UV irradiation, depending on initial HA concentration (A_0 – absorbance of not irradiated HA solution, A – absorbance of irradiated HA solution). Irradiation time 60 min.

(LH) kinetics which is usually observed in the case of many other contaminants. Looking for the most probable explanation of that fact the very strong adsorption of HA on the TiO_2 surface must be invoked in the first instance. In the derivation of the kinetic equation based on LH kinetics one assumes that the reaction rate is proportional to the surface coverage of the (photo)catalyst by the substrate of the reaction. However the results of the adsorption studies and the results of the other experiments strongly suggest that even at rather low concentration of HA in solution the surface is covered by the substrate in almost 100%. On the other hand it should be stated that humic acids are composed also by the substances that do not adsorb at the TiO_2 surface (see Fig. 3). The results of the experiment presented in Figs 9 and 10 suggest that those substances are also decomposed in the photocatalytic process.

4. CONCLUSIONS

Humic substances adsorb strongly at the surface of TiO_2. More than 50% of humic acid may be removed from the solution simply by adsorption on the surface if the concentration of TiO_2 in suspension is high enough. The presence of at least two types of humic species with diverse tendency to adsorption on TiO_2 surface was observed. Some part of HA does not adsorb at the TiO_2 surface in a measurable extent, however both the strongly adsorbing part of humic acid as well as that part which adsorb to only very limited extent may be removed from the solution by the photocatalytic process using UV radiation. The energy of the artificial sunlight appeared not to be high enough to cause the degradation of humic substances in a photocatalytic process at the TiO_2 surface – at all conditions applied the rate of degradation of HA by ASL was very low. 100% removal of HA substances may be achieved even at relatively low dosage of TiO_2 (100 mg dm^{-3}) if UV radiation and sufficiently long time of irradiation is applied. However time required for the complete removal of HA from water with the use of the photocatalyst only is relatively long. Three hours of irradiation was necessary at the 100 mg dm^{-3} TiO_2 concentration in the suspension to attain almost 100% removal of HA from solution at rather high UV irradiation intensity (48.8 mW cm^{-2}). Because rather high yield is required in the potable water treatment it is rather doubtful if the photocatalytic process alone may lead to the required efficiency.

The results of the experiments suggests that the process that HA decomposition does not follow the Langmuir – Hisnshelwood kinetics and is controlled rather by the rate of the generation of the reactive radicals in the photoexcitation process. If so, it means that either more active photocatalyst or additional destructive component (oxidant) is needed in the system, to speed up the process of HA decomposition. The works in both directions are being conducted now in our laboratory.

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