New photocatalyst for decomposition of humic acids in photocatalysis and photo-Fenton processes

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Humic acid Leonardite IHSS standard was decomposed on TiO_2 and TiO_2 modified by FeC_2O_4 via the photocatalysis and photo-Fenton processes under UV irradiation. Humic acid (HA) were favorable adsorbed on TiO_2 surface and followed decomposition during UV irradiation faster on TiO_2 than on the modified samples. However, when H_2O_2 was added to the solution, the photo-Fenton process occurred on the prepared TiO_2 samples, contained iron together with photocatalysis and high acceleration of HA decomposition was observed. In this case the mineralization degree was much higher than in the applied photocatalysis only, around 75% HA (with concentration of 18 mg/L) was mineralized after 3 h of adsorption and 5 h of UV irradiation in the presence of H_2O_2 and modified TiO_2 whereas on TiO_2 mineralisation of HA occurred in around 45% only. The measured fluorescence spectra of HA solutions showed that in the presence of H_2O_2 polycyclic aromatics were rapidly oxidized to the lower size products such as alcohols, aldehydes, ketones and carboxylic acids, what accelerated the process of HA decomposition.

Keywords: Humic acid (HA), photodecomposition, photo-Fenton, TiO_2, FeC_2O_4.

INTRODUCTION

Humic acid is a natural organic compound, a component of humic substances which is derived from the decomposition of plants and animals materials. HA in water can cause undesirable taste and colour, therefore has to be removed during the water treatment system[1]. However, HA is hard to remove in water by the conventional methods such as coagulation, percipitation and filtration, to achieve a complete removal of HA a large amount of coagulant is needed, which increases both, the amount of sediments and the cost of the process. HA is a high risk, because it can be a precursor of trihalomethanes (THMs) formation during chlorination of water. THMs are classified as carcinogenic compounds[2]. Therefore applying Advanced Oxidation Processes (AOP) seems to be reasonable. These processes are characterised by their ability to form strong oxidising species, the hydroxyl radicals. It was reported that hydroxyl radicals oxidise wide range of organic compounds significantly faster than ozone[2]. Fenton and photo-Fenton processes have been also used for the degradation of HA[2–4], although there are not many reports on it. In Fenton process hydroxyl radicals are produced during the decomposition of hydrogen peroxide in the presence of ferrous salts:

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\bullet} + HO^- + Fe^{3+}$$

This process has an optimum at pH around 3 and can be enhanced by irradiation with near-UV and visible light, then this process is called photo-Fenton:

$$Fe^{3+} + HO^- + h\nu \rightarrow Fe^{2+} + HO^{\bullet}$$
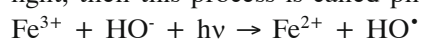
Katsumata et al.[4] reported that in the photo-Fenton process the acceleration of decomposition of organic compounds was due to the hydrolysis of iron aquacomplex $Fe(OH)^{2+}$. During this process the regeneration of Fe(II) is achieved, so the low concentration of Fe^{2+} is needed to run this process in comparison to the classical Fenton:

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + HO^{\bullet}$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet}$$
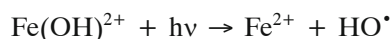
They reported that under optimal conditions of pH, H_2O_2 and ferrous ions, 10 mg/L of HA could be mineralised in 80% after 15 h of UV irradiation, whereas the initial absorbance UV_{254} and UV_{400} for this dose of HA disappeared after 8 h of UV irradiation. The large molecular weight components in HA were easily degraded to the smaller one, which appeared to be more resistant to oxidation[3–4].

Murray et al.[2] reported that under optimum conditions of pH, Fe: H_2O_2 ratio and Fe^{2+} dose significant removal of DOC (Dissolved Organic Compounds) and reduction of absorbance at UV_{254} could be achieved, even over 90% which reduced trihalomethanes formation potential of the water from 140 to below 10 $\mu g/L$.

Fukushima et al.[3] reported that the decomposition of large molecular weight fraction in HA via the photo-Fenton process could be caused by the degradation of cinnamic acid moieties which were in high level in this fraction and disappeared during UV irradiation, moreover the majority of iron species were complexed with the high molecular weight HA fraction, so the degradation of these active sites was responsible for the decreasing of molecular size of HA.

It was already reported that HA can be decomposed through the photocatalysis with using different photocatalysts, among these TiO_2 was widely tested[1,5–8]. Improving the photocatalytic activity of the photocatalyst towards HA decomposition by metal coating such as Pt on ZnO and TiO_2 or Ag on TiO_2 was also reported[6,9–10].

Applying TiO_2 photocatalysts coated silica was found to be effective for HA degradation[11]. TiO_2 coated hematite was reported to be effective in removing HA, with the reduction of TOC 61.58%) and color (93.25%) at 180-minutes illumination time for the starting solution of 20 mg/l[12]. TiO_2 nanotubes were also applied for the degradation of humic acids with a repeated activity and their good separation through the membrane techniques[13].

HA is easily adsorbed on the surface of TiO_2 under acidic conditions[1,8–9]. However, it was reported that in an acidic pH direct whole oxidation of HA adsorbed on TiO_2 was less effective compared to OH radicals attacks, which took place in neutral and alkaline pH. It was explained by the nature of HA, large size molecules adsorbed on TiO_2 were decomposed into smaller fragments and oxidation of these fragments and non-adsorbing HA fractions was a limiting step of this process. This hypothesis was confirmed when H_2O_2 was added to the solution and enhanced removal of HA was observed. In the process of UV/TiO_2 also the reduction of THMs formation potential was observed to the value below 20 μg/L and reduction of DOC above 80% and absorbance UV_{254} 90 % of 9.3 mg/L of initial concentration of HA after 2.5 h of UV illumination[1].

Ozonation and oxidation by OH radicals attack or directly by H_2O_2 have high significance in the process of HA destruction[1]. HA can be decomposed in the presence of H_2O_2 and UV irradiation[14]. However, carbonate and bicarbonate ions in water inhibit the degradation of HA, because of scavenging the OH radicals.

It was reported that the optimal addition of H_2O_2 to TiO_2 solution can enhance the yield of HA degradation, because H_2O_2 can serve as an electron scavenger, however in the access of H_2O_2 it works as an scavenger for OH radicals and forms less reactive HO_2 radicals[15].

Decomposition of HA in the presence of TiO_2 during irradiation with visible light ($\lambda > 420$ nm) was reported[9]. The adsorbed HA acted as a sensitizer for injecting electrons from their excited state to the conduction band of TiO_2, which were subsequently transformed and decolorized through a series of electron transfer reactions. However, the visible light irradiation was not efficient for the mineralisation of HA, this mineralisation proceeded under UV irradiation only.

In this paper the decomposition of HA on TiO_2 and TiO_2 modified by FeC_2O_4 is presented. The authors previously reported that the prepared TiO_2 samples modified with FeC_2O_4 were active in both, the photocatalysis and photo-Fenton processes in the presence of UV and H_2O_2 and they could successfully decompose phenol and dyes from the aqueous solutions[16, 17]. In this paper the enhanced effect of HA destruction by applying the photo-Fenton process together with photocatalysis is reported. UV-Vis absorbance is a commonly used method for controlling the HA concentration. In the present work besides UV-Vis absorbance the fluorescence spectroscopy was applied for controlling the destruction of HA particles, together with Total Organic Carbon (TOC) analysis.

EXPERIMENTAL

Materials

TiO_2 of anatase type has been obtained from the Chemical Factory Police S.A. in Poland. It contained a small amount of rutile nuclei, about 3.5 wt %, and exhibited a relatively high BET surface area, around 300 m^2/g. FeC_2O_4 of an analytical grade was purchased from Sigma-Aldrich Co. Leonardite humic acid was purchased from the IHSS (International Humic Substances Society).

According to the elemental analyses obtained from the list of IHSS products Leonardite HA standard (IS104H) contains in % (w/w): 63.81 C, 3.70 H, 31.27 O, 1.23 N, 0.76 S, < 0.01 P, and 2.58 ash.

Preparation of photocatalysts

The photocatalysts were prepared by mechanical mixing of TiO_2 and FeC_2O_4 powders in the mass ratio of 10:1 and heating at 500–800°C with a heating rate of 10°/min in a pipe furnace under Ar atmosphere. The samples were kept for 1 h at a final temperature of heat treatment.

Analytical methods

The phase composition of the original TiO_2 and the prepared samples were characterised by XRD powder diffraction. XRD measurements were performed in the X'Pert PRO diffractometer of Philips Company, with CuKα lamp (35 kW, 30 mA). The obtained XRD patterns were compared with JCPDS (Joint Committee on Powder Diffraction Standards) cards. The content of carbon in the prepared samples was determined by the combustion of carbon in air using TG analysis coupled with FTIR measurements. The samples were gradually heated up to 1000°C in air with simultaneous recording of FTIR spectra of the decomposed gas products. The carbon content in the samples was calculated from the mass loss on the TG curve accompanied by appearing of CO_2 bands in the spectrum.

The concentration of humic acid was controlled by the measurements of absorbance at UV_{254} and Total Organic Carbon (TOC) analyses. The fluorescence spectra of HA solutions were taken in order to observe the changes in their structure during the UV degradation process. Fluorescence synchronous scan spectra were acquired in Hitachi F-2500 spectrofluorymeter in the excitation wavelength range of 300–650 nm using the bandwidth of $\Delta\lambda = 18$ nm between the excitation and emission monochromators, the measurement method was described elsewhere[18].

Photocatalytic activity test

HA degradation was performed in a batch type reactor of 500 ml. The solution of HA was prepared by dissolving of Leonardite HA in an ultra pure distilled water with addition a little amount of 1 M NaOH to increase their solubility and followed filtration through the membrane filter of 0.45 μm. The concentration of HA of the prepared solution was estimated on the basis of TOC analyses and calculation regarding to the amount of carbon given by the IHSS. Preliminary adsorption of HA on the photocatalyst surface was performed. The Photodegradation of HA was conducted under UV irradiation. As a source of UV six lamps of Philips company with power of 20 W each were applied. These lamps emit the radiation at the visible region of about 108 W/m^2 and at UV range of 96 W/m^2 intensities, in the range of 312–553 nm with a maximum at around 350 nm. The reaction mixture contained 500 ml of HA with concentration ca. 18 mg/L and 0.1 g photocatalyst. The solutions were first magnetically stirred in the dark for 3 hours in order to estimate the adsorption on the photocatalyst surface and then were irradiated under UV irradiation within 5 hours. For the photo-Fenton

process, 4.4 mmol of H_2O_2 (30%) was added to the reaction mixture after HA adsorption. Every hour a small amount of titania slurry solution was sampled, filtrated through the membrane filter 0.45 μm and analysed for UV_{254}, TOC and fluorescence. The blank experiment with degradation of HA under UV irradiation without any photocatalyst was also performed, then the solution of HA was irradiated with UV for 5 hours.

RESULTS AND DISCUSSION

XRD measurements

XRD patterns of TiO_2 and prepared samples are presented in Fig. 1. The original TiO_2 consisted of the anatase phase and trace amount of rutile. After heating at 500°C the peaks attributed to the anatase phase became more narrow, it means that anatase crystals grew and were better crystalized, a small amount of rutile remained, and Fe_3O_4 with Fe_2O_3 (hematite), as new phases were formed. At higher temperatures of the heat-treatment, the 600–800°C, Fe_2O_3 phase was present and anatase was transformed to rutile.
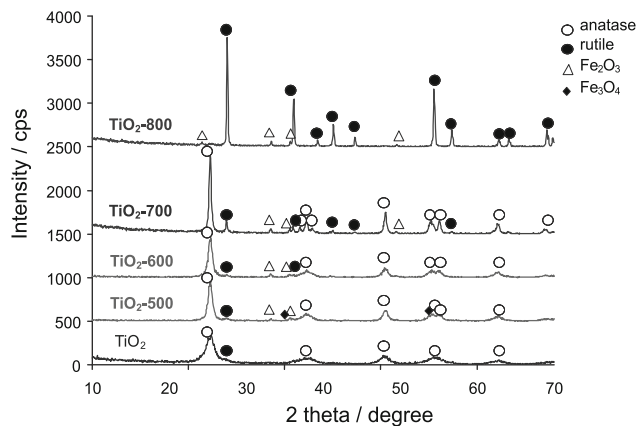

Figure 1. XRD patterns of TiO_2 and prepared photocatalysts

Content of carbon

The prepared samples contained the residue carbon, which came from the carbonization of oxalate. In Table 1 the content of carbon and the conditions of heat treatment are listed.

The highest content of carbon, 1.6 wt % was found in the sample prepared at 500°C, the other samples contained less than 1 wt % of carbon. The lower content of carbon in the samples prepared at higher temperatures could be effected by a carbon oxidation through TiO_2 and its evolving during gas flow. Oxidative conditions resulted also in iron oxidation and formation of iron oxides such as Fe_3O_4 and Fe_2O_3.

Adsorption and decomposition of Leonardite HA under UV irradiation

The results from the adsorption and decomposition of

Table 1. Characteristics of TiO_2 and prepared photocatalysts

Sample name	HTT (°C)	Content of carbon by TG (wt. %)
TiO_2	–	–
TiO_2-500	500	1.6
TiO_2-600	600	0.3
TiO_2-700	700	0.3
TiO_2-800	800	0.15

HA on TiO_2 and prepared Fe-C-TiO_2 samples monitored by absorbance at UV_{254} and TOC analyses are shown in Fig. 2.
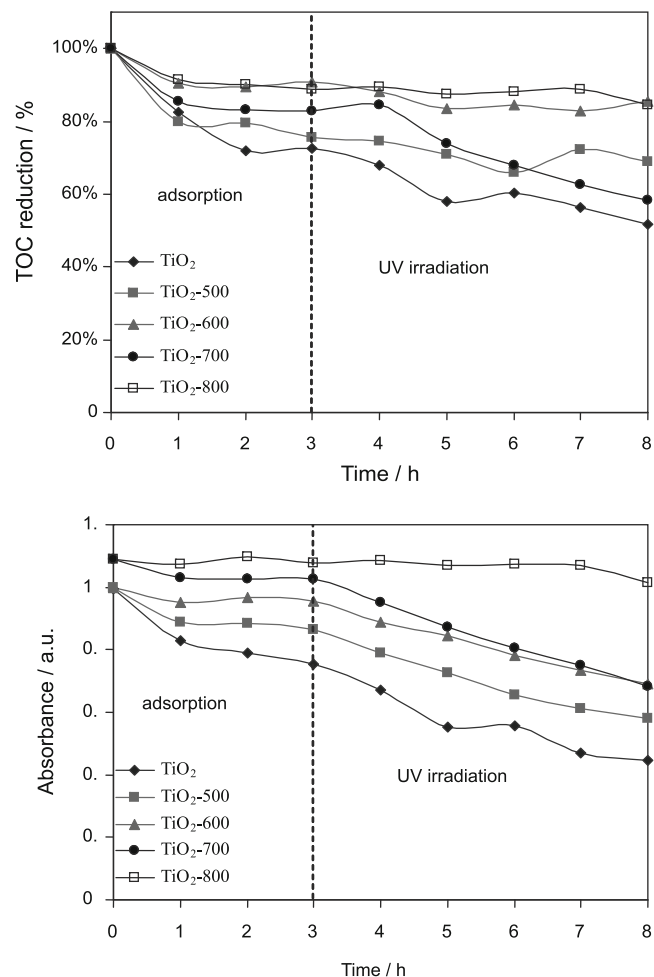

Figure 2. Changes in a) absorbance at UV_{254}, b) content of TOC, during adsorption and decomposition of Leonardite HA under UV irradiation on TiO_2 and prepared photocatalysts

It can be noticed that TiO_2 photocatalyst exhibited the highest capability for HA adsorption and also the highest decomposition rate. The prepared photocatalysts showed lower adsorption of HA than TiO_2, especially that heat treated at high temperature such as 800°C. Decomposition of HA on the prepared samples was also lower than on the original TiO_2. Mineralisation of HA reached around 50% in the case of TiO_2 after 5 h of UV irradiation, and was lower on the prepared samples, reaching 40% on TiO_2-700 and only 10% in the case of sample heat treated at 800°C. Low photocatalytic activity of TiO_2-800 sample could be caused by the presence of inactive rutile.

In Fig. 3 the fluorescence spectra of HA are shown after its adsorption on the photocatalysts surface and degradation under UV radiation.

The initial concentration of HA at time 0 h shows two peaks on the fluorescence spectra, with the maximum at around 380 and 460 nm. The latter is attributed to the presence of polycyclic ring hydrocarbons, and the former to the lower molecular weight compounds, which are the ingredients of the HA molecules[19]. It can be noticed that the peak attributed to the polycyclic ring hydrocarbons decreased significantly after adsorption process on TiO_2 and TiO_2-500 photocatalysts, whereas
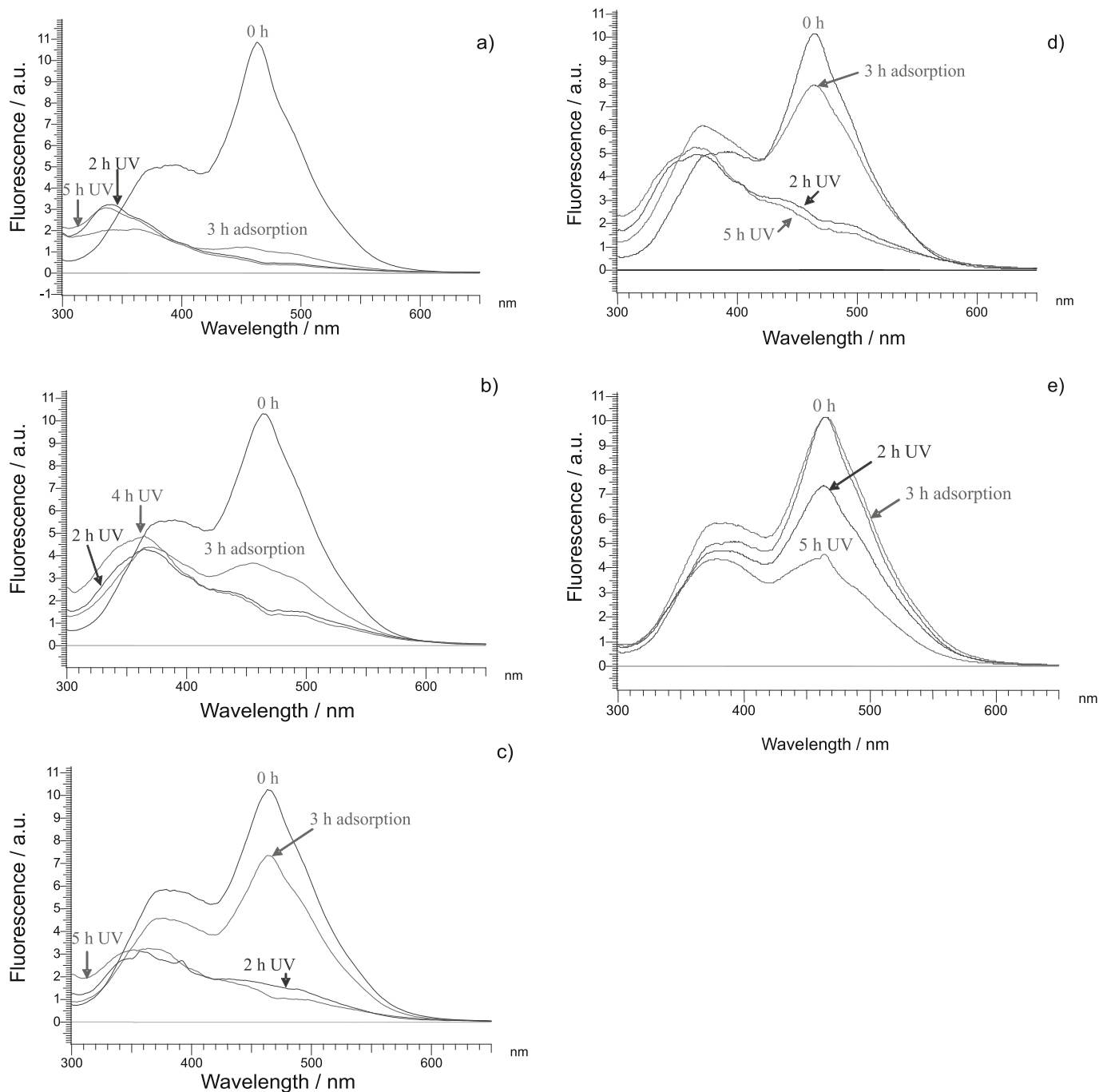
Figure 3. The fluorescence spectra of HA after its adsorption and decomposition under UV irradiation on TiO$_2$ and prepared photocatalysts: a) TiO$_2$, b) TiO$_2$-500, c) TiO$_2$-600, d) TiO$_2$-700, and e) TiO$_2$-800

on the samples prepared above 500°C it was slightly reduced. Within UV irradiation the fluorescence peak at 460 nm completely disappeared in the case of all the investigated samples, whereas the peak at 380 nm was shifted to the lower values. These results showed that in the photocatalytic degradation of HA under UV irradiation the ring polycyclic hydrocarbons are firstly decomposed giving low molecular weight byproducts, which are further decomposed with following the time of UV irradiation.

Adsorption and decomposition of Leonardite HA under UV irradiation and H$_2$O$_2$

The same experiment was performed as described above but with an addition of H$_2$O$_2$ to the reaction mixture after the adsorption of HA on the photocatalyst surface. The results from the measurements of UV$_{254}$ and TOC after adsorption of HA on the photocatalysts

surface and UV irradiation are presented in Fig. 4.

In the presence of H$_2$O$_2$ and UV irradiation higher reduction of absorbance at UV$_{254}$ was clearly observed in the case of all the investigated samples by comparison with the experiment without an addition of H$_2$O$_2$. In the case of the prepared samples at 500 and 600°C this absorbance was reduced almost to zero after 5 h of UV irradiation, and for these samples the highest mineralisation degree was achieved, around 75%. H$_2$O$_2$ and caused strong oxidation of aromatic rings, which resulted in fast reduction of absorbance at UV$_{254}$. However, in the case of TiO$_2$, although the reduction of absorbance at UV$_{254}$ was significant, the the mineralisation degree was much lower than in the experiment without an addition of H$_2$O$_2$. Probably some adsorbed compounds were easily desorbed after an addition of H$_2$O$_2$, causing an increase of the organic compounds in the solution and the increase of absorbance at UV$_{254}$, These desorbed compounds were
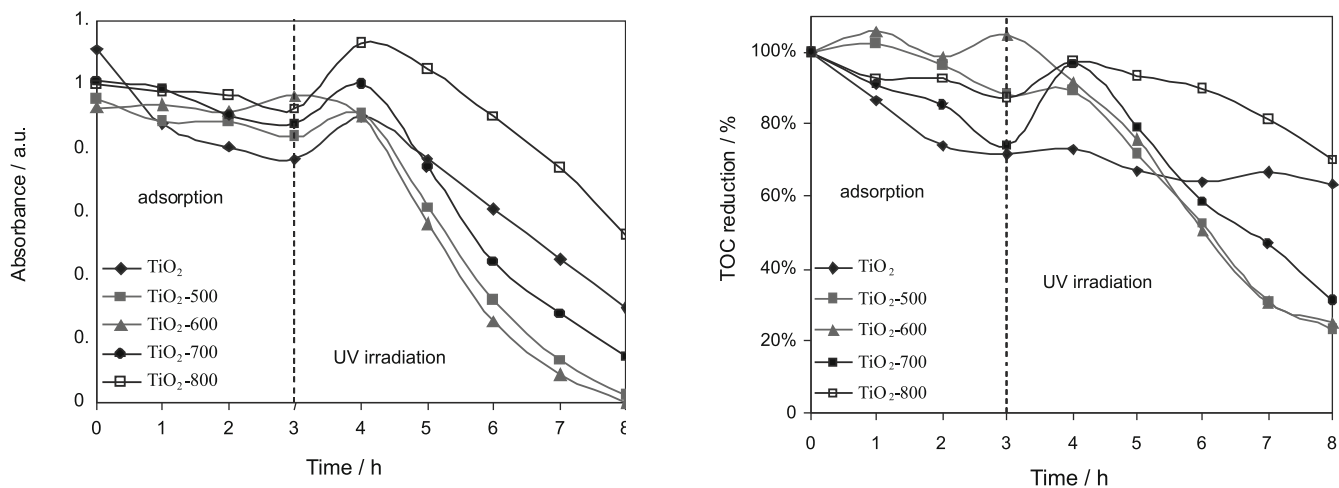
Figure 4. Changes in a) absorbance at UV_{254}, b) content of TOC, during adsorption and decomposition of Leonardite HA under UV irradiation with H_2O_2 on TiO_2 and prepared photocatalysts
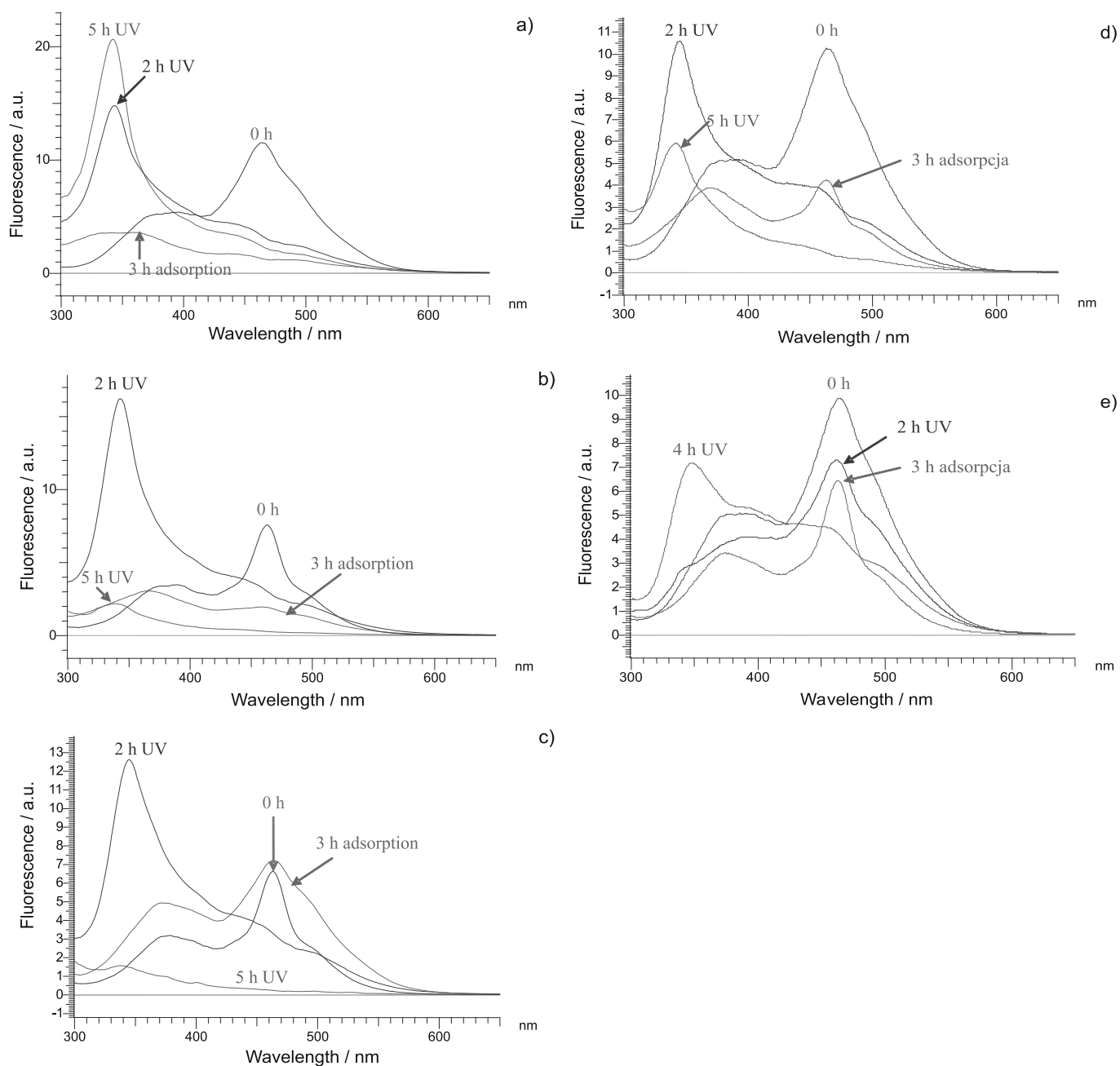

Figure 5. The fluorescence spectra of HA after its adsorption and decomposition under UV irradiation with H_2O_2 on TiO_2 and prepared photocatalysts: a) TiO_2, b) TiO_2-500, c) TiO_2-600, d) TiO_2-700, and e) TiO_2-800

following degradation together with other ingredients of HA in solution, increasing the potential of OH radicals needed for a complete mineralisation of HA. However, in the case of TiO_2 samples modified with FeC_2O_4, the reduction of absorbance at UV_{254} and mineralisation degree was much higher with addition of H_2O_2 than without, because of the occurrence of the photo-Fenton process, which supplies in OH radicals. This experiment confirmed that HA were favorably decomposed by the OH radicals attack (similar as it was reported by Liu et al.[1]), and the photo-Fenton process could support photocatalysis by increasing the yield of OH radicals formation. The blank experiment of HA decomposition without photocatalyst under UV irradiation with addition of H_2O_2 was also performed, although the data are not presented here. Both, the absorbance at UV_{254} and TOC did not change significantly with the time of UV irradiation, indicating poor oxidation of HA by H_2O_2. OH radicals were not generated in the presence of used UV irradiation, because its range was above 300 nm. The fluorescence spectra of HA solution measured after its adsorption on the photocatalyst surface and degradation under UV irradiation with H_2O_2 are shown in Fig. 5.

The fluorescence spectra were in a good agreement with the measurements of UV_{254} and TOC, showing that after an addition of H_2O_2 peak at 460 nm attributed to the polycyclic ring hydrocarbons disappeared, but a new peak with a maximum at around 340 nm appeared, suggesting that there appeared the low chain byproducts, such as alcohols, aldehydes, ketones and carboxylic acids[19], which were further degraded with the time of UV irradiation. In the case of the samples prepared at 500 and 600°C this peak was almost completely reduced after 5 h of UV irradiation, whereas for TiO_2 and sample prepared at 800°C was of high intensity, confirming the lower mineralisation degree of HA in the case of the later samples.

CONCLUSIONS

Modification of TiO_2 by FeC_2O_4 through the mechanical mixing and heating in Ar at 500–800°C caused formation of Fe_3O_4 and Fe_2O_3 phases on its surface, however the former was present only in the sample prepared at 500°C. The iron phases were active in the photo-Fenton process under UV irradiation with H_2O_2 enhancing the decomposition rate of Leonardite HA. Higher temperature of modification such as 800°C caused a complete transformation of anatase to rutile, which decreased the activity of the prepared photocatalyst. Lower temperatures of the modification such as 500 and 600°C were favorable for obtaining the photocatalyst active for HA degradation in both photocatalysis and photo-Fenton. Photodegradation of Leonardite HA on the sample prepared at 500°C proceeded partly through its adsorption on the photocatalyst surface, but in case of sample prepared at 600°C through the OH radicals attack mainly, however similar degradation rate and mineralisation degree were observed, which proves the significance of OH radicals formation in HA oxidation. High adsorption of HA on the surface of TiO_2-500 sample could be caused by the formation of HA complexes with iron (magnetite). Leonardite HA was favorably adsorbed on the surface of unmodified TiO_2, accelerating the process of HA degradation, however in the presence of H_2O_2 the rate of HA degradation was mostly determined by the formation of OH radicals, so in that case the photo-Fenton process was more efficient. The presented results showed that the photo-Fenton process could support photocatalysis enhancing the rate of HA degradation and modification of TiO_2 by FeC_2O_4 at 500–600°C could give photocatalysts active in both, photocatalysis, and photo-Fenton processes.

LITERATURE CITED

1. Liu, S., Lim, M., Fabris, R., Chow, C., Chiang, K., Drikas, M. & Amal, R. (2008). Removal of humic acid using TiO_2 photocatalytic process – Fractionation and molecular weight characterisation studies. *Chemosphere*. 72, 263–271. DOI: 10.1016/ j. chemosphere. 2008. 01. 061.

2. Murray, C.A. & Parsons, S. (2004). Removal of NOM from drinking water: Fenton's and photo-Fenton's processes. *Chemosphere*. 54, 1017–1023. DOI: 10.1016/j.chemosphere.2003.08.040.

3. Fukushima, M. & Tatsumi K. (2001). Degradation characteristics of humic acid during photo-Fenton processes. *Environ. Sci. Technol*. 35, 3683–3690.

4. Katsumata, H., Sada, M., Kaneco, S., Suzuki, T., Ohta, K. & Yobiko, Y. (2008). Humic acid degradation in aqueous solution by the photo-Fenton process. *Chem. Eng. Journal*. 137, 225–230. DOI: 10.1016/j.cej.2007.04.019.

5. Al-Rasheed. R. & Cardin, D.J. (2003). Photocatalytic degradation of humic acid in saline waters. Part 1. Artificial seawater: influence of TiO_2, temperature, pH, and air flow. Chemosphere. 51, 925–933. DOI: 10.1016/S0045-6535(03)00097-3.

6. Al-Rasheed, R. & Cardin, D.J. (2003). Photocatalytic degradation of saline waters. Part 2. Effects of various photocatalytic materials. *Appl. Catal. A: Gen*. 246, 39–48. DOI: 10.1016/S0926-860X(02)00667-1.

7. Selcuk, H., Sene, J.J, Sarikaya, H.Z., Bekbolet, M. & Anderson, M.A. (2004). An innovative photocatalytic technology in the treatment of river water containing humic substances. *Water Sci. & Techn*. 49, 153–158.

8. Wiszniowski, J., Didier, R., Surmacz-Gorska, J. & Miksch, K. (2002). Photocatalytic decomposition of humic acids on TiO_2: Part I: Discussion of adsorption and mechanism. *J. Photochem. Photobiol. A: Chem*. 152, 267–273.

9. Cho, Y. & Choi, W. (2002). Visible-light induced reactions of humic acids on TiO_2. *J. Photocham. Photobiol. A: Chem*. 148, 129–135.

10. Bansal, A., Madhavi, S., Yang Tan, T.T. & Lim, T.M. (2008). Effect of silver on the photocatalytic degradation of humic acid. *Catal. Today*. 131, 250–254. DOI: 10.1016/j. cattod.2007.10.078.

11. Moriguchi, T., Tahara, M. & Yaguchi, K. (2006). Adsorbability and photocatalytic degradability of humic substances in water on Ti-modified silica. *J. Coll. Interf. Sci*. 297, 678–686. DOI: 10.1016/j.jcis.2005.11.002.

12. Qiao, S., Sun, D.bD., Tay, J.bH. & Easton, C. (2003). Photocatalytic oxidation technology for humic acid removal using a nano-structured TiO_2/Fe_2O_3 catalyst. *Wat. Sci. & Techn*. 47, 211–217.

13. Zhang, X., Pan, J.H., Fu, W., Du, A.J. & Sun, D.D. (2009). TiO_2 nanotube photocatalytic oxidation for water treatment. *Water Science & Technology*. 9, 45–49. DOI: 10.2166/ws.2009.075.

14. Wang, G.-S., Hsieh, S.-T. & Hong, C.-S. (2000). Destruction of humic acid in water by UV light-catalyzed oxidation with hydrogen peroxide. *Water Res*. 34, 3882–3887. DOI:

15. Bekbolet, M. & Balcioglu, I. (1996). Photocatalytic degradation kinetics of humic acid in aqueous TiO_2 dispersions: The influence of hydrogen peroxide and bicarbonate ion. *Wat. Sci. Techn*. 34, 73–80.

16. Tryba, B. Morawski, A.W., Inagaki, M. & Toyoda, M. (2006). The kinetics of phenol decomposition under UV irradiation with and without H_2O_2 on TiO_2, $Fe-TiO_2$ and $Fe-C-TiO_2$ photocatalysts. *Appl. Catal. B: Environ*. 63, 215–221. DOI: 10.1016/ j.apcatb. 2005 .09. 011.

17. Tryba, B. (2007). Effect of TiO_2 precursor on the photoactivity of $Fe-C-TiO_2$ photocatalysts for Acid Red (AR) decomposition. *J. Adv. Oxid. Techn*. 10, 267–272.

18. Uyguner, C.S., Bekbolet, M. (2005). Evaluation of humic acid photocatalytic degradation by UV-Vis and fluorescence spectroscopy. *Catal. Today*, 101, 267–274. DOI: 10.1016/j. cattod.2005.03.011.

19. Fasurova, N., Cechlovska, H. & Kucerik, J. (2006). A comparative study of South Moravian lignite and standard IHSS humic acids, optical and colloidal properties. *Petroleum & Coal*. 48, 24–32.