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 TiO₂ and TiO₂ modified by FeC₂O₄ via the photocatalysis and photo-Fenton processes under UV irradiation. Humic acid (HA) were favorable adsorbed on TiO₂ surface and followed decomposition during UV irradiation faster on TiO₂ than on the modified samples. However, when H₂O₂ was added to the solution, the photo-Fenton process occurred on the prepared TiO₂ 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 H₂O₂ and modified TiO₂ whereas on TiO₂ mineralisation of HA occurred in around 45% only. The measured fluorescence spectra of HA solutions showed that in the presence of H₂O₂ polyyclic 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, TiO₂, FeC₂O₄

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. However, HA is hard to remove in water by the conventional methods such as coagulation, precipitation 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. 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. Fenton and photo-Fenton processes have been also used for the degradation of HA, 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:

\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{HO}^- + \text{HO}^+ + \text{Fe}^{3+} \]

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:

\[ \text{Fe}^{3+} + \text{HO}^- + \text{hv} \rightarrow \text{Fe}^{2+} + \text{HO}^- \]

Katsumata et al. reported that in the photo-Fenton process the acceleration of decomposition of organic compounds was due to the hydrolysis of iron aqua-complex Fe(OH)²⁺. During this process the regeneration of Fe(II) is achieved, so the low concentration of Fe²⁺ is needed to run this process in comparison to the classical Fenton:

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(OH)}^{2+} + \text{HO}^- \]

They reported that under optimal conditions of pH, H₂O₂ and ferrous ions, 10 mg/L of HA could be mineralised in 80% after 15 h of UV irradiation, whereas the initial absorbance UV₂₅₄ and UV₄₀₀ 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.

Murray et al. reported that under optimum conditions of pH, Fe: H₂O₂ ratio and Fe²⁺ dose significant removal of DOC (Dissolved Organic Compounds) and reduction of absorbance at UV₂₅₄ could be achieved, even over 90% which reduced trihalomethanes formation potential of the water from 140 to below 10 μg/L.

Fukushima et al. 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 TiO₂ was widely tested. Improving the photocatalytic activity of the photocatalyst towards HA decomposition by metal coating such as Pt on ZnO and TiO₂ or Ag on TiO₂ was also reported.

Applying TiO₂ photocatalysts coated silica was found to be effective for HA degradation. TiO₂ 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. TiO₂ nanotubes were also applied for the degradation of humic acids with a repeated activity and their good separation through the membrane techniques.
HA is easily adsorbed on the surface of TiO₂ under acidic conditions. However, it was reported that in an acidic pH direct whole oxidation of HA adsorbed on TiO₂ 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 TiO₂ 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 H₂O₂ was added to the solution and enhanced removal of HA was observed. In the process of UV/TiO₂ also the reduction of THMs formation potential was observed to the value below 20 μg/L and reduction of DOC above 80% and absorbance UV₉₅₄ 90% of 9.3 mg/L of initial concentration of HA after 2.5 h of UV illumination.

Ozonation and oxidation by OH radicals attack or directly by H₂O₂ have high significance in the process of HA destruction. HA can be decomposed in the presence of H₂O₂ and UV irradiation. 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 H₂O₂ to TiO₂ solution can enhance the yield of HA degradation, because H₂O₂ can serve as an electron scavenger, however in the access of H₂O₂ it works as an scavenger for OH radicals and forms less reactive HO₂ radicals. Decomposition of HA in the presence of TiO₂ during irradiation with visible light (λ>420 nm) was reported. The adsorbed HA acted as a sensitizer for injecting electrons from their excited state to the conduction band of TiO₂, 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 TiO₂ and TiO₂ modified by FeC₂O₄ is presented. The authors previously reported that the prepared TiO₂ samples modified with FeC₂O₄ were active in both, the photocatalysis and photo-Fenton processes in the presence of UV and H₂O₂ and they could successfully decompose phenol and dyes from the aqueous solution. 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 concentration of HA particles, together with Total Organic Carbon (TOC) analysis.

EXPERIMENTAL

Materials

TiO₂ 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 m²/g. FeC₂O₄ 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 TiO₂ and FeC₂O₄ 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 TiO₂ 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 CO₂ bands in the spectrum.

The concentration of humic acid was controlled by the measurements of absorbance at UV₉₅₄ 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 spectrofluorimeter in the excitation wavelength range of 300–650 nm using the bandwidth of Δλ = 18 nm between the excitation and emission monochromators, the measurement method was described elsewhere.

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 FTIR spectra 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.
process, 4.4 mmol of \( \text{H}_2\text{O}_2 \) (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 crystallized, a small amount of rutile remained, and Fe\(_3\)O\(_4\) with Fe\(_2\)O\(_3\) (hematite), as new phases were formed. At higher temperatures of the heat-treatment, the 600–800°C, Fe\(_2\)O\(_3\) phase was present and anatase was transformed to rutile.

![Figure 1. XRD patterns of TiO\(_2\) and prepared photocatalysts](image)

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\(_3\)O\(_4\) and Fe\(_2\)O\(_3\).

Adsorption and decomposition of Leonardite HA under UV irradiation
The results from the adsorption and decomposition of

<table>
<thead>
<tr>
<th>Sample name</th>
<th>HLT (°C)</th>
<th>Content of carbon by TG (wt. %)</th>
</tr>
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<tbody>
<tr>
<td>TiO(_2)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiO(_2)-500</td>
<td>500</td>
<td>1.6</td>
</tr>
<tr>
<td>TiO(_2)-600</td>
<td>600</td>
<td>0.3</td>
</tr>
<tr>
<td>TiO(_2)-700</td>
<td>700</td>
<td>0.3</td>
</tr>
<tr>
<td>TiO(_2)-800</td>
<td>800</td>
<td>0.15</td>
</tr>
</tbody>
</table>

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](image)

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 H₂O₂ on TiO₂ and prepared photocatalysts.

Figure 5. The fluorescence spectra of HA after its adsorption and decomposition under UV irradiation with H₂O₂ on TiO₂ and prepared photocatalysts: a) TiO₂, b) TiO₂-500, c) TiO₂-600, d) TiO₂-700, and e) TiO₂-800.
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 TiO₂ samples modified with FeC₂O₄, the reduction of absorbance at UV₂₅₄ and mineralisation degree was much higher with addition of H₂O₂ 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.), 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 H₂O₂ was also performed, although the data are not presented here. Both, the absorbance at UV₂₅₄ and TOC did not change significantly with the time of UV irradiation, indicating poor oxidation of HA by H₂O₂. OH radicals were not generated in the presence of used photocatalyst, 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 H₂O₂ are shown in Fig. 5.

The fluorescence spectra were in a good agreement with the measurements of UV₂₅₄ and TOC, showing that after an addition of H₂O₂ 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, 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 TiO₂ 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 TiO₂ by FeC₂O₄ through the mechanical mixing and heating in Ar at 500–800°C caused formation of Fe₂O₃ and Fe₃O₄ 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 H₂O₂, 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 TiO₂-500 sample could be caused by the formation of HA complexes with iron (magnetite). Leonardite HA was favorably adsorbed on the surface of unmodified TiO₂, accelerating the process of HA degradation, however in the presence of H₂O₂ 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 TiO₂ by FeC₂O₄ at 500–600°C could give photocatalysts active in both, photocatalysis, and photo-Fenton processes.

LITERATURE CITED


