Chapter 03

Advanced Materials, Artificial Intelligence, and Sustainable Technologies for Energy and Environmental Engineering
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Use of nano substances for environmental safety

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ABSTRACT

Purification of aquatic ecosystems using nanotechnological methods is one of the most important problems from an environmental point of view and for this purpose, environmentally friendly TiO_2 nanoparticles were used. TiO_2 nano particles have excellent catalytic properties in photochemical processes as they are also environmentally friendly.Chemical-physical properties of TiO_2 nanoparticles have been investigated.The main aims of this study are to investigate the photochemical degradation of phenol with TiO_2 nanoparticles in the nitrogen mediun and nitrogen-free medium. Photochemical reactions were carried out in the presence of TiO_2 nanoparticles having the size of 10-30 nm. In this study, TiO_2 nanoparticles that have been used in photochemical reaction with phenol were synthesized by sol-gel method. TiO_2 nanoparticles were characterized by SEM and XRD-methods. Photochemical degradation of phenol was found to be better at pH>5. Decomposition of 1 mgL^{-1} phenol was 99 % in the nitrogen-free medium. However, in the medium containing nitrogen,the decomposition of phenol decreased, the decomposition rate was determined 52 %. Quantitative analyzes were performed using high sensitivity Agilent 5975 mss detector equipped with an Agilent 6890N gas chromatograph. The process was carried out under the same conditions in the presence of the same amount of TiO_2 for 1 hour in the "Varian Cary 50" spectrophotometer. Was also studied the effect of the pH of the reaction medium on the course of the photochemical reaction. At the same time the adsorption properties of TiO_2 nanoparticles were studied.It has been found that TiO_2 nanoparticles have very poor adsorption capacity properties.

Keywords: Decomposition; Nano-TiO_2; XRD; SEM; GC-MSD.

INTRODUCTION

Currently, water pollution treatment is one of the widespread environmental problems in the world. It is essential to develop an efficient, economical, and environment-friendly process of wastewater treatment in order to allow the discharge of wastewater to the receiving environment. Phenol is known as a stubborn compound due to its toxicity and non-biodegradable properties, and is therefore difficult to treat.[1,2] The treatment technologies of phenol in wastewater are based either on separation or destruction. The known separation techniques are steam distillation, extractions, adsorption, membrane pervaporation, and membrane-based solvent extractions, while destructive techniques include ectrochemical oxidation, photocatalytic oxidation, chemical oxidation, and biochemical reduction. There is a lot of research on these techniques.[3] Since nanotechnology is a one of the rapidly evolving areas nowadays, purification methods based on nanoparticles for various purposes leads to new directions.

Many photochemical processes take place in the presence of TiO_2 nanoparticles.[4,5,6,7] Decomposition of organics materials using TiO_2/Ce systems is widely discussed in the literature.

[8] Such systems have a high level of active oxygen which leads to the rapid degradation of organic compounds. It is very useful because it is cheap, durable and most importantly, environmentally friendly. In many cases photochemical reactions have been carried out to remove toxic substances from the aquatic environment, mainly using TiO_2 in the form of anatase and mixed composites: for example, photocatalytic oxidation or mineralization of phenol in the presence of a Degussa P25-TiO_2 suspension (consisting of 80 % anatase and 20 % rutile phase). A vital piece of information is available in the literature on methods of depositing precious metals such as silver, gold, platinum on the TiO_2 surface. Heterogeneous photocatalysis is a transferable oxidation process. Large-scale decomposition of pollutants in the air and water also occurs on the basis of this process.[9,10,11] In addition, many doping systems and modifications are being developed to ensure that TiO_2 undergoes photochemical reactions in the visible field. TiO_2 systems with non-metals are of great interest: mainly alloyed with nitrogen and carbon. It is theoretically explained that the photocatalytic properties of TiO_2[12] based on doping with carbon and nitrogen atoms can increase from the UV radiation field to the visible portion of spectrum. Systems doped with a nitrogen atom are very common in the literature, and thus air purification is carried out.[13]

Nitrogen is alloyed with TiO_2 by various methods. For example; The TiO_2/N system modified with Ar/N_2 has very good photocatalytic activity in the visible field.[14] Since titanium dioxide is structurally resistant to UV radiation, it is also important to obtain nanoparticles based on it and apply it in various fields. Both anatase and rutile forms of TiO_2 nanoparticles are important for chemical processes. The anatase form of TiO_2 is metabolic and converts to rutile when heated. The permissible amount of TiO_2 in an aqueous medium is 0,7-16,0 mgL^{-1}.In this regard it is effective to use small amounts of nanoparticles. The behavior of nanoparticles in water depends on pH. Taking into account the above we can say that nano technological methods are the most modern methods of water purification from toxic compounds. The most effective of them was the purification of wastewater from phenol, an organic toxic substance based on the GO/Al_2O_3 composite by 99,9 %.[15]

The main aims of this study are to investigate the photochemical degradation of phenol with TiO_2 nanoparticles in the nitrogen and nitrogen-free medium to determine of adsorption properties of TiO_2 nanoparticles.

Experimental Part

TiO_2nanoparticles have been investigated in order to carry out photochemical reactions. TiO_2 nanoparticles were synthesized by the sol-gel method. In the system TiO_2+Ph (phenol) the process took place only in the UV-radiation area. For the this system it was taken 0,05 gr TiO_2 equally distributed in the water of 10 mL. Then 5 ml of obtained mixture has been added to 20 mL of the 1 mgL^{-1} phenol solution. In this system the decomposition of phenol was 99 %.

For the TiO_2+Ph/N system was taken 0,05 g TiO_2+0,05 g N compound: ethyl-3,3,5,5-tetraciano-2-hydroxide-2-metil-4,6-diphenylcyclohexane carboxylate($C_{26}H_{22}N_4O_3$).Their solution has been equally distributed in the water of 10 mL. In the Ph+TiO2/N system the process took place in the UV-Vis area. As it is mentioned above TiO_2 nanoparticles are not toxic and gets excited by UV radiation; this contributes to the reaction process. Complete mixing of TiO_2 nanoparticles in the participation of UV radiation has been carried out in advance for their equal distribution in the water. 5 mL of obtained mixture has been added to 20 ml 1 mgL^{-1} phenol solution and then 0,05 g N-compound has been added. The viewed mixture has been subject to photochemical dissociation for 60 minutes. All quantitative analyzes were performed on Agilent 6890N /5975 device. The device has a very high sensitivity. After photolysis process the dependence of the solution's absorption coefficient on wavelength has been measured in UV "Varian Cary 50" spectrophotometer. Although the decomposition of phenol occurs in a lower yield compared to Ph+TiO_2 system it has been found that the photochemical process extends from the UV area to the Visible area. In the Ph+TiO_2/N system the decomposition of phenol was less than 52 %.

X-ray structure of the $C_{26}H_{22}N_4O_3$-ethyl-3,3,5,5-tetracyano-2-hydroxy-2-methyl-4,6-diphenylcyclohexane carboxylate obtained for the first time by us «Bruker APEX II CCD " (T = 100K, λMoKα - radiation, graphite monochromator, φ- and ω-scanning, 2θmax = 56˚) was analyzed in the diffractometer and the following structure was obtained. The obtained carboxylate consists of white crystals.[16]

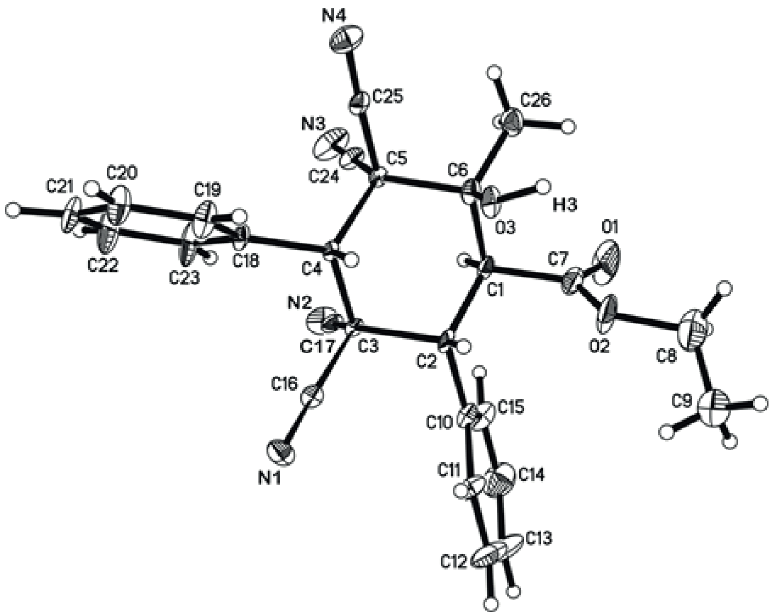

Figure 1. Structure of the $C_{26}H_{22}N_4O_3$-ethyl-3,3,5,5-tetracyano-2-hydroxy-2-methyl-4,6-diphenylcyclohexane carboxylate

RESULTS AND DISCUSSION

TiO_2 nanostructures are synthesized by the sol-gel method. It was obtained by the hydrolysis of titanium IV isopropoxide.This process usually proceeds through hydrolysis of titanium (IV) isopropoxide followed by condensation of formed $Ti(OH)_4$.The high rate of hydrolysis contributes to the formation of $Ti(OH)_4$ which interrupts the development of the chain Ti-O-Ti. The presence of a large number of Ti-OH groups and the low development of a three-dimensional polymer structure leads to a low particles packing 1 mgL^{-1} of phenol solution was used during the process.The purity and crystalline properties of the TiO_2 nanoparticles were investigated by powder X-ray diffraction (XRD) method. Figure 2 shows the XRD patterns of the synthesized TiO_2 nanoparticles. XRD peaks were well defined and corresponded to TiO_2 at rutile phase. X-ray structure analysis graphs of the studied nanocomposite materials were recorded on the Rigaku Mini Flex 600spowder diffractometer. Its features are given below:

X-ray tube with copper anode (Cu-Kα radiation, 30 kV and mA) was used to draw the diffraction specters at room temperature. At 2θ = 20°-80° with discrete growth mode these specters were obtained as Δ2θ = 0,05°and the exposure time was τ = 5 seconds (figure 2).

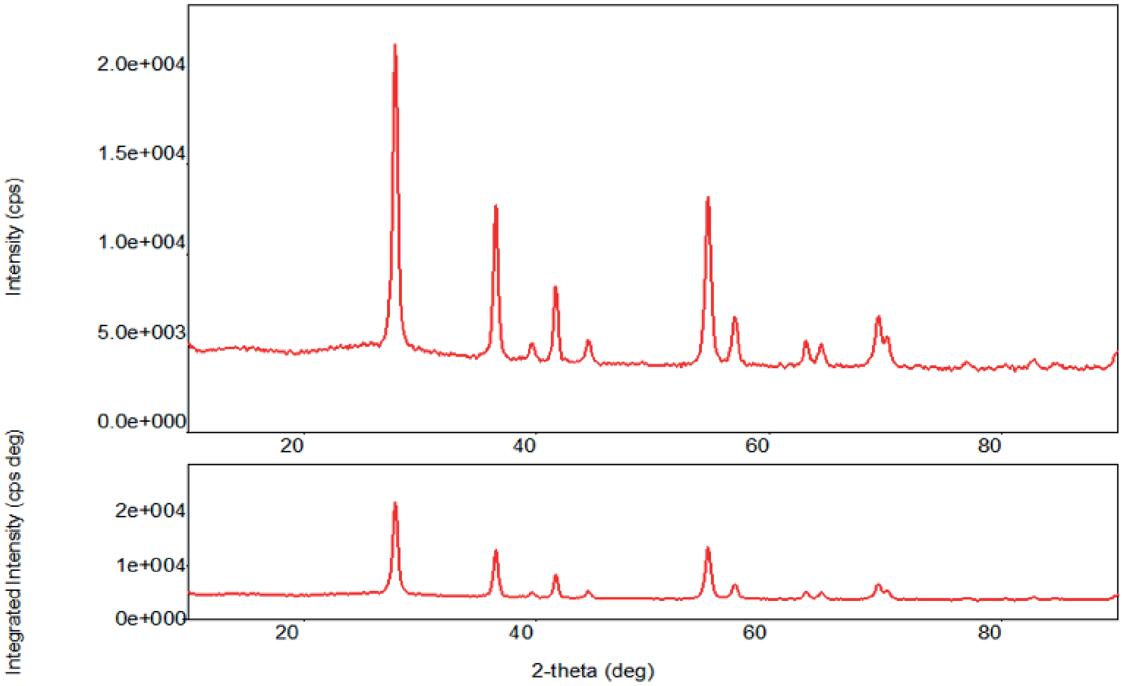

Figure 2. XRD patterns of the rutile phase TiO_2 nanoparticles

Figure 3 show the SEM patterns of the synthesized TiO_2 nanoparticles. Based on the SEM analysis of TiO_2 the nanoparticles were 10-30 nm in size.

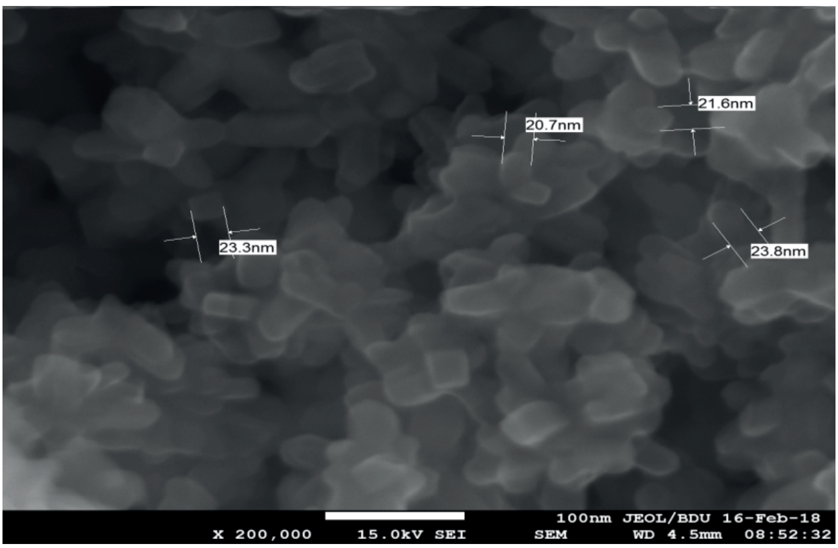

Figure 3. SEM patterns of the rutile phase TiO_2 nanoparticles

As can be seen from figure 4 the highest peaks for TiO_2 were obtained at 300-350 nm wavelengths after UV irradiation of TiO_2 nanoparticles. Starting from this wavelength (350 nm) the emission of the UV spectrum increases sharply in the figure 4.

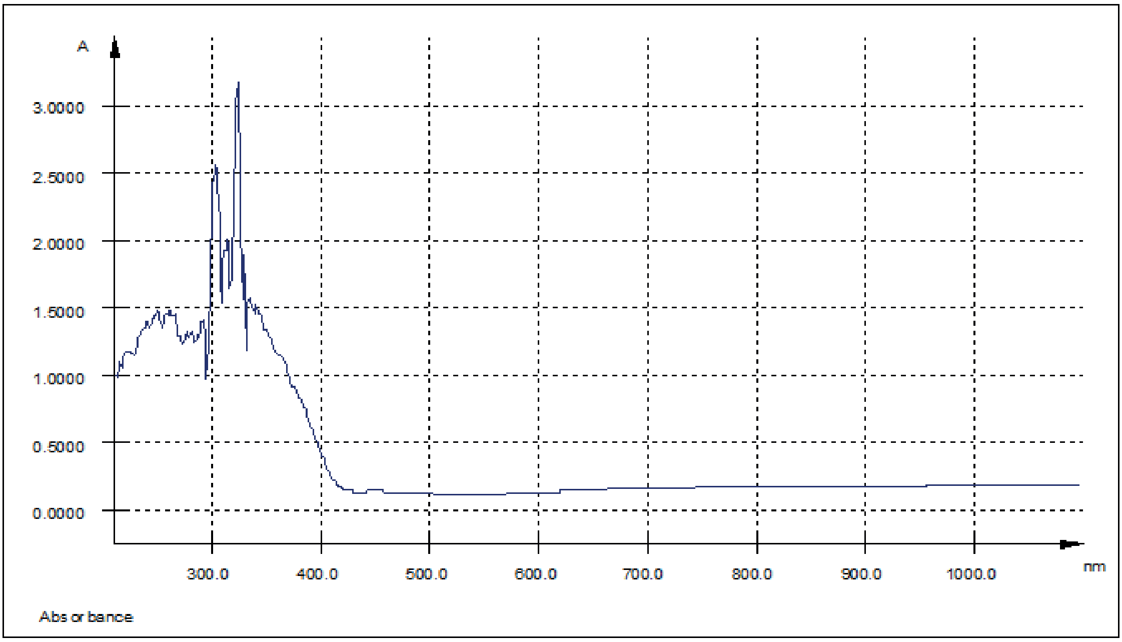

Figure 4. Light absorption of TiO_2 nanoparticles

The process of decomposition of phenol in the presence of UV in the system Ph + TiO_2 is shown below (figure 5).

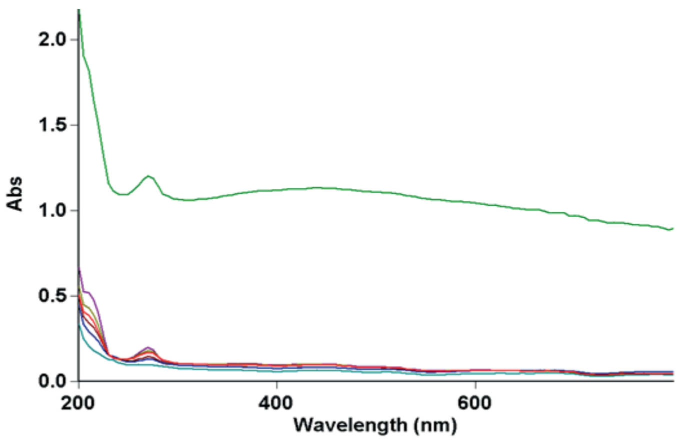

Figure 5. Photochemical decomposition of the Ph+TiO_2 in the presence of UV

As shown in figure 5 for the 1 mgL^{-1} Ph+TiO_2 system the characteristic wavelengths (270 nm) for phenol are not observed in the last (blue) curve compared to the other curves.This is due to the lack of or insufficient quantity of phenol after photolysis (sensitivity of the device) in the solution. The sample was then analysed in a gas chromatographic mass detector for more sensitive and accurate analysis. Amount of phenol has dropped from 1 mg to 10 µg. This means that 99 % of phenol has degraded.(17)

It may be noted that TiO_2 nanoparticles has very good photo dissociation together in combinations with N atom. The matter is that we have considered more appropriate to use TiO_2 nanoparticles as the works done by us have been carried out in the participation of UV radiation, since TiO_2 nanoparticles gets excited only during UV radiation (A<387 mm) it has only 5 % excitement in the Visible area. Furthermore TiO_2 is chemically sustainable it is obtained in soft condition that's easily seen in the viewed case and the most important is that it is considered ecologically clean. In addition the photochemical reaction in the Ph+TiO_2/N system was considered. The reaction range ranged from the UV radiation range to 400-600 nm in the visible area (figure 6). In the Ph+TiO_2/N system photolysis process has been done in UV radiation device; the dependence of absorption coefficient on the wavelength has been determined by "Varian Cary 50" device the concentration of phenol remained in the solution after photochemical reaction has been determined.

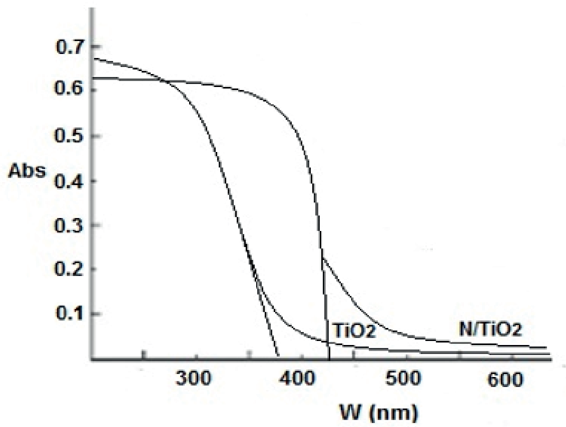

Figure 6. The dependence of the absorption coefficient on the wavelength for Ph +TiO_2 and Ph +TiO_2/N systems

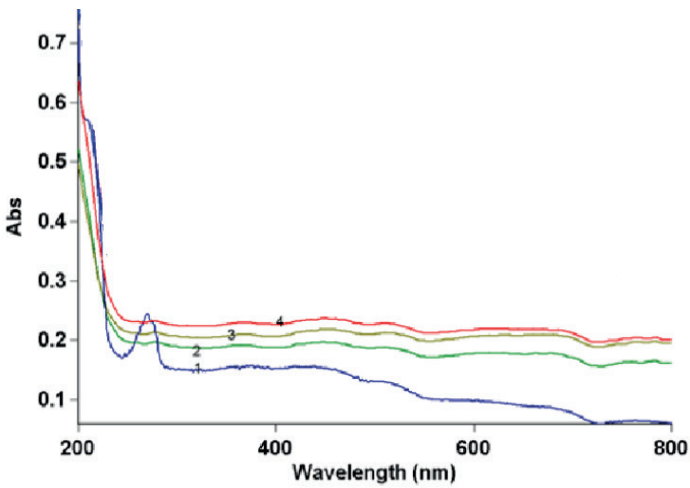

Figure 7. Photochemical decomposition of the Ph + TiO_2/N in the presence of UV

1. Curve before irradiation.
2. Curve obtained at the 20th minute of the photocatalytic process.
3. Curve obtained at the 40 th minute of the photocatalytic process.
4. Curve obtained at the 60th minute of the photocatalytic process.

As can be seen in figure 7 for the Ph +TiO_2 system (1) the light absorption of the solution was intense in the UV irradiation area up to 400 nm while the light absorption of the Ph+TiO_2/N system (2,3,4) covered the area after 400 nm. The transition in the UV-Vis areas occurs with the transition of the adsorption wavelength dependence curve to the area after 400 nm in the presence of N-retaining substance.

The effect of pH on the photochemical reaction was also studied in the process. pH was determined by taking samples from the reaction solution at different times of the photochemical process. It has been determined that photochemical decomposition occurs at best in an acidic area: pH>5 (figure 8).

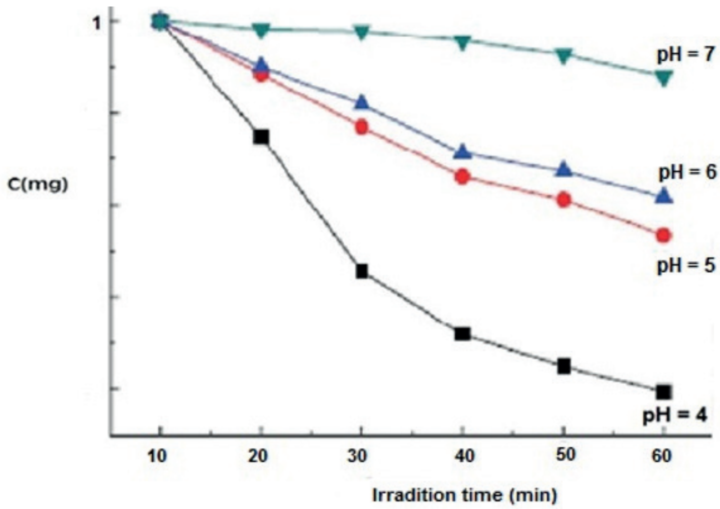

Figure 8. Effect of the pH of the reaction medium on the course of the photochemical reaction

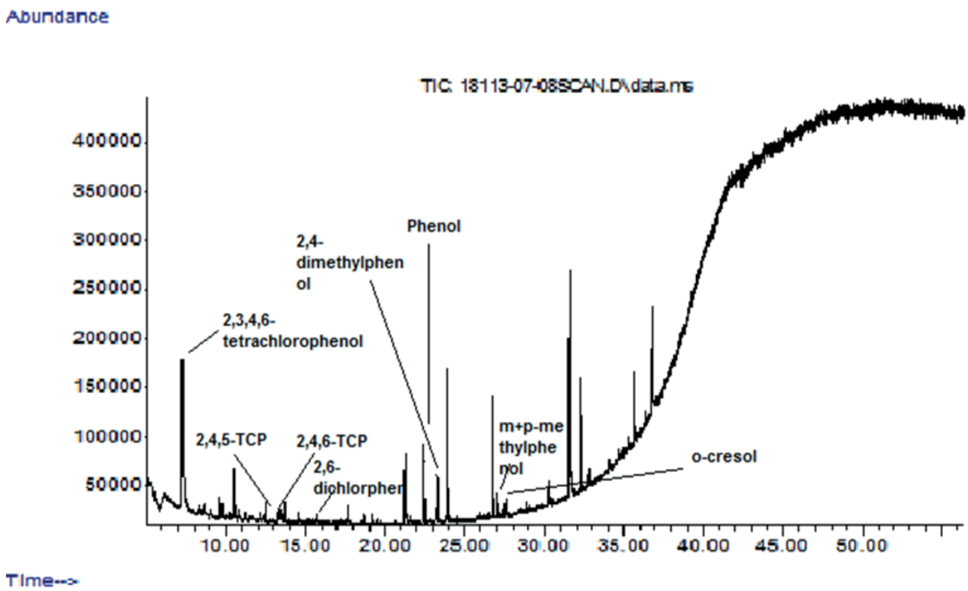

Figure 9. GC-MSD analysis of the Ph+TiO_2 solution after photochemical decomposition

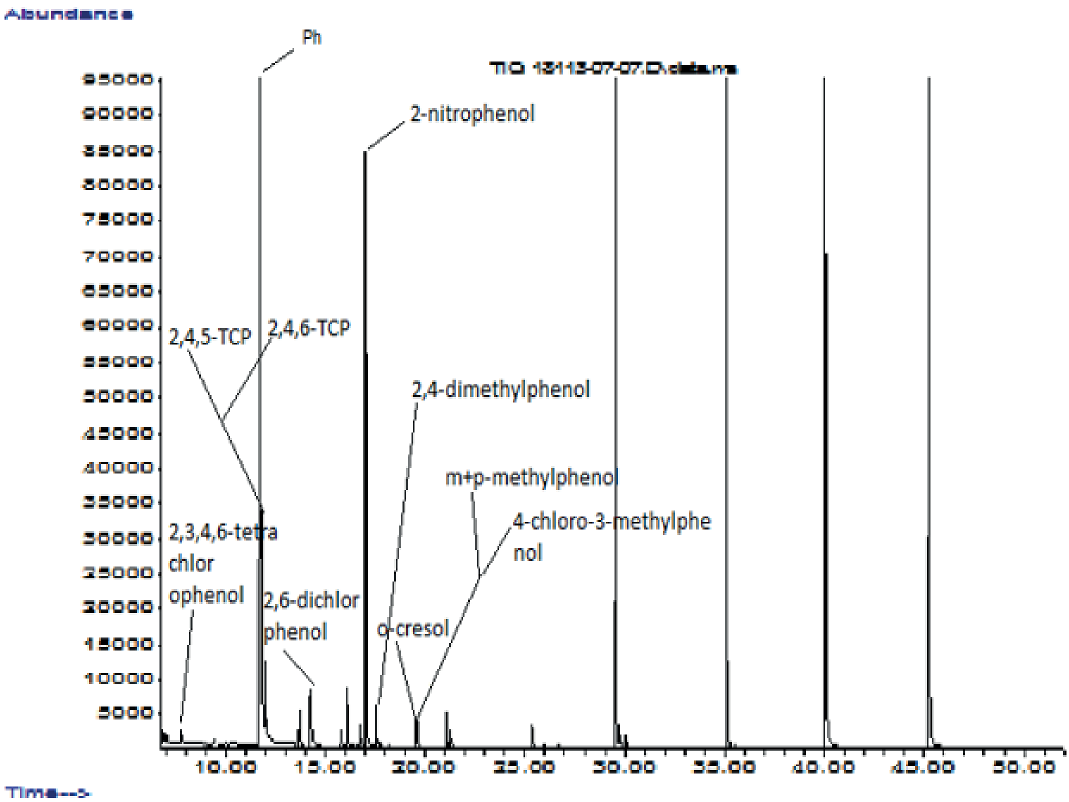

Figure 10. GC-MSD analysis of the Ph+ TiO_2/N solution after photochemical decomposition

In the systems Ph+TiO_2 (figure 8) and Ph+ TiO_2/N (figure 9) a quantitative analysis of treated samples after photolysis were carried out on a 6890N GC-MSD gas chromatograph with an Agilent 5975 high-performance mass-selective detector manufactured by Agilent Technologies (USA).

Also it was studied the adsorption process in the presence of TiO_2 nanoparticles which was carried out at room temperature (25°C) for 2 hours. The process was monitored on a “Varian Cary 50” instrument. It was found that the adsorption process was very weak. This suggests that TiO_2 is a very poor adsorbent despite the fact that it is a good photo catalytic reagent. It should be noted that the TiO_2 nanoparticles belonged to the rutile phase. The process was monitored on a “Varian Cary 50” spectrophotometer. During the 2-hour process solution samples were taken and peaks were observed in the phenol-specific region of 270 nm every time (figure 10). This suggests that the adsorption process was absent. It is possible that the adsorption did not take place due to chemisorption. This can be said according to the Langmuir-Hinshelwood (LH) hypothesis.

Thus the work on the photochemical decomposition of phenol from wastewater in the presence of TiO_2 nanoparticles was studied and a high percentage of photochemical decomposition of phenol was achieved but as an adsorbent TiO_2 had a weak property. In conclusion it should be noted that in our time wastewater treatment by nanotechnological methods is one of the most developed and modern areas therefore work in this direction will continue in the future.

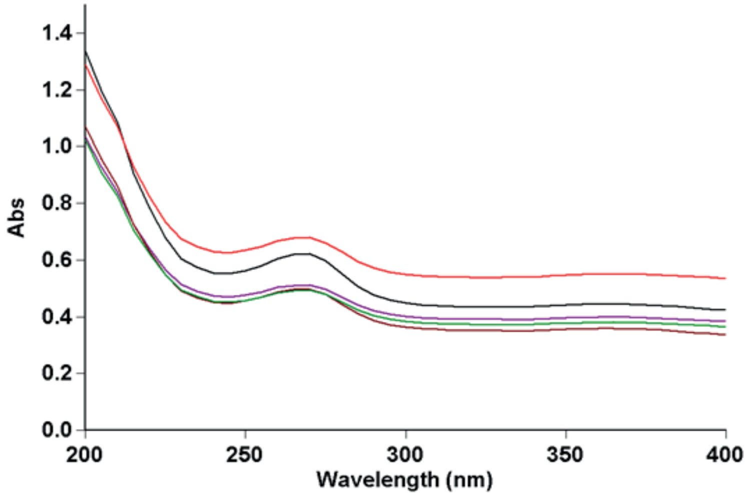

Figure 10. Comparison of phenol adsorption curves in the presence of TiO_2

CONCLUSIONS

1. The article deals with the decomposition of phenol in the Ph+TiO_2 and Ph+TiO_2/N systems.
2. For the first time, a new synthesized organic matter: $C_{26}H_{22}N_4O_3$ containing nitrogen was used in the photochemical process.
3. In the Ph+TiO_2 system, the decomposition of phenol was 99 % and the decomposition of phenol in the Ph+TiO_2/N system was 52 %.
4. The purpose of using a nitrogenous substance was to carry out a photochemical reaction in the visible area in the presence of TiO_2 nanoparticles in the UV area of radiation. This increases the practical significance of the process.
5. XRD and SEM analyzes of the TiO_2 nanoparticles were carried out.
6. The sizes of TiO_2 nanoparticles used ranged from 10 to 30 nm.
7. Decomposition of 1 mg/L phenol was carried out for 1 hour. In this case, the influence of the pH of the medium on the course of the reaction was determined.
8. The photochemical process was monitored on a "Varian Cary 50" spectrophotometer.
9. Quantitative analyzes were performed using an Agilent 6980N/5975 GC/MSD.
10. It was studied that TiO_2 nanoparticles have a very poor adsorption capacity.

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CONFLICT OF INTEREST

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AUTHORSHIP CONTRIBUTION

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Writing - proofreading and editing: Elmina Gadirova, S.R. Hajiyeva.