



Modern Methods for Wastewater Treatment

Atık Su Arıtımı için Modern Yöntemler

Elmina Gadirova[®]

Department of Ecological Chemistry, Baku State University, Baku, Azerbaijan.

ABSTRACT

The article considers the photochemical degradation of the phenol solution in the presence of TiO₂ nanoparticles, which synthesized in moderate conditions and dimensions vary between 10-30 nm and the 100 mg/ml NH₄OH solution. The appearance of photochemical dissociation was confirmed on the basis of the absorption curves taken before and after the process and Abs curves were drawn on the "Varian" device. Phenol's photochemical dissociation in UV-visible area has been confirmed by experiments.

Key Words

NH₄OH, degradation, phenol, UV-visible area.

Öz

Makale, ılımlı bir ortamda sentezlenen ve 10-30 nm ve 100 mg/ml NH₄OH ölçülen TiO₂ nanopartiküllerinin varlığında çözelti içinde fenolün fotokimyasal bozunmasını incelenmiştir. UV görünür alanda fenolün fotokimyasal bozunması deneylerle doğrulanmıştır.

Anahtar Kelimeler

NH₄OH, bozunması, fenol, UV-görünür alan.

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Correspondence to: E. Gadirova, Department of Ecological Chemistry, Baku State University, Baku, Azerbaijan.

E-Mail: elmina2010@mail.ru

INTRODUCTION

We know that wastewater treatment is currently one of the environmental problems in the world. Pollution of water basins through toxic organic substances are considered to be one of the global environmental issues and therefore implementation of new methods are needed for the solution. Nowadays, heterogeneous photocatalytic techniques are considered as the most effective methods for environmental protection and purifying wastewater from phenol compounds. On the other hand, the processes involved in nanoparticles regarding to the development of nanotechnology are very interesting and new. In the viewed case, waste materials are taken in very small quantities, so this is considered to be ecologically positive. In this regard, effective purifying methods by using nanoparticles are now widely used [1]. Phenol is always found in wastewater as it comes from petrochemicals, medicines, plastic, coal, paint and paper industry. Generally, phenol is one of the most important hazardous pollutants due to poor biological degradation, high concentrations, and high toxicity in terms of long-term adverse environmental effects [2]. The gradual decline of freshwater and the increased pollution are now a major environmental problem in the world. Currently, millions of people in the world suffer from freshwater shortages. Generally, phenol, which is the most important among water pollutants, creates serious environmental problems. So far, many methods have been used to purify phenol from waste water. The use of physical, chemical and biological methods is not tremendous today. In the process of chemical processing, intermediate products are obtained, which are harmful to the environment too. Membrane filtration is a unique method for the purification of pollutants from water; currently membrane filtration method is on the focus, as it is an energy efficient and ecologically efficient process for water purification. However, the separation of the toxic substances contained in the water requires other methods [3,4]. Therefore, the subject of the new methods maintains its relevance.

EXPERIMENTAL

According to literature data, we can note that, it is possible to extract phenols from waste water based on photochemical reactions by TiO_2 nanoparticles. It has also been studied that these nanoparticles generate systems with carbonized and nitrogenous compounds and such systems expands the UV radiation range to the visible region and ultimately reactions in the N/TiO_2 participation occur

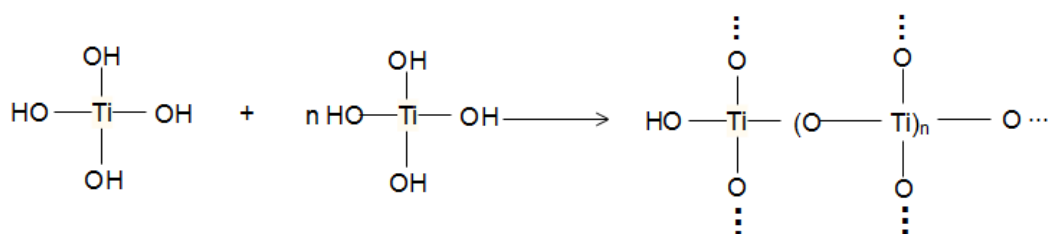
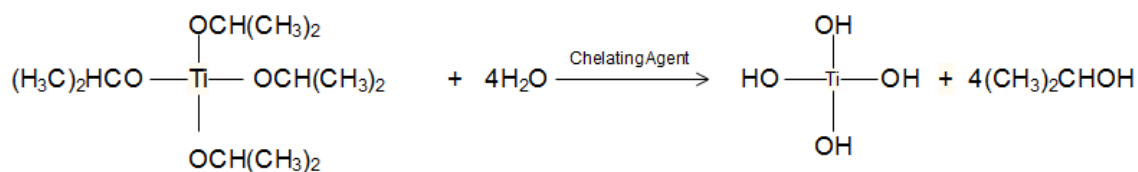
in the visible region; which enhances the practical importance of the reactions. TiO_2 nanoparticles are excited only during UV radiation ($\lambda < 387 \text{ nm}$) and in the visible region, no reactions occur with these nanoparticles ($\lambda < 400 \text{ nm}$). Because, in the TiO_2 compound bonding energy between Ti-O is high, so that, the UV rays cause TiO_2 excitement. The reason of process going on in the visible region is based on the fact, in N/TiO_2 doped systems the bonded energy between Ti-N is smaller than the bonded energy between Ti-O [5].

TiO_2 nanoparticles are very useful; so that, it is chemically stable, easy to handle, non-toxic and ecologically clean.

Phenol decomposition reactions were carried out through photochemical reactions using TiO_2 nanoparticles and NH_4OH solution to purify phenol from wastewater. The aim was to determine how effective the new synthesized nitrogen compound is effective in photochemical reactions. For this purpose, 0,05g of TiO_2 and NH_4OH in 10 ml of distilled water was prepared. Sanification of the solution is carried out beforehand in order to provide the equal distribution of TiO_2 nanoparticles in distilled water. 5 ml of taken mixture was added to 20 ml of 1 mg/l of phenol solution, followed by addition of 0,05 g of ammonia and subjected to photochemical dissection in UV-visible region. After the photolysis process, dependent of the wavelength of the absorption coefficient on the reaction solution has been obtained in the UV radiating device and thereby the photolitic dissolution has been proved. In the photolysis process, dependence of the absorption coefficient (Abs) on the wavelength was determined by the «Varian» device the reduction of solids concentration of the phenol remaining in the solution. The reduction of solids concentration of the phenol has been determined in the remaining solution after photochemical reaction based on the graphic 1. The process took about 5 hours.

ANALYSIS of RESULTS

In the sol gel process forms the colloidal suspension, or sol by the hydrolysis and polymerizing reactions of TTIP precursor substance. Complete polymerisation or solvent removal converts the liquid sol to a solid gel phase. TiO_2 nanostructures are synthesized by the sol - gel method by the hydrolysis of titanium IV isopropoxide. This process usually proceeds through hydrolysis of titanium (IV) isopropoxide, followed by condensation of formed $\text{Ti}(\text{OH})_4$.



The development of the chain of Ti–O–Ti bonds is promoted by a low water content (low level of hydrolysis) and an excess of titanium alkoxide in the reaction mixture. The formation of chains leads to the formation of a three-dimensional polymer structure with a short degree of order. The high rate of hydrolysis contributes to the formation of $\text{Ti}(\text{OH})_4$, 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 [6,7].

The TiO_2 nanoparticles of rutile phase prepared for the process were determined by the TEM method and the results are shown in Figure 1. As shown in figure 1, the obtained nanoparticles are homogeneous and range from 10 to 30 nm, the results are consistent with the calculations of the Sherrer method. The total surface area of the nanoparticles is $159.6 \text{ m}^2/\text{g}$.

Crystallization and purification of TiO_2 nanoparticles are determined by the XRD method. Figure 2 shows the X-ray structure of TiO_2 nanoparticles which has been the synthesized by us.

All XRD signals were determined to correspond to the rutile phase of TiO_2 . The diameter of the nanoparticles was 10.3 nm according to the Sherrer method (101). The total area of TiO_2 was $159.6 \text{ m}^2/\text{g}$. Specific alerts for

TiO_2 nanoparticles were -27.90° (110), 36.01 (101), 41.58 (111), 54.71 (211) [3].

SEM-Field Emission Scanning Electron Microscope JEOL JSM-7600F at an accelerating voltage of 15.0 kV, SEI regime XRD X-ray diffraction analysis was performed on Rigaku Mini Flex 600 XRD diffractometer at ambient. In all the cases, Cu K α radiation from a Cu X-ray tube (run at 15 mA and 30 kV) was used. The samples were scanned in the Bragg angle 2θ range of 20 – 70 .

According to literature data, the photochemical dissociation of phenol passes through the UV radiation region to the visible region gradually in the doped systems of TiO_2 nanoparticles, generated from chemical compounds that stores C or N. That is why, ammonia solution has been used for this purpose that are synthesized by us for the first time and contain both C and N. In the process, it is assumed that the process proceeds to the visible region, based on the reaction between the electron pair of the N atom and TiO_2 .

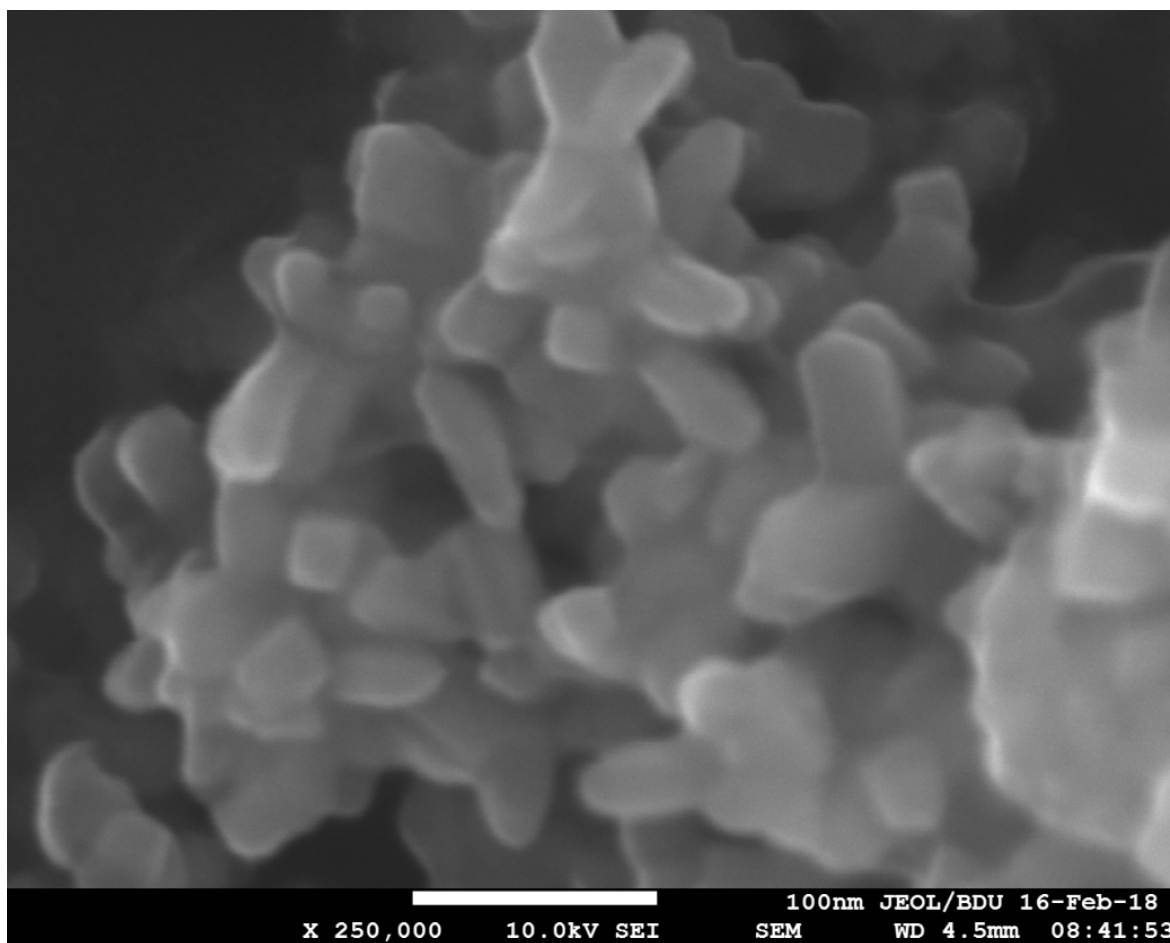


Figure 1. SEM view for TiO_2 nanoparticles

20 ml 1 mg/l phenol solution, 5 ml solution in which 0,05 g of TiO_2 nanoparticles distributed equally and 0,05 g of ammonia solution were taken for the process.

The increased effectiveness of photochemical dissociation in the visible region and with the participation of composites generated from the modification of nitrogen compounds with TiO_2 nanoparticles is characterized by the external energy level of the N and O atoms: a decrease in the number of oxygen atoms in the 2 p e- boundary of the excited O atom and the entry of N atoms to the cavities [8,9].

The pH was determined during the photochemical reaction (1-2; 2-3; 3-4 and 4-5 hours). The dependence of photochemical dissociation on pH was determined too. The pH-change was determined by the PHS-25 pH meter. In the last one the pH of environment was equal to 4. The dissociation of $\text{N/TiO}_2+\text{Ph}$ is better, when $\text{pH}=4$.

The article considers the use of nanoparticles in the solution of environmental problems created by waste water. For example, in the last 30-35 years, due to the development of nanotechnology, the pollution of toxic substances from waste water or contamination of waste water is considered to be one of the topical issues. The freshwater resources around the globe is gradually decreasing, so discovering new methods for maximum waste water treatment do not lose its relevance.

RESULTS

The dimensions of TiO_2 nanoparticles synthesized by us have varied between 10 and 30 nm.

Photochemical reaction of $\text{NH}_4\text{OH}+\text{TiO}_2+\text{phenol}$ system in UV-visible area was carried out. pH of environment was equal to 4.

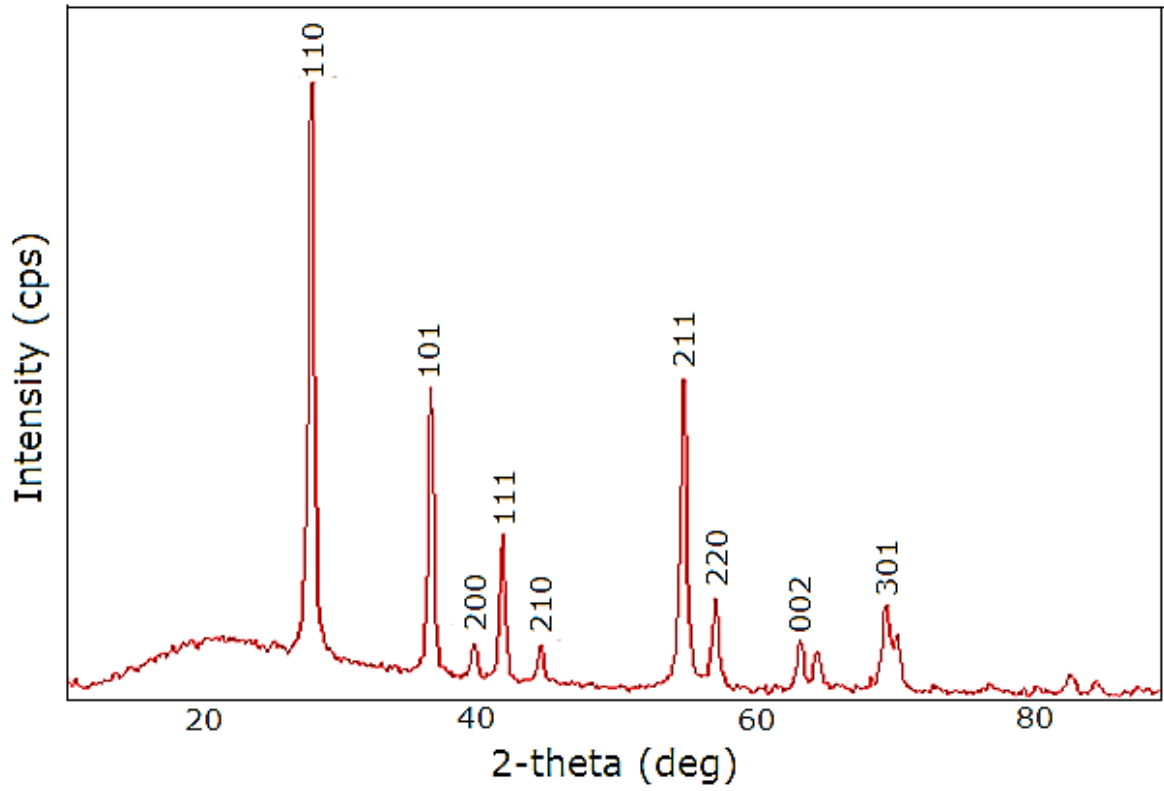
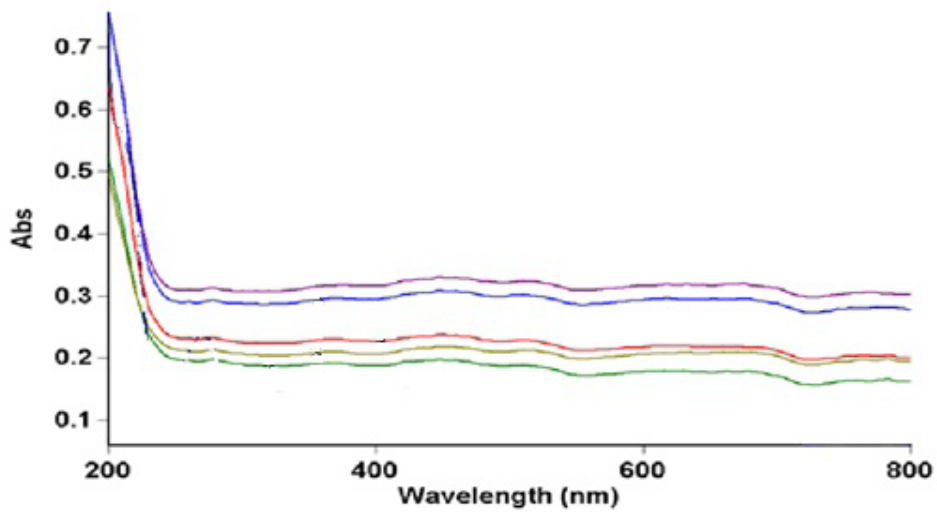
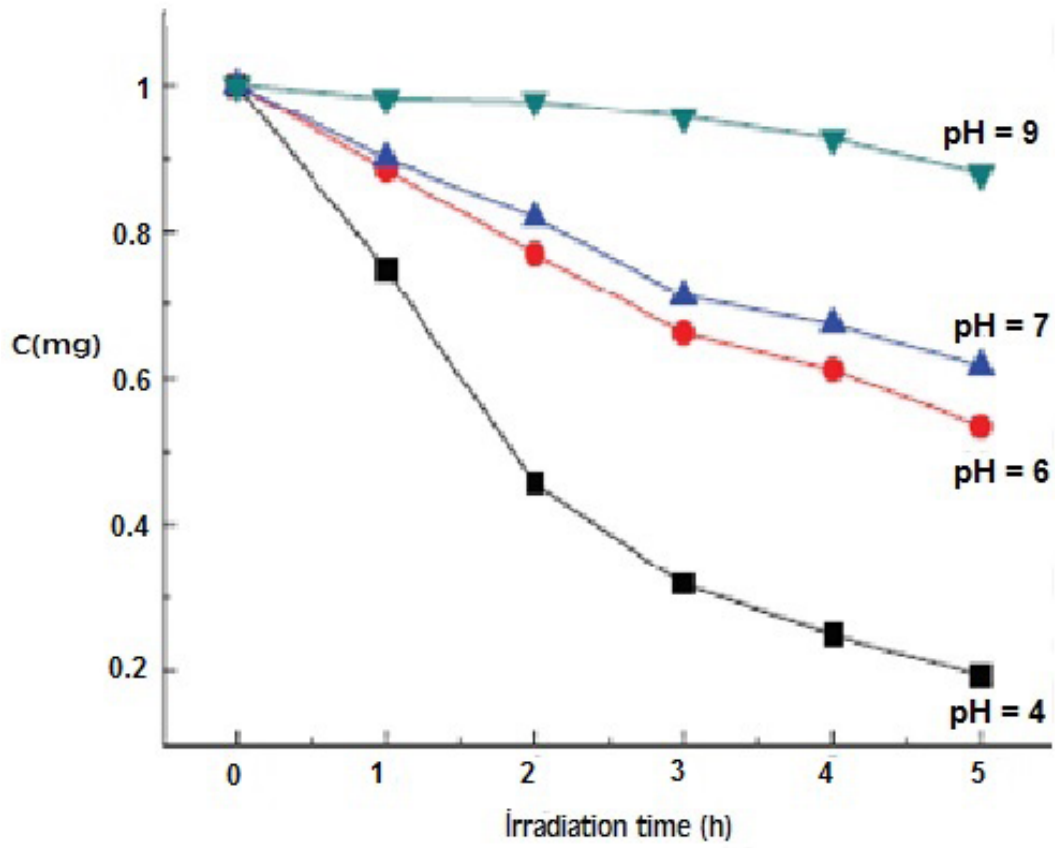


Figure 2. X-ray of TiO_2 nanoparticles (XRD).



Graphic 1. Comparison of radiation curves received before and after the photolysis process of the phenol + N/TiO_2 system in UV-visible areas.



Graphic 2. Dependence of N/TiO₂+phenol solution on the pH.

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