Chapter 04

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Using nanoparticles to protect aquatic ecosystems

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ABSTRACT

Recently, the use of modern chemical methods for the protection of aquatic ecosystems has become very important. These methods are used to remove certain toxic organic substances. Using nanotechnology, a method has been developed to clean the aquatic ecosystem from toxic phenol. The main objectives of this study are: (1) to study the photochemical degradation of phenol by TiO_2 nanoparticles in nitrogenous and nitrogen-free media; (2) to determine the adsorption properties of rutile phase TiO_2 nanoparticles. Many photochemical reactions have been carried out in the presence of TiO_2 nanoparticles of 10-32 nm size. In this study, TiO_2 nanoparticles used in the photochemical reaction with phenol were synthesized by sol-gel method. TiO_2 nanoparticles were characterized by SEM and XRD. The adsorption properties of TiO_2 nanoparticles were also studied.

Keywords: Degradation; Phenol; Nano-TiO_2; XRD; SEM.

INTRODUCTION

Phenol is a toxic, persistent compound that is difficult to degrade.(1,2) Degradation of organics using TiO_2/Ce systems has been widely reported in the literature.(3) They are in great demand, economical and most importantly environmentally friendly.(4,5) Currently, research on wastewater treatment is of great importance worldwide.(6) Therefore, it is important to develop efficient, economical and environmentally friendly methods to ensure that wastewater is discharged to the receiving environment at phenol concentration values that meet regulatory standards. Wastewater treatment technologies for phenol are based on either separation or destruction. Well-known separation methods include steam distillation, extraction, adsorption, membrane pervaporation and membrane solvent extraction, while destructive methods include electrochemical oxidation, photocatalytic oxidation, chemical oxidation and biochemical reduction. Many studies have been conducted on these methods. Since nanotechnology is currently one of the rapidly developing fields, nanoparticle-based cleaning methods for various purposes are important. It is worth mentioning that recently $Fe+H_2O_2$ systems have been used for the purification of phenol from wastewater.(7) In this context, studies based on TiO_2 are still relevant today. Many photochemical processes occur in the presence of TiO_2 nanoparticles.(8,9,10,11,12,13) In particular, many photochemical reactions have been carried out using TiO_2 in the form of anatase and mixed composites for the removal of toxic substances from the aquatic environment: for example, photocatalytic oxidation or mineralization of phenol in the presence of Degussa P25-TiO_2 suspension (80 % anatase and 20 % rutile phase). There is considerable information in the literature about the deposition of precious metals such as silver, gold and platinum on the TiO_2 surface. Heterogeneous photocatalysis is a portable oxidative process. On the basis of this process, large-scale degradation of pollutants in air and water also takes place.(14) In addition, many alloy systems and modifications are being developed to enable photochemical reactions of TiO_2 in the visible region. Non-metallic TiO_2 systems are of great interest: especially alloyed with nitrogen and carbon. It has been theoretically described(15) that the photocatalytic properties of TiO_2 can be enhanced from the UV region to the visible region of the spectrum due to doping with carbon and nitrogen atoms. In the literature, systems doped with nitrogen atoms are very common and thus air purification is realized.(16)

METHOD

TiO_2 nanoparticles were synthesized by sol-gel method and obtained by hydrolysis of titanium (IV) isopropoxide. In the TiO_2+phenol (Ph) (1) system, the process was carried out only in the UV region, while in the TiO_2+nitrogen+phenol (Ph) (2) process in nitrogen-containing medium, the process was carried out in the UV and visible region. For system (1), 0,05 g of TiO_2 was taken and evenly distributed in 10 ml of water. Then 5 ml of the mixture was added to 20 ml of phenol solution with a concentration of 1 mg/l.

For system (2), 0,05 g of TiO_2 was taken and evenly distributed in 10 ml of water. Then, 5 ml of the resulting mixture was added to 20 ml of phenol solution with a concentration of 1 mg/l followed by the addition of 0,05 g of nitrogenous compound. The mixture was subjected to photochemical decomposition for 60 min. The degradation of phenol was 60 %. All quantitative analyses were performed on a high precision Agilent 6890N/5975 instrument. After photolysis, the wavelength dependence of the absorption coefficient of the solution was measured on a Varian Cary 50 UV spectrophotometer. It was found that the photochemical process extends from the UV region to the visible region, although the degradation of phenol in system (2) occurs with a lower efficiency compared to system (1). Methyl 3-aminocrotonate ($CH_3C(NH_2)=CHCOOCH_3$) was taken as the nitrogen-containing component for the reaction.

The purity and crystalline properties of TiO_2 nanoparticles were investigated by powder X-ray diffraction (XRD).

RESULTS AND DISCUSSION

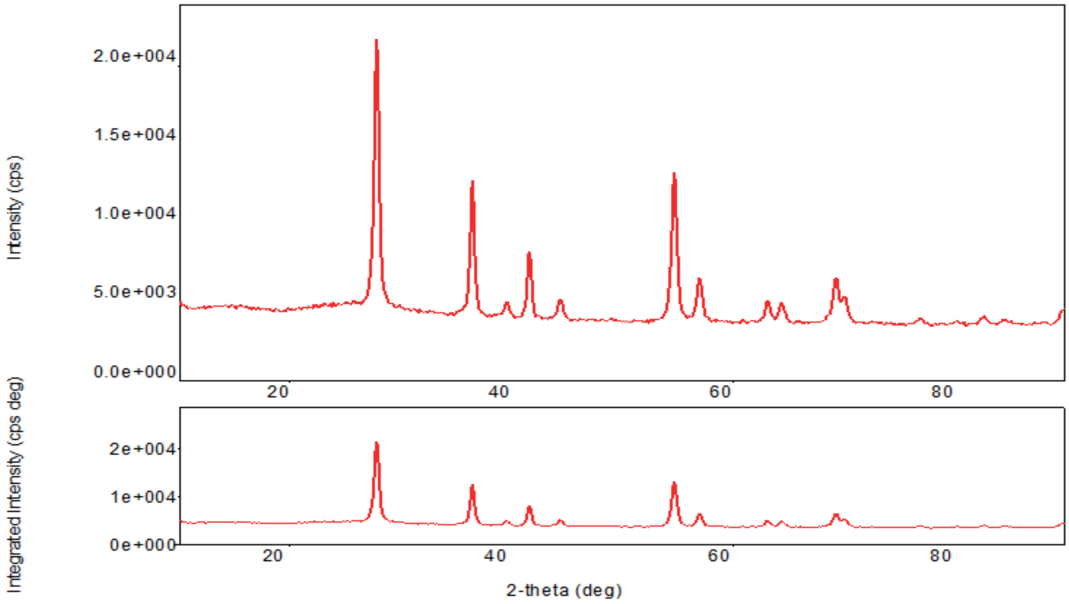

Figure 1. X-ray diffraction patterns of rutile phase TiO_2 nanoparticles

Figure 1 shows the X-ray diffraction patterns of the synthesized TiO_2 nanoparticles. The peaks are well defined and correspond to TiO_2 in the rutile phase. X-ray diffraction analysis plots of the investigated nanocomposite materials were recorded on a Rigaku Mini Flex 600 powder diffractometer. Their properties are given below: a copper anode X-ray tube (Cu-Kα radiation, 30 kV and mA) was used to generate diffraction spectra at room temperature. These spectra were acquired at $2\theta = 20°-80°$ in discrete increment mode with $\Delta 2\theta = 0{,}05°$ and exposure time $\tau = 5$ seconds (figure 1).

According to SEM analysis of TiO_2, the size of the nanoparticles was 10-32 nm. Figure 2 shows SEM photographs of the synthesized TiO_2 nanoparticles.

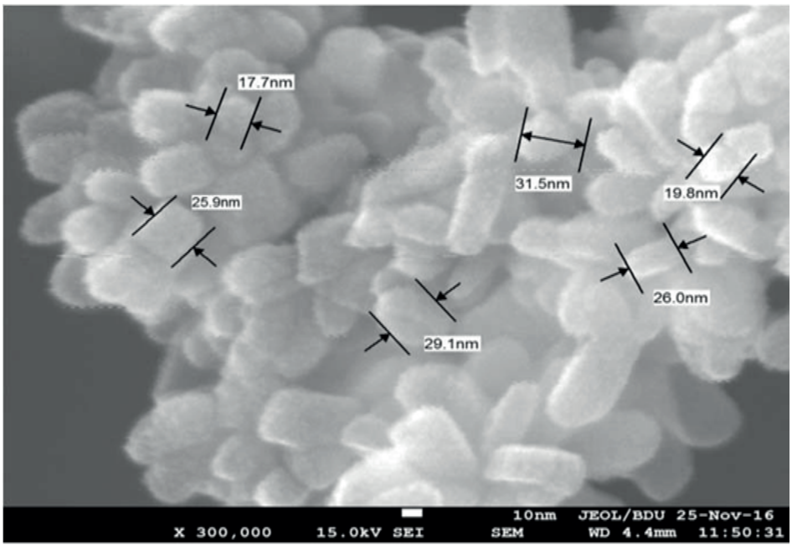

Figure 2. SEM analysis of rutile phase TiO_2 nanoparticles

TiO_2 nanoparticles used in the experiments were obtained by sol-gel method. The reaction proceeded with the formation of TiO_2 layers and a suspension solution was obtained. However, there are other ways to obtain TiO_2: for example, TiO_2 has also been obtained from white liquid isopropoxide-$Ti(OCH(CH_3)_2)_4$ under mild laboratory conditions. The general formula is $C_{12}H_{28}O_4Ti$.

It is prepared by reaction of tetrachloride with isopropanol:

$TiCl_4 + 4(CH_3)_2CHOH \rightarrow Ti(OCH(CH_3)_2)_4 + 4HCl$

TiO_2 was obtained by reacting the resulting compound with water.

$Ti(OCH(CH_3)_2)_4 + 2H_2O \rightarrow TiO_2 + 4(CH_3)_2CHOH$

Since TiCl4 is very soluble in water, TiO_2 was obtained from it and the reaction proceeded as follows:

$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$

This method is easy to use, but is not often used in the laboratory because $TiCl_4$ is toxic.

Therefore, organotitanium compounds are more often used to obtain small TiO_2 layers. It is believed that the oxidation of phenol under the influence of UV radiation in a medium containing TiO_2 nanoparticles occurs as follows:

TiO_2+hv→ TiO_2 (e- + h+)
TiO_2(h+) +H_2O →TiO_2 +H+ +OH.
Phenol+OH. → oxidation products
Phenol + (e-) → oxidation products
Phenol + (h+) → oxidation products

In general, these types of photochemical processes are carried out in four stages:

1. Photolytic excitation.
2. Activation and displacement of oh groups.
3. Molecular displacement.
4. Fragmentation of the molecule.

The degradation process of phenol in the presence of UV radiation in the Ph+TiO_2 system is shown below (figure 3).

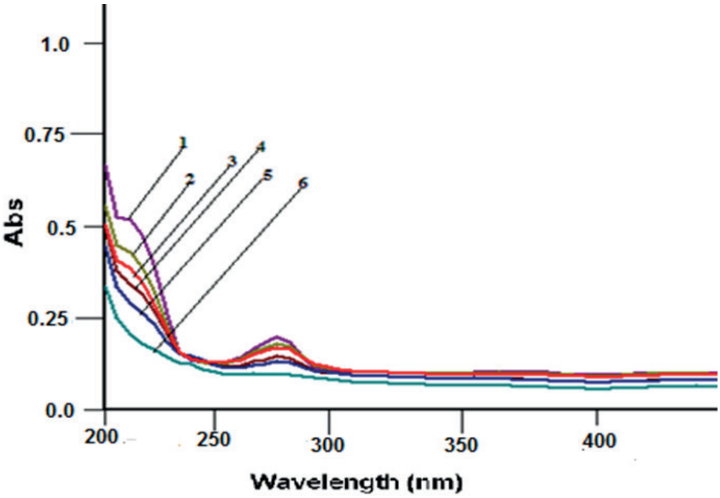

Figure 3. Photochemical decomposition of TiO_2+phenol in the presence of UV radiation

Comparison of UV radiation curves obtained during photolysis for TiO_2+phenol system: curve 1 - 10 min photolysis; curve 2 - 20 min photolysis; curve 3 - 30 min photolysis; curve 4 - 40 min photolysis; curve 5 - 50 min photolysis; curve 6 - 60 min photolysis.

As shown in figure 3, for the 1 mg/L phenol + TiO_2 system, the characteristic wavelengths of phenol (270 nm) are not observed in the last curve (curve 6) in contrast to the other curves. This is due to the absence or insufficient amount of phenol in the solution after photolysis. The sample was then analyzed in a gas chromatography mass detector for more sensitive and accurate analysis. The amount of phenol decreased from 1 mg to 10 µg. This means that 99 % of phenol is degraded.(17)

It can be noted that TiO_2 nanoparticles have very good photodissociation in combination with nitrogen atom. The point is that we considered it more convenient to use only the property of TiO_2 nanoparticles to be excited by ultraviolet radiation. Only 5 % of the nanoparticles are excited in the visible region. In the system where the reaction extends from the UV radiation range to 400-600 nm in the visible region, a photochemical reaction in the phenol + TiO_2 + nitrogen compound (Ph + TiO_2/N) was considered (figure 4). Photolysis in the phenol + TiO_2/N system was carried out in the UV region; the wavelength dependence of the absorption coefficient was determined on a Varian Cary 50 instrument. Then, the concentration of phenol remaining in solution after the photochemical reaction was determined.

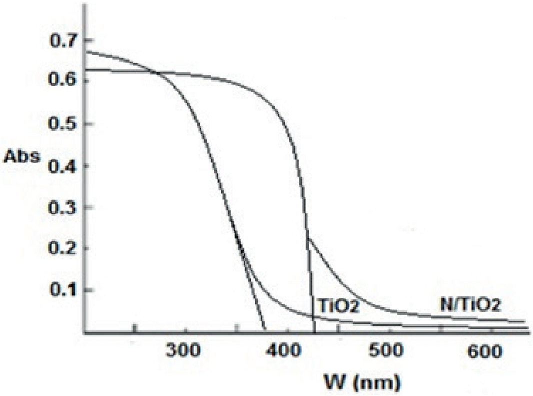

Figure 4. Wavelength dependence of absorption coefficient for phenol + TiO_2/N system For phenol + TiO_2/N system

Comparison of UV radiation curves obtained during photolysis for TiO_2+phenol and TiO_2/N+phenol systems:

1. Photolysis curve for TiO_2+phenol system.
2. Photolysis curve for TiO_2/N+phenol system.

As can be seen from figure 4, the photochemical decomposition of phenol in the presence of TiO_2 nanoparticles occurred in the UV region, i.e., in the region up to 400 nm (1). However, in the presence of N and TiO_2, the process extended from the UV region to the visible region between 400 and 600 nm (2).

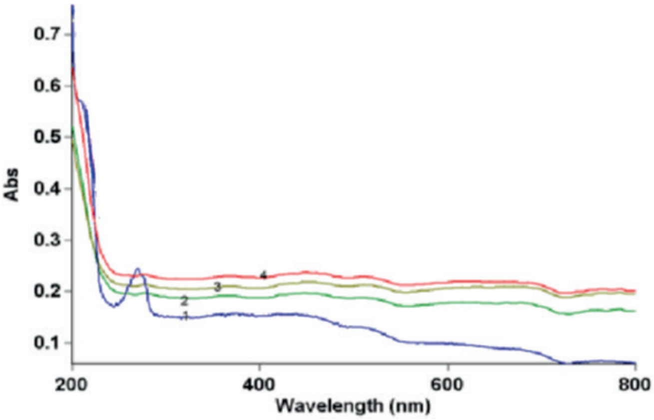

Figure 5. Photolysis for phenol+N/TiO2 system

1. Curve 1 - obtained before photolysis.

2. Curve 2 - obtained at 45 minutes of photolysis.
3. Curve 3 - obtained at 55 minutes of photolysis.
4. Curve 4 - obtained at 60 minutes of photolysis.

The light absorption for the phenol+TiO_2 system (1) is intense in the UV irradiation region up to 400 nm, while the light absorption of the phenol+N/TiO_2 system (2,3,4) covers the region after 400 nm. The transition from the UV region to the visible region occurs in the presence of N-containing material.

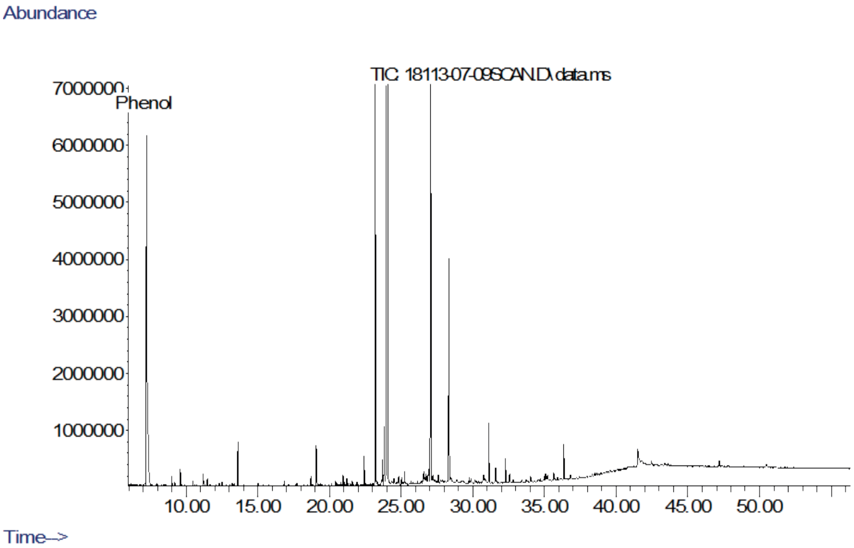

Figure 6. GC-MSD analysis of phenol+TiO_2 solution after photochemical decomposition

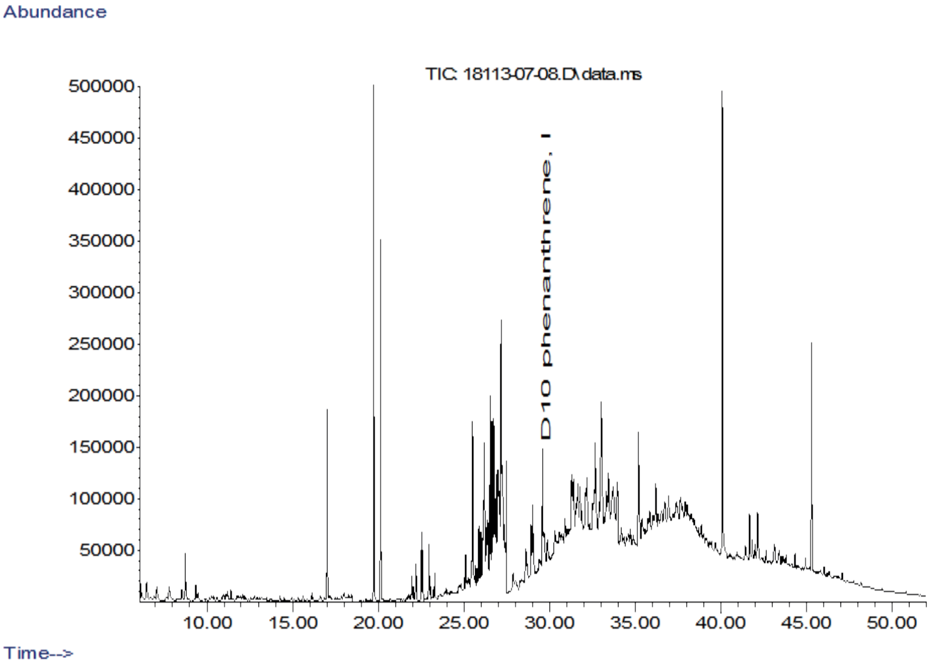

Figure 7. GC-MSD analysis of phenol+N/TiO_2 solution after photochemical decomposition

The adsorption process of phenol by TiO_2 nanoparticles was also studied. The process continued for 2 hours at room temperature. Long after the start of the process in the phenol+nanoTiO_2 mixture: characteristic peaks of phenol (270 nm) were observed in the curves of 30, 60, 90 and 120 minutes, indicating that adsorption does not occur in the presence of these nanoparticles.

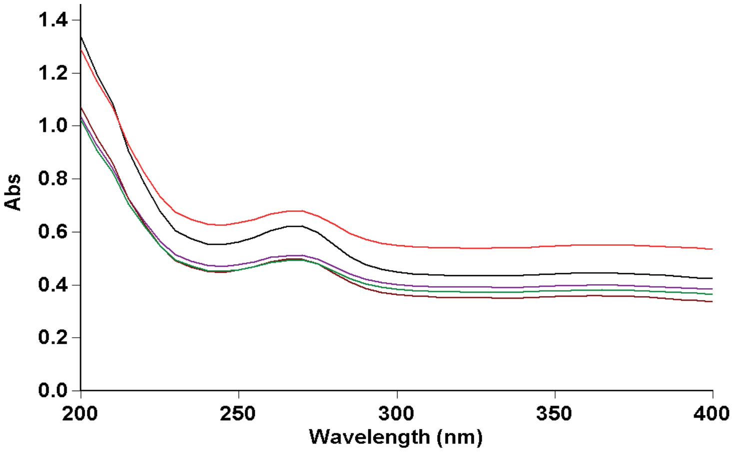

Figure 8. Comparison of curves obtained for phenol adsorption in the presence of TiO_2

Figure 8 shows the comparison of the curves obtained during the adsorption process (every 25 min). At this time, swelling was observed at the wavelength corresponding to phenol (240-270 nm) along the horizontal line.

CONCLUSIONS

1. This paper discusses the degradation of phenol in Ph+TiO_2 (1) and Ph+N/TiO_2 (2) systems.
2. In system (1), 99 % of degradation of phenol occurred under UV influence, whereas in the Ph+N/TiO_2 system (2), 60 % of degradation of phenol occurred.
3. The purpose of using a nitrogenous agent was to carry out a photochemical reaction in the visible and UV radiation region in the presence of TiO_2 nanoparticles. This increases the practical importance of the process.
4. The sizes of TiO_2 nanoparticles used ranged from 10 to 32 nm.
5. The degradation of 1 mg/l phenol was carried out in 1 hour. At the same time, the influence of the pH of the medium on the course of the reaction was determined. The process was monitored on a Varian Cary 50 spectrophotometer.
6. XRF and SEM analyses of TiO_2 nanoparticles were performed.
7. Quantitative analyses were performed using an Agilent 6980N/5975 GC-MSD.
8. The adsorption process of phenol by TiO_2 nanoparticles was studied.

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FINANCING

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CONFLICT OF INTEREST

None.

AUTHORSHIP CONTRIBUTION

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Data curation: Elmina Gadirova, S.R. Hajiyeva.
Formal analysis: Elmina Gadirova, S.R. Hajiyeva.
Drafting - original draft: Elmina Gadirova, S.R. Hajiyeva.
Writing - proofreading and editing: Elmina Gadirova, S.R. Hajiyeva.