



Photodegradation of Phenol Using N/TiO₂ System

N/TiO₂ Sistemi Kullanarak Fenolün Fotobozulması

Elmina Gadirova[®]

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

ABSTRACT

In the article the photochemical dissociation of phenol in the participation of TiO₂ nano-particles and methyl-3-aminocrotonate was done for the first time, the period was taken as 60 minutes, the processing of photochemical dissociation was verified by the curves drawn for reaction solution in the UV radiation device and the 60% decomposition of phenol was defined. Light absorption of a system with TiO₂ is observed only in the UV area, whereas absorption of a system with N/TiO₂ falls on the visible area of the spectrum.

Key Words

UV radiation, visible area, methyl-3-aminocrotonate, TiO₂ nano-particles.

Öz

Makalede ılımlı ortamda sentezlenen 10-30 nm boyutlarındaki TiO₂ nanopartikülleri ile 100 mg/ml NH₄OH varlığında fenolün fotokimyasal bozunması çalışılmıştır. Fotokimyasal bozunma sürecinden önce ve sonra çekilmiş "Varian" cihazında absorpsiyon verileri temelinde ispatlanmıştır. Fenolün UV-görülebilir bölgede fotokimyasal bozunması deneylerle doğrulanmıştır.

Anahtar Kelimeler

UV ışını, görünür bölge, metil-3-aminokrotonat, TiO₂ nano-partiküller.

Article History: Received: Feb 7, 2020; Revised: Sep 15, 2020; Accepted: Dec 22, 2020; Available Online: Jan 18, 2021.

DOI: <https://doi.org/10.15671/hjbc.686550>

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

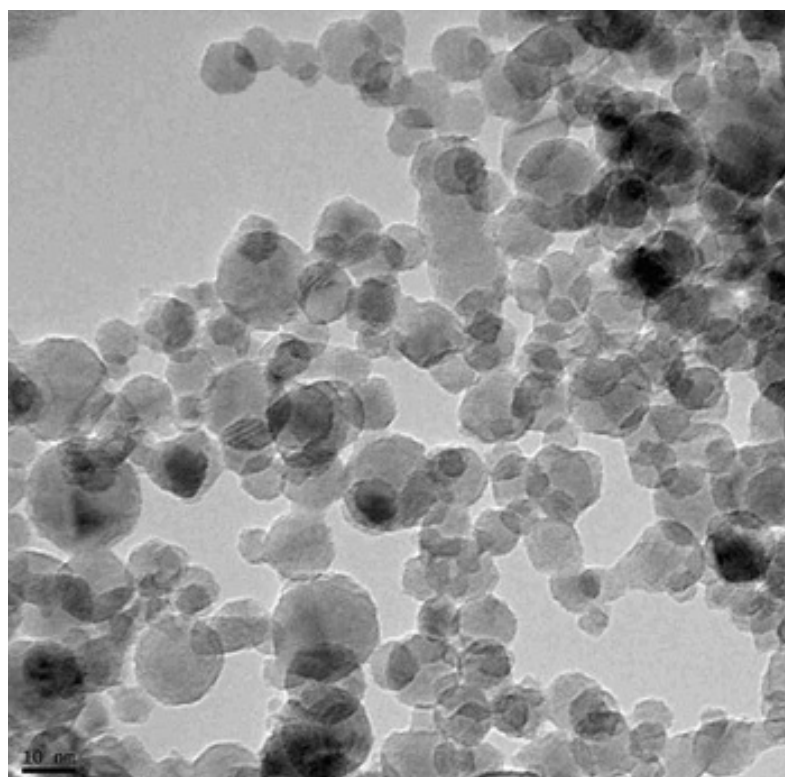
E-Mail: elmina2010@mail.ru

INTRODUCTION

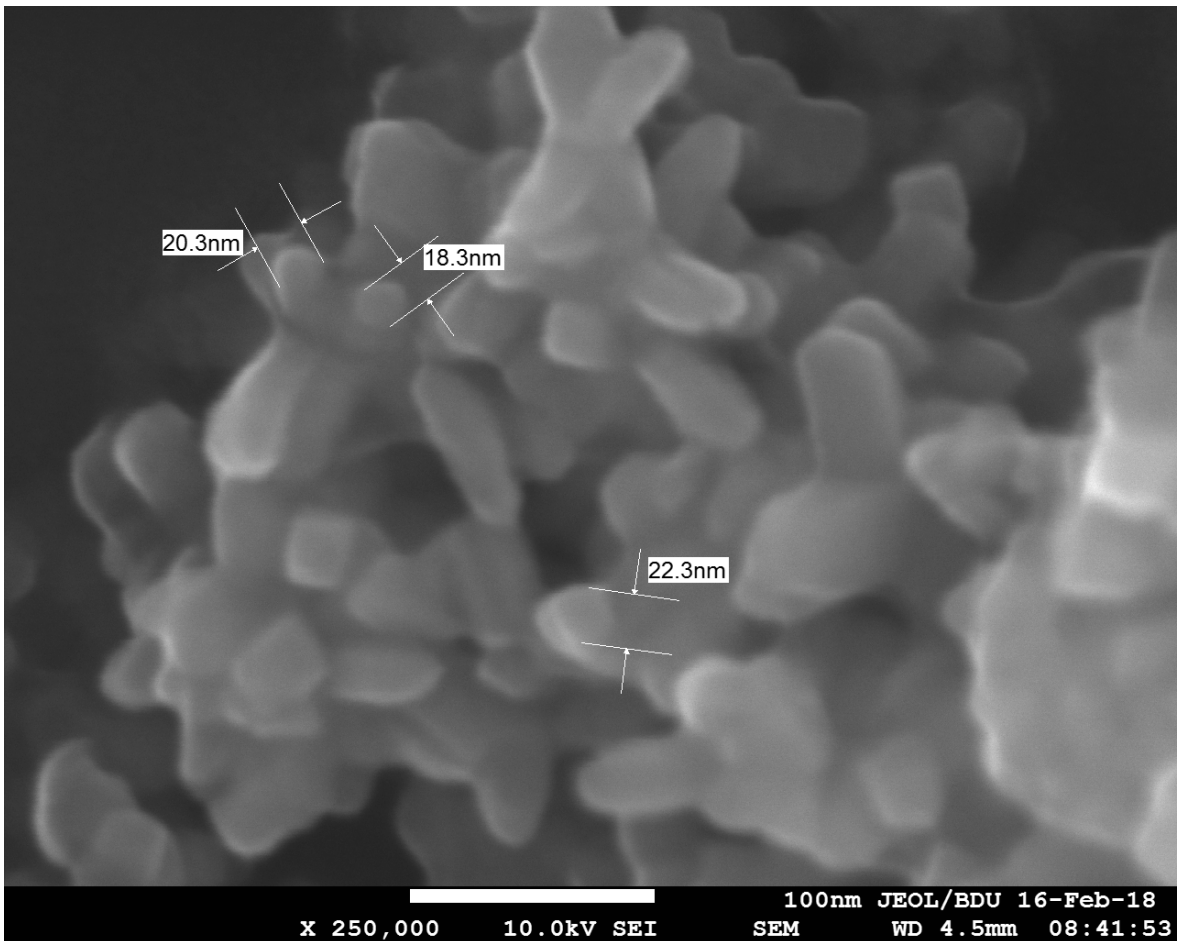
The contamination of water basins with high toxic organic substances is considered as global ecological issues recently and therefore the works done in the direction of the solution of this problem are very topical. In modern era heterogenic photocatalysis is considered one of the most effective processes in the environmental protection and treatment of waste waters from phenol-type combinations. Reduction in the fresh water reserve, growth in the amount of waste water is increasing the demand to the clean water or purified water. In this regard, different cleaning methods are proposed for dissociation of organic toxic substances from the waste water. As it is impossible to carry out complete treatment with the classic chemical, physical and biological methods in this case, recently the process of working out of new methods is going on [1-2]. In this direction the treatment of waste water was achieved by using nano-particles. In this regard, recently effective treatment methods by using nano-particles have got a wide scope.

By looking through the world literature, recently treatment methods by nano-composites are encountered very much: i.e. GO/Al₂O₃ nano-composite has been prepared with spin locking method for better treatment of phenol from waste water; at that time graphene oxide layer has been tightly covered with Al₂O₃ nano-particles, it was possible to treat phenol from waste water by 99.9% on the basis of this obtained composite [3]. There are also other references on the viewed works.

Phenol is always encountered in waste water as it is obtained from petroleum chemistry, medicine, plastics, coal production, and color and paper production. Generally, phenol is one of the most important contaminants because of high toxicity in the regard of its weak biological dissociation, being in high concentration and harmful influence to environment for a long time [4]. As it is noted, gradual reduction of clean water and increase of contamination are already among the significant ecological issues in the world. Currently, millions of people are suffering from the shortage of fresh water in the world. Totally, phenol, the most important of water contaminants leads to sig-



Picture 1. TEM appearance of TiO₂ nano-particles.

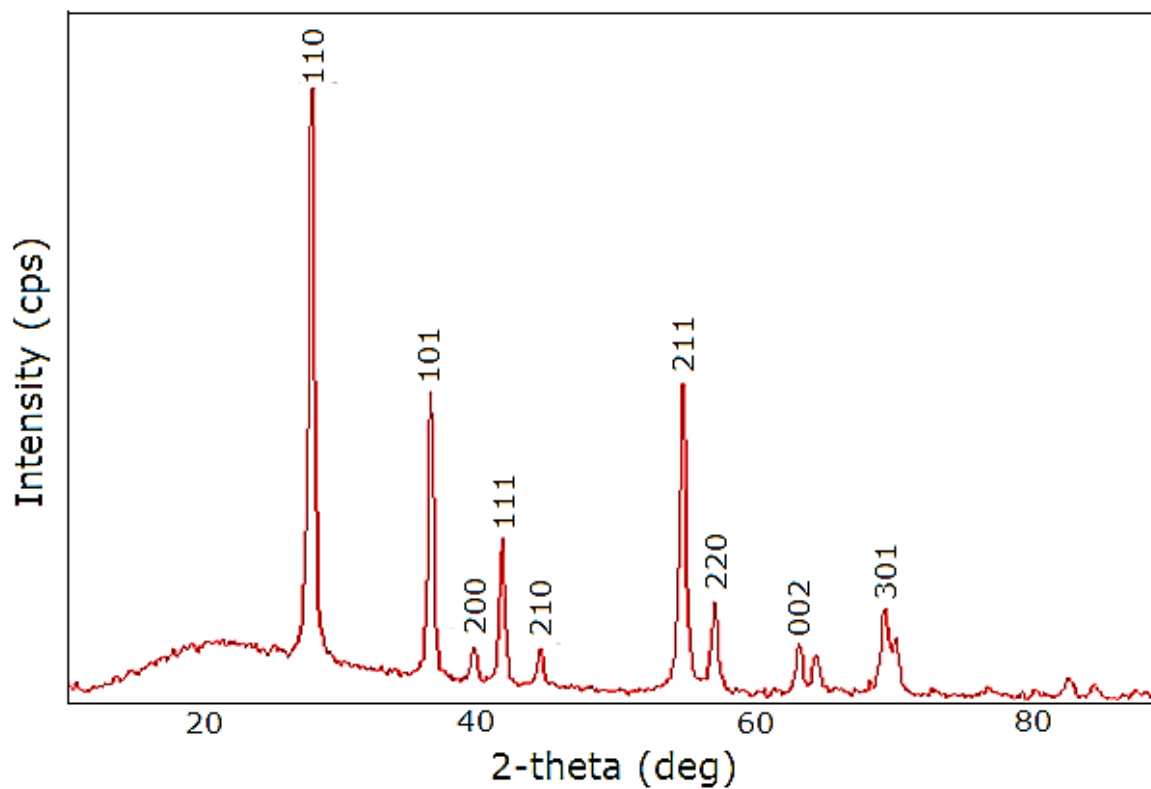


Picture 2. SEM of TiO₂ nano-particles.

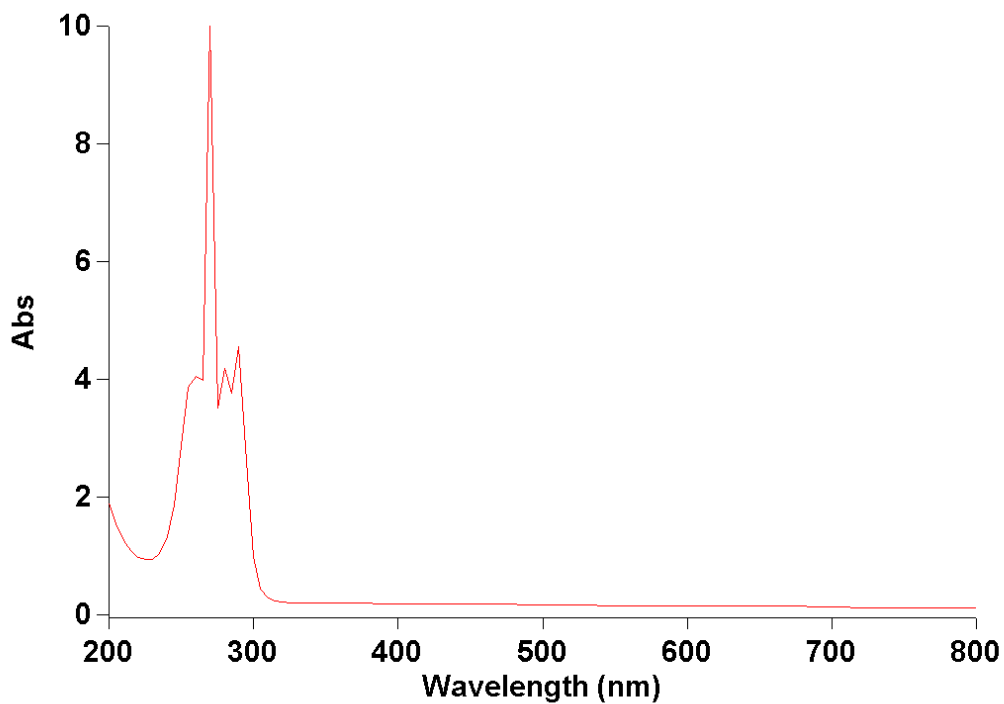
nificant ecological problems. So far many methods have been used for removal of phenol from waste water. Usage of physical, chemical and biological methods is less trendy today [5-6]. During the chemical processing intervening products are obtained so that they are also harmful for environment. Biological processing methods are less influencing for the acceleration of biological reactions, and in physical treatment absorption and membrane filtration methods are mainly used [7]. Membrane filtration is a unique method for treatment of water from contaminating substances, i.e.; currently, the method of membrane filtration is paid much attention as an effective process in the regard of ecology and energy effectiveness for the water treatment. However at this time dissociation of toxic substances in the composition of water requires other methods. Therefore, the subject of working out new methods does not lose its actuality.

EXPERIMENT and ANALYSIS OF THE RESULTS

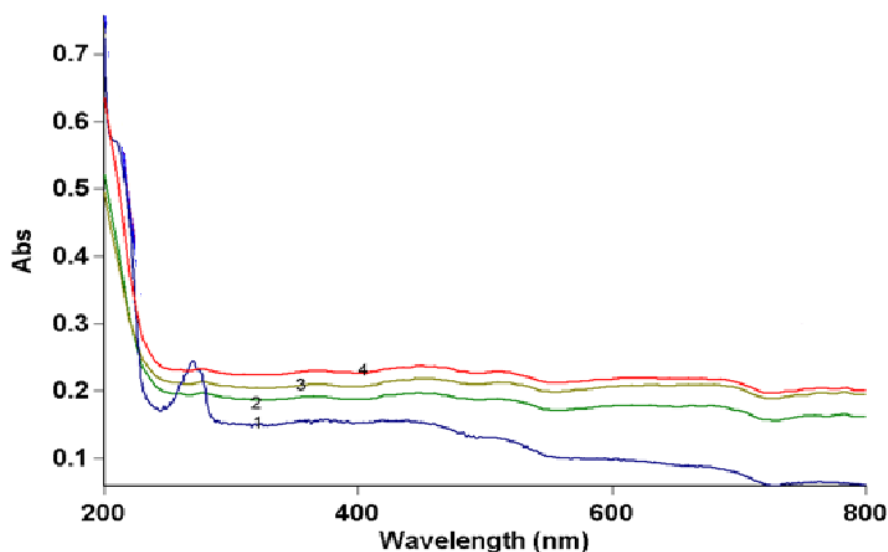
The works on the treatment of phenol from waste water in the participation of other composites with nano-particles are encountered in the world literature. It may be noted by referring the information that TiO₂ nano-particles has very good photo-dissociation together with combinations with N atom [8-9]. And why has namely the usage of TiO₂ been paid less? The matter is that we have considered more appropriate TiO₂ nano-particles as the works to be done by us have been carried out in the participation of UV radiation, since TiO₂ nano-particles gets excited only during UV radiation ($\lambda < 387 \text{ nm}$), it has only 5% excitement in the visible region. Furthermore, TiO₂ is chemically sustainable, it is obtained in soft condition, that's easily in the viewed case, and the most important is that it is considered ecologically clean [10-11].



Picture 3. XRD patterns of the TiO₂ nano-particles.



Graphic 1. UV radiation curve of phenol+methyl-3-aminocrotonate+TiO₂ solution before the radiation.



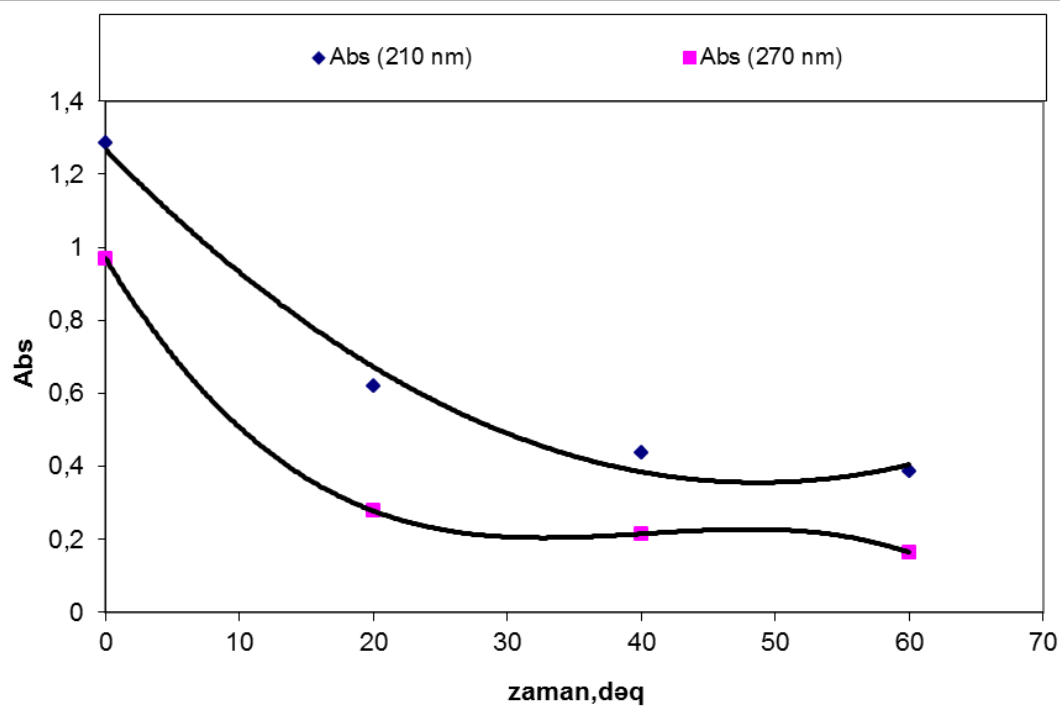
Garphic 2. The comparison of UV radiation curves obtained from the photolysis process.

The reaction of phenol dissociation through photochemical reactions by using TiO_2 nano-particles and methyl-3-aminocrotonate for the treatment of phenol from waste water has been carried out for the first time by us. For this purpose, it has been prepared the solution 0.05 g TiO_2 and methyl-3-aminocrotonate being in 0.05 g weight by being equally distributed in the distillation water of 10 ml. As it is mentioned above, TiO_2 nano-particles are not dangerous for environment, are considered ecologically clean in the regard of toxic and gets excited by UV radiation and serve to the processing of the reaction. Complete mixing of TiO_2 nano-particles in the participation of UV radiation has been carried out in advance for their equal distribution in the distillation water. 5 ml has been added to 20 ml 1 mg/l phenol solution (totally 25 ml) by being taken from the obtained solution and then 0.05 g methyl-3-aminocrotonate has been added. The viewed mixture has been subject to photochemical dissociation for 60 minutes. After photolysis process the dependence of the absorption coefficient of reaction solution on the wavelength has been drawn in UV radiation device. On the basis of the obtained curves the photolytic dissociation has been proved. The photolysis process has been done in UV radiation device; the dependence of absorption coefficient on the wavelength has been determined by "Varian" device, the concentration of phenol remained in the solution after photochemical reaction has been determined upon the degreed graphics. Photolytic dissociation has been 60%.

TiO_2 nano-particles preaped for the process has been determined by TEM method and the results has been given in Picture 1. As seen from Picture 2, the sizes of the obtained nano-particles are homogenous and vary between 10-30 nm, the results are according to the calculation with the Scherrer method. General surface area of nano-particles has consisted of 159.6 m^2/g . TEM results have been according to the analysis of XRD.

Picture 3 shows the XRD patterns of the synthesised TiO_2 nanoparticles. It can be seen that all the XRD peaks are well-defined and correspond to rutile phase TiO_2 . From the line broadening of the (101) diffraction peak by Scherrer's method, the average crystal size TiO_2 is about 10.3. The specific surface areas for TiO_2 is 159.6 m^2/g . In the pattern all lines can be indexed, using the ICDD (PDF-2/ Release 2011 RDB) DB card number 00-001-1292. The pattern of TiO_2 nanoparticles has characteristic peaks at 27.90° (110), 36.01° (101), 41.58(111), 54.71° (211) [12].

20 ml 1 mg/l phenol solution, 5 ml from the solution full equal disturbing 0.05 g TiO_2 nano-particles in it and 0,05 g methyl-3-aminocrotonate have been taken for using in the process.



Graphic 3. Diagram of reduction of the concentration of phenol in the solution in 20,40,60 minutes of UV radiation in the system of TiO₂+methyl-3-aminocrotonate+phenol3-aminocrotonate+phenolt.

Table 1. Abs coefficients of phenol depending on time.

Time, minute	Abs (210 nm)	Abs (270 nm)
0	1.285	0.969
20	0.619	0.278
40	0.438	0.215
60	0.387	0.164

In Graphic 1, it was given the dependence of absorption coefficient of the 5 ml solution with TiO_2 , 20 ml 1 mg/l phenol solution, methyl-3-aminocrotonate before the radiation on the wave length. It is clear from the graphic curve that the existence of curve in the 270 nm part which is characteristic for phenol in the solution is the evidence of the existence of the same substance.

In Graphic 2 it is given the comparison of the curves obtained during the photolysis process. It is seen from the graphic that the curves which are characteristic for phenol (270 nm) is reducing gradually so that it is the dissociation of the certain part of phenol in the process. Light absorption of a system with TiO_2 is observed only in the UV area, whereas absorption of a system with N/ TiO_2 falls on the visible area of the spectrum (after 400 nm).

According to the indicators of UV radiation device, Abs coefficient has been 0,164 nm in 60th minute for phenol. Upon this unit the concentration of phenol remained in the solution after photolysis has been calculated and has been 40% in the comparison with the initial concentration. Upon this it may be noted that dissociation has been 60%. This article has been directed to the solution of ecological problems for the environmental protection. So, the dissociation of toxic substances from contaminated water through nano-particles is considered one of the most important and topical issues. In the modern area the contamination of water basin is the most important of the global ecological problems. As the fresh water reserve is getting reduced, maximum working out of treatment methods of waste water and reducing the toxic substances to minimum are the most topical issues.

RESULTS

- The sizes of TiO_2 nano-particles are homogeneous and vary between 10-30 nm, the results are according to the calculations with Scherrer method.
- General surface area of nano-particles has consisted of 159.6 m²/g. TEM results coincide with the results obtained from the analysis of XRD.
- Dissociation of phenol in the participation of TiO_2 nano-particles and methyl-3-aminocrotonate has been 60%.

References

1. D. Gümüş and F. Akbal, Photocatalytic degradation of textile dye and wastewater, *Water, Air, and Soil Pollution*, 216 (2011) 117-124.
2. A. M. De Luis, J. I. Lombrana, A. Menendez, and J. Sanz, Analysis of the toxicity of phenol solutions treated with $\text{H}_2\text{O}_2/\text{UV}$ and $\text{H}_2\text{O}_2/\text{Fe}$ oxidative systems, *Industr. Engineer. Chem. Res.*, 50 (2011) 1928-1937.
3. H. Xuebing, Y. Yun, R. Shuang, L. Na, W. Yongqing, Z. Jianer, Highly efficient removal of phenol from aqueous solutions using graphene oxide/ Al_2O_3 composite membrane, *J. Porous Mater.*, 25 (2018) 719-726.
4. C. Santhosh, V. Velmurugan, G. Jacob, S.K. Jeong, A.N. Grace, A. Bhatnagar, Role of nanomaterials in water treatment applications: a review, *Chem. Eng. J.*, 306 (2016) 1116-1137.
5. F. Wang, Novel high performance magnetic activated carbon for phenol removal: equilibrium, kinetics and thermodynamics, *J. Porous Mater.*, 24 (2017) 1-9.
6. S. Mohammadi, A. Kargari, H. Sanaeepur, K. Abbassian, A. Najafi, E. Mofarrah, Phenol removal from industrial wastewaters: a short review, *Desalin. Water Treat.*, 53 (2015) 2215-2234.
7. S.N. Gosling, N.W. Arnell, A global assessment of the impact of climate change on water scarcity, *Clim. Change*, 134 (2016) 371-385.
8. D. Yue, X. Qian, Y. Zhao, Photocatalytic remediation of ionic pollutant, *Sci. Bullet.*, 60 (2015) 1791-1806.
9. X. Qiu and C. Burda, Chemically synthesized nitrogen-doped metal oxide nanoparticles, *Chem. Phys.*, 339 (2017) 1-10.
10. Y. Li, W. Cao, F. Ran, and X. Zhang, Photocatalytic degradation of methylene blue aqueous solution under visible light irradiation by using N-doped titanium dioxide, *Key Engineer. Mater.*, 336-338 (2007) 1972-1975.
11. A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C*, 1 (2000) 1-21.
12. E.M. Gadirova, Photochemical degradation of phenol in the presence of titanium dioxide nanoparticles, *Proceedings of Universities, Appl. Chem. Biotechnol.*, 9 (2019) 176-182.