Advances in Biology & Earth Sciences
Vol.8, No.1, 2023, pp.36-43

ECOLOGICALLY IMPORTANT PHOTOCHEMICAL REACTIONS

S.R. Hajiyeva, E.M. Gadirova*, U.N. Rustamova, H.F. Hajiyeva

Baku State University, Baku, Azerbaijan

Abstract. TiO_2 nanoparticles have been investigated to carry out photochemical reactions. TiO_2 nanoparticles (10-32 nm) were used for the first time to purify phenol from seawater.Investigation of the TiO_2 nanoparticles has been proven using SEM and XRD analysis. For this purpose water samples were taken from Shikh and Boulevard for analysis. The Khazar Ecological Laboratory analyzed water samples and all quantitative analyses were performed using Agilent 6890N/5975 GC/MSD. 15 compounds of polycyclic aromatic hydrocarbons (PAHs) and 11 compounds of phenolic compounds have been identified. In the water samples, the permissible concentrations of organic toxic compounds were exceeded. Also, physical and chemical indicators were determined for water samples taken from Shikh and Boulevard.

Keywords: *PAHs, TiO_2, SEM, XRD, organic compounds, analysis, seawater.*

Corresponding Author: *E.M. Gadirova, Baku State University, Z. Khalilov 23, Baku, Azerbaijan, e-mail: elmina2010@mail.ru*

Received*: 18 October 2022;* ***Accepted****: 13 February 2023;* ***Published****: 18 April 2023.*

1. Introduction

Organic compounds such as polycyclic aromatic hydrocarbons (PAHs) are a global environmental concern as they cause inflammation and skin cancer. There are two types of anthropogenic sources of hydrocarbons: petrogenic and pyrogenic sources. Petrogenic sources include crude oil and petroleum-derived hydrocarbon compounds. Pyrogenic sources of hydrocarbon compounds are formed as a result of the incomplete combustion of organic substances such as oil, wood, coal, etc.

The Caspian Sea is a very sensitive ecosystem. Over the past decades under the influence of anthropogenic and biochemical factors, the state of ecosystems,in general,has deteriorated sharply and especially in the northeastern part of the sea. Observations of recent years show that the waters of the Caspian Sea especially along the coast of the National Park are also polluted by oil and sewage. Industrialization and urbanization in the Caspian region have developed rapidly over the past several decades and the associated increase in hydrocarbons is a concern in the region (Hajiyeva *et.al*, 2020).

Offshore production and accidental oil spills, industrial wastes, wastewater, and discharges flowing down from river water are considered the main source of anthropogenic hydrocarbons in the marine environment.The industry is believed to be the main source of oil pollution in the Caspian Sea. The total amount of industrial waste discharged into the Caspian Sea averages 2342.0 million m^3 per year. Such waters

How to cite (APA):
Hajiyeva, S.R., Gadirova, E.M., Rustamova, U.N., & Hajiyeva, H.F. (2023). Ecologically important photochemical reactions. *Advances in Biology & Earth Sciences*, *8*(1), 36-43.

contain 122.5 thousand tons of oil, 1.1 thousand tons of phenols, and 9.9 thousand tons of organic chemistry products. The total content of hydrocarbons in the North-Western part of the South Caspian was small 32-54.2 $\mu g g^{-1}$. Water and bottom sediments are polluted throughout the Absheron Peninsula and in Baku. The main volume of pollution (total 90%) enters the Caspian Sea with river runoff (Mohammadi *et al*., 2019). Sources of pollution of seawater with toxic organic compounds are known. However, it is very important to take serious measures to prevent them (Gosling *et al*., 2016). Because both PAHs and phenolic compounds are very dangerous for the flora and fauna of the aquatic ecosystem (Hajiyeva *et al.*, 2019).

2. Experımental

It is known from the literature that according to the latest indicators,every year 6 mln tons of oil and oil products are discharged into the world's ocean. Pyrogen and petrogenic pollution of seawater contamination with ballast water, and so on cause pollution of common water basins. These hydrosphere segments are a dynamic system that leads to a decrease and depletion of freshwater supplies over time (Hajiyeva *et al.*, 2014).

Water samples were taken from the two fields with the "12 L Niskin" sample taker for analysis at depths of 0.5 m from the sea level at the Shikh and Boulevard areas. Chromatographic analyzes were carried out by the gas chromatograph detector with a flame-ionizing GC-FID 6890 (Agilent, USA) equipped with a ZB-1 (Phenomenex, USA) device. Helium was also used as a gas bearing in the analysis (Chen *et al*., 2019). Identification of organic toxic substances in sea waters taken from the Shikh and Boulevard areas was carried out with the support of the Hazar Ecology Laboratory. In the end 15 PAHs also 11 phenolic compounds were analyzed in the water samples.

The first time, in the presence of TiO_2 nanoparticles photochemical degradation of phenol in the seawater samples (20ml) under UV radiation was carried out for 1 hour. The spectra of water samples were taken before and after the photochemical process on a Varian Cary 50 spectrophotometer. When comparing the spectra dissociation of phenol is observed in the presence of 0.05 g of TiO_2 nanoparticles (Gadirova, 2019).

3. Results and dıscussıon

The amount of PAHs in the analyzed water samples is shown in Table 1 below. So the amounts obtained for PAHs were in many cases higher than the norm.

Table 1. Amount of the PAHs in the water samples taken from Shikh and Boulevard

PAHs, $\mu g L^{-1}$ $\mu g L^{-1}$ = $mkg L^{-1}$(or 0.001$g L^{-1}$)	**Shikh**	**Boulevard**
Naphthalene	0.07	0.04
Acenthylene	<0.01	<0.01
Acenaften	0.01	0.05
Fluoren	0.04	0.07
Fenantren	0.06	0.17
Anthracene	0.01	0.01

Fluoranten	<0.01	0.01
Piren	<0.01	0.01
Benz (a) anthracene	<0.01	0.00
Chrizsen	<0.01	0.01
Benz (b + j + k) fluorantene	0.03	0.03
Benz (a) pyrene	<0.01	0.01
Inden (1,2,3-cd) pyrene	<0.03	<0.03
Benzo (ghi) perylene	<0.01	<0.01
Dibenz (ah) anthracene	<0.01	<0.01

It should be noted that the standard value for PAHs is 0.01 μgL^{-1}. Table 1 shows that some PAHs are too much in aqueous samples. This naphthalene is the most dangerous. Thus, the amount of naphthalene in the water sample taken from Shikh was greater than in the water sample taken from Boulevard however in both cases the permissible limit was exceeded. Acenaphthene, fluorine and phenanthrene were above the water test taken from the Boulevard.

Based on the analysis 15 PAHs were appointed and according to the results the amount of naphthalene which is very dangerous in the sample of seawater extracted from Shikh was approximately twice more than, in water sample taken from Boulevard (Kochana *et al*., 2012). In general, a large amount of naphthalene can affect erythrocytes in people and even destroy them. By the International Cancer Research Society (CRS) naphthalene is classified as a substance that causes cancer in humans and animals. According to scientists, naphthalene is in first place among toxic substances even in the first place. From this point of view it is called a "chemical substance that causes death".This substance penetrates the lungs through the respiratory system and makes a carcinogenic effect.Fluorene is a toxic organic substance but no carcinogenic properties such as naphthalene have been detected.Phenanthrene is a polycyclic aromatic carbohydrogen consisting of a combination of three benzene rings. It is found in cigarette smoke purely and has irritating properties that make the skin sensitive to light. Phenanthrene appears as a blue fluorescent white powder.According to research in America, the first discovered substance was phenanthrene in investigating substances that cause genetic exposure to smokers. This toxic substance creates mutations that cause cancer.The results in the table show that the amount of polycyclic aromatic hydrocarbons (PAHs)in sea water received from Shikh has been very high.Both pyrogenic and petrogenic pollutants play a major role here (Khan *et al*., 2022).

Phenol and its derivatives such as PAHs are considered hazardous to aquatic ecosystems. Lethal effects occur when the concentration of phenol is already 1 gL^{-1} and at a concentration of less than 0.5 gL^{-1} there is practically no harmful effect but at a phenol concentration of 0.2mgL^{-1} waters have already an unpleasant taste. The amount of phenolic compounds in the analyzed water samples is shown in Table 2.

Table 2 shows the results of the analysis of phenol compounds in two sea water samples. It should be noted that phenolic compounds are considered hazardous to the aquatic ecosystem if they exceed 0.01 mgL^{-1} in sea water (in drinking water 0.001 mgL^{-1}). Chlorinated phenol derivatives are more dangerous than phenol. They have a pungent odor. Even with the chlorination of phenol derivatives at a concentration of 0.001 mgL^{-1} such sea waters have a negative effect. Too much phenol in water is

damaging to living things. It causes serious illness in aquatic life and through the food chain poses a threat to human health (Khan *et.al.*, 2021) .

Table 2 shows that the amount of phenol was more in the Boulevard. This can be explained by the strong contamination of the Baku Bay. Other substances did not exceed the norm.

Table 2. Amount of the phenolic compounds in the water samples taken from Shikh and Boulevard

Phenol and its derivatives, μgL^{-1} μgL^{-1}= mkgL^{-1}(or 0.001gL^{-1})	**Shikh**	**Boulevard**
phenol	0.10	0.14
o-kresol	0.02	0.03
2-nitrophenol	<0.04	0.04
2,4-dimethylphenol	0.02	0.04
2,4-dichlorophenol	<0.02	<0.02
2,6-dichlorphenol	0.02	0.04
4-chloro-3-methylphenol	<0.04	0.05
2,4,5-trichlorphenol	<0.04	<0.04
2,4,6-trichlorphenol	<0.04	<0.04
2,3,4,6-tetrachlorophenol	<0.04	<0.04
pentachlorphenol	<0.04	<0.14

There was more phenol in the water sample taken from the Boulevard than in the Shikh.In fact, the standard amount should be 0.04 μgL^{-1} but amounts are higher for phenol in water samples taken from Sikh and Boulevard.

It should be noted that the content of toxic organic compounds in the samples of water selected in both districts was above the norm. Other analyzes were performed on analyzed water samples of the Shikh and Boulevard.

Table 3. Physical-chemical parameters of the water samples

Areas	tem. ^{o}C	pH	salinity, %	Electrical conductivity, mS/sm
Shik	26.2	8.1	11.2	18.6
Boulevard	26.4	8.2	11.0	18.8

Although the physicochemical parameters in the considered samples of seawater are normal the pollution with toxic substances of organic origin has exceeded the norm.

It is known from the literature that TiO_2 nanoparticles are used in wastewater treatment (Yan *et.al*., 2015; Gadirova, 2022). To this end we have carried out research

in this area. The use of TiO_2 nanoparticles for purifying phenol from seawater samples was also considered.

First time TiO_2 nanoparticles of the rutile phase were used for the purification of water from phenol which is a very serious toxicant for aquatic ecosystems (Santhosh, 2016). It is known that TiO_2 nanoparticles have the ability to decompose phenol from water contaminated with phenol under the action of UV radiation. Using this method the decomposition of phenol under the action of UV irradiation of the studied water samples for 1 hour was studied. Nanoparticles of TiO_2 had a rutile phase and the size of the nanoparticles ranged from 10 to 32 nm. Scanning Electron Microscopy(SEM) analysis of the TiO_2 nanoparticles is shown below.

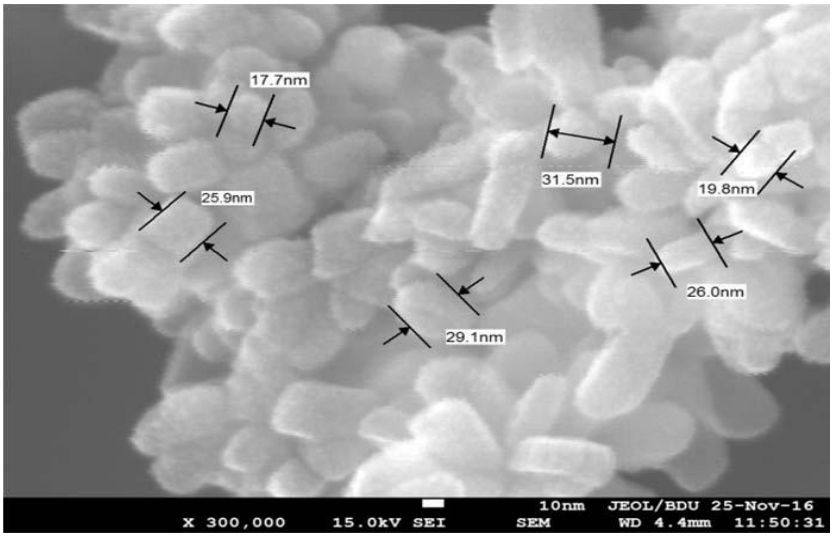

Fig.1. Scanning Electron Microscopy (SEM) analysis of the TiO_2 nanoparticles

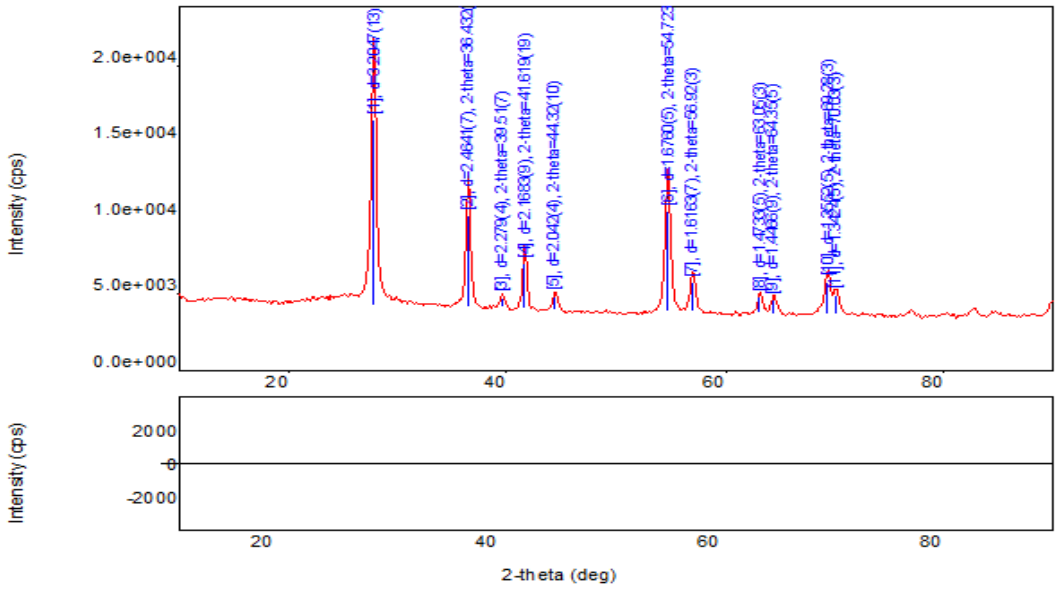

Fig. 2. XRD analysis of the TiO_2 nanoparticles

The purity and crystalline properties of the TiO_2 nanoparticles were investigated using the powder XRD method. Figure 2 shows the XRD patterns of the TiO_2 nanoparticles.X-ray tube with copper anode (Cu_{Ka} radiation, 30 kV and mA) was used to draw the diffraction spectrum at room temperature. At $2\theta = 20°\text{-}80°$ with discrete growth mode these spectrums were obtained as $\Delta 2\theta = 0.05°$and the exposure time was $\tau = 5$ seconds (Gadirova *et al*., 2021).

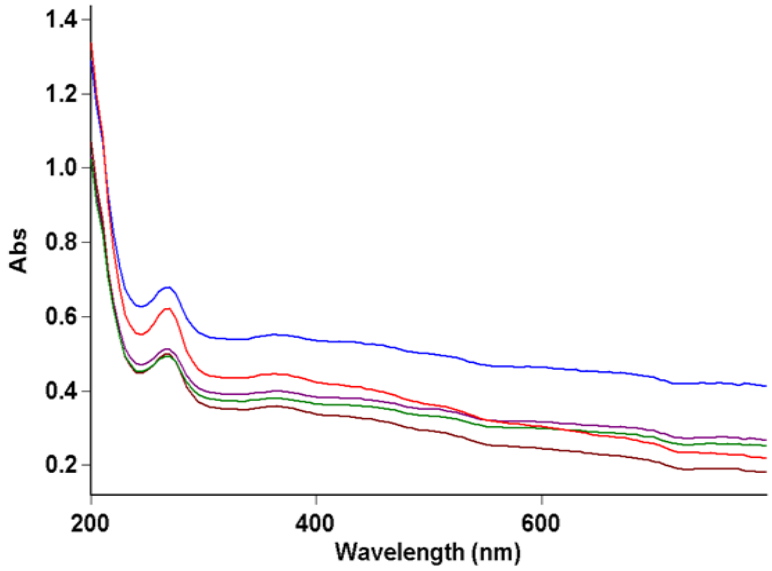

Fig.3. Curves after the photochemical decomposition process

Photochemical decomposition of phenol in wastewater with the participation of TiO_2 nanoparticles was carried out and scientific results were obtained. Since the amount of phenol in the seawater samples taken at the Shikh and Boulevard sites is close(0.10 μgL^{-1} and 0.14 μgL^{-1})the degradation of phenol under UV radiation was considered only in one of the seawater samples (Shikh).In this case, partial decomposition of phenol was observed after photolysis on a spectrophotometer.In this case, partial decomposition of phenol was observed from the difference in the curves drawn after photolysis on a spectrophotometer (Fig.3). After the photochemical process signals were obtained corresponding to phenol at 270 nm.This indicates that the phenol is not completely photolyzed. There can be many reasons for this: firstly sea water is multi-component and in order for a full-fledged photochemical process to take place, it is necessary either to take a large number of nanoparticles or to reduce the viscosity of water, because the effect of TiO_2 nanoparticles in liquid solutions is greater. This fact was also confirmed on the basis of analysis by the Agilent 6890N/5975 GC-MSD method. At the same time 60% (0.06 μgL^{-1}**)** of phenol remained in the solution which means that 40% (0.04 μgL^{-1}**)** of the decomposition was gone.

The following are the chromatographic curves of the sample after the photolysis process (Fig.4).

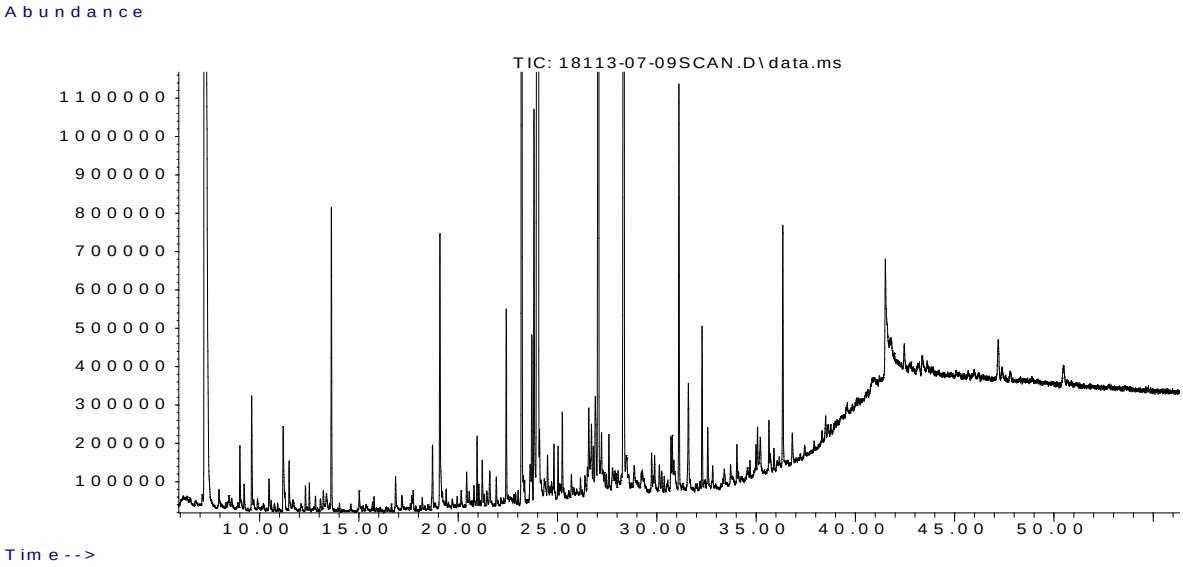

Fig.4. General view of the analysis by the GC-MSD method

4. Conclusıon

TiO_2 nanoparticles were studied by SEM and XRD. The use of TiO_2 nanoparticles(10-32nm) for purifying phenol from sea water samples is considered. From Shikh and Boulevard areas water samples were taken and analyzed. In the water samples 15 PAHs,11 phenol,and its derivatives were analyzed.In the water samples permissible concentrations of organic toxic compounds were exceeded. So as the amount of naphthalene in the water sample taken from Shikh was greater than in the water sample taken from Boulevard. From PAHs acenaphthene, fluorine and phenanthrene were above the water test taken from the Boulevard. There was more phenol in the water sample taken from the Boulevard than in the Shikh.Quantitative analyzes were performed by the Agilent 6890N/5975 GC-MSD method.Degradation of phenol under UV radiation was 40%. Also was determined physical-chemical parameters of the water samples taken from Shikh and Boulevard.

Recently, the purification of aquatic ecosystems using nanotechnological methods is one of the most important issues from an environmental point of view. Research in this direction will be continued in the future.

References

Chen, C. F., Ju, Y. R., Lim, Y. C., Hsieh, S. L., Tsai, M. L., Sun, P. P., ... & Dong, C. D. (2019). Determination of polycyclic aromatic hydrocarbons in sludge from water and wastewater treatment plants by GC-MS. *International Journal of Environmental Research and Public Health*, *16*(14), 2604.

Gadirova, E.M. (2019). Photochemical degradation of phenol in the presence of titanium dioxide nanoparticles. *Proceedings of Universities. Applied chemistry and Biotechnology*, *9*(2), 176-182.

Gadirova, E.M., Hajiyeva, S.R., Sujayev, A.A. (2021). Investigation of photocatalytic properties of TiO_2 nanoparticles belonging to rutile phase. *Journal of Molecular Structure*, *1227*(11), 129534.

Gadirova, E.M. (2022). Research of wastewaters from the Oil Refinery, 2022, *PPOR, 23*(1), 46-54.

Gosling, S.N., Arnell, N.W. (2016). A global assessment of the impact of climate change on water scarcity. *Climatic Change*, 134, 371-385.

Hajiyeva, S., Gadirova, E., Ozdemir, O., Demirak, A. (2019). Determination of phenol in wastewater. *3th International UNIDOKAP Black Sea Symposium*, Turkey, Tokat, 21-23 June, 48-53.

Hajiyeva, S.R., Gadirova, E.M., etc. (2014). Methods for cleaning water contaminated with oil. *Chemistry Journal of Azerbaijan*, 1, 35-38.

Hajiyeva, S.R., Gadirova, E.M. (2020). Monitoring of the petrogenically polluted territories. *Belarus, E3S Web of Conferences ICBTE*, 01006, p.212.

Kochana, J., Adamski, J., & Parczewski, A. (2012). A critical view on the phenol index as a measure of phenol compounds content in waters. Application of a biosensor. *Ecological Chemistry and Engineering S*, *19*(3), 383-391.

Zadeh, C.M., Saify, A., & Shalikar, H. (2010). Polycyclic aromatic hydrocarbons (PAHs) along the eastern Caspian Sea coast. *Glob. Environ. Res.*, *4*, 59-63.

Santhosh, C., Velmurugan, V., Jacob, G., Jeong, S. K., Grace, A. N., & Bhatnagar, A. (2016). Role of nanomaterials in water treatment applications: a review. *Chemical Engineering Journal*, 306, 1116-1137.

Khan, S., Naushad, M., Govarthanan, M., Iqbal, J., & Alfadul, S.M. (2022). Emerging contaminants of high concern for the environment: Current trends and future research. *Environmental Research*, 207, 112609.

Khan, S., Naushad, M., Al-Gheethi, A., & Iqbal, J. (2021). Engineered nanoparticles for removal of pollutants from wastewater: Current status and future prospects of nanotechnology for remediation strategies. *Journal of Environmental Chemical Engineering*, *9*(5), 106160.

Yan, H., Wu, H., Li, K., Wang, Y., Tao, X., Yang, H., ... & Cheng, R. (2015). Influence of the surface structure of graphene oxide on the adsorption of aromatic organic compounds from water. *ACS Applied Materials & Interfaces*, 7(12), 6690-6697.