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COMPARED THE EFFICIENCY OF TiO_2 AND N-DOPED TiO_2 TO DEGRADE BTEX

S.A. Hasanova*

Department of Ecology, Azerbaijan University of Architecture and Construction, Baku, Azerbaijan

Abstract. The point of this research is to define the effectiveness of the degradation of BTEX from wastewaters under irradiation with ultraviolet (UV) and visible light (VIS). The photocatalyst used for this article is TiO_2 nanopowder by company Sigma Aldrich. N-Doping was prepared from 20% of diethyl amine solution was achieved by using 97% diethyl amine solution. The processes were carried out of temperature 293-323 K, irradiation time (0-360 min.) initial pH 2-12, dose of catalysts 0.1-2 mg/L. The powder was analyzed with X-ray diffraction (XRD) and was determined that this composed of anatase crystallite. The results showed that the photocatalytic degradation best effect for N-Doping samples, achieving 91.6% of UV degradation.

Keywords: *Advanced oxidation process, photocatalysis, BTEX, TiO_2, N-Doped TiO_2.*

Corresponding Author: *S.A. Hasanova, Department of Ecology, Azerbaijan University of Architecture and Construction, AZ-1073, Baku, Azerbaijan, e-mail: seynure.ibrahimova@gmail.com*

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1. Introduction

The precept of adsorption and the potential of sure strong substances to do away with dissolved materials from water have lengthy been known. For approximately a hundred years, the adsorption era has been used to a broader volume for water treatment, and for the duration of this time, it has now no longer misplaced its relevance. On the contrary, new utility fields, except the traditional utility in consuming water treatment, had been introduced in latest a long time, which include groundwater remediation or more advantageous wastewater treatment (Worch, 2012). This method is called superior oxidation method and is appropriate for the oxidation of a huge variety of natural compounds. Among AOPs, heterogeneous photocatalysis had been verified to be of hobby because of its performance in degrading recalcitrant natural compounds. Developed with inside the 1970s, heterogeneous photocatalytic oxidation has been given big interest and with inside the beyond a long-time research had been accomplished at the utility of heterogeneous photocatalytic oxidation method to be able to decompose and mineralize recalcitrant natural compounds. Heterogenous photocatalysis (HPC) has become the most distinctive, popular, effective and promising treatment technique for the removal of recalcitrant contaminants, such as organic pollutants, in wastewater (Juan C. García-Prieto *et al.,* 2022) Several semiconductors (TiO_2, ZnO, Fe_2O_3, CdS, ZnS) can act as photocatalysts but TiO_2 is the most commonly studied due to its ability to degrade organic pollutants. Apart from TiO_2, ZnO is one material that has been heavily explored for photocatalysis. The greatest advantage of ZnO is that absorbs a large fraction of the solar spectrum and has higher quanta of light than TiO_2 (Kundan & Anirban, 2018*).* The photocatalytic and hydrophilic properties of TiO_2 make it close to an ideal catalyst due to

its high reactivity, reduced toxicity, chemical stability and reduced costs (Gaya & Abdullah, 2008; Fujishima *et al*., 2000).

The key to these successes is the use of nanosized TiO_2 photocatalyst powders dispersed on a substrate with an extremely large surface areas and spread over the ground capture sunlight. The concentration of environmental pollutants is general low, the UV light contained in sunlight in sufficiently strong to decompose them by TiO_2 photocatalysis, if we can collect the light from a broad area (Ibrahimova, 2015,).

BTEX is an acronym that stands for Benzene, Toluene, Ethylbenzene and Xylenes. These compounds are volatile organic compounds (VOCs) that are found in petroleum and petroleum products such as gasoline (Julien *et al*., 2018). Application of advanced oxidation processes (AOPs) appears to be an effective way of treating contaminated groundwater. Titanium dioxide (TiO_2) is a photocatalyst, providing heterogeneous photocatalysis in the presence of semiconductor that can decompose organic substances in aqueous solution, generating hydroxyl radicals and superoxide under ultraviolet radiation (Fujishima *et al*., 2000).

In this study, Titanium Dioxide (TiO_2) nanoparticles (NPs) and N-Doped TiO_2 were tested for the decomposition of aromatic hydrocarbons on produce water samples. Some process parameters such as pH and irradiation time were optimized. The experiments the degradation efficiencies of remediation methods were scrutinized on the treatment of real polluted of Garadagh.

2. Material and methods

2.1. Reagent and chemicals

All chemicals were purchased from Sigma Aldrich with 98-99.5% purity (Germany), expect hydrogen peroxide which had a purity level of 30% v/v. NaOH (1M) and H_2SO_4 (1M) from Sigma Aldrich with 95-97% purity (Germany) were used to adjust pH values (3.5, 7.0 and 10.5). TiO_2 NPs (Aeroxide P25, ≥99.5 % purity) were supplied by Sigma Aldrich (Germany). According to the company, the TiO_2 particle size was expected to be 21 nm and its specific surface area was 50±15 m^2/g.

All Photocatalyst experiments were conducted in a 0.5 L vessel reactor. The images of setup were prepared by using 3DMax that were shown in (Fig. 1).

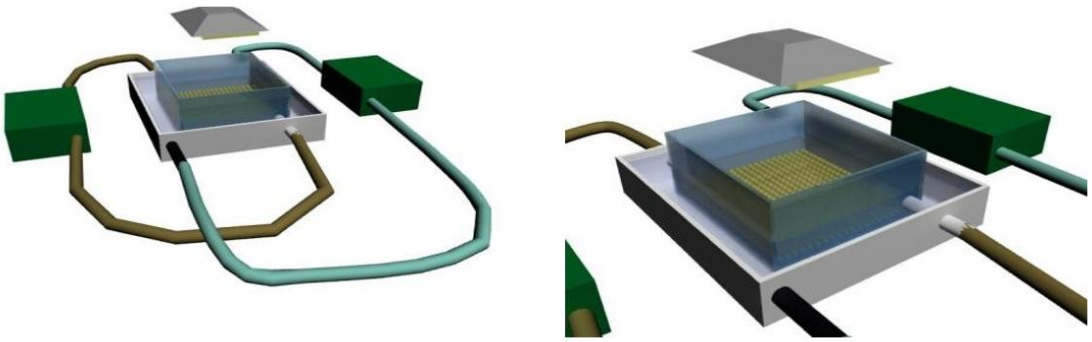

Fig. 1. The images of the setup

The image does not include a vessel, 500 ml in capacity, positioned in a cooled bath along the recycling circuit. This arrangement is required to stabilize at 30-35 °C the temperature of solution submitted to the treatment, in order to remove the heat released

by the lamp to the liquid in reaction vessel. An UV lamp of 125 W medium-pressure and 160 W visible lamp was placed on the above. The above-mentioned UV lamp was put over the rector vessel 10 cm far from the liquid layer.

The setup includes 2 peristaltic pumps, 1 vessel and lamp. One of the pumps was worked for agitation of wastewater in the reaction vessel and the other one was worked for to recirculate of cooling water.

2.2. Preparation of N-Doped TiO_2

TiO_2 NPs were added into a glass beaker then beaker was put into a cold water bath and hydrogen peroxide 30% was added drop by drop. This process was really important because adding hydrogen peroxide faster caused turning the gel fastly. The color of the sol gel was orange and the solution appeared transparent.

After Sol- Gel was synthesized, the next step was the doping process. For this process firstly, 20% of diethyl amine solution was prepared by using 97% diethyl amine solution. The reaction was exothermic, that's why 20% of diethyl amine solution was added into Solution A poured drop wises into the cold-water bath. Color of the solution changed from orange to the yellowish. We let the solution under a magnetic stirrer for 2 hours, so that Solution B was ready (Ibrahimova *et al.*, 2016; Sajid *et al.*, 2016)

2.3. Experimental procedure

2.3.1. Transmission electron microscopy (TEM)

The images given by TEM are reported in Fig. 2: the normal size of the nanoparticles is about 21 nm and agrees with the features included in the product card present in Evonik database. The specific surface area is about 50±15 m^2/g.

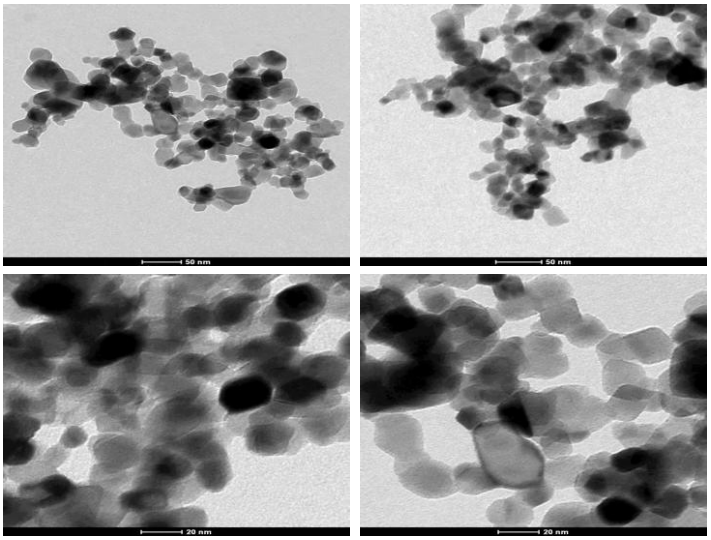

Fig. 2. TEM images of TiO_2 P25

2.3.2. X-Ray Diffractometer (XRD)

The composition of TiO_2 and also the ratio between anatase and rutile is evaluated with XRD: it's well-known that P25 consists of anatase and rutile crystallites, but it seems that no-one knows the precise crystalline composition, presumably thanks to a

scarcity of methodology for determination of crystalline contents in nanometer-sized particulate samples (Ohtani *et al*., 2010).

In Fig. 3 and in Table 1 the diffractogram and the main peaks are reported. Blu line is that the diffractogram of TiO_2 P25 powder, red line regarding anatase phase and green line rutile phase. Peak at 25.30 and 27.45 are associated with the most crystallographic plane and respectively the previous to anatase and also the latter to rutile.

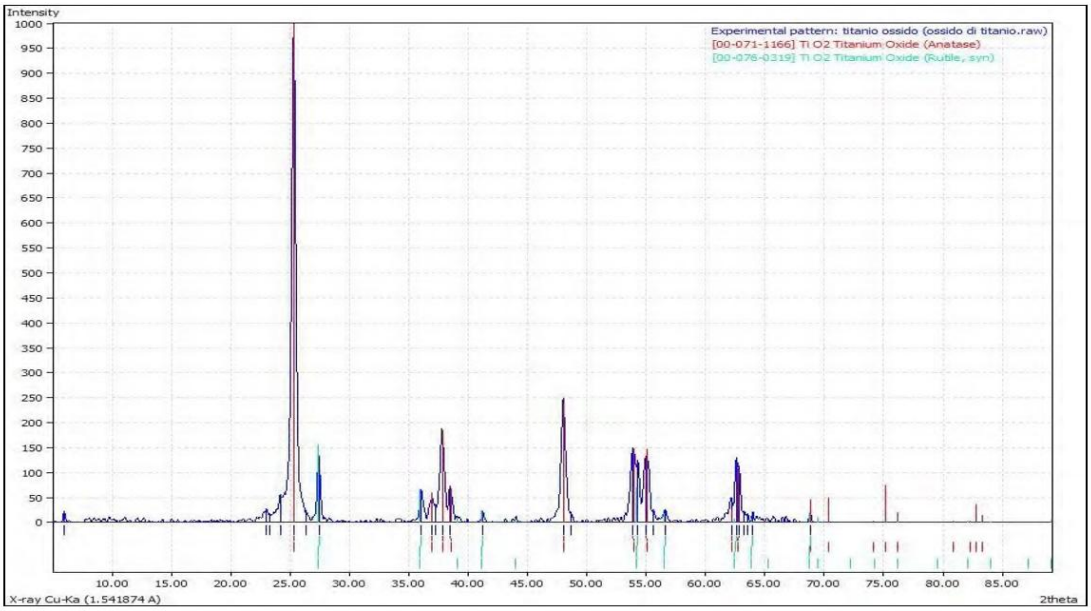

Fig. 3. X-ray diffractometer (XRD) pattern of TiO_2 Degussa P25: Blu line is the diffractogram of TiO_2 P25 powder, red line regarding anatase phase and green line rutile phase

Table 1: XRD peaks of TiO_2.

2theta	Intensity
25.3	995.43
27.45	153.73
36.04	78.45
37.8	192.52
38.5	85.27
48.03	276.48
53.98	160.29
54.26	139.09
54.99	140.36
56.66	35.2
62.83	129.76
68.97	72.51

2.3.3. Experimental set-up

Before conducting the experiments, all vials and containers were washed dichloromethane and distilled water twice, and then dried at 150 °C for 3h. then petroleum wastewater was centrifuged as a preliminary treatment to eliminate the solid residues

remaining from the produce water. This technique presents an advantage with respect to other methods because it can be economically used as was used in the extraction of wastewater. Furthermore, it gives as the possibility of operating only mechanically without any chemical additives and in a short time. In the present case, a centrifuge (Avanti J-20XP) was used; 1 L of wastewater was filled into each tube of the system, maintained for two hours at a speed of 7500 rpm at 22 °C.

The concentrations of each BTEX compound in the samples were determined to (by gas chromatography) 2000 mg/L.

Both of experiments (TiO_2 and N-Doped TiO_2) were carry out six hours under irradiation with ultraviolet (UV) and visible light (VIS).

To evaluate the effect of pH on the performance of the reactor, the initial pH was adjusted to 3.5, 7.0 and 10.5. The concentration of H_2O_2 was 30 mg/L in all experiments.

3. Results and discussions

The effect of pH on the efficiency of BTEX photodegradation is difficult because pH has multiple roles withen the process (Konstantinou & Albanis 2004). The pH is associated with to surface ionization of TiO_2 per the subsequent reactions (Fard *et al*., 2013).

$$TiOH + H^+ \leftrightarrow TiOH_2^+$$
$$TiOH + OH^- \leftrightarrow TiO^- + H_2O$$

The variation in BTEX degradation efficiencies for pH values is shown in Table 2. The most BTEX degradation was achieved under UV lamp at pH 3.5 after 2 hours by the 1 mg/L N-Doped TiO_2 catalyst.

Table 2. Variation in BTEX degradation efficiencies at different Ph values for UV/N-Doped TiO_2 system (BTEX=2000 mg/L, reaction time=2 hours)

Degradation efficiency (%)				
pH	**Benzene**	**Toluene**	**Ethylbenzene**	**Xylene**
3.5	90.7	91.6	90.5	89.8
7.0	80.5	85.1	79.5	82.1
10.5	85.4	83.4	86.6	88.9

Given the close degradation efficiencies for 30 and 50 mg/L H_2O_2 concentrations and the cost of hydrogen peroxide, 30 mg/L was selected as the operational H_2O_2 concentration. The effect of reaction time on the all-oxidation processes was investigated using natural sources and artificial radiation.

4. Conclusion

Effective decomposition of petroleum aromatic hydrocarbons is possible using UV/N-Doped TiO_2 /H_2O_2 system. The priority of treatment processes based BTEX degradation efficiencies within the 2 hours. This study also revealed that the using UV/ TiO_2 and UV/N-Doped TiO_2 /H_2O_2 system were effective in treating the contaminated industrial wastewater.

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