Photo-degradation of P-Nitro Toluene using Modified Bentonite Based Nano-TiO2 Photocatalyst in Aqueous Solution

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1. INTRODUCTION

Due to the global shortage of water resources and their continuous depletion, along with the growth of human communities and the manufacturing of a wide range of chemicals in various industries, the need to develop efficient methods in water and wastewater treatment have become more considerable and the wastewater reuse will be vital [1, 2].

Aromatic compounds are one of the most polluting objects in the world and also in Iran. Some organic compounds are disposed by biological methods in effluents, but despite their dominance, they also have inferiorities such as incompetence in the presence of biodegradable organic compounds and the production of noxious intermediates. Types of compounds It is essential to use novel processes such as advanced oxidation that can convert non-biodegradable molecules into molecules that can be degraded by microorganisms or into inert molecules such as water, carbon dioxide, nitrogen, and so on [3, 4].

Toluene and its nitrate derivatives are widely used in differing industries. These compounds are employed in defense industries, chemicals, rubber, insecticides, textile and paper industries, paint industries, and so on. These compounds are often recognized as environmental pollutants, especially in industrial

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wastewater treatment. Nitro-Toluene derivitives include 2-nitro-toluene, 3-nitro-toluene, and 4-nitro-toluene. These aromatic derivitives are toxic, and their demolition is mandatory. It is noteworthy that 4-nitrotoluene or the same PNT is the most abundant derivitive available [5]. Many procedures including preparation of pesticides, textiles and paper use nitroaromatics, which are damaging to human and environment if discharged into water lacking proper treatment. The p-nitrotoluene (PNT) is one of the public nitroaromatics and studies exhibited that it is a suspected hormone disrupter. So, some studies have been made to the degradation of PNT in wastewater.

One of the effective methods to degradation of PNT contaminants is the use of advanced oxidation processes, which were discussed below.

Advanced oxidation processes are generally referred to processes in which a strong oxidizing agent such as oxygenated water, ozone, and a catalyst such as titanium dioxide, zinc oxide, iron, and manganese are applied in the presence or absence of UV radiation [6,7]. These processes rely on the production of hydroxyl radicals with high oxidation activity, which convert organic chemical pollutants into minerals that are most efficient in oxidizing of durable organic compounds. When the energy of a photon is equal to or greater than that of semiconductor, it leads to excitation of the electron energy gap ($E_g$) from the capacitance band to the conduction band, which due to the excitation of the electron generate a gap in capacitance band. Excited electrons can directly or indirectly create hydroxyl radicals, in which these radicals alter the organic matter to minerals. The use of titanium dioxide photocatalyst is recognized as an efficient method of advanced oxidation methods [8,9].

In this study, TiO$_2$ was used as a photocatalyst. TiO$_2$ exists in the three main phases of Rutile, Anatase, and Brucite. Of these three phases, the Rutile phase is the most reliable, and the other two phases, namely Anatase and Brucite, are transformed into the Rutile phase by gaining heat. Spatially, the Rutile and Anatashe phases are tetragonal, and the Brucite has an orthorhombic shape. However, for some applications such as conventional solution filtration, the crystal phase is not required. The crystalline phase is necessary when a particular application, such as photocatalytic or semiconductor, is considered. [10,11].

Different materials can be combined with TiO$_2$ as a base to serve different purposes. Therefore, in this study, in order to increase the contact level and reduce the cost, bentonite was used as a cheap and available material. Bentonite is a clay material composed of swollen minerals, which are mainly Montmorillonite and, to a small extent, is Bidellite. Most bentonites are created by weathering and alteration of volcanic ash, often in the presence of water, and their source rocks are mostly basalt. Volcanic ash decomposition is mainly carried out in saline and swampy environments, and as we move away from the volcano, the thickness of bentonite decreases. Bentonite has an alumina silicate structure and belongs to the three-layer silicates classes. Bentonite has two quadrilateral layers and one octahedral layer [12].

In recent years, studies have been done on the combination of TiO$_2$ with other materials, which have been referred to in the following: Nasirian et al. [13] reported the photocatalytic behaviors of the Fe$_2$O$_3$ / TiO$_2$ on the degradation of ordinary dyes. In their research, the degradation of Congo Red (CR) and Methyl Orange (MO) was investigated, and the results revealed that by using 0.01 wt% Fe$_2$O$_3$ / TiO$_2$ as a photocatalyst, 62% of MO and 46.8% of CR could be degraded. Also, the optimum temperature in this process was 300°C, where the highest color degradation occurs [13].

Sethau et al. [14] studied the elimination of the methylene blue dye using a TiO$_2$ zeolite photocatalyst. In their research, after describing the synthesizing procedure, the performance of the synthesized zeolite TiO$_2$ photocatalyst is exposed in comparison with the pure TiO$_2$ which highlights the higher performance and greater efficiency of the synthesized photocatalyst [14].

Hosseini and et al. [15] presented a study on photocatalytic degradation of 4, 2-dichlorophenol using TiO$_2$ nanoparticles and also Co/TiO$_2$ containing mixed matrix membranes. They synthesized TiO$_2$ with different amounts of cobalt by the sol-gel method. The best combination occurred with 1.34 molar percent of Co, which had the highest degradation rate. They also studied the TiO$_2$ degradation with mixed membranes and also applied PES membranes and found that adding 1 wt% of Co/TiO$_2$ (1.34%) to Polyethersulfone (PES) had a greater passing flux. They also reported the best method for the separation of 2, 4 dichlorophenols [15].

Also, Gharibshahian [16] investigated the influence of the concentration of Polyvinyl Alcohol on the progress kinetics of KTiOPO$_4$ nanoparticles produced by the co-precipitation Method. Preparation, identification and optical features of LaFeO$_3$ nanoparticles through sol-gel combustion method was explored by Theingi et al. [17].

Aby et al. [18] published an article on how to make a nano-silver and zinc (Ag/ZnO) photocatalyst and demonstrated its elevated efficiency. The effect of photocatalyst degradation on organic pollutants such as some dyes was investigated, and it was concluded that the efficacy of ZnO <Ag / ZnO (% 1wt) <Ag / ZnO (4 wt%) [18].

As has been observed, many studies have been done, but studies are at the boundary of knowledge and have the potential to be expanded. Therefore, the present study investigates the combination of TiO$_2$ and bentonite to reduce photocatalyst cost and Finally, the
efficiency of the photocatalyst made on PNT degradation was evaluated.

2. EXPERIMENTAL

2.1. Materials and Methods The used materials of this study involve PNT manufactured by Merck Company, TiO\textsubscript{2} produced by the US Research Nano Materials Company (APS of 20 nm and BET surface area of 200 m\textsuperscript{2}/g). Bentonite soil was purchased from the Chinese DAE JUNG Company. Agilent 8453 spectrophotometers, KBr-PerkinElmer Fourier transform infrared (FT-IR) analyzer, PW1730 Philips-Diffractometer X-ray diffraction (XRD) analyzer, Phenom ProX Scanning electron microscopy (SEM) and Spectroscopy and energy dispersive X-ray (EDX) for characterizing the synthesized photocatalyst and all the experimental activities were performed in a home-made laboratory pilot (semi CREC reactor with capacity of 1.4 liters and height of 41 cm) [19,20].

2.2. Synthesis of the TB Photocatalyst In this research, at the first step, the photocatalyst was synthesized by the co-precipitation protocol. The purpose of the photocatalyst manufacturing is to enhance the accessible surface for the TiO\textsubscript{2} and diminish the extra cost so that the catalyst can be operated with a low-priced base. To reach this aim, compounds of 5 wt %, 10 wt %, and 20 wt % of TiO\textsubscript{2} and bentonite were formulated. The mixture was stirred gently for 20 hours and by adding ethanol, a gel-like mixture was created. The created precipitate was washed with distilled water and the prepared gel was dried for about 2 h in the oven. The dried precipitate was heated in the furnace for 4 h at 450 \degree C. Finally, the precipitate was slowly cooled down and sifted and for better sample recognition and tracking of the experimental results the catalysts were named TB 5, TB 10, TB 20 [21,22].

2.3. UV Irradiation Experiments A solution containing 50 mg/L of PNT and 0.2 g/L TB was prepared and circulated for 120 minutes in the reactor with irradiation. Samples were taken at certain reaction intervals, centrifuged and then analyzed by a UV–vis spectrophotometer at 286 nm. The degradation of the studied wastewater by the process was estimated using the following Equation (1). According to photocatalytic processes, when TiO\textsubscript{2} excitation occurs, it creates an electron and electron hole. The hole next to the water causes the production of OH\textsuperscript{\textminus} radicals. These radicals are very active and carry PNT and convert it into minerals. Figure 1 illustrated the degradation mechanism.

\[ \text{Degradation of PNT(\%)} = \frac{C_0 - C}{C_0} \times 100 \]

where \( C_0 \) and \( C \) are initial and current concentration of PNT, respectively.

3. RESULTS AND DISCUSSIONS

3.1. Evaluation of Modified TB Photocatalyst Properties

3.1.1. TB Samples XRD Test Figure 2 depicted the XRD diffraction pattern of the synthetic samples. The spectrum of the bentonite sample is shown in section (a). As illustrated in this figure, the sample consists of three main phases: Montmorlite, Quartz, and Feldspar. Section (b) fully complies with the formation of TiO\textsubscript{2} in the Anatase phase with the JCPDS card number of 1272-21-00 [23]. The bandwidths also confirm that the particles are all in a nano-sized scale. For the nanocomposite sample, as it is shown in sections (c-e), the Anatase phase peak intensities soar with increasing TiO\textsubscript{2} percentage from 5 wt% to 20 wt%. This intensity variation occurs specifically in the crystalline plates (101), (200) and (105) [24]. The simultaneous presence of TiO\textsubscript{2} and bentonite diffraction verifies the favorable synthesis of 5 wt%, 10 wt% and 20 wt% nanocomposites. However, in some angles, there is a high overlap between the two distinct components.

3.1.2. TB Samples FTIR Test As Figure 3 illustrated, the (a) spectrum demonstrates the TiO\textsubscript{2} sample. The peak of Ti-O vibration is shown in the range of 400-500 cm\textsuperscript{-1}. The peaks at 3350 cm\textsuperscript{-1} and 1640 cm\textsuperscript{-1} are related to O-H tensile and bending vibrations, respectively [25]. Figure 3(b) spectrum is related to the bentonite sample. The bands observed at 460 cm\textsuperscript{-1} and 540 cm\textsuperscript{-1} are related to the bending vibrations of Si-O-Si and Al-O-Si. The peak observed at 626 cm\textsuperscript{-1} is attributed to off-plane vibrations of Al-O and Si-O bonds. The peak observed at 915 cm\textsuperscript{-1} is related to the tensile vibration of Al – O– (OH) –Al. The strong peak in the 1040 cm\textsuperscript{-1}
Figure 2. XRD patterns of (a) Bentonite, (b) Pure TiO$_2$, (c) TB 5, (d) TB 10 and (e) TB 20

However, in some cases, small displacements are observed at the peak location, which confirms the successful formation of the composite. These results are in full agreement with XRD and EDX analyses.

3.1.3. TB Sample EDX and SEM Tests Figure 4 depicts the SEM test for TB 5, TB 10, and TB 20 samples. This figure well indicates the presence of TiO$_2$ particles on the bentonite particles. The catalyst morphology is fixed in all the proportion of the compounds; likewise, the dispersion of TiO$_2$ particles is uniform on the surface. Figures illustrate that as the amount of TiO$_2$ enhanced, the number of particles on the surface escalated.

The EDX test was used for determination of different elements in various materials [27]. On the other hand, EDX tests were performed for the samples, and the results are shown in Figure 5.

The peaks imply the identification of major catalyst materials such as Si, C, Br, Ti and O. The results confirm the existence of Ti elements in the fabricated samples (peak 0.2 and 4.5 KeV) [28]. The composition percentage of the major elements is listed in Table 1.

Figure 3. FT-IR spectra of (a) Pure TiO$_2$, (b) Pure Bentonite, (c) TB 20

region belongs to the Si-O-Si group of tetrahedral sheets. The peak observed at 1645 cm$^{-1}$ is related to the bending vibration of the hydroxyl group of water molecules remaining in the bentonite matrix. The broadband at the 3420 cm$^{-1}$ is attributed to the O-H tensile vibrations of the silanols (Si-OH) as well as the absorbed water [26].

The spectrum in Figure 3(c) highlights the composite sample of the TB 20 catalyst. The Ti-O peak is shown in the range of 400-500 cm$^{-1}$ and the other peaks of the bentonite sample are fully preserved.

Figure 4. SEM of (a) Pure Bentonite (10 µm), (b) Pure Bentonite (5 µm), (c) TB 5 (10 µm), (d) TB 5 (5 µm), (e) TB 10 (10 µm), (f) TB 10 (5 µm), (g) TB 20 (10 µm), (h) TB 20 (5 µm)
3.2. Evaluation of the Modified TB Photocatalyst on PNT Removal Performance

After fulfilling the characteristics tests for evaluation of the synthesis method and well-creation of the hybrid photocatalyst, its performance was measured on the degradation of PNT. Experiments were carried out in the reactor setup. The prepared solution contained 50 mg/L of PNT, and the pH of the solution was kept at 5 (normal solution pH). These values were consistent by considering the previous results in all experiments. Also, the catalyst content was 0.2 g/L [20].

It should be noted that the intended values are optimal so that the rate of degradation depends on the initial concentration of paranitrotoluene. It changes with increasing initial concentration of the pollutant. The reaction between the hydroxyl radicals produced by the active sites on the surface of titanium dioxide and the paranitrotoluene molecule occurs from the solution. When the initial contaminant content is high, the number of these active sites available by the paranitrotoluene molecules decreases as their absorption onto the surface of titanium dioxide decreases. On the other hand, there is an increase in the rate of transfer of paranitrotoluene molecules. When the initial concentration of paranitrotoluene is low, although there are more active sites and more hydroxyl radicals, the rate of contaminant transport to the catalyst surface is low, so it can be seen that the contaminant concentration has positive and negative effects [29].

pH has an important effect, and at low and high pH values, the rate of degradation is variable. The best pH for degradation is near the zero point of titanium dioxide, and this concept illustrates the effect of pH on the amount of degradation based on its effect on titanium dioxide particles. The zero point for titanium dioxide is in the pH range between 5.6 and 6.4 [30,31]. It appears that the maximum value of PNT destruction happens at the Neutral pH which may be originated from the superior production of total radicals at this pH. Truly, the PNT removal efficiency was improved due to keeping higher levels of radicals which are employed to decompose the structure of a refractory organic compound such as PNT.

The results showed that the rate of degradation increased with increasing concentration of titanium dioxide and then decreased. Excessive catalyst overload may cause solution obstruction and light penetration. Therefore, the catalyst increase has a positive effect until the turbidity effect is dominated, but afterwards it has a completely undesirable effect on the degradation process [32-34].

As it is shown in Figure 6, the degradation rate enhanced with increasing TiO$_2$ content and reaches its highest value of 59% for TB 20.

It is noteworthy that the degradation was very slow in the first half-hour due to the opacity of the solution, which diminished the illumination and consequently shortened photocatalytic activity. The highest catalytic activity occurs in the early hours and then the catalytic activity decreases and the reaction does not sensible change in the final hours. By the way, in the experiments that utilized pure TiO$_2$, the catalytic activity was low in the early hours and thereafter, the catalytic activity increased, with a maximum degradation rate of 64%.

![Figure 6. Photocatalytic degradation of PNT](image-url)
4. CONCLUSION

In this study, the TB catalyst was synthesized by precipitation method, and its catalytic activity on PNT decomposition was explored. The catalyst was made of 5 wt%, 10 wt% and 20 wt% TiO₂. Furthermore, the characterizations of the nano catalyst were evaluated by the XRD, FT-IR and SEM techniques. Observations of this work reveal that modification of TiO₂ nano catalyst with Bentonite has a prominent impact on the degradation of PNT in a suspension reactor for the PNT values of 50 mg/L and TB of 0.2 g/L. The residence time of two hours was considered and it was observed that in the early hours of the reaction, the highest catalytic activity attains to develop and then the catalytic activity reduces and finally fixed at the equilibrium value. The results confirm that with increasing TiO₂, degradation rate increased and the highest value for TB 20 catalysts was 59% (COD = 53%). Therefore, it can be said that although the usage of bentonite as a base does not have much impact on enhancing the final efficiency, it can have a favorable role in terms of economic cost and reduction of reaction time.

5. ACKNOWLEDGEMENT

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6. REFERENCES


**Persian Abstract**

چکیده

کشور ایران در طول‌الزمان به‌طور گسترده‌ای به دلیل افزایش مصرف صنعتی از مواد شیمیایی و مواد آلی به‌طور بسیار کمی کثرت از مایعات و مواد آلی، زیرا عملکرد صنعتی بسیار ضروری است. به‌طور کلی، مصرف مواد شیمیایی و مواد آلی در صنعت تولید تولیدکننده‌ها به‌طور مداوم رشد می‌کند. این به‌طور کلی باعث افزایش مصرف مواد شیمیایی و مواد آلی، زیرا عملکرد صنعتی بسیار ضروری است. به‌طور کلی، مصرف مواد شیمیایی و مواد آلی در صنعت تولید تولیدکننده‌ها به‌طور مداوم رشد می‌کرده است. این به‌طور کلی باعث افزایش مصرف مواد شیمیایی و مواد آلی، زیرا عملکرد صنعتی بسیار ضروری است. به‌طور کلی، مصرف مواد شیمیایی و مواد آلی در صنعت تولید تولیدکننده‌ها به‌طور مداوم رشد می‌کرده است.

[TA 20]