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# Photocatalytic degradation of acetaminophen in aqueous solution in the presence of montmorillonite nanosheets modified with titanium dioxide

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## ABSTRACT

In this study, the photocatalytic degradation of acetaminophen was investigated using montmorillonite nanosheets modified with titanium dioxide ($TiO_2$). This study was experimental and conducted on a laboratory scale. Identification of montmorillonite nanosheets modified with $TiO_2$ was performed by various techniques such as Fourier transform infrared (FT-IR), X-ray diffraction, and TEM. For degradation of acetaminophen, aqueous solutions with different concentrations of acetaminophen, ultraviolet (UV) radiation, and a montmorillonite nanoparticles modified with $TiO_2$ catalyst were used. Parameters affecting photocatalytic reactions including pH (3–11), catalyst dose (0.1–1 g $L^{-1}$), initial concentration (2–25 mg $L^{-1}$), and contact time (15–150 min) were investigated. The concentration of acetaminophen was determined by spectrophotometer at 243 nm wavelengths. The FT-IR confirmed the presence of $TiO_2$ on the montmorillonite nanosheets modified with $TiO_2$. Using two other methods of detection, it was found that montmorillonite nanoparticles modified with $TiO_2$ is more than 100 nm. The results showed that the maximum removal efficiency (100%) of acetaminophen was achieved at pH = 7, catalyst dose of 0.75 g $L^{-1}$, the concentration of 2 mg $L^{-1,}$ and contact time of 120 min. The results of this study showed that montmorillonite nanosheets modified with $TiO_2$ catalyst under the UV radiation is an effective method for removal of acetaminophen from aqueous solution.

*Keywords:* Montmorillonite nanosheets; $TiO_2$; Photocatalyst; Acetaminophen

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## 1. Introduction

Water is a basic need for maintaining life and health. The water is also important from an economic standpoint. Various pollutants threaten water resources. Among the pollutants of water, the new pollutants have attracted more attention. Since 2000, personal care products and pharmaceuticals (PPCP) are the worst contaminants [1–3]. Compared with conventional pollutants, many PPCPs are generally soluble in water, and some of them have acidic and alkaline groups. Large amounts of these drugs are transmitted through the transfer of water and food chain in the environment [4,5]. Acetaminophen is a commonly used anti-inflammatory and analgesic drug that is used worldwide at a rate of $1.45 \times 10^5$ t $y^{-1}$ [6]. The solubility of acetaminophen in water is 12.78 g $kg^{-1}$ at 20°C, which is often detected in the water pathway [7]. More than 65 μg $L^{-1}$ acetaminophen is detected in surface water, and the concentration

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of acetaminophen in the pharmaceutical industry is much higher [8]. Acetaminophen is not completely removed from urban wastewater, which is why today it is one of the important compounds in natural and drinking water [9]. To determine acetaminophen, methods such as spectrophotometry [10], high-performance liquid chromatography [11], electrophoresis [12], and ion chromatography [13] have been used. Recently, various methods of biological treatment [14], advanced oxidation [15], advanced oxidation with Fenton [16], or ultrasound [17] have been used to remove acetaminophen. Among the advanced oxidation processes, ultraviolet (UV) radiation is one of the effective methods to remove pollutants [18]. However, some pollutants such as acetaminophen cannot effectively be destroyed by UV due to the presence of $NH_2$ in their structure. The degradation efficiency in UV systems can be significantly increased by using oxidant compounds such as $H_2O_2$, persulfate, or titanium dioxide ($TiO_2$) catalyst. These compounds lead to the production of radical hydroxyl and radical sulfate. These free radicals are active species that are capable of oxidizing a variety of organic compounds [19]. $TiO_2$ is a nontoxic substance used in wastewater treatment processes. Ultra-fine $TiO_2$ powder has a high specific surface area which catalytic performance well on these levels is expected. However, $TiO_2$ is hardly recovered in the practical area. This problem is solved through the stabilization of $TiO_2$ on materials such as clay and zeolite without losing its function. The use of clay such as montmorillonite nanosheets has been considerable in recent years in the field of wastewater treatment. Clay catalytic performance can be improved by using $TiO_2$ particles between clay layers because these composite structures can stabilize $TiO_2$ and maintain a crystalline $TiO_2$ surface for access to different molecules [20].

Dehghani et al. investigated the photocatalytic oxidation of oganophosphorus pesticides using zinc oxide, and the result showed that the optimal concentration of catalyst was found to be 100 mg $L^{-1}$ at acidic conditions [21].

Oskoei et al. investigated the removal of humic acid from aqueous solution using UV/ZnO nano-photocatalysis and adsorption, and the result showed that the efficiency of this process was found higher under acidic conditions. The maximum removal efficiency of humic acid for the single-stage process was found to be 0.2 g $L^{-1}$ ZnO and for that of two-stage process was found to be 0.5 g $L^{-1}$ ZnO [22].

Dehghani et al. also investigated the removal of acid 4092 dye from aqueous solution by zinc oxide nanoparticles and UV irradiation, and the result showed that the best result was obtained in the treatment with concentration of dye = 0.5 mg $L^{-1}$, radiation time = 12 min, pH 5, and dosage of catalyst = 0.2 g $L^{-1}$ [23].

Najafi Saleh et al. evaluated the data on the acid black 1 dye adsorption from aqueous solutions by low-cost adsorbent *Cerastoderma lamarcki* shell collected from the northern coast of Caspian Sea, and the result showed that the optimum conditions for AB1 adsorption using CLS adsorbent were found to be 2 g of adsorbent, pH 2, and a contact time of 60 min. The adsorption data of CLS fit well with the Langmuir model and pseudo-second-order model [24].

The aim of the present study was to use montmorillonite nanosheets modified with $TiO_2$ in the photocatalytic degradation of acetaminophen with UV radiation.

## 2. Materials and methods

In this study, materials such as montmorillonite nanosheets from nano Pioneer Company (Iran), titanium and hydrochloric acid from Merck Company (Germany), and acetaminophen powder with 100% purity from Sigma-Aldrich Company (USA) were purchased.

### 2.1. Montmorillonite nanosheets modified with $TiO_2$

One gram of montmorillonite nanosheets were added to 100 mL distilled water, and the resulting suspension was placed on a heater for 2 h at 80°C. To prepare the titanium hydrate, HCl (1 M) was added to the compound $Ti(OC_3H_7)_4$ to a ratio of $(Ti)/(H^+) = 1:4$ and mixed for 4 h, and then titanium hydrate was added to the initial solution to a ratio of 30 mmoL $g^{-1}$ montmorillonite nanosheets and mixed for 6 h. The resulting solution was centrifuged and washed with deionized water. Then, the cake was placed in an oven at 80°C for 48 h. It was then calcined at a temperature of 550°C at a rate of increase of 2°C $min^{-1}$. Finally, the catalyst was ground and further used for acetaminophen photocatalytic degradation tests [22]. Identification of montmorillonite nanoparticles modified with $TiO_2$ was performed by various techniques such as Fourier transform infrared (FT-IR), X-ray diffraction (XRD), and TEM.

### 2.2. Specifications of the reactor used for photocatalytic experiments

The reactor used for photocatalytic experiments shown in Fig. 1, with a volume of 300 mL, was equipped with a UVC ultralow lamp with a length of 20.1 cm and a production wavelength of 254 nm. The radiation intensity was 282–294 W $m^{-2}$ at a distance of 1 cm. This lamp was placed in a quartz tube with a diameter of 5 cm at the center of the reactor.

### 2.3. Solubilization and photocatalytic experiments

To prepare different concentrations of acetaminophen, the stock solution was first prepared by dissolving 0.1 g of acetaminophen powder in 1,000 mL of deionized water with

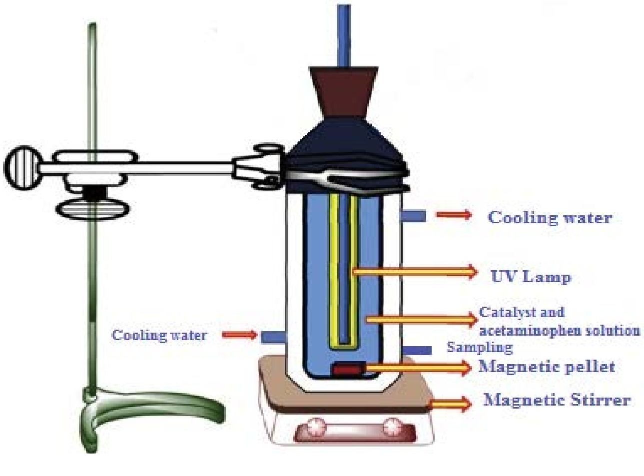


Fig. 1. Schematic diagram of the photocatalytic reactor.

a concentration of 100 mg $L^{-1}$, and then the desired concentrations were prepared by dilution from the stock solution. In this reactor, a suspension consisting of a solution containing acetaminophen and a catalyst of 300 mL were introduced and the mixing was done by a stirrer. In all the experiments to reach adsorption equilibrium before UV radiation, the solution was mixed in the reactor for 30 min in the dark and then irradiated. The effective parameters on photocatalytic reactions were pH (3–11), catalyst dosage (0.1–1 g $L^{-1}$), initial concentration (2–25 mg $L^{-1}$), and contact time (15–150 min). The desired samples were extracted by sampling valve and analyzed by spectrophotometer at 243 wavelengths. Then, the removal efficiency of acetaminophen was calculated from Eq. (1):

$$\%\text{Removal} = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

where $C_0$ is the initial concentration of acetaminophen and $C_t$ is the concentration of acetaminophen after time $t$ from the start of the reaction.

## 3. Results and discussion

### 3.1. Characteristics of montmorillonite nanoparticles and montmorillonite nanosheets modified with $TiO_2$

In Figs. 2–4, the FT-IR, XRD, and TEM spectra are shown for montmorillonite nanosheets and montmorillonite nanosheets modified with $TiO_2$.

Infrared spectroscopy is a method for identifying molecules and in particular molecular functional groups. Each substance has its own infrared spectrum and is unique to the same molecule as the fingerprint. As shown in Fig. 2 (montmorillonite nanosheets modified in comparison with the crude montmorillonite nanosheets), peaks higher than 1,630 $cm^{-1}$ are related to the tensile bonding of the hydroxyl group, and peaks in the range of 3,430 are related to the water molecules between the layers, which makes the interaction between Si with Ti. A new peak at around 913 $cm^{-1}$ corresponds to Si–O–Ti bond which also discloses that $TiO_2$ combines with montmorillonite by the formation of Si–O–Ti chemical bond and stretching vibration of short Ti–O bonds involving non-bridging oxygen coordinated with sodium ions [25–28]. Also, the stretching vibration in 432 $cm^{-1}$ is

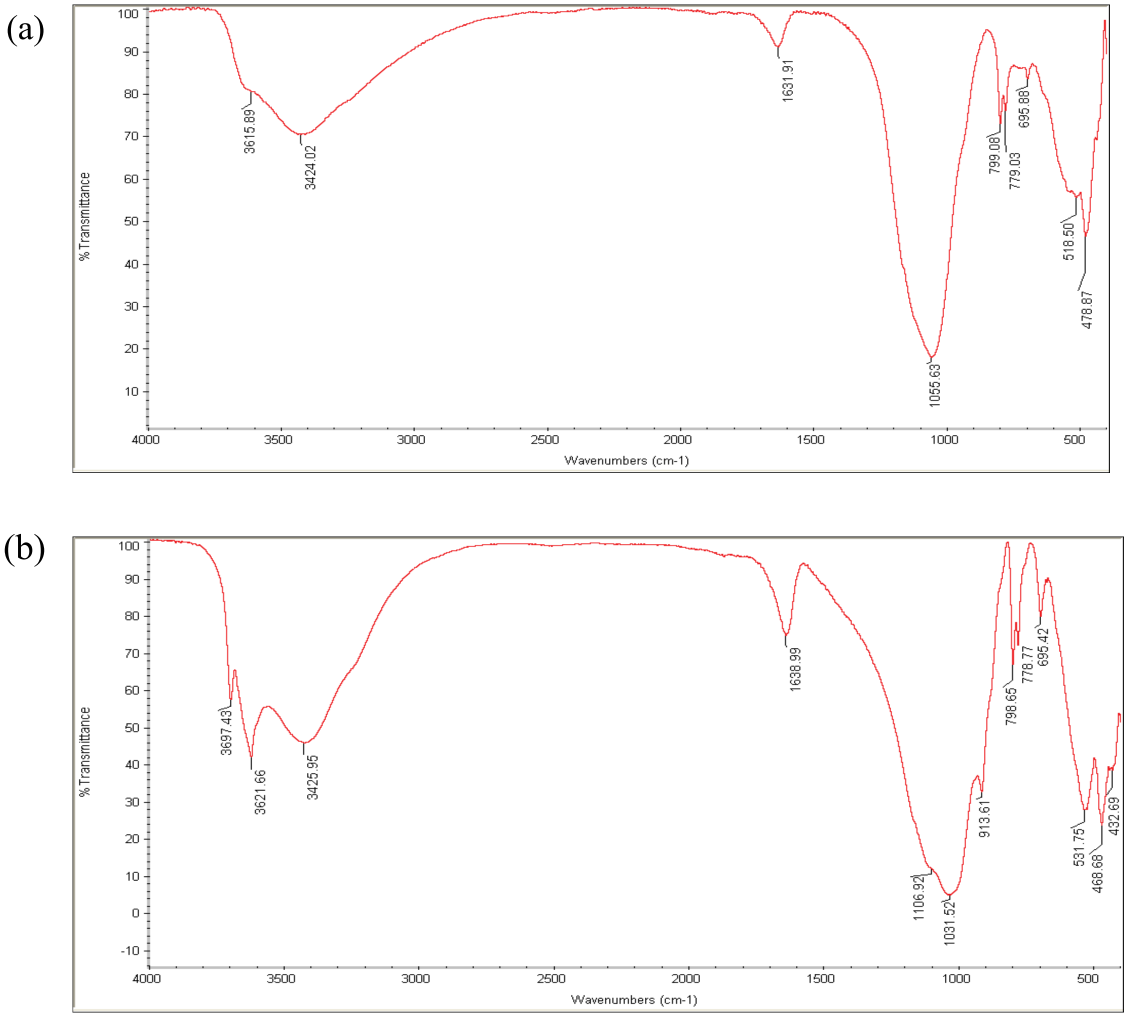


Fig. 2. The FT-IR spectra of montmorillonite nanoparticles (a) and montmorillonite nanosheets modified with $TiO_2$ (b).

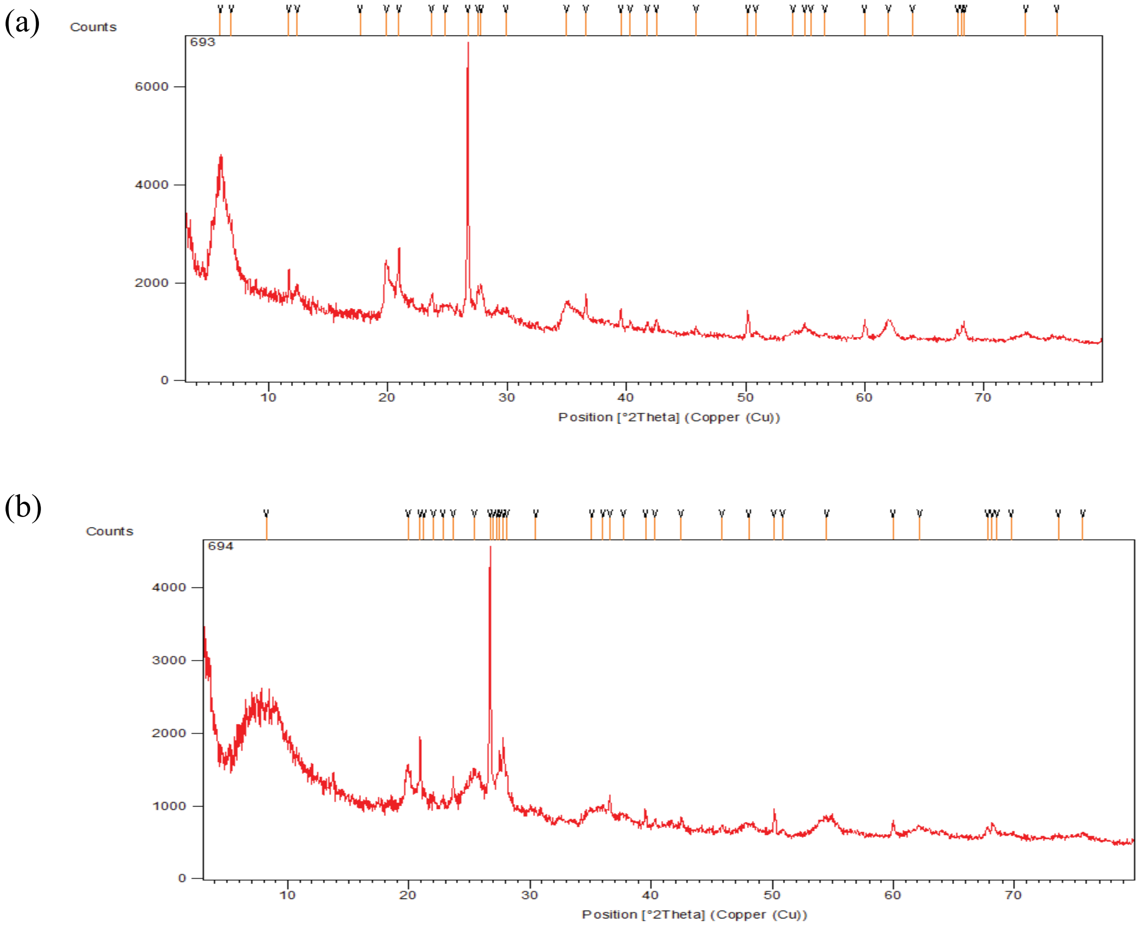
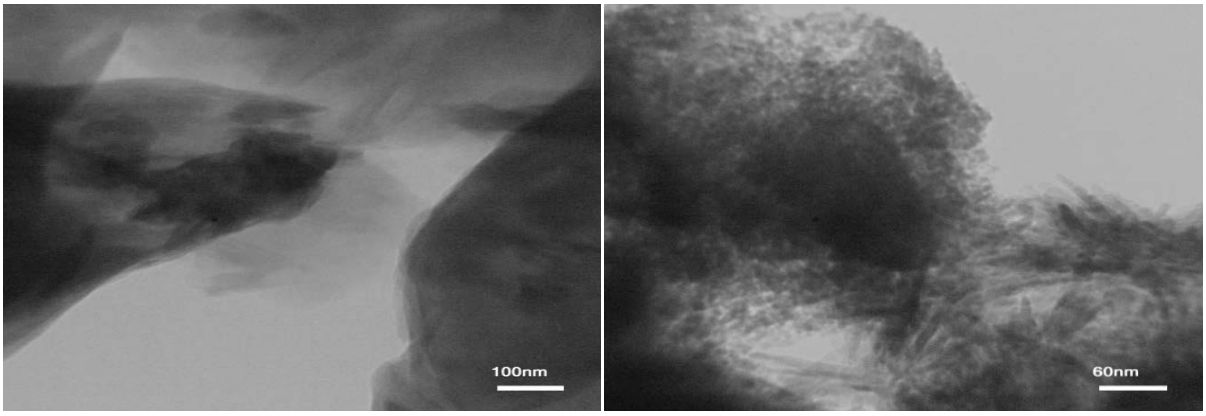


Fig. 3. The XRD spectra of montmorillonite nanosheets (a) and montmorillonite nanosheets modified with $TiO_2$ (b).



(a) (b)

Fig. 4. The TEM images of montmorillonite nanosheets (a) and montmorillonite nanosheets modified with $TiO_2$ (b).

ascribed as the stretching vibration of Ti–O–Ti bonds [29]. These vibration peaks confirmed the presence of $TiO_2$ on montmorillonite.The X-ray region in the electromagnetic spectrum is in the range between gamma and UV rays. Using this spectral region, information can be obtained about the structure and the determination of the number of elements [30]. XRD patterns (Figs. 3(a) and (b)) indicate that the dispersion of titania does not affect the structure of montmorillonite. However, in XRD pattern of $TiO_2$/montmorillonite, the d001 reflection at around 2θ = 6.24°

is shifted to 2θ = 9.3° and broadened which indicates the increased basal spacing of layers by the insertion of titania as indication of silicate sheets [31].

Also, the reflection at 2θ = 25.31° (101), which shows the crystalline phase of $TiO_2$ as anatase (by comparison with a $TiO_2$ standard), confirmed the presence of $TiO_2$ in montmorillonite [32,33]. Furthermore, the reflection at around 2θ = 38° and 58° also confirmed the presence of $TiO_2$ in montmorillonite [31]. The most useful template for using XRD to calculate the particle size is the maximum peak width multiplied by half of the height. The Scherer formula in Eq. (2) determines the crystalline particle size in the diffraction peak width of the X-ray multiplied by half of the height:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

where $D$ is the crystalline particle size, $\lambda$ is the wavelength of the X-rays, and β is the maximum peak width multiplied by half of its height. Using the Scherer study, the size of the sheets of montmorillonite nanosheets at the largest peak is 113 nm, and its size after modification with $TiO_2$ is 164 nm.

Using electron microscopic images, we can determine the shape, size, and accumulation of particles clearly and precisely. As shown in Fig. 3, the sheet size before modification (a) and after modification with $TiO_2$ (b) is greater than 100 nm but the thickness of the sheets is lower than 100 nm.

### *3.2. Determination of pH of the zero point of charge of montmorillonite nanosheets modified with $TiO_2$ and effect of pH on the photocatalytic degradation of acetaminophen by montmorillonite nanosheets modified with $TiO_2$*

In Fig. 5, pH of the zero point of charge ($pH_{zpc}$) of montmorillonite nanosheets modified with $TiO_2$, which is about 6.7, is shown. In Fig. 6, the effect of pH on the photocatalytic degradation of acetaminophen is shown. The pH is one of the most important parameters in the removal of pollutants in sewage treatment. Also, one of the most important factors in photocatalytic reactions is the pH of soluble. This is due to its effect on the catalyst surface load and electron transfer process in this process. As shown in Fig. 6, the highest removal rates in pH values 3, 5, and 7 are 63.94%, 62.35%, and 64.24%, respectively. The results of this study indicate that the removal of pollutants in acidic to neutral environments is far more than removal of it in alkaline environments. As shown in Fig. 5, the $pH_{zpc}$ of the catalyst is 6.7. Therefore, the modified montmorillonite nanoparticle surface has a positive load at pH below 6.7 and has a negative load in the alkaline range. On the other hand, acidic pH values of 3 and 5 are lower than $pk_a$ of acetaminophen (9.71). In these conditions, acetaminophen has a positive load and is in the form of cation in solution. Therefore, in acidic conditions, the catalyst and pollutant load are similar, and there is a repulsive force between them, and absorption does not occur. This causes the hydroxide ions derived from the water degradation be absorbed on the surface of the catalyst, and by UV radiation, the OH groups present at the catalyst level are changed to form OH or $O_2$. This free radical will cause further degradation of the target contaminants [34–36]. In alkaline pH, it is also possible that the formation of superoxide anion $O_2$ is stopped by the resuscitation of oxygen by electrons which will eventually lead to a reduction in the degradation of acetaminophen [36–38]. In a study by Ming-Chun et al. about the photocatalytic degradation of acetaminophen by $K_2S_2O_8$-doped $TiO_2$ catalyst and visible light, it was concluded that at pH = 9 the highest degradation of acetaminophen was obtained, since in alkaline conditions pH = 9, the catalyst surface load ($pH_{zpc}$ of $TiO_2$ equals 6.3) is negative and acetaminophen is also cationic, which increases the contact of catalyst and acetaminophen, and consequently, its degradation increases [37]. In the present study, the reason for the increase of degradation at pH = 7 could be interpreted as having adsorbed surface load in these conditions and acetaminophen is cationic, so increasing electrostatic gravity leads to a further degradation of acetaminophen at pH = 7. Therefore, the remaining test stages were performed at pH = 7.

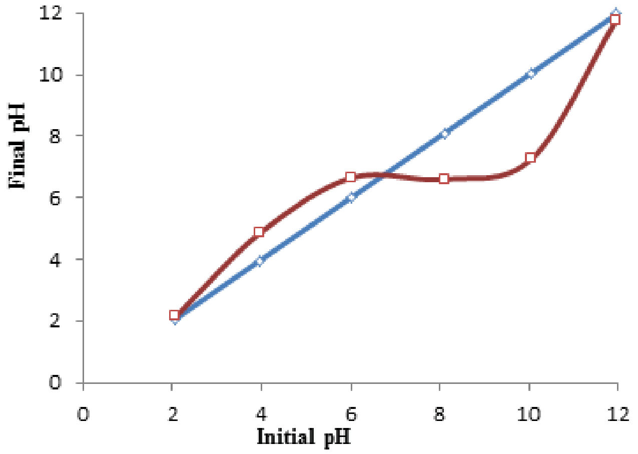


Fig. 5. $pH_{zpc}$ of montmorillonite nanosheets modified with $TiO_2$ (adsorbent dose: 25 mg, solubility: 50 cc, time: 24 h).

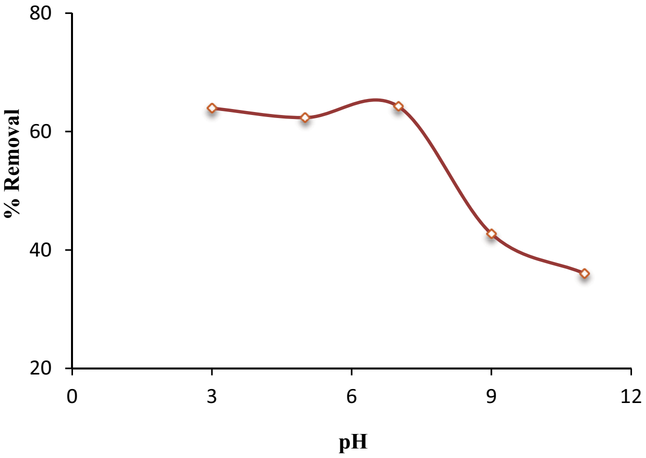


Fig. 6. The effect of the initial pH of the solution on the removal of acetaminophen (volume of solution: 300 mL, initial concentration of acetaminophen: 5 mg $L^{-1}$, catalyst dose: 0.25 g $L^{-1}$, contact time: 90 min).

### *3.3. Effect of montmorillonite nanosheets modified with $TiO_2$ catalyst dose on the acetaminophen photocatalytic degradation*

In Fig. 7, the effect of catalyst dose on the acetaminophen degradation process is shown. As shown in Fig. 6, with increasing catalyst dose from 0.1 to 0.75 g $L^{-1}$, the amount of acetaminophen removal increased after 90 min, and the highest removal rate of 90.28% is related to the dose of 0.75 g $L^{-1}$. While the catalytic dose increased to 1 g $L^{-1}$, the amount of acetaminophen removal decreased to 89.48% compared with the previous dose. These results can be explained by the fact that by increasing the catalyst dose, the number of electrons produced increased as a result of the molecules of acetaminophen more degraded. By increasing the catalytic dose, the number of active sites available for photocatalytic reactions increases. However, with the excessive increase in the catalysts in the turbidity solution, it prevents the light from reaching the particles completely, and the removal rate will be reduced. The results of this study are consistent with Yang et al. [36]. Xiong et al. in Singapore have reported similar results of this study [15].

### *3.4. Effect of the initial concentration and contact time in photocatalytic degradation of acetaminophen by montmorillonite nanosheets modified with $TiO_2$*

In Fig. 8, the effects of the initial concentration of acetaminophen and the contact time of acetaminophen degradation are shown. As shown in Fig. 8, the removal efficiency of acetaminophen has been decreased with increasing concentrations. At 120 min, the initial concentration of 2 mg $L^{-1}$ of acetaminophen has been removed 100%, but with increasing concentrations of 25 mg $L^{-1}$ after 120 min of photocatalytic reaction, the removal rate was reduced to 52.1%. The reason for the reduction in efficiency can be explained by the fact that at all concentrations, the catalyst dose, pH, and contact time are the same and the amount of radicals produced is the same. Therefore, removal of acetaminophen in samples with lower concentrations is higher. On the other hand, by increasing the concentration of contaminants, the radiation emitted by the pollutant molecules is absorbed faster and prevents it from reaching the catalyst, and with increasing the concentration of acetaminophen, more active sites of $TiO_2$ may be occupied and reduced its efficiency [38]. Malekootian et al. reported similar results [39].

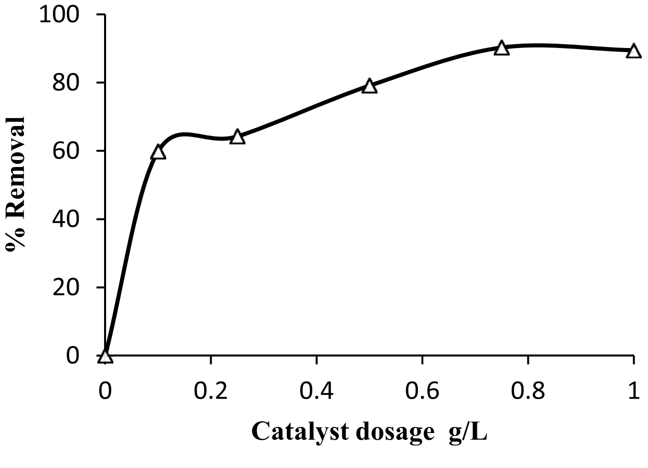


Fig. 7. Effect of catalytic dose on acetaminophen removal (volume of solution: 300 mL, initial concentration: 5 mg $L^{-1}$, pH = 7, contact time: 90 min).

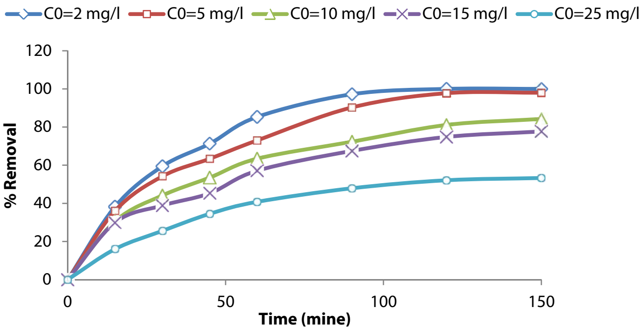


Fig. 8. Effect of acetaminophen concentration on contact time on acetaminophen removal (volume of solution: 300 mL, catalyst dose: 0.75 g $L^{-1}$, pH = 7).

## 4. Conclusion

In this research, the photocatalytic decomposition of acetaminophen was studied using montmorillonite nanosheets modified with $TiO_2$. Overall, the results of the FT-IR tests showed that the bonds between Si and Ti were formed. According to the SEM analysis, the particles size before modification (a) and after modification with $TiO_2$ (b) is less than 100 nm. The experimental data obtained from the photocatalytic experiments of acetaminophen using montmorillonite nanosheets modified with $TiO_2$ showed that the maximum removal rate of acetaminophen achieved was 100% at pH = 7, catalyst dose of 0.75 g $L^{-1}$, concentration of 2 mg $L^{-1,}$ and 120 min from the beginning of the photocatalytic reaction. The results of this study show that one of the effective methods for removing acetaminophen is the use of photocatalytic process.

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