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Research Article

Optimization of Nano-TiO_2 Photocatalytic Reactor for Organophosphorus Degradation

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The photocatalytic decontamination of triethyl phosphate (TEP) is studied by the UV/nano-TiO_2 process. The nano-TiO_2 concentration and pH value for the complete oxidation of TEP were investigated in different concentrations of TEP. The kinetic reaction was calculated for TEP as a function of initial concentration of TEP. Results of adsorptions showed that TEP was adsorbed better in alkalinity pH, and the natural pH had the highest reaction rate for complete degradation. Also, the zero-kinetic order with the lag time as a function of initial concentration of TEP and TiO_2 was suggested for oxidation of TEP. The optimized concentration of nano-TiO_2 was 400 mg/lit which had the best conversion and the lowest lag time in the reaction.

1. Introduction

Nowadays, an important environmental constrain is the effort to improve water quality and remove pollution from waste water. One of the most widespread methods of water purification is biodegradation which has a low reaction rate [1–3]. A novel method that has become popular in recent decades is the advanced oxidation processes (AOPs) which are very potent in oxidization, decolorization, mineralization, reducing heavy metals, and degrading organic pollutants [2–4].

Organophosphate is a very complicated contaminant in waste water which contains insecticides, pesticides, and detergents. These types of pollutants are found in industrial, agricultural, and also domestic waste water. Organophosphate degrades to several intermediate materials; phosphate appears as a solution when it degrades completely. The triethyl phosphate (TEP) is an organophosphate used as an industrial catalyst, a polymer resin modifier, a plasticizer, an intermediate for pesticides and other chemicals, a stabilizer for peroxides, a strengthening agent for rubbers and plastics including vinyl polymers and unsaturated polyesters, and so forth [4–8]. The intermediate products of TEP degradation are diethyl phosphate and monoethyl phosphate which are known as pollutants in wastewater. The final products of TEP degradation are phosphate, carbon dioxide, and water. Therefore, it can be said that phosphate can see end of TEP degradation [9].

One of the most common AOPs methods for both academic and industrial researches is photocatalytic process [10, 11]. TiO_2 photocatalyst was considered as one of the most practical candidates due to its high stability and photocatalytic efficiency [12–14]. Recently, more attention has been paid to increasing the reaction rate and enhance its catalytic efficiency [15–17]. Several reports have been presented for the nano-TiO_2 photocatalytic process; the effects of important parameters such as pH values, TiO_2 dosage, light intensities, dissolved oxygen levels and other operating conditions were investigated for heavy metals and some organic materials [17–21]. There is not any report on optimization of effective parameters for degradation of organophosphates which are important factors for photocatalytic reactor design; therefore, a study on the optimization of effective parameters is important and promising, which is yet to be done.

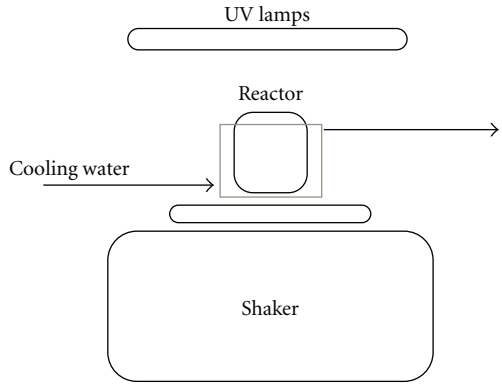


Figure 1: Schematic diagram of the photocatalytic system.

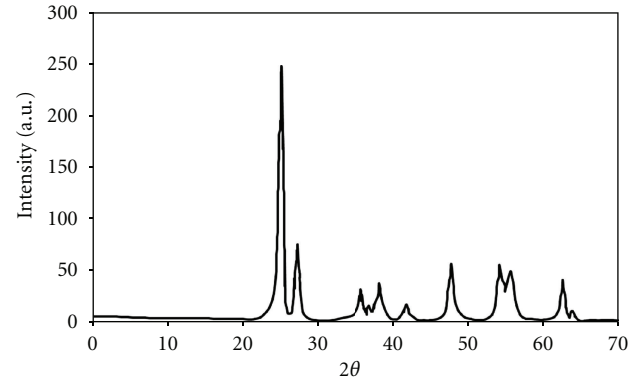


Figure 2: The XRD pattern of nano-TiO_2 particle.

In this research, the decontamination of organophosphates by the UV/nano-TiO_2 process has been investigated, and optimized conditions have been obtained. Firstly, nano-TiO_2 particles were characterized by X-ray powder diffraction (XRD), Field-Emission Scanning Electron Microscope (FESEM), and Dynamic Light Scattering (DLS), and the best pH for TEP adsorption was calculated in dark condition. Then, the optimum concentration of nano-TiO_2 and pH in photocatalytic process was studied. At the end, the kinetic reaction of TEP degradation was suggested as a function of initial concentration of TEP, nano-TiO_2 concentration and pH.

2. Experimental

2.1. Materials. Triethyl phosphate (TEP) with purity above 99.5%, sodium hydroxide (NaOH) and nitric acid were obtained from Merck Co. (Germany). Titanium dioxide nanoparticle (P-25, ca. 80% anatase and 20% rutile) with an average particle size of 20 nm and a BET surface area of 50.4 m^2g^{-1} was supplied by Degussa, Germany.

2.2. Analysis. The phosphate concentration was measured by a UV/visible spectrophotometer at a wavelength of 640 nm. The samples were filtered to remove nanoparticles of nano-TiO_2 particles. The gas chromatograph (GC) was equipped with a flame-ionization detector and a WCOT fused silica column (50 m × 250 μm × 0.4 μm) to measure the TEP concentration.

The X-ray diffraction (XRD) pattern was obtained using a Philips X'Pert diffractometer (X'pert diffractometer using CuK α radiation). The average crystal dimension was calculated using Scherrer's equation, which was also confirmed with DLS test. The FESEM (Hitachi, model S-4160) was used to determine the particle size distribution of nano-TiO_2 crystals.

2.3. Adsorption Measurements. The oxidation of TEP was carried out in a glass batch reactor with six 15 W UV-C lamps at 25.0 ± 0.1°C (Figure 1). The concentration of nano-TiO_2 and TEP was changed from 100 to 1000 mg L^{-1} and from 10 to 50 mg L^{-1}, respectively. The adsorption value measurements were carried out with 400 mg/L nano-TiO_2 in dark condition. The pH of solution was stabled with 0.1 M of NaOH and HNO_3 solutions. For complete degradation of TEP, the phosphate concentration was measured during the reaction.

Table 1: Adsorption of TEP on nano-TiO_2 surface (nano-TiO_2 = 0.4 g L^{-1}, TEP = 30 mg L^{-1}).

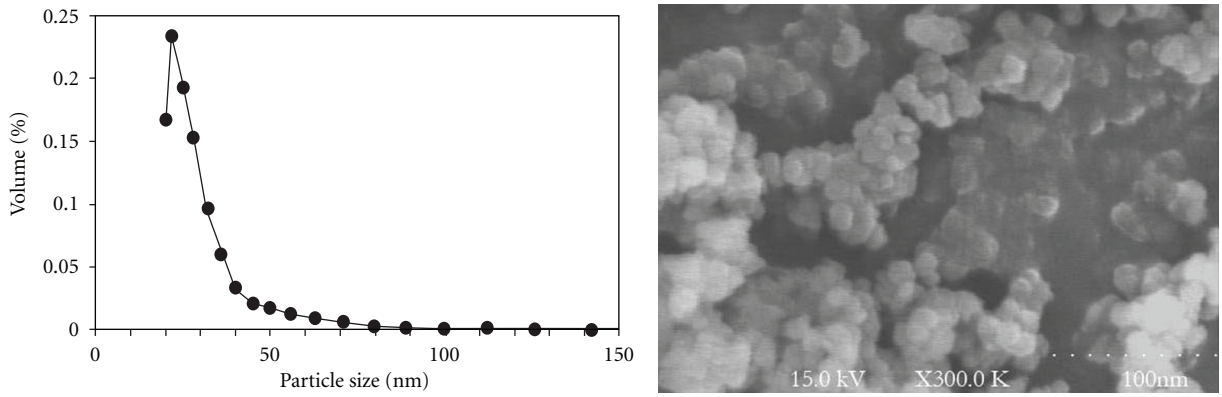
pH value	2	4	7	10	12
TEP	14.01 ± 0.5	22.3 ± 0.7	24.7 ± 0.7	27.2 ± 0.7	34.02 ± 0.7

3. Results and Discussion

3.1. Structure and Surface Characterization of TiO_2. The XRD patterns of the nano-TiO_2 in rutile and anatase phases are shown in Figure 2. The XRD patterns exhibit strong diffraction peaks at 27°, 36°, and 55°. Ordinary peaks seen at 25° and 48° indicate that TiO_2 has been in the rutile and the anatase phase with the ratio of approximately 20 : 80, respectively. Also, the Degussa materials were random spherical nanomaterials 10–50 nm in size and composed of a mixture of ~8 : 2 anatase (JCPDS card no. 00-21-1272): rutile (JCPDS card no. 00-21-1276). The crystallite size of the prepared particles obtained from the width of XRD peaks using Scherrer's equation is 20 nm, which can be confirmed with DLS FESEM image (Figure 3).

3.2. Adsorption of TEP and Cr(VI) Mixture on TiO_2. The effect of the pH values on adsorption behaviour of TEP on nano-TiO_2 particles was investigated. TEP adsorptions percentages at different pH levels are shown in Table 1. At the pH value of 12, the adsorption of TEP on nano-TiO_2 particles is the highest and minimum percentage of TEP adsorption is seen at the pH value of 2. In the acidic pH, TEP is protonized to carry the positive charges, while the surface of TiO_2 is electropositive [8]. Therefore, the acidic pH does not favour the adsorption of TEP on the TiO_2 particles.

3.3. Photocatalytic Degradation of TEP by UV/TiO_2. The intermediate materials such as diethyl phosphate and ethanol



(a) (b)

Figure 3: FESEM image and particle size distribution of nano-TiO_2 patricle.

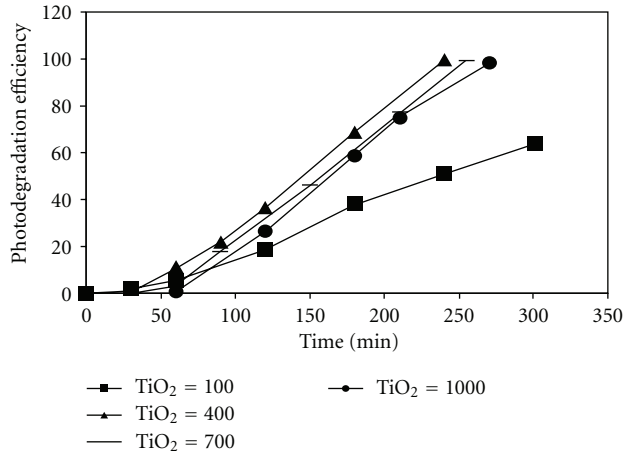


Figure 4: Effect of nano-TiO_2 concentration on TEP degredation (TEP = 30 mg/li, pH = 7).

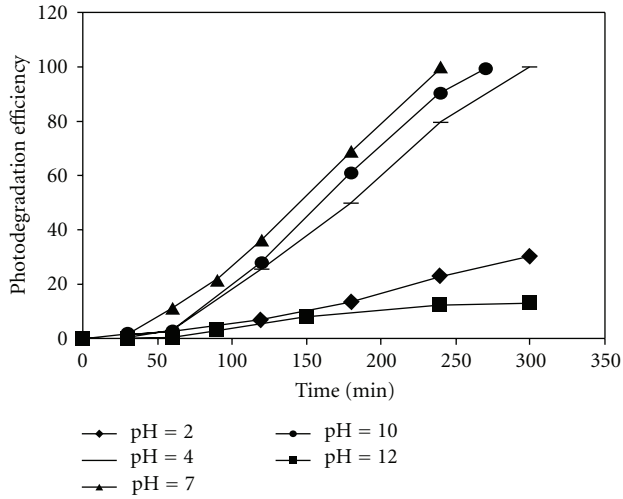


Figure 5: The effect of pH on reaction rate (TEP = 30 mg/li and nano-TiO_2 = 400 mg/li).

are produced from TEP photocatalytic degradation, and subsequently monoethyl phosphate is formed from TEP and diethyl phosphate. In the final step, TEP and intermediate products degrade to phosphate, which is known as the end of TEP degradation. To study the photocatalytic reduction of TEP by UV/TiO_2 process, the kinetic experiments were carried out at different pH values, TEP and nano-TiO_2 concentration by analyzing the phosphate concentration. The effect of nano-TiO_2 concentration on photocatalytic reaction is shown in Figure 4. In the high concentration of nano-TiO_2 (1000 mg/li), the solution is very dark, which decreases diffusion zone of UV radiation in the solution and causes the reaction rate to decline. On the other hand, low concentration of nano-TiO_2 causes the reaction zone to decrease. Therefore, the best concentration of nano-TiO_2 is 400 mg/lit which shows the highest reaction rate.

The effect of pH values on reaction rates is shown in Figure 5. At acidic pH values, because of proton releasing in solution, the photocatalytic reaction rate is higher than alkaline pH. Therefore, it hardly reaches the criteria for ready photocatalytic degradation. Also, the adsorption of TEP over the nano-TiO_2 particles is another crucial factor in the photocatalytic reaction rate. Increasing the amount of TEP adsorption leads to more TEP concentration in the reaction zone which can improve the reaction rate. The experimental results show that natural pH has the highest reaction rate. Degradation rate of TEP at lower pH values is lower than that of at pH value of 7.0. This can be explained by the less adsorption amount of TEP on the TiO_2 at acidic pH compared to the pH value of 7; therefore, it can be said that the adsorption process plays an important role in photocatalytic reactions.

In Figure 6, the effect of TEP concentration on kinetic degradation is shown at the pH level of 7. A little trace of phosphate is observed at an early stage of the photocatalytic reaction because phosphate forms after the degradation of TEP, diethyl phosphate, and monoethyl phosphate. After a lag time, phosphate amount suddenly increases up to final concentration. These lags were 21.1, 35, and 47 min

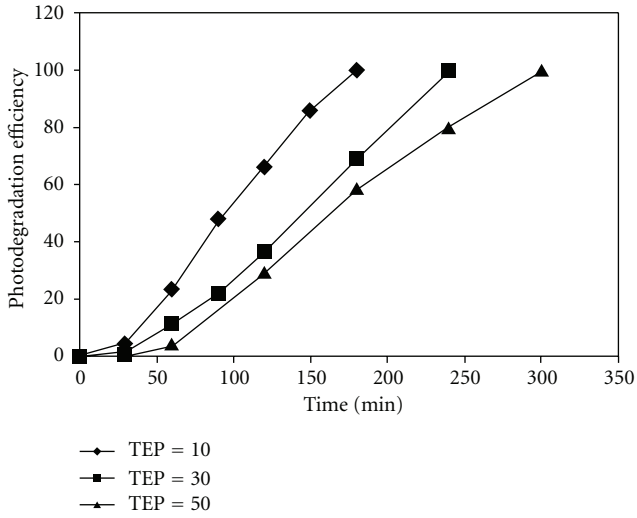


FIGURE 6: The kenetic rate of TEP (nano-TiO_2 = 400 mg/li and pH = 7).

for 10, 30, and 50 mg L^{-1} of TEP concentration in solution, respectively.

The effects of TiO_2 and TEP concentration were studied, and the results are shown in Figure 6. The photocatalytic reaction rate is very low in low concentration of nano-TiO_2 (100 mg/li). As the concentration of nano-TiO_2 increases to 400 mg/li, the reaction rate rise to the highest value. Results show that the reaction rate is only as a function of initial TEP concentration and TiO_2 does not have any effect on it. Also, it can be seen that total degradation of TEP has a lag time which is as a function initial concentration of TEP and TiO_2 concentration. The suggested kinetic reaction is a zero-order equation with a lag time as a function of initial concentration of TEP. The final equation is

$$\frac{dC_{\text{phosphate}}}{dt} = k_{\text{red}}, \quad t > t_{\text{lag}}, \tag{1}$$

where $k_{\text{red}} = 0.756C_{\text{TEP}_0}^{-0.29}$ (hr^{-1}) and $t_{\text{lag}} = 0.567C_{\text{TiO}_2}^{0.454}C_{\text{TEP}_0}^{0.492}$ (hr).

4. Conclusion

The optimum condition of TEP degradation in nano-TiO_2 photocatalytic reaction was obtained. Also, effects of nano-TiO_2 and TEP concentration as well as pH values were studied using a batch reactor. The results show that the neutral pH has highest photocatalytic reaction rate while the highest TEP adsorption is calculated at alkaline pH. Also, increasing the concentration of nano-TiO_2 declines the photocatalytic reaction rate and rises the lag time which was seen as TEP concentration increased. At the end, a zero-order kinetic reaction rate with a lag time was suggested for complete oxidation of TEP.

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