Studying the Photocatalytic Degradation of Tri-n-Butyl Phosphate Using Nano Nd-Doped TiO2

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Abstract

Photocatalytic method was used as an efficient and simple way for degradation of tri-n-butyl phosphate (TBP). In contrast to other methods, in this method the mineralization occurs and no twin pollution is generated. Nd doped TiO2 was synthesized via sol gel process and characterized by XRD and TEM tecniuqes. Then it was used as photocatalyst for TBP degradetion. It was found that the solution pH has important effect on degradation efficiency and kinetic. Degradation was more efficient in both acidic and alkali media. The kinetic studies indicated that the second order model at neutral pHs range was the dominant while in acidic or alkali conditions the kinetic models were first and third order respectively. By proceeding the degradation process, some products and byproducts are generated, which lead to the change of the solution pH and change of degradetion mechanism and kinetic. The LC MS was used to detect the intermediate and final products. Results showed that the method has high efficiency and is a promising procedure for decomposition of TBP.

Keywords: TBP; Photodegradation; TiO2.

Introduction

TBP, as a complexing agent, is being used widely in liquid–liquid extraction and separation of many valuable radionuclides such as uranium, plutonium, hafnium, etc. ions, in nuclear science and technology [1]. Despite its advantages such as high selectivity and great stability when radiationis is concerned, it has some disadvantages such as solubility in water (about 400 mg/L) which causes some problems such as formation of red oil in evaprators [2]. The red oil is a red substance formed by reaction between the TBP and nitrates (supplied by nitric acid or uranyl nitrate). In evaporators, the red oil can be exploded at elevated temperature during nuclear fuel reprocessing [3]. Moreover, the TBP has many other applications. It is used as a solvent, herbicide, fungicide, defoamer, and plasticizer in various application fields. So it can leach to the aquatic environment and cause pollution problems. Even low TBP concentration in water may cause toxicity to fresh water living organisms, and if ingested by human it also causes cholinergic toxicity and neurotoxicity [4-6].

Considering the mentioned hazards of TBP, its removal from water necessitates a simple, albeit an efficient method. Some physico-chemical processes has been employed to treat TBP which are expensive and also they do not degrade the TBP, but only move it from one phase to another. Photocatalytic degradation

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process is a simple and very efficient procedure which can be used to degradation of the TBP to the minerals without production of toxic intermediates. It has been adopted for degradation of many organic pollutants in many researches [8-12]. Some various materials were used as photocatalyst in this process. The TiO_2 is among the photocatalysts which have been employed extensively, because of their high activity and efficiency, low toxicity, no twin pollution, chemical stability and insolubility in water [13-18]. To increase the photocatalytic activity, the TiO_2 is doped with transition metals and rare earth ions, which prevent the electron-hole recombination produced by UV light irradiation. Lanthanide ions could also form a complex with lewis bases organic moleculs (because of f-orbital configuration) such as amines, alcohols, etc. in addition to the mentioned effect, so the decomposition process can proceed faster [19-22].

Considering our previous works [23, 24] which revealed that doping with neodymium had a significant effect on increasing the photocatalytic activity of the TiO_2 compared with other dopants. In this study the TiO_2 was doped with neodymium and used for degradation of the TBP. The solution pH as an important factor affecting the degradation efficiency, and degration kinetic was investigated.

Materials and Methods

Synthesis and characterization

Sol gel method was used to synthesize of catalyst. The method was developed in the following steps: an appropriate amount of Titanium Tetra iso-Propoxide (TTiP) was dissolved in 100 ml of ethanol to form solution A. Then 0.2 g of hydroxypropyl cellulose was added to solution A under stirring condition as a stabilizer. Solution B was prepared by addition of 0.18 ml nitric acid to 10 ml ethanol. Neodymium nitrate was dissolved in 5 ml ethanol and considered as solution C. The Nd/Ti molar ratio was 1:500 in as-prepared solution. Then the solution B was added to the solution A drop by drop, under vigorous stirring condition to form a clear sol. Then the solution C was added slowly to this (sol) solution. The obtained mixture was continuously dispersed for 30 minutes by a homogenizer at ~20000 rpm.

The sol was sonicated for 30 minutes, aged at room temperature (25–30°C) for 48 hours to form gel, and dried at 70°C overnight to remove water and organic solvents. Finally the dried gel was calcinated in an electric furnace at 500°C for 4 hours [23].

Then the synthesized sample was characterized as fallow: X-Ray diffraction was employed to identify the crystalline phases of as prepared TiO_2/Nd sample. The diffractometer was STOE STADI MP with Cu Kα radiation (λ=0.15406 nm). TEM ananlysis was used to investigate the morphology and particle size of nanostructure. A Philips EM 208 S electron microscopy instrument was used for this purpose. Average particle size of the catalyst was estimated using the Sherrer equation and compared with TEM images.The surface area of the samples were determined through nitrogen adsorption-desorption isotherms analysis (BET method:Quantachrome Nova 2200). The samples were degassed in a vacuum chamber for 3 hours at 300 °C before BET analysis. TBP concentration was determined by GC, using standard addition method. The solutions were spiked with n-decanol as internal standard. To detect the intermediate species, LC MS analysis was used (Agilent MSD1100 system).

Photocatalytic degradation

Photocatalytic degradation process was studied in a cubic glass photoreactor. The UV lamp was placed in a quartz tube which was placed in the middle of reactor and surrounded by the TBP solution. 500 ml of the solution and 0.5 g of catalyst were irradiated in a run (as previous work [23]). The irradiation source was a UV lamp (15 W). The sampling (about 5 ml) was done every 30 minutes and then it was filtered. The TBP concentration was determined by GC analysis. Before determination of TBP in irradiated solution, it should be extracted from aqueous to an organic phase. The extraction was done by dichloromethane. Extraction time was optimized by determination of extraction efficiency of TBP in various shaking times.

LC-Mass was used during photodegradation to analyze the intermediate species. Five solutions with pHs of 2, 4, 6, 8 and 10 were chosen to investigate the pH effect on degradation rate and mechanism of TBP. The initial solution pH, was adjusted by nitric acid and ammonia solutions.

Results and Discussion

X-Ray diffraction pattern of the TiO_2/Nd (figure1) showd that the major part of the synthesized sample was anatase phase, and the rutile existed as minor phase. No other crystalline impurities were seen in synthesized samples.

Peak broadening in XRD pattern indicated the nano size of particles. The crystallite size of the samples were estimated by the Scherrer equation:

$D = 0.89\lambda/\beta\cos\theta$

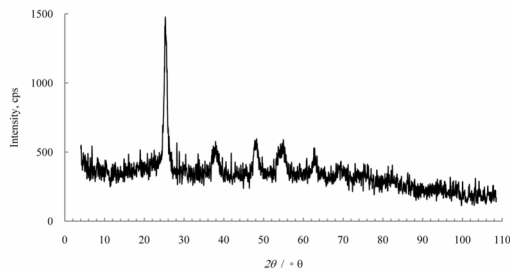where D is the crystal size, β is the full width at half maximum of the peak and λ is the wavelength of
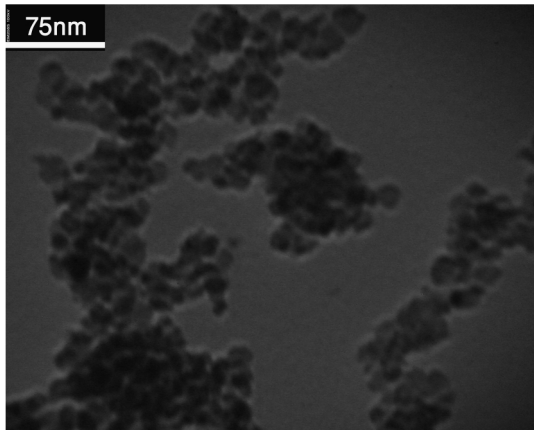
Figure 1. XRD pattern of TiO$_2$/Nd

Figure 2. TEM image of TiO$_2$/Nd

Figure 3. Extraction percent of TBP in various contact times

Figure 4. Degradation of TBP versus the time

incident X-Ray [25]. The average crystal size of the Nd-doped TiO$_2$ were calculated about 35 nm, being in line with the TEM results.

Figure 2 shows the TEM image of the synthesized sample. As can be seen from image the particle size is less than 30 nm. It is also clear that the particles size distribution range is narrow and all particles are in the range of 20-30 nm. Close examination cleared that the particles are agglomerated to form semi-spherical structure.

The sample surface area estimated from BET method was 153 m^2/g with meso size pores (the pores formed between the spheres as can be seen in TEM image). The high surface area improves the catalytic performance of sample. The GC analysis was used to determine the TBP concentration in extracted samples. Dichloromethane was employed as an extracting solvent. To optimize the time of extraction, a determined amount of TBP was contacted with solvent and extracted at different contact times for GC analysis. Figure 3 shows the extraction percent versus the shaking time. It can be seen that the extraction percent increased with time and maximum was achieved at initial 10 minutes. So the 10 minute time was selected for shaking of decanter using a shaker with a fixed shaking speed and temperature.

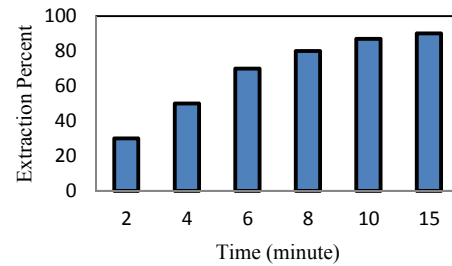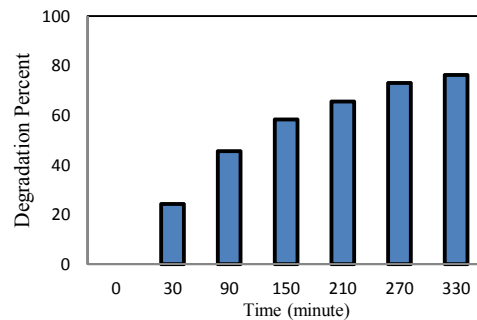Degradation of TBP was studied versus the time. It can be seen (Figure 4) that about 80% of TBP was degraded at 5 initial hours. The first order and the second order kinetics were examined to fit the experimental data. It was found that the data were fitted better with the pseudo second order model.

Figure 5 shows the fitting of experimental data with the pseudo second order kinetic. It was seen that the regression coefficient was more than 0.99 for the pseudo second order while it was 0.97 for the first order kinetic model, so the pseudo second order kinetic model can describe better the TBP degradation rate. Various kinetic models were also used to fit the experimental data obtained in different initial pHs. It was found that at the pHs of 4, 6 and 8 the second order model is suitable for fitting the experimental data and the regression coefficients are higher than 0.99. At the pH=2 the experimental data are better fitted with the first order model indicating that the degradation mechanism was changed. However at the pH=2 the rate constant was not the same for whole of process. The rate constant changing during degradation, indicates the change of reaction mechanism. The results also showed that the obtained data at initial pH=10 was not fitted in second order kinetic model and fallows the third order kinetic model, and varies during the process. Figure 6 shows the degradation of TBP at various pHs.

In addition to affecting the reaction rate and kinetic, the solution pH, can affect the degradation percent.
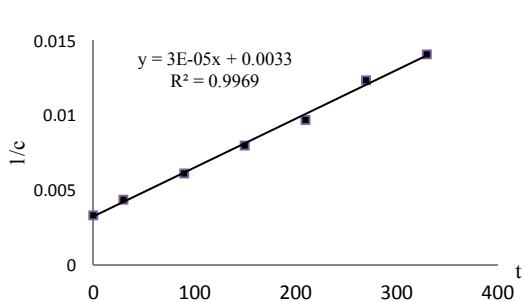
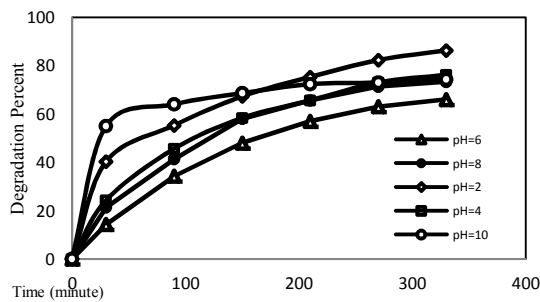**Figure 5.** The second order kinetic fitting for degradation process at pH=4

Figure 6. The effect of solution acidity on degradation of TBP

Table 1. Solution pH during the photodegradation process with initial pH=10

T (min.)	30	90	150	210	270	330
pH	9.8	6.58	5.18	4.29	3.98	3.62

Table 2. Solution pH during the photodegradation process with initial pH=8

T (min.)	30	90	150	210	270	330
pH	6.58	4.28	3.91	3.63	3.40	3.35

From figure 6, it is clear that the maximum degradation percent occurs at pH=10 and pH=2, so both acidic and basic solutions are more favorable than neutral media for degradation process. It was found that solution pH varies during the degradation reaction. So the mechanism and the rate of reaction will be vary during the degradation process. In two individual run, the pH of solution was measured during the degradation process. Tables 1 and 2 show the pH of solution during the degradation period, with initial pHs of 8 and 10. As
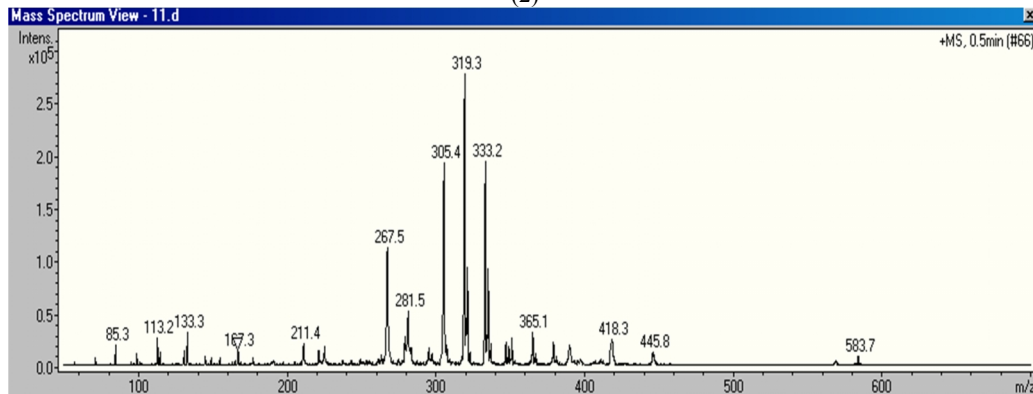
(1)
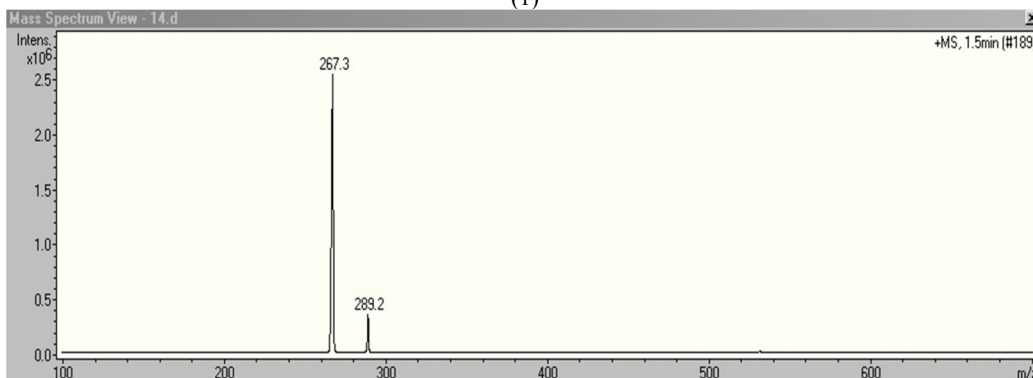
(2)

Figure 7. LC MS for undegraded (1) and degraded TBP (2)

can be seen, the pH decreases with proceeding the degradation process. It was found that the pH change was the main reason of changing the kinetic with proceeding the degradation reaction (from the third to the second order at initial pH=10). The solution pH was not reached to 2 in any run, so the first order kinetic (which was seen in pH=2) was not observed at these initial pHs. Due to multiple roles of solution pH, it is difficult to interpret the pH effects on the efficiency of photodegradation process. The first role is because of the following reactions:

$$TiOH + H^+ \rightarrow TiOH_2^+$$
$$TiOH + OH^- \rightarrow TiO^- + H_2O$$
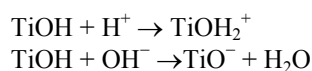
Since the surface adsorption of TBP on the photocatalyst is an important step in its photocatalytic degradation, the surface charge change with pH, affects the reaction rate and mechanism. TBP can also be protonated and change the reaction mechanism. Through alkaline media, more hydroxyl radicals can also be formed by the reaction between hydroxide ions available on TiO_2 and positive holes which giving rise to an increase in the degradation rate [26].

Degradation process proceeds through several stages and various intermediates. Moreover various intermediate and final products are also produced during the degradation because of butyl groups separation. LC MS was used to detect the intermediates and final products. Figure 7 shows the LC MS analysis for the TBP before and after degradation process.

In the first part, it was seen that only TBP species was present. The two observed peaks are result of proton or sodium ions adduction on the TBP molecule. In the second part several peaks can be seen. The probable products (according to their mass) are presented in Figure 8. We guess that the three highest peaks are belong to three adducting product presented in the first row of figure 8. Except the m/z = 305 which belongs to TBP, the others belongs to final products. Both of them are minerals, so the mineralization has been achieved extentsively. Other two guessed products are also minerals. The organic byproducts can be subjected to more degradation until complete mineralization. The peaks with low intensity which has small m/z, can be result of adducting the potassium, sodium or other cations on the produced butanol.
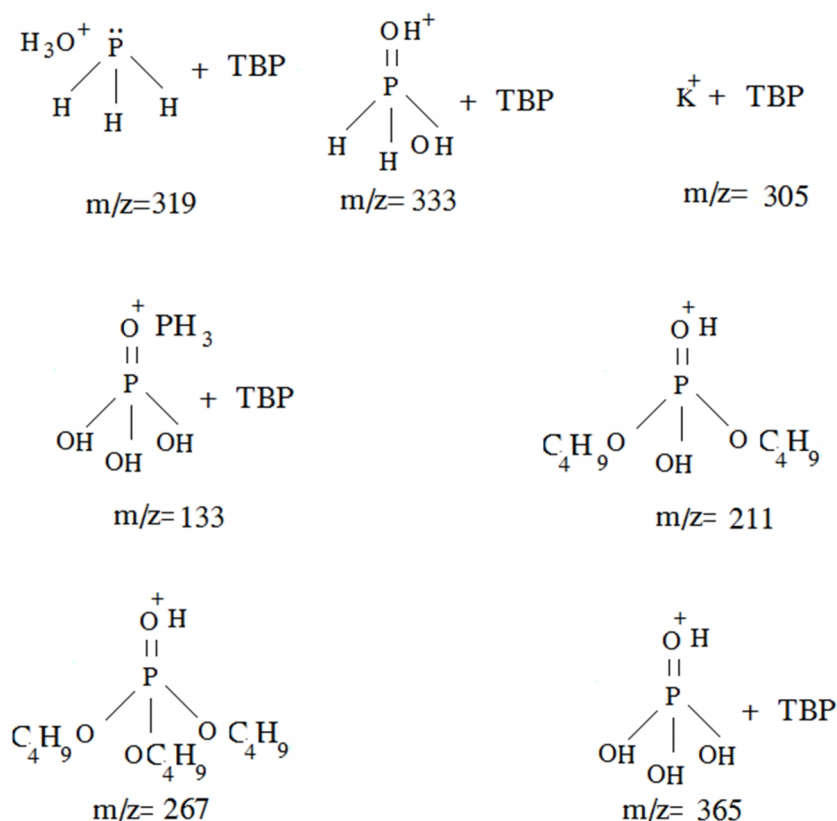

Figure 8. Some intermediates which are guessed to be produced regarding the observed m/z

Conclusion

Photocatalytic method was used as a simple albeit promising process for degradation of TBP. The photocatalyst was synthesized through the sol gel method. The XRD ,TEM and BET techniques were used to characterization of products. The effect of solution pH on kinetic and efficiency of degradation was studied. It was found that the solution pH could affect both the kinetic and efficiency of degradation reactions. The efficiency was increased in acidic and alkali media, but decreased when the solution pH was nearly neutral or under weak acidic and alkali conditions.

A careful investigation of the kinetic models revealed that at pHs of 4, 6 and 8 the second order kinetic model best fitted the experimental data. At pH=2, the data fit better the first order kinetic, indicating the mechanism of degradation is changed in acidic solution.

The data obtained at initial pH=10 fitted with the third order kinetic model, but varied during the the degradation process. By determination of the solution pH during the degradation for some samples, it was found that the solution becomes acidic with proceeding the reaction due to generation of acidic products.

The maximum degradation percent was observed at pH=10 and pH=2, so both acidic and alkali solutions are more favorable than neutral media for degradation of TBP. LC MS was used to detect the intermediate and final products. Most of the generated products were minerals. The results showed that the method has high efficiency and is a promising process for mineralization of TBP without generation of twin pollution.

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