Boron Doped TiO$_2$ For The Photodegradation of 4-nitrophenol: Optimization of The Doping Parameters

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ABSTRACT

In this work we prepared boron doped TiO$_2$ (B-TiO$_2$) photocatalysts and evaluated their photocatalytic activity for the degradation of our model organic pollutant, 4-nitrophenol (4-NP). The photocatalysts were prepared using wet impregnation method with different calcination times, calcination temperatures and dopant amounts in order to determine the optimum parameters. The degradation of the pollutant was carried out in a specially designed degradation chamber and characterized by UV-Vis spectrophotometry. The degradation kinetics were evaluated with pseudo-first order kinetics by comparing rate constants and half-lives of various photocatalytic reactions. It was found that the highest removal rate was obtained for 0.50 % boron doping with calcination at 450°C for 3 hours. The results showed that TiO$_2$ could be doped with boron, which is in abundance in our country, and used for the photocatalytic degradation of a toxic pollutant in water. The promising results for the organic matter removal could pave the way for further studies of environmental applications.

Keywords:

Boron doped TiO$_2$; Photocatalysis; 4-Nitrophenol; Pseudo first order kinetics; Doping parameters.

INTRODUCTION

With diminishing resources for drinkable water in the world, wastewater treatment is more relevant than ever today. There are a number of physical, chemical, electrochemical and biological treatment methods [1-5] to remove harmful pollutants from aqueous systems. One of these methods is photocatalysis which is one of the advanced oxidation processes (AOPs) and basically includes the use of a photocatalyst for the mineralization of the pollutant into harmless small molecules such as CO_2 and H_2O [6, 7]. This is made possible by oxidation with reactive oxidizing radicals produced from the combined use of a photocatalyst and an appropriate light source.

Heterogeneous photocatalysis is an economically feasible choice among AOPs since it has low operational costs and it is possible to work at ambient conditions without the need of other chemicals [8]. The most widely researched and utilized photocatalyst is TiO$_2$ which is a semiconductor with a band gap energy of approximately 3.2 eV [9, 10]. Due to this band gap energy, photocatalytic degradation using TiO$_2$ is performed under ultraviolet (UV) light which has the corresponding energy to initiate the excitation and transfer of an electron from the valence band to the conduction band of TiO$_2$, leaving behind a positively charged hole. The formation of these electron-hole (e$^-$ / h$^+$) pairs leads to the subsequent oxidation of adsorbed organic matter on TiO$_2$ surface through the generation of reactive oxidizing species such as HO$_2\bullet$, HO$\bullet$ and O$_2\bullet^-$ [11, 12].

There is a variety of approaches and strategies such as surface modification [13, 14], doping with another element [15, 16] or synthesizing composite materials [17, 18] to enhance the activity of TiO$_2$ under solar light or to obtain a more powerful photocatalyst. We have found through our previous research that doping with metals [19, 20], non-metals [21] or co-doping [16, 22] could influence the photocatalytic activity of TiO$_2$ for the degradation of a variety of pollutants. In this work, we have used boron as the dopant and obtained B-TiO$_2$ which has previously been utilized as a catalyst [23-25]. It is known that doping with transition metals narrows the band-gap of TiO$_2$, making it more efficient under solar light and reduces the recombination rate of electron-hole (e$^-$ / h$^+$) pairs [26].

Boron deposits in Turkey are estimated to be 948 million tons according to 2017 report of Turkish National Boron Research Institute, which constitutes 73% of

the world's boron reserves [27]. Because of its natural abundance in various mineral forms in Turkey, we chose boron as the dopant. We have used boric acid (H_3BO_3) as the boron source for doping. Boric acid also finds use in a myriad of areas from glass industry to detergents, nuclear reactors, and medicine.

Phenols and their derivatives are pollutants that are known to cause toxicity in wastewaters. Especially nitrophenols that are highly toxic are released in water as effluents of numerous industries [28]. One of these compounds is 4-nitrophenol (4-NP) which has a maximum allowed concentration of 20 ppb in water [6]. We have chosen 4-NP as the pollutant to be studied because of its environmental relevance and toxicity.

In this work, we prepared B-doped TiO_2 photocatalysts by altering the experimental conditions. Successful doping was shown by SEM-EDX measurements. The photocatalytic activity of the catalysts were determined from the heterogeneous photocatalytic degradation of 4-NP. We have investigated the effects of calcination time, calcination temperature and dopant amount in order to find the most promising photocatalyst in terms of activity. We used pseudo-first order kinetic model to obtain and compared rate constant values of the photocatalytic reactions. We also studied the removal percentages of the pollutant for assessing the photocatalytic efficiencies of the newly prepared B-TiO_2 photocatalysts. We compared our results with the photocatalytic removal of 4-NP by bare TiO_2.

MATERIAL AND METHODS

We used Evonik P25 TiO_2 as the precursor to be doped. Evonik P25 is a mixture of anatase (79%) and rutile phases (21%). The doping procedure was achieved using the well-established wet impregnation method. Boric acid (H_3BO_3) was used as the dopant source. It was obtained from Merck and used without further purification. All the solutions were prepared with distilled water.

Preparation of Doped Photocatalysts

Boron doped photocatalysts were obtained via wet-impregnation method where TiO_2 is impregnated with the dopant solution, which in our case was boric acid. Briefly, we mixed 10 g TiO_2 with 15 mL aqueous boric acid solution at different concentrations and stirred at room temperature for 1 hour. Dopant concentration was varied between 0.25 – 1.00% wt. Obtained photocatalysts were then washed with distilled water and dried for 24 hours at 373 K. After the drying process, the samples were calcined at 350, 450 and 550°C for predetermined amounts of time. In order to achieve a narrow size distri-
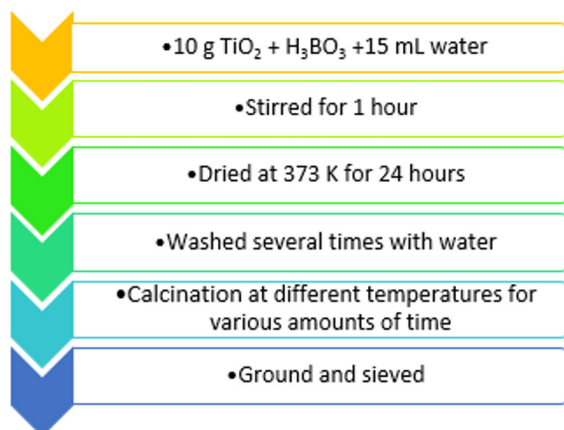

Figure 1. Preparation steps for the B-doped photocatalysts

bution of the particles, the calcined photocatalysts were ground and sieved from a 32 Micron sieve. The complete preparation process is summarized in Figure 1.

The abbreviations for the obtained photocatalysts stand for their preparation conditions. For example, 0.25-450-3 B-TiO_2 stands for the photocatalyst that has 0.25% wt. boron and was calcined at 450°C for 3 hours. All photocatalysts were named accordingly and presented in Table 1.

Table 1. RBoron Dose(% wt.), Calcination Times and Temperatures for the Preparation of Doped Photocatalysts.

Photocatalyst	Boron Dose (%wt.), Calcination Temperature and Time
0.25-B-450-3	0.25% B, 450°C, 3hr
0.50-B-450-3	0.50% B, 450°C, 3hr
0.75-B-450-3	0.75% B, 450°C, 3hr
1.00-B-450-3	1.00% B, 450°C, 3hr
0.50-B-450-1	0.50% B, 450°C, 1hr
0.50-B-450-5	0.50% B, 450°C, 5hr
0.50-B-350-1	0.50% B, 350°C, 1hr
0.50-B-350-3	0.50% B, 350°C, 3hr
0.50-B-350-5	0.50% B, 350°C, 5hr
0.50-B-550-1	0.50% B, 550°C, 1hr
0.50-B-550-3	0.50% B, 550°C, 3hr
0.50-B-550-5	0.50% B, 550°C, 5hr

Characterization of Photocatalysts

In order to show that the wet impregnation of TiO_2 with boron was indeed achieved successfully, we have used scanning electron microscopy with energy dispersive X-Ray analysis (SEM-EDX). The analysis was carried on a FEI-Philips XL30 instrument equipped with EDAX unit operating at 5 kV. Photocatalyst powders were supported on carbon tape prior to analysis.

Photocatalytic Degradation Experiments

In order to assess the photocatalytic capabilities of the B-TiO₂ samples, we have investigated the degradation reaction of 4-NP under UV-A light in a specially designed reactor. The reactions were carried out in a double-jacketed pyrex photoreactor. Five 8-watt black fluorescent lights were used as the light source. The reactor was connected to a water bath to utilize constant temperature at 25°C. 600 mL solution containing 4-NP (1.0×10^{-4} mol/L) with 0.2 g/100 mL B-TiO₂ photocatalyst was suspended in an ultrasonic bath for 30 minutes in dark in order to reach adsorption equilibrium. The solution was then introduced to the photocatalytic reactor and mechanically stirred through the reaction. The photocatalytic experiments were carried out at the natural pH of the solutions without pH adjustment. 10 mL samples were collected at predetermined time intervals and were immediately filtered through 0.45 μm Millipore HA (cellulose acetate) filters to separate TiO₂ from the solution. Absorbance values of the samples at λ = 317 nm were determined with a Perkin Elmer LS 55 UV-Visible spectrophotometer, and the concentrations of the solutions were calculated from calibration curves.

Photocatalytic efficiencies were compared using removal percentages of 4-NP with B-TiO2 photocatalysts. These were calculated from Eq.1 where C0 is the initial 4-NP concentration and C is 4-NP concentration at time t.

$$\text{Removal \%} = \left(\frac{C_0 - C}{C_0} \right) x100 \qquad (1)$$

Experiments in identical conditions were also carried out for bare Evonik P25 TiO₂ for comparison purposes.

Kinetic Calculations

The degradation was estimated to follow pseudo-first order kinetics as was the case in our previous works [16, 29]. The degradation rate constant was obtained from Eq. 2 where C₀ is the initial concentration (mol/L), C is the concentration (mol/L) after time (t) (mins) of the degradation reaction, and k is the first-order rate constant:

$$\ln \left(\frac{C}{C_0} \right) = kt \qquad (2)$$

RESULTS AND DISCUSSION

Effect of Dopant Amount

Photocatalysts were prepared using different amounts of dopant and their efficiencies on 4-NP degradation were investigated. With this purpose, 0.25, 0.50, 0.75 and 1.00
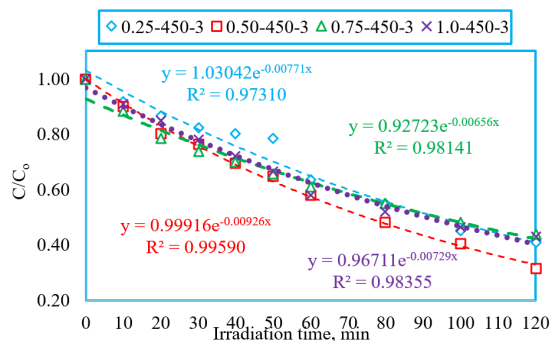

Figure 2. PC/C₀ – t plots for photocatalysts with different dopant amounts

% wt. boric acid was used as dopant and 3 hours of calcination at 450°C was performed. Degradation reaction was continued for 120 mins and C/C₀ values were plotted against time in Fig.2.

Kinetic data was modeled by pseudo first-order reaction kinetics and rate constants (k, min⁻¹), as well as half-lives ($t_{1/2}$, min) were calculated from Fig. 2 using Eq. 2 and listed in Table 2. Removal % values were calculated according to Eq. 1 and also presented in Table 2.

It can be seen that the photocatalytic degradation rate of 4-NP increased and then decreased and it was found that among the studied range, 0.50 % wt. showed the best result in terms of degradation with 68.47% removal. Photocatalytic degradation rate constant was also found to be highest for 0.50-450-3 which consequently yielded the lowest half-life. A similar behavior was observed for selenium doping of TiO₂ by Gurkan et. al. [30] which was attributed to two conflicting effects of doping. Enhanced photocatalytic activity is caused by the energy levels generated by the dopant ion, which acts as an electron or a hole trap. Also, the reaction rate is directly proportional to the absorption of photons, which again is increased by doping. But if the dopant concentration is high (i.e. higher than 0.50% wt.), increase in the recombination rate of the charge carriers is observed because of the decreased average distance between trap sites. We continued our experiments with 0.50% wt. dopant as the optimum amount since it provided the highest photocatalytic activity of the studied photocatalysts.

Table 2. Effect of dopant amount of B- TiO₂ photocatalysts for the degradation of 4-NP

Photocatalyst	Removal (%)	k (10^{-3}.min⁻¹)	$t_{1/2}$ (min)
0.25-450-3	59.02	7.71	89.90
0.50-450-3	68.47	9.26	74.85
0.75-450-3	56.13	6.56	105.66
1.0-450-3	56.99	7.29	95.08

Effects of Calcination Time and Temperature

In order to investigate the effects of calcination properties on the photocatalytic activities of the photocatalysts, we used three different calcination times and three temperature values. Studied calcination times and temperatures were 1, 3 and 5 hours, and 350, 450 and 550°C, respectively. The removal % value for each photocatalyst was calculated and given in Fig. 3.
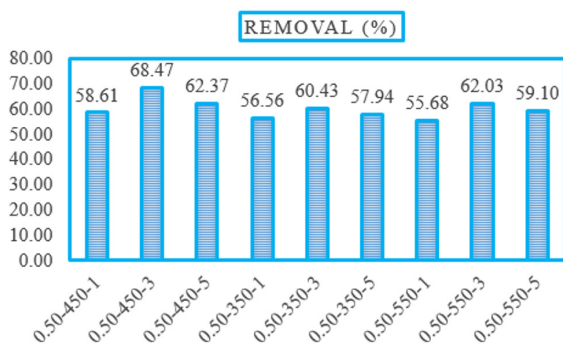

Figure 3. Removal % values for photocatalysts with different calcination times and temperatures.

When Fig. 3 is taken into account, we can conclude that highest removal percentages were obtained with photocatalysts prepared by 3 hours calcination time for every temperature value. This finding suggests that the optimum calcination time is 3 hours. For a better comparison, we also give the dependence of removal % values to calcination temperatures in Fig. 4.
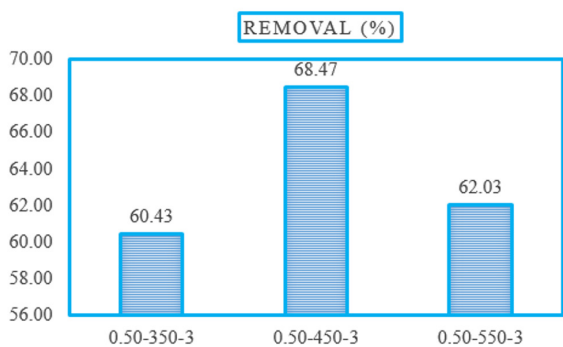

Figure 4. Dependence of removal % values for photocatalysts with different calcination temperatures.

We can conclude that out of the studied calcination temperature values, photocatalyst prepared at 450°C had the highest photocatalytic efficiency for the degradation of 4-NP. The exact ranking was 450°C > 550°C> 350°C with 68.47%, 62.03% and 60.43%, respectively.

The kinetic parameters of the photocatalytic degradation reactions were also calculated and given in Table 3 for each photocatalyst prepared by different calcination times and temperatures.

Table 3. Effect of dopant amount of B- TiO2 photocatalysts for the degradation of 4-NP

Photocatalyst	Removal (%)	k $(10^{-3}.min^{-1})$	$t_{1/2}$ (min)
0.50-450-1	58.61	7.44	93.16
0.50-450-3	68.47	9.26	74.85
0.50-450-5	62.37	7.82	88.64
0.50-350-1	56.56	7.48	92.67
0.50-350-3	60.43	7.60	91.20
0.50-350-5	57.94	7.20	96.27
0.50-550-1	55.68	6.57	105.50
0.50-550-3	62.03	8.20	84.53
0.50-550-5	59.10	7.69	90.14

Table 3 shows that once again 0.50-450-3 yields the best photocatalysis efficiency for the degradation of 4-NP. The obtained rate constant for this photocatalyst was $9.26x10^{-3}$ min^{-1}, which is higher than all other prepared photocatalysts. $t_{1/2}$ value suggests that the degradation of half of the initial 4-NP concentration takes approximately 75 mins where it could be as high as 105.50 mins, which is the case for 0.50-550-1.

Taking into consideration the removal % values, rate constants and half-lives, we have concluded that calcination at 450°C for 3 hours yields the most efficient boron doped photocatalyst for the degradation of 4-NP. Calcination temperature and times could alter the crystallographic properties of TiO_2 [31]. It is known that with increased calcination times, the particle size also increases [32], which could be the reason for lower photocatalytic efficiency obtained for 550°C. This increase in size is attributed to the fact that calcination at high temperatures or for long periods cause the doped ions to be desorbed [22]. The increase in the photocatalytic activity when calcination temperature is increased from 350°C to 450°C, can be caused by the greater formation of hydroxyl radicals per unit surface area [33]. We could conclude that calcination at 450°C for three hours yields the highest radical formation and smallest crystal size than other studied values.

Comparison of Doped and Bare TiO₂ Efficiencies

We have also compared the photocatalytic efficiencies of doped and bare TiO_2 under UV light in order to reveal the effect of doping with boron. The results of photodegradation of 4-NP with doped (0.50-450-3) and bare P25 TiO_2 under identical experimental conditions of photocatalyst amount, 4-NP concentration and irradiation time are given in Fig. 5.

When the removal rates were compared, 0.50-450-3 was found to be more efficient with a removal rate of 68.47

% than TiO_2 with 64.40 %. Kinetic parameters of reaction rate and half-life were also improved by doping. Rate constant and half-life values were 7.29 10^{-3} min^{-1} and 95.08 min for bare TiO_2 while they were found to be 7.82 10^{-3} min^{-1} and 88.64 min for 0.50-450-3. Although the difference may not seem significant, one should keep in mind that the main purpose of doping is to make TiO_2 more efficient under sunlight. The results of solar photocatalysis could show a more enhanced activity for B-doped samples since there is no direct correlation between the visible light activity and the photocatalytic activity [30]. But at this time, solar photodegradation is beyond the scope of our study and we could conclude that doping with boron enhances the photodegradation efficiency under UV light.
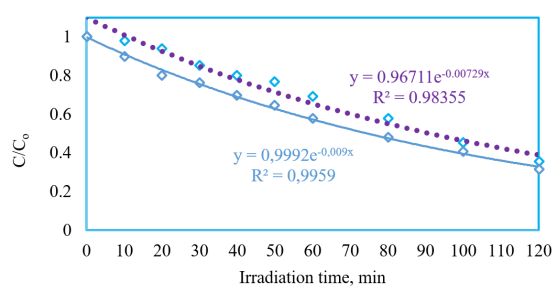

Figure 5. C/C_0 – t plots for bare (purple) and doped (blue) photocatalysts (P25 and 0.50-450-3, respectively.)

Morphology of the Photocatalysts

In this secton we have compared the morphologies of doped and bare photocataysts and shown that doping has indeed taken place, using elemental analysis. SEM images and EDX spectra of B-doped TiO_2 (0.50-450-3) and bare TiO_2 are given in Fig. 6.
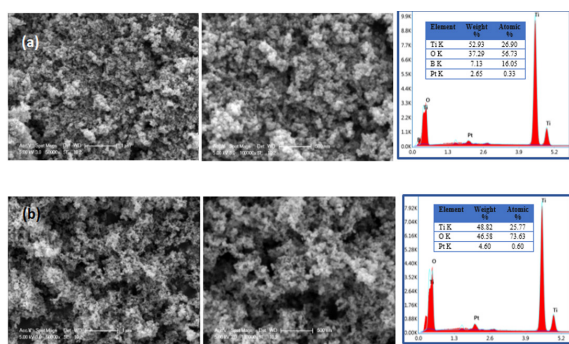

Figure 6. SEM images (left) x 50000, (right) x 100000 and elemental analysis (a) B-doped TiO_2, (b) bare TiO_2.

The SEM images of both B-doped TiO_2 (450-5-3 TiO_2) and bare TiO_2 consist of almost spherical particles with an average particle size of ~20 nm. Because of the doping effect of TiO_2, B-doped TiO_2 nanoparticles show a slight aggregation and the particle size is increased. The EDX spectra that are used to analyze the elemental composition of the photocatalysts demonstrate that the main components are Ti and O elements for both of the photocatalysts, as expected.

No impurities are observed in EDX spectra. The presence of boron in the EDX spectrum of B-doped TiO_2 confirms the doping procedure is successfully achieved.

CONCLUSION

Here, we investigated the heterogeneous photocatalytic degradation reaction of 4-NP, using the newly prepared, boron doped TiO_2 photocatalysts. We prepared these photocatalysts using the well-established wet-impregnation technique and evaluated the effects of doping conditions on the photocatalytic activities of B-TiO_2 catalysts. The doping was proven by SEM-EDX results. Optimization of dopant amount, calcination times and temperatures were performed. The photocatalytic activity and performance of the B-TiO_2 photocatalysts were evaluated in terms of removal percentage of 4-NP and also rate constants obtained from pseudo-first order kinetics model. The optimum amount of dopant was found to be 0.50% wt which yielded the best result in terms of pollutant removal. Highest removal of 4-NP was 68.47 % which was achieved by calcination of the photocatalyst at 450°C, 3 hours. Photocatalysis was performed with both doped catalyst, 0.50-450-3 and bare TiO_2 in order to show the effect of doping. The results indicated that the 4-NP removal as well as kinetic parameters were improved after doping. The findings of this work showed that TiO_2 could be doped with boron and used for the photocatalytic degradation of a toxic pollutant in water. In a time when water treatment is more relevant than ever, we think this work could provide a valuable insight for preparing photocatalysts by doping with an element that is in abundance in Turkey. Solar efficiency of boron-doped photocatalysts could be studied in the future, which would be promising for commercial applications.

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