Original Article

Photocatalytic Degradation of Bisphenol A from Aqueous Solutions using TiO_2 Nanoparticles and UV Illumination

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Abstract

Background and Purpose: Bisphenol A (BPA) is used to make certain plastics and epoxy resins. It is a non-biodegradable compound, and poses health risks to both humans and animals. The purpose of this study was to evaluate decomposition efficiency of BPA from aqueous solutions using UV irradiation.

Materials and Methods: In this study, the photodegradation of BPA in water were carried out in a reactor equipped 6 W UV lamp. In order to obtain the optimum operational conditions, parameters such as BPA concentration (1-50 mg/l), TiO_2 dosage (0.025-2 g/l), and pH (3-11) were evaluated. BPA concentration was measured by high-performance liquid chromatography.

Results: The highest degradation was 90% and achieved in 60 min. BPA degradation efficiency can be effectively improved by increasing pH, decreasing the initial concentration and increasing TiO_2 dosage. The optimal dose of TiO_2 was measured at 0.5 g/l. The degradation decreases with increasing TiO_2 dosage.

Conclusion: Photocatalytic degradation by using TiO_2 and low power UV lamp is applicable.

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***Key words*:** Photocatalytic degradation, Bisphenol A, Low power UV lamp

1. Introduction

Bisphenol A (BPA) is a non-biodegradable compound that is used to make plastics and epoxy resin. Plastics containing BPA is used to make some goods such as water bottles and sports equipment since this type of plastics are tough and clear. Some application of epoxy resins are lining of water pipes and coating of cans and thermal papers (1). BPA (Figure 1) is suspected to having estrogenic activity and can cause an imbalance in the endocrine system (2-5).

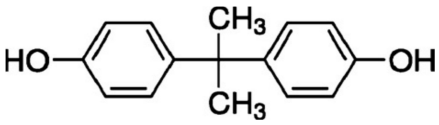


Figure 1. Chemical structure of Bisphenol A (6)

To having estrogenic activity and can cause an imbalance in the endocrine system (2-5). This compound can be found in natural waters as a result of untreated industrial effluents (7). The capability of conventional biological wastewater treatment systems for biodegradation of these compounds is low (8). These compounds can potentially pose a risk to fish and other aquatic organisms even at low concentrations of 0.1-10 ng/l (9). Various methods to remove phenolic compounds are presented such as ozonation, photo-fenton, ultrafiltration, adsorption on activated carbon, ultrafiltration (10) and phyto remediation (11). However, the most of these physical and chemical methods are non-destructive method for the removal of this contaminant (12). Methods that is based on heterogeneous photocatalysis, and production of hydroxyl radicals is applicable for treatment of BPA in wastewater (13). Because these methods have a high mineralization efficiency, low toxigenicity, ideally producing carbon dioxide, water, and inorganic mineral ions as end products (6). Over the past few years, several photocatalytic processes were investigated. The degradation of organic compounds using catalysts such as titanium dioxide in the presence of UV radiation has attracted much attention as a promising method for its potential application in decomposition of various environmental pollutants (14-16). Titanium dioxide can further produce hydroxyl free radicals ($OH^{\bullet}$), and eventually leads to the breakdown of pollutants into the CO_2 and H_2O. It is also very efficient due to its photoactivity, physical and chemical stability, resistance to corrosion, low toxicity, low cost, and easy access. A major advantage of photocatalytic oxidation is a high rate of reaction (15,17,18). TiO_2photocatalysis with UV light presence Leads to excite an electron from TiO_2 to produce an electron-hole pair (19).

$$TiO_2 + h\upsilon \rightarrow TiO_2\ (e^-\_\ h^+)$$

The aim of this study was to evaluate the applicability of using low power UV lamp (6 W) as energy source in the photocatalytic process to decompose BPA in aqueous solutions. Furthermore, the effect of several parameters, including pH, contact time, initial BPA concentration and catalyst dosage was evaluated on the BPA removal by the photocatalytic process.

2. Materials and Methods

The BPA was from Sigma-Aldrich Company and titanium dioxide nanoparticles was purchased from Iranian nanomaterials Co. (Nano Sany) Mashhad-Iran. Shows the in figure 2, X-ray diffraction pattern and scanning electron microscope (SEM) photo of nanoparticles used in this study is shown. H_2SO_4 and NaOH were used by PH meter (EUTECH pH 5500) for adjusting initial pH of the aqueous solution. The reactor was made by glass cylinder with diameter and height 4 and 25 cm, respectively. The reactor equipped with magnetic stirrer (HP-3000) and cooling system and UV lamp (power 6 W).

Physical properties of TiO_2 nanoparticles are: color is white, bulk density is 0.46 g/ml, specific surface is 10-45 m^2/g and particle size is 20 nm.

In order to obtain the optimum operational conditions, the studied parameters on present process including initial BPA concentration (1-50 mg/l), TiO_2 dosage (0.025-2 g/l), initial pH (3-11) were evaluated (11,19). A certain amount of TiO_2 (0.5 g) was added to the solution and stirred for 30 min by shaker (SIBATA rotary shaker CMS-05). The mixture was placed in a dark environment in order to reach equilibrium. Then the solution was transferred into the reactor to carry out the process. The temperature was kept constant for all time experiments around 25°C. The samples were centrifuged (Roxette II) for 15 min in 4000 rpm and then filtered, by 0.45 µ syringe filter to remove the TiO_2 particles.

To clarify the effect of pH on the photocatalytic decomposition of BPA and determine the best conditions in terms of pH, the experiments were performed in the pH 3, 7, 9 and 11 in presence of a constant amount of nanoparticles (0.5 g/l) and the concentration of BPA at 50 mg/l. To determine the optimum nanoparticle concentration, different amounts of TiO_2 (0.025, 0.05, 0.2, 0.3, 0.5,1, and 2 g/l) and BPA (50 mg/l) were prepared. Then optimum pH was adjusted, and the samples were placed in the dark without UV irradiation for 30 min to reach equilibrium. The effect of BPA concentration on the efficiency of photocatalytic process was investigated by varying the BPA concentration including 1, 3, 5, 10, 20, 30, 40, 50 mg/l. To determine the effect of contact time on decomposition of BPA, experiments were conducted in contact times including 15, 30, 45, 60, 75, 90, 120 min.

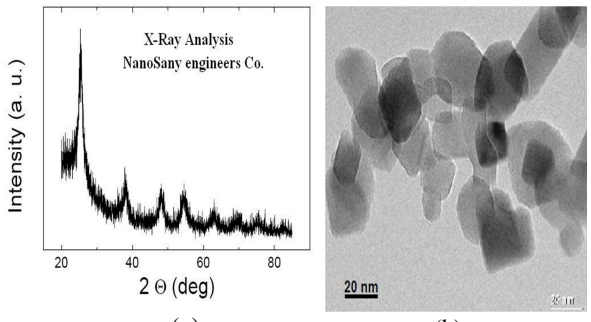
To analyze the concentrations of BPA, a standard curve was plotted in the 6 concentrations of the compound (1, 3, 5, 10, 20, 30, 40, 50) and with $R^2 = 0.999$. The BPA concentration was measured by using a high-performance liquid chromatography (HPLC) (Knauver HPLC instrument) with a UV detector, the column was C18, the mobile phase was 30% water and 70% acetonitrile and analysis undertaken at 280 nm.

3. Results

3.1. The characteristic of nanoparticles

Figure 2a shows XRD pattern of the TiO_2 particles, as it is shown, the examined TiO_2 particles are in the anatase phase and so it is a good photocatalyst.

As it can be seen from figure 2b the SEM images shows TiO_2 growth homogeneity which its particle size is 20 nm.



(a) (b)

Figure 2. X-ray diffraction pattern (a) and scanning electron microscope photo (b) of TiO_2 nanoparticles used in this study

3.2. Effect of contact time

As it can be seen from figure 3, the optimum time for BPA degradation was 60 min. because after that, the removal efficiency was constant. Removal efficiency increases by increasing contact time and reach equilibrium within 60 min.

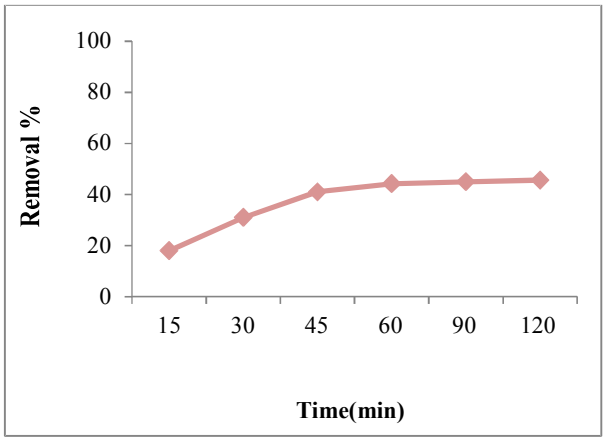


Figure 3. Effect of contact time on removal efficiency of bisphenol A (BPA) (pH = 3.4, TiO_2 dosage 0.5 g/1, BPA concentration: 50 ppm)

3.3. Effect of initial pH

Figure 4 shows the effect of different pH (3, 7, 9, 11) on the removal of BPA. The photocatalytic decomposition of BPA in the presence of titanium dioxide nanoparticles depends on pH, so the efficiency of the process increases by increasing pH and the highest removal efficiency was obtained at alkaline pH. Removal efficiency was significantly decreased in acidic condition.

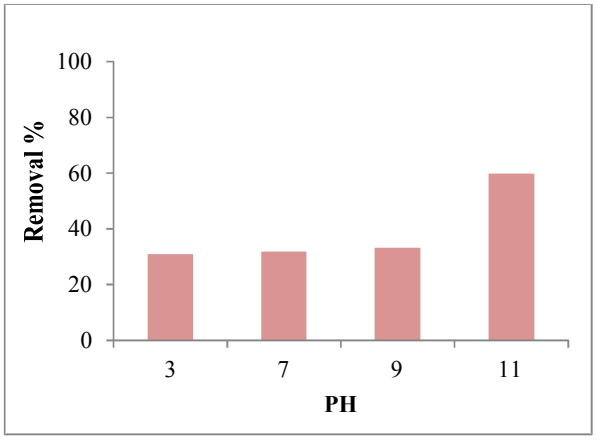


Figure 4. Effect of pH on removal efficiency of bisphenol A (BPA) (TiO_2 dosage 0.5 g/1, time = 60 min, BPA concentration: 50 ppm)

3.4. Effect of catalyst dosage

In order to obtain optimum TiO_2 dosage, various amounts of catalyst (0.025, 0.05, 0.1, 0.2, 0.3, 0.5, 1 and 2 g/l) were added to solutions containing constant concentration of BPA (50 ppm). Figure 5 shows removal efficiency increases by increasing dosage of TiO_2. Removal efficiency of 78% was achieved in 0.5 g/l catalyst dosage and 60 min contact time. By increasing the catalyst dosage > 0.5 g/l, the removal efficiency was decreased.

3.5. Effect of initial BPA concentration

Figure 6 shows the efficiency of photocatalytic decomposition of BPA at different initial concentration. Various concentrations of BPA (1, 3, 5, 10, 20, 30, 40, 50 ppm) were studied in pH and optimum dose of catalyst.

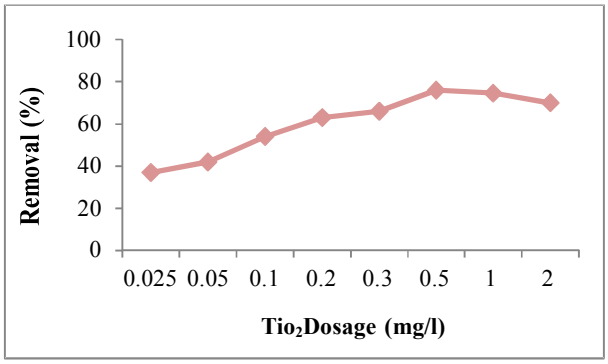


Figure 5. Effect of TiO_2 dosage on removal efficiency of bisphenol A (BPA) (pH = 3.4, time = 60 min, BPA concentration: 50 ppm)

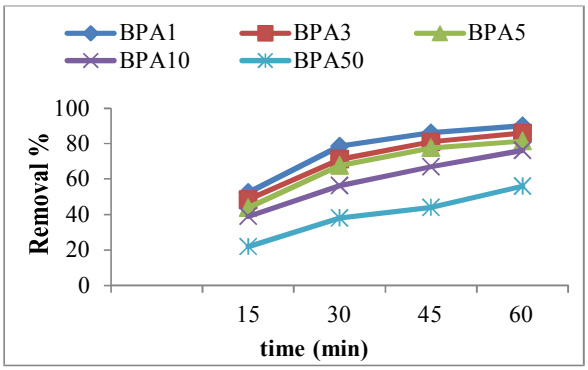


Figure 6. Effect of bisphenol A (BPA) concentration on removal efficiency of BPA (pH = 11, time = 60 min, TiO_2 dosage 0.5 g/l)

4. Discussion

4.1. Effect of pH on BPA degradation

Since most semiconductor has amphoteric properties so pH roles in the catalytic process is significant. The concentration of H^+ and OH^- in the aqueous solutions determines the surface charge of catalyst, so it effects on surface charge properties and reaction rate that occurs at the surface of nanoparticles (20). The effect of the initial pH 3, 7, 9, and 11 on the photodegradation of BPA was investigated at the initial BPA concentrations of 50 ppm and TiO_2 dosage of 0.5 g/l. As shown in figure 3, the removal of BPA increases with increasing pH, and the highest removal efficiency was observed at alkaline pH. Removal efficiency is obtained for pH 3, 7, 9 and 11, were 31, 32, 36 and 60% respectively. The variation of the pH, can

change the positive or negative charge of nanoparticles (21). At neutral and alkaline pH, the released electrons react with molecules of H_2O or OH, and the production of hydroxyl free radicals ($OH^{\bullet}$) had accelerated effect on the organic matter decomposition (14).

4.2. Effect of TiO_2 dosage on BPA degradation

Amount of catalyst is an important parameter in the photocatalytic process. Figure 5 shows the removal efficiency increases by increasing the catalyst dosage. As the results show that the performance is increased by increasing the amount of TiO_2, and the optimal dosage of catalyst for the process, 0.5 g/l, respectively. Proper dosage of catalyst gives the increase production rate of electron-hole pairs and hydroxyl radicals; therefore, will improve photocatalytic process. It also enhances the performance of the catalyst in greater concentrations, which it is due to the presence of active sites on the catalyst surface and the possibility of further effect on its UV rays. The results are consistent with the conducted studied by Lee et al. (16). However figure 2 indicated that larger amounts of catalyst can lead to slightly reducing the removal efficiency during the process. Therefore, there is an optimum TiO_2 dosage, so when the titanium dioxide catalyst dosage 0.5 g/l, and the pH optimum removal efficiency reached a maximum value. Reduce the efficiency of the process. By increasing the catalyst dosage, the decomposition rate was decreased this could be due to aggregation of nanoparticles, which reduces the penetration of UV radiation.

4.3. Effect of concentrations of BPA on the degradation

As shown in figure 4, the removal efficiency of nano-photocatalytic reactor, UV/TiO_2 has an inverse relationship with increasing initial concentration of BPA. The findings show that decomposition efficiency was decreased by increasing the initial concentration of BPA. For initial concentrations of 1, 3, 5, 10, 20, 30, 40, and 50 ppm, the removal efficiency were 90, 85.9, 81.3, 76.1, 71, 67, 61, 23, 55.4% respectively. In conditions that the contact time was 60 min and pH was 11, and catalyst dose was 0.5 g/l the best decomposition was occurred. This is due to fixed rate of hydroxyl radical formation in this condition. In the high concentration of BPA, the available hydroxyl radical is insufficient for decomposition, and the limited adsorption sites available for the adsorption of BPA. The results are consistent with those studied by Zacharakis et al. (8)

The results indicated that photocatalytic degradation of bisphenol is applicable by low power of UV lamp (6 W). This system is a method with high efficiency to remove BPA from water and it can be applied to industrial effluent treatment. These results were consistent with those reported by some researchers (3-13).

The highest degradation was 90% and achieved in 60 min. BPA degradation efficiency can be effectively improved by increasing pH, decreasing the initial concentration and increasing TiO_2 dosage. The optimal dose of TiO_2 was measured at 0.5 g/l. The degradation decreases with increasing TiO_2 dosage. Photocatalytic degradation using Tio_2 and UV is applicable and has high efficiency for BPA.

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