

[Research]

Fabrication of UV/ TiO₂ nanotubes / Pd system by electrochemical anodization for furfural photocatalytic degradation

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(Received: Sept. 08. 2016 Accepted: Feb. 05. 2017)

ABSTRACT

The aim of this study was to degrade furfural by a new nanotube system. To degrade some organic pollutants as well as to reduce the amount of furfural which is a well-known pollutant in oil industry, the photocatalytic process along with ultraviolet (UV) irradiation may be employed. In this study, the UV/TiO₂/Pd system in which the nanoparticles of palladium doped into the titanium dioxide was proposed for degradation of furfural. The rate of furfural decomposition in the proposed system was more than that of the system without TiO₂ foils due to the degradable reactions. The experimental results demonstrate that the maximum degradation occurs at a distinct pH and specific temperature under the UV irradiation. After 100-minute UV-irradiation duration, the maximum and minimum degradations were 97.8% (pH 3), and 95.8% (pH 12), respectively. Also, the degradation values were as parabolic function at the pH values. The values of efficiency of decomposition for this irradiation duration at optimum pH 3 were 96.7% and 98.5% at 30°C and 40°C, respectively. Also, the minimum degradation under photolysis was 93.52% at 30°C under 20-minute UV-irradiation duration. Furthermore, while the irradiation duration was 70-75 min, the degradation values were independent of pH approximately. The difference between the degradation values at 30 and 40°C was decreased with increasing the UV-irradiation duration till 60min, and then this difference was increased with increasing the UV-irradiation duration.

Key words: Furfural; UV/TiO₂/Pd system; Photocatalytic degradation; Temperature; pH.

INTRODUCTION

The hydrology as well as the health may be affected by the pollution of environment. One of the pollution sources is the release of complex chemical materials from the various plants and facilities (Iliev *et al.* 2002). These materials are toxic and non-biodegradable in the biological systems which have a long life in natural environment because their decay and decomposition are insignificant. For instance, "Phenols" and "Furfural" are the cyclic and

aromatic organic compounds that the latter is an aromatic aldehyde with the cyclic structure. As known, furfural is an excellent organic solvent to be employed to extract industrial effluents from other hydrocarbons and oil in the petrochemical and refineries which is consistent with the tissues and body organs due to high adsorption coefficient, as shown in Fig. 1. Recently, the oxidation techniques have been used to decompose the complex and heavy molecules. These oxidation reactions are

included the Ultraviolet (UV) irradiation and/or a combination of other oxidizing agents and mineral catalysts (Wenqi *et al.* 2006; Faramarzpour *et al.* 2009; Borghei *et al.* 2008; Kang *et al.* 2009). Within the last few years, there are efforts to develop the some methods such as homogeneous and heterogeneous chemical oxidation, photo oxidation and photo catalysis in order to detoxify waste water efficiently. Also, the processes of silica-modified TiO₂, titania-supported bimetallic catalyst, and TiO₂/MgO are proposed as efficient ones to remove the various chemical complexes from waste water, and also as alternative for filtration, adsorption, reverse osmosis and incineration in environmental cleaning processes, dealing with complex

nonbiodegradable chemicals (Boopathy *et al.* 1993; Nomeir *et al.* 1992; Haque 2007; He *et al.* 2013; Assadi *et al.* 2010; Huang *et al.* 2015; Chiou *et al.* 2008; Dixit *et al.* 2010; He *et al.* 2002; Ferrari-Lima *et al.* 2015; Kim *et al.* 2012; Sun *et al.* 2009). In this study, a new method, combination of UV radiation and the nanoparticles of palladium were doped into the titanium dioxide (UV/TiO₂/Pd) is proposed to degrade and to decompose the furfural in which the rate of furfural decomposition is more. The efficiency of various advanced oxidation processes (AOPs) and the effect of experimental parameters of pH, UV-irradiation duration, and temperature are also investigated on the rate of reactions.

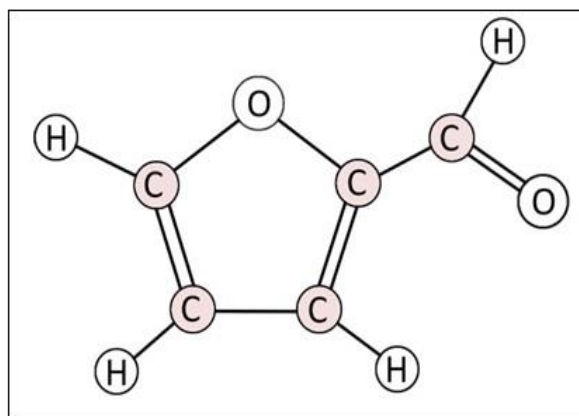


Fig. 1. The structure of furfural.

MATERIALS AND METHODS

The titanium foils (1-mm thickness, 5×5 cm², purity 99.5%), furfural (99.9%), palladium, platinum, stannous chloride II (SnCl₂) and double distilled water were purchased from laboratory grade in Merck company. The technical specifications of furfural were as C₂H₄O₂; molecular weight 96.09 g.mol⁻¹; maximum UV-absorption wavelength 270 nm; boil point 11 Torre; density 1.159 mg.L⁻¹ for standardization of pure analysis.

Experimental Procedures

Preparing TiO₂ nanotube arrays by anodization process

As shown in Fig. 2, the titanium foils were anodized at three stages as follows; (a)

polishing with sand-paper, as shown in Fig. 3 A and B, (b) cleaning by the 100-ml solution consisting of HF (10 ml), HNO₃ (40 ml), and (c) twice distilled water (50 ml) during 5 second and washing by distilled water.

These foils with the thickness 1mm, the surface area 25 cm² and the purity 99.5% were ultrasonically cleaned in the detergent, acetone, ethanol, nitric acid, and deionized water in turn during 10 minutes, and then dried in an oven prior to the anodization process. For the anodic oxidation process, a two-electrode configuration was used with platinum foil as the counter electrode at a fixed potential, as shown in Fig. 4. The distance between two electrodes approximately was 3cm. The voltage value and duration of anodization were 60V

and 120 min, respectively. The mixture of the HF (2 mL) and DMSO (98 mL) was used in different concentrations as electrolyte. The stirring rate was 150 rpm (Rui *et al.* 2011; Hee-Yeon *et al.* 2011; Yajun *et al.* 2011; Sreekantan *et al.* 2011; Robin *et al.* 2014; Hoyer 1996; Prakasam *et al.* 2007; Minagar *et al.* 2012; Regonini *et al.* 2013).

Samples were washed by deionized water and ultrasonicated to remove the ions from the surface of the TiO₂ foils after anodization. All experiments were carried out at room temperature. The SEM images of TiO₂

nanotubes /Pd were prepared by the scanning electron microscope, Zeiss evo 18, Germany, as shown in Fig. 5.

Gong *et al.* fabricated the TiO₂ nanotube arrays by the anodic oxidation of titanium foil into the fluoride-electrolyte solution primarily that its mechanism is as follows (Gong *et al.* 2001); The TiO₂ passive layer is formed by the elemental titanium undergoing oxidation and hydrolysis in aqueous acidic medium (Macak *et al.* 2005) as:

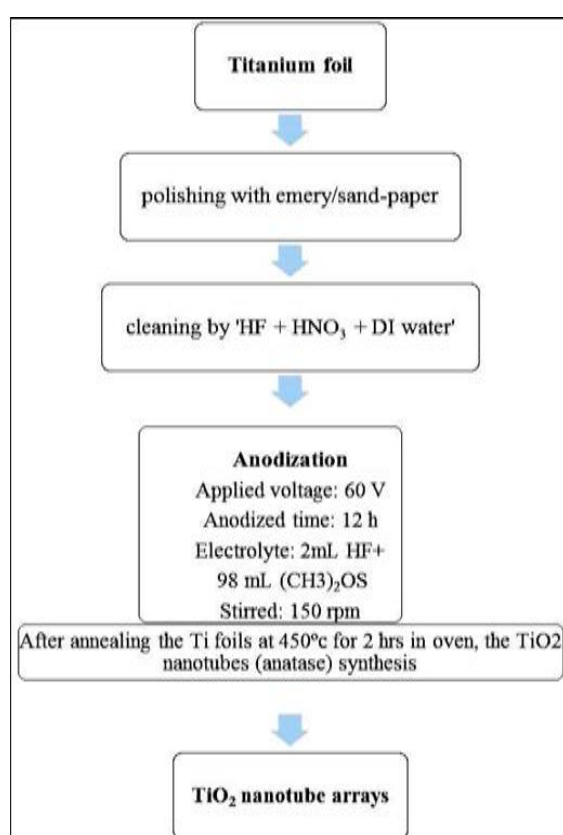
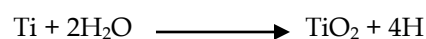


Fig. 2. Flowchart of implementation of the proposed method.

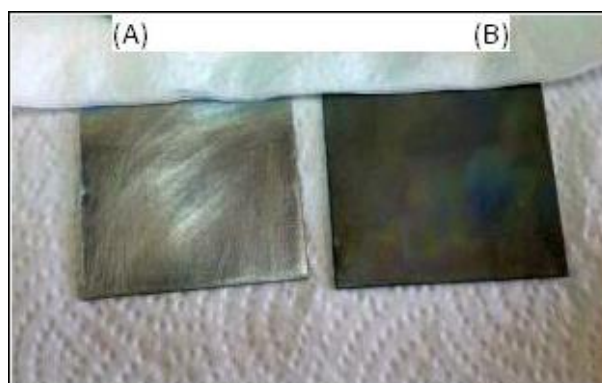


Fig. 3. Images of titanium foils before (A), and after anodization process (B).

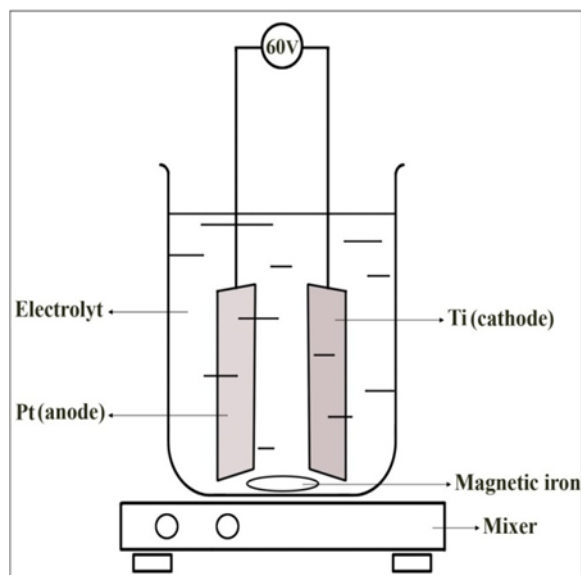


Fig. 4. Two-electrode electrochemical cell for anodization process.

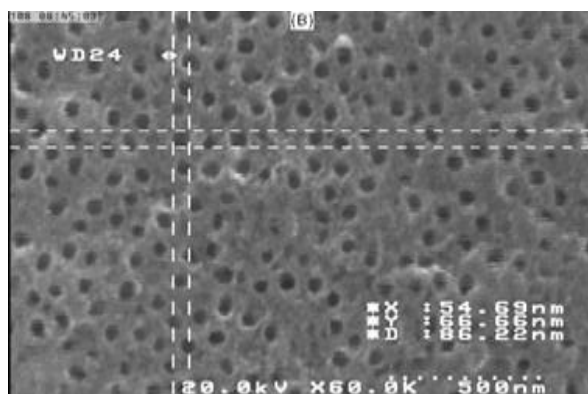
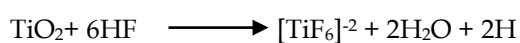


Fig. 5. SEM images of anodized TiO₂ (A), and TiO₂/Pd (B).

To form soluble $[\text{TiF}_6]^{-2}$ complexes, the TiO₂ undergoes rapid etching in the presence of acidic HF or neutral fluoride containing solutions in spite of stability at the pH values from 2 to 12 thermodynamically. The Ti-O bond is weakened by the polarization so that the dissolution of metal oxide is increased at higher applied electric field.

This dissolution at higher voltage values leads to the field-assisted chemical dissolution of the oxide appeared at the oxide/electrolyte interface. The F⁻ ions are produced by the pits as follows,



Basically, the porous layer is dependent on the equilibrium between electrochemical formation and the chemical dissolution of TiO₂

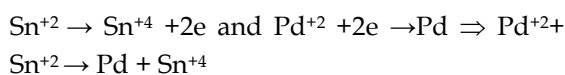
in solution of F⁻ ion. In this study, chemical composition of electrolyte was 2% HF in DMSO, and the nanoparticles were formed at duration of 12 h under the anodizing voltage 60V.

The localized dissolution of TiO₂ and anodization of Ti in HF may occur simultaneously which the latter involves the electrochemical dissolution of titanium metal into Ti ions, the oxidation of Ti⁺ and/or Ti³⁺ to TiO₂. After annealing the Ti foils at 450°C for 2 h in oven, the TiO₂ nanotubes (anatase) synthesis is completed (Rui *et al.* 2011).

Doping Pd

It was carried out at two synthetic stages. At first, TiO₂ foils were dipped into the stannous chloride II (SnCl₂) solution of 0.1M during two minutes before the ultrasonic process. At the

second, the samples were settled in the PdCl_2 solution of 0.01M during four minutes (Fig. 5A and B). The reactions were as follows,



Experimental reactor consists mainly of a two-layer beaker with 1-litre capacity and a two-layer quartz mounting in the center of the

photoreactor, as shown in Fig. 6. The heater was used to obtain a constantly suitable temperature in experiments. The cooling water system is used and injected to the annulus surrounding the beaker and lamp. To decrease errors and avoid noise, this reactor was placed in the cubic dark box at dimensions of 1m covered by the aluminum foil. The samples were drawn out from the reactor at the certain intervals for analysis by UV lamp (250W).

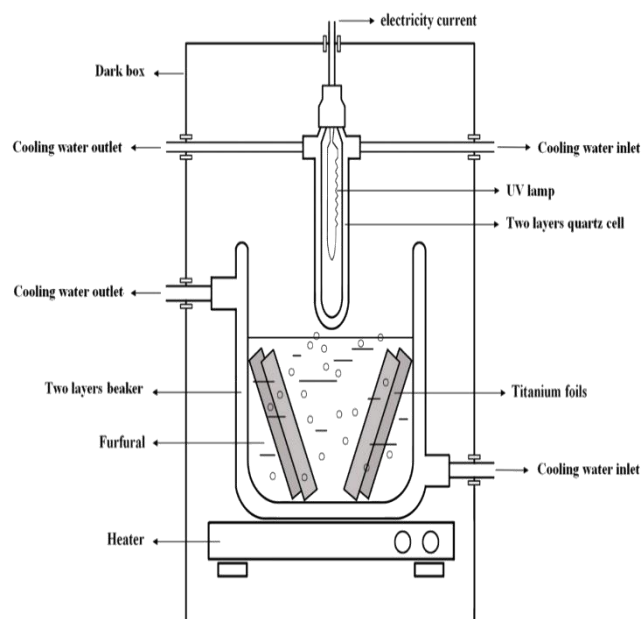


Fig. 6. The schematic representation of the photoreactor.

RESULTS AND DISCUSSION

The absorptiveness effect of titanium foil

To obtain the spectra of absorption, the system with/without titanium foil was irradiated by UV light during 100 minutes, as shown in Fig. 7.

The peak of 270 nm was considered as a criterion of the photocatalytic activity. The results show that the amount of absorption was increased in the presence of the titanium foil. After 100-minute UV-irradiation duration, the concentrations of the samples with/without titanium foil were 12.1 and 10.94 mg.L^{-1} , respectively. To evaluate the photo degradation behavior of furfural in the UV/ TiO_2 /Pd system, the second series of experiments were carried out in which the concentration of furfural was 250 mg.L^{-1} along with a medium pressure mercury lamp (250W) as the UV source. In the system without

titanium foil, the amount of absorption is decreased with increasing the wavelength value as exponential, while in the system with titanium foil, the minimum and maximum values are 1.22 and 1.38 at the 255nm and 270nm, respectively. Also, it decreased as exponential function approximately at more than 270nm.

The effect of various UV-irradiation durations

The photocatalytic test was done on the TiO_2 /Pd foils. The spectra were obtained during 100-minute UV irradiation, as shown in Fig. 8.

The photocatalytic activity was characterized by the peak intensity of 270 nm. The furfural has a configuration of absorption because there are the OH⁻ ions on the surface of TiO_2 foils. To

more deliberation, the efficiency of degradation was defined as follows:

$$d = (C_0 - C) / C_0 \times 100\% \quad [1]$$

Where C_0 and C are the concentrations of furfural before and after degradation, respectively.

The degradation of furfural took place up to 100-minute UV-irradiation duration in all the

samples here. The efficiency of degradation severely increases with increasing duration of irradiation because of improving the photocatalytic activity of TiO₂ (Pd).

To assess degradation of furfural, the first set of experiments was carried out under UV irradiation without the TiO₂ foils. The minimum degradation under photolysis was 93.52 % at 30 °C after 20-minute UV-irradiation duration.

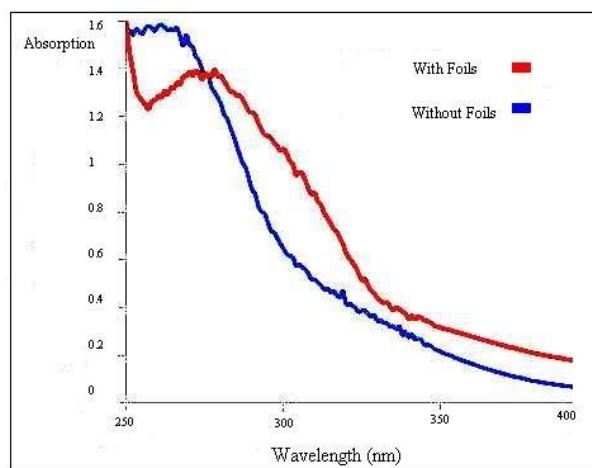


Fig. 7. The UV Spectra of furfural with and without Titanium foil at concentration of 250 mg.L⁻¹ under 250W 100-minute UV-irradiation duration.

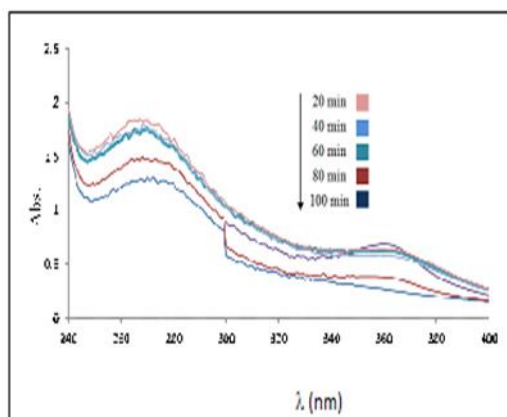


Fig. 8. The UV-VIS reflectance spectra of some samples at various degradation UV-irradiation durations for furfural ($C = 250 \text{ mg.L}^{-1}$) at pH 12 in the UV/TiO₂/Pd system.

The effect of pH

As well known, the reactions involving ionic solutions are dependent on pH. The photocatalytic activity can be changed by the pH. Several sets of experiments were performed to determine the effect of initial pH

on the degradation of furfural. The furfural solutions were adjusted at a distinct pH by augment 1 M sulfuric acid and/or 1 M sodium hydroxide. They are also investigated at the pH of 1, 3, 7 and 12 (250 mg.L⁻¹) under 250 W-UV

irradiation in duration intervals of 20 min from 20 to 100 minutes.

After 100-minute UV-irradiation duration, the maximum degradation was 97.8% at pH 3 while the minimum was 95.8% at pH 12. The

degradation values were as a parabolic function at various pH values. Also, while the irradiation duration was 70-75 min, the degradation values were independent of the pH values, as shown in Fig. 9.

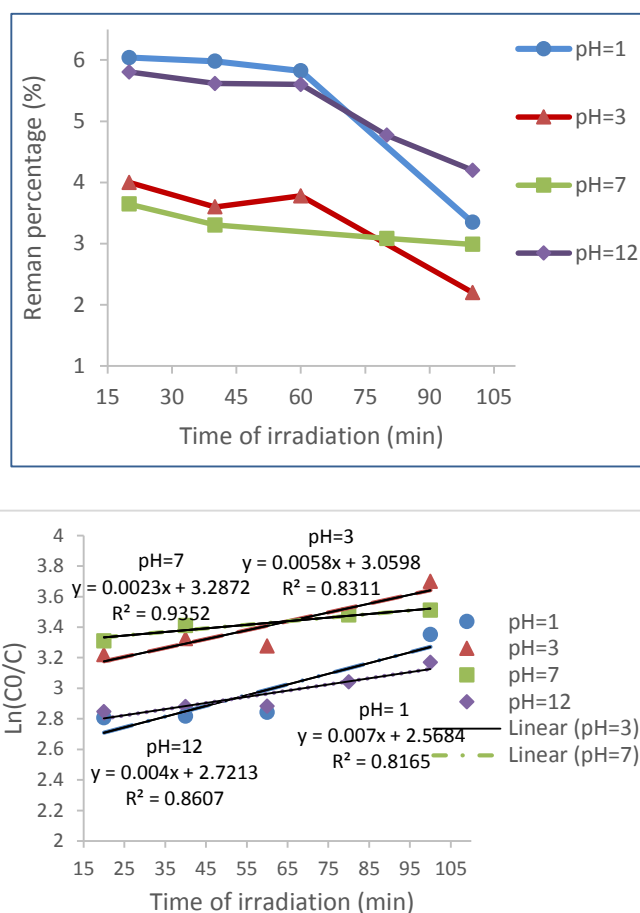


Fig. 9. The effect of pH values on photocatalytic removal of furfural in the UV/TiO₂/Pd system

The effect of temperature

In the UV/TiO₂/Pd system, the efficiency of decomposition was measured at 30 °C and 40 °C under UV-250W irradiation in duration intervals of 20 min from 20 to 100 minutes.

This efficiency for 100-minute UV-irradiation duration at optimum pH 3 was 96.70% and 98.5% at 30°C and 40 °C, respectively. The results indicate that the maximum degradation (98.5%)

gives rise to the pH 3 and 40 °C under UV irradiation.

The difference between the degradation values at 30 °C and 40 °C is decreased with increasing the UV-irradiation duration till 60 min, and then this difference is increased with increasing the UV-irradiation duration approximately, as shown in Fig. 10.

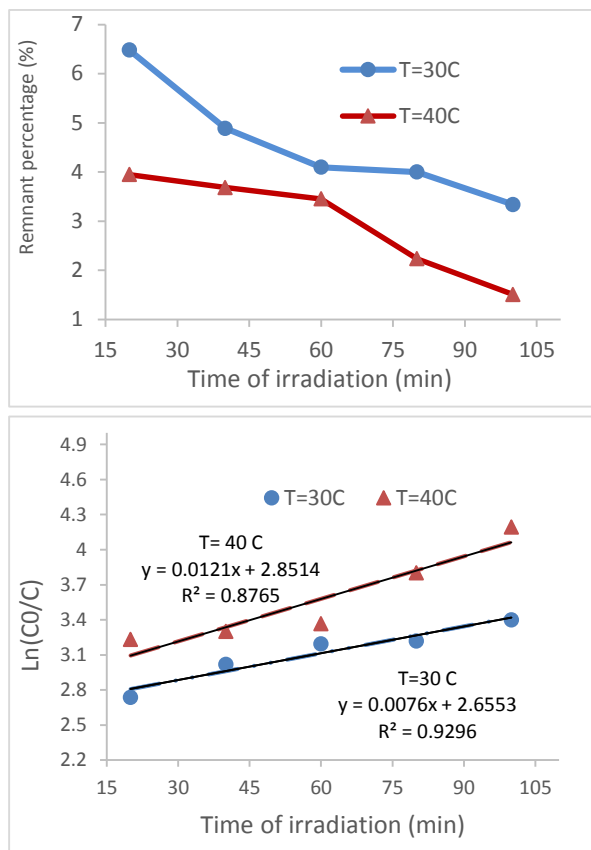


Fig. 10. The effect of temperature on photocatalytic removal of furfural at the optimum pH 3 in the UV/TiO₂/Pd system.

CONCLUSION

In this study, the UV/TiO₂/Pd system in which the nanoparticles of palladium were doped into the titanium dioxide is proposed for degradation of furfural.

The experimental parameters of temperature, pH and UV irradiation duration may improve the photocatalytic process.

This process may be employed to reduce the furfural.

The results indicate that the maximum degradation occurs at a distinct pH and specific temperature under the UV irradiation.

The efficiency of furfural decomposition increases with increasing the UV-irradiation duration.

Also, while the irradiation duration is 70-75 min, the degradation values are independent of the pH values.

The difference between the degradation values at 30 °C and 40 °C is decreased with increasing the UV-irradiation duration till 60 min, and

then this difference is increased with increasing the UV-irradiation duration approximately.

ACKNOWLEDGEMENTS

We gratefully acknowledge the Nuclear Science and Technology Research Institute for financial and technical supports.

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تخریب فوتوکاتالیزوری فورفورال به وسیله فویل تیتانیوم دوپ شده با نانوذرات پالادیوم و بررسی پارامترهای موثر بر آن

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(تاریخ دریافت: ۹۵/۰۶/۱۸ تاریخ پذیرش: ۹۵/۱۱/۱۷)

چکیده

فورفورال از آلاینده‌های زیست محیطی موجود در پساب‌های صنعتی به ویژه پالایشگاه‌ها است و وجود این ماده سرطان‌زا در فاضلاب پالایشگاه‌های روغن موتور یکی از مشکلات عمده محسوب می‌شود. از این رو در تحقیق حاضر تلاش شده است این ترکیب آلی با استفاده از فرایند فوتوکاتالیستی تحت تابش UV که امروزه کاربرد فراوانی در تصفیه آلاینده‌های زیست محیطی یافته است، تخریب شود. در این تحقیق آزمایش‌های تخریب فوتوکاتالیستی فورفورال در یک فوتوراکتور و با فویل تیتانیوم صورت گرفت. به این منظور، فویل تیتانیوم آندیزه شده و پس از تشکیل نانولوله‌های دی اکسید تیتانیوم، نانوذرات پالادیوم در فویل تیتانیوم دوپ شدند. سپس فویل تیتانیوم در محلول فورفورال با غلظت اولیه ثابت (۲۵۰ ppm) و تحت تابش UV با شدت ثابت (۲۵۰ وات)، قرار داده شده و اثر پارامترهای زمان، pH و درجه حرارت مورد بررسی قرار گرفت. نتایج این تحقیق نشان داد که بیشترین میزان تخریب فورفورال در pH برابر با ۳ به میزان ۹۶/۷٪ و ۹۸/۵٪ به ترتیب در دماهای ۳۰ و ۴۰ درجه سانتی‌گراد، بعد از ۱۰۰ دقیقه تابش UV صورت گرفته است. با توجه به آن که حداقل تخریب در آزمایش‌های متعدد انجام گرفته در این پروژه به میزان ۹۳/۵۲٪ در دمای ۳۰ درجه سانتی‌گراد به مدت ۲۰ دقیقه تابش UV مشاهده شده است می‌توان فرایند فوتوکاتالیستی را روش مناسبی برای حذف فورفورال از محیط زیست ارزیابی کرد.

*مؤلف مسئول