Eco. Env. & Cons. 28 (2) : 2022; pp. (606-609)
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ISSN 0971–765X

DOI No.: http://doi.org/10.53550/EEC.2022.v28i02.004

Assessment of the treatment efficiency of some polycyclic aromatic hydrocarbon (PAHs) in the water by doped TiO_2

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(Received 5 July, 2021; Accepted 31 August, 2021)

ABSTRACT

Treatment of persistent organic pollutants by advanced oxidation processes is a trend nowadays because of its efficiency. Through studies it has been found that enhanced oxidation processes can treat organic pollutants that are difficult to decompose due to OH radicals and can convert those substances into non-toxic substances which areH_2O và CO_2. $TiO_2$is a strong oxidizing agent; especially with the addition of catalysts, it is highly likely to be able to to treat persistent pollutants. PAHs are a class of polycyclic aromatic hydrocarbons that are highly toxic and persistent in the environment. The treatment of PAHs with 1% Fe-doped TiO2 coated on silica gel combined with using a 365nm UV lamp model initially produced certain results. Treatment efficiency is up to over 90% after 48 hours. On that basis, the article proposes a feasible solution for the treatment of PAHs in particular and toxic organic substances in general.

Key words : *Persistent organic pollutants, Doped, PAHs*

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are products of incomplete combustion of fuels (gasoline, diesel...) in vehicles' engines. In addition, domestic activities (cooking with sawdust, charcoal, honeycomb charcoal...), straw burning in the field, domestic waste burning, and industrial processes (thermal power, fuel consumption…) also contribute significantly to PAHs emissions (Duc Toan, 2009). PAHs from the above sources have entered the river and lake environment in urban areas of Vietnam, affecting humans and aquatic animals. PAHs can cause acute impacts (skin and eye irritation, nausea, vomiting, inflammation) or chronic impacts (DNA damage and genetic mutations, organ failure and cell damage, cancer, death). There are over 200 PAHs with different structures and toxicity. However, studies around the world often focus on some typical, highly toxic PAHs such as Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene.

To treat PAHs pollution in water, one of the promising solutions is to use advanced oxidation processes with selective photocatalysis.

In the world, there have been several works in PAH treatment with advanced oxidizing agents. According to Li *et al.,* 2016; Wu, Zhou *et al.,* 2011; Yap *et al.,* 2012, the treatment efficiency of PAHs in soil and leachate by advanced oxidation processes is up to 90%.

PAHs pollution in water in Hanoi has been as-

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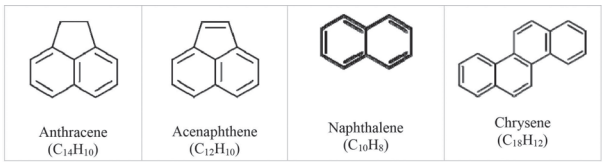


Fig. 1. Structural and molecular formulas of some typical PAHs

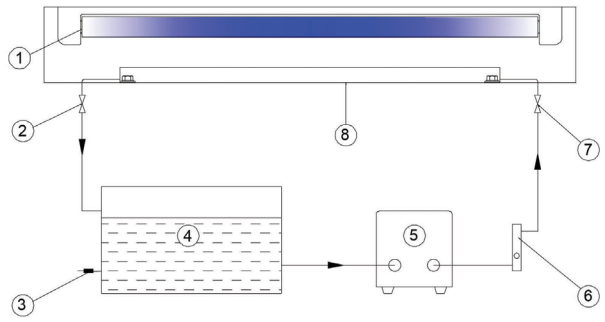
sessed in Kim Nguu and Cau Bay rivers. The concentration of PAHs in the water of Kim Nguu and Cau Bay rivers ranges from 0.18 -2.084 µg/l and from 0.14 to 2.47 µg/l, respectively ([2], [3]). Therefore, it is necessary to study and assess the treatment efficiency of some PAHs in water by advanced oxidation processes, contributing to solving the above pollution problems.

Currently, TiO_2 photocatalyst materials are attracting a lot of attention because of its ability to treat persistent pollutants. The treatment capacity and environmental friendliness of TiO_2 are relatively good. However, due to its wide band gap (3.0eV - 3.2eV), TiO_2 cannot produce catalytic effects in visible light and the presence of UV light is required. To improve the efficiency of PAHs treatment, this study proposes a treatment method for Naphalene, Acenaphthylene and Acenaphthene with 1% Fe-doped TiO_2 material deposited on silica gel combined with using a 365nm UV lamp model.

Research Method

Analytical method

The 14 samples taken after the experiment were analyzed using the method of *Kadokami et al. (2009).* The samples were extracted, evaporated, and reduced by N2 stream to 1ml. After that, the concentration of PAHs was identified by gas chromatography–mass spectrometry method(GC-MS) to determine the efficiency of the treatment process.



Remark:

1: UV light system	4: Water tank	7: Water valve02
2: Water valve 01	5: Peristaltic pump	8: Material storage tube
3: Sampling valve	6: Flowmeter	

Fig. 2. Laboratory photocatalyst test system

Experimental method

Assessment of PAHs treatment capacity through the experimental system of 250 ml/day.

The photocatalytic capacity of Fe-doped TiO_2 samples coated on SiO_2 particles is evaluated through the ability to decompose PAHs solution under UV light. 2 grams of material is used to treat 250ml of a solution of the test substances with an initial concentration of 50 ppb. The test medium has a pH value of 6.5 – 7.5. The schematic diagram of the treatment system is shown in Figure 2.1.

Diagram explanation

250 ml of PAHs solution is stored in a beaker (4). From the beaker (4), water is pumped through the flowmeter (6) and through the water valve (7) into a tube containing 2g of 1% Fe-dopped TiO_2 material coated on the silicagel. Here, the PAHs solution is flowed through a tube containing 1% Fe-modified TiO_2 material coated on the silica gel under the effect of UV light. The water after being treated at the material storage tube (8) is flowed to the cup (4) through the water valve No. 01 (2). The water at the beaker (4) is periodically checked by taking an analytical sample at the sampling valve (3). The peristaltic pump (5) maintains a flow rate of 100 ml/min. The material tube (8) is a glass tube that is 300 mm long, 5 mm in diameter, through which UVA light (365 nm) is transmitted. The lamp (1) used in the photocatalytic test is a 365 nm/18 W UV lamp that is illuminated at a close distance from the glass tube containing the sample.

Results and Discussion

The model runs continuously for 48 hours, and 14 samples are collected: Sample 0 is the sample taken before treatment, sample 14 is the sample taken after 48 hours, and the remaining samples are taken at the following time intervals:

After sampling, the sample was extracted and analyzed by gas chromatography to determine the ability to treat PAHs of doped TiO_2.

PAHs treatment efficiency of TiO_2

Mechanism of photocatalytic reaction of TiO_2 materials to PAHs under illumination
Under illumination

$$TiO_2 + hv \rightarrow TiO_2(h^+ + e^-) \quad .. (1)$$

$$TiO_2(h^+) + H_2O \rightarrow OH^* + H^+ + TiO_2 \quad .. (2)$$

$$TiO_2(h^+) + HO^- \rightarrow OH^* + TiO_2 \quad .. (3)$$

$$TiO_2(h^+) + R \rightarrow R^* + TiO_2 \quad .. (4)$$

$$TiO_2(e^-) + O_2 \rightarrow O_2^{-*} + TiO_2 \quad .. (5)$$

$$TiO_2\ (e^-) + H_2O_2 \rightarrow\ OH^- + OH^* +\ TiO_2 \quad .. (6)$$

$$O_2^{\bullet-} + H^+ \rightarrow\ HO_2^{\bullet} \quad .. (7)$$

$$HO_2^{\bullet} \rightarrow\ O_2 + H_2O_2 \quad .. (7)$$

$$H_2O_2 + O_2 \rightarrow O_2 + OH^- + OH^{\bullet} \quad .. (9)$$

$$OH^- + \text{PAH inorganic ions, } CO_2, H_2O \quad .. (10)$$

In addition to the OH radical, the HO2 radical also participates in advanced oxidation reactions with similar reactants

The basic principle of photocatalysis on semiconductors is that when excited by light with energy high or equal to the band gap of the semiconductor (in this study it is ultraviolet light because the band gap width of TiO_2 is quite large: ~3.2eV), electron-hole pairs (e, h+) in the conduction and valence bands (1) are created. These electron-hole pairs will move to the surface to perform an oxidation - reduction reaction. The holes can participate directly in the oxidation reaction of toxic substances, or can participate in the intermediate stage to form active free radicals such as (2), (3), (4), (5). Similarly, electrons will participate in reduction processes to form free radicals. The free radicals will further oxidize organic substances adsorbed on the surface of the catalyst into non-toxic end products of CO_2 and HO_2 (6), (7), (8), (9), (10).

The selected catalyst must have the largest surface area; for the hole width, it is not important because the treatment process uses UV lamp. The material must have a large surface area with good adsorption capacity, easy for TiO_2 and catalysts to adhere. In addition, the catalyst must be a strong photocatalyst. Based on the above requirements as well as some studies on the treatment of persistent pollutants with similar structure to Phenol and MB (Methylene Blue), the treatment capacity of 1% Fe-doped TiO_2 coated on silica gel is found to have the best effect. For MB treatment, the above material gives a treatment efficiency of 80% after 6 hours, for Phenol treatment, the treatment efficiency is over 90% after 2 hours. ([4], [5]).

Treatment effect for PAH

For PAH with structure consisting of 2 benzene rings (Figure 3).

After the first 20 minutes, the Naphalene treatment ability of 1% Fe-doped TiO2 was clearly effective. Specifically, the concentration of Naphalene decreased by 90% in the first 24 hours (1320 minutes); after 24 hours, the concentration of Naphalene decreased slowly.

For PAHs with 3 benzene rings (Figure 4+5)

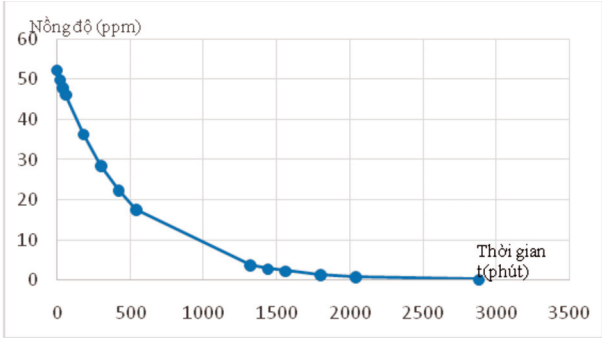


Fig. 3. Naphalene treatment by doped TiO_2

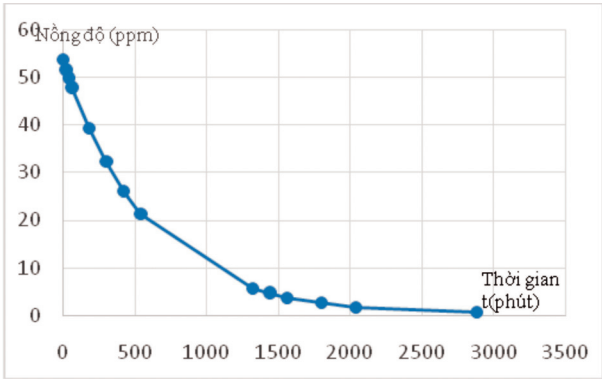


Fig. 4. Acenaphthylenetreatment bydoped TiO_2

Table 1. Sample of PAHs treated over time

Sample	M0	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12	M13
Time (Minute)	0	20	40	60	180	300	420	540	1320	1440	1560	1800	2040	2880

Table 2. The k coefficient of the reaction

PAHs	Naphalene	Acenaphthylene	Acenaphthene
Constant k (1/minute)	0.002	0.0017	0.0015

From Figure 4 and 5, it can be seen that the treatment rate of TiO_2 in the first 24 hours of Acenaphthylene and Acenapthene is over 80%; after 24 hours, the reaction rate slows down.

The PAHs treatment capacity decreases in the following order: Nap < Acenaphthylene < Acenapthene substances. This can be explained by the Naphalene structure consisting of 2 aromatic rings and the remaining substances having 3 aromatic rings, so doped TiO_2treats Naphalene better than other PAHs.

Order of the reaction equation.

We have the first-order reaction equation:

lnCO/C1 = KT

Where C_0 is the initial concentration

C_1 is the concentration after treatment

t is the processing time

We can easily calculate the coefficient k:

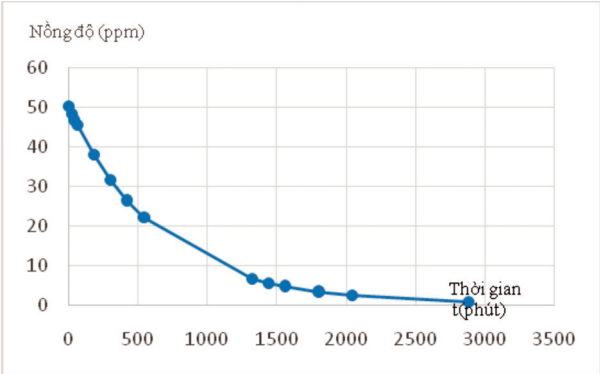


Fig. 5. Acenaphthenetreatment by doped TiO_2

Conclusion

The 1% Fe-doped TiO2 photocatalyst material coated on silica gel shows good catalytic capacity to decompose PAHs when combined with the 365 nm UV lamp. At selected conditions, the capability to handle Naphalene after 24 hours is 90% and after 48 hours is over 90%. For Acenaphthylene and Acenaphthene, the treatment capacity after 24 hours and 48 hours is over 80% and over 90, respectively. %.

The PAHs included in this paper are L-PAHs - PAHs with low molecular weight and molecular structure of 2-3 aromatic rings. These substances have the characteristics of high water solubility; therefore, the treatment capacity by TiO_2 is relatively feasible.

This research is funded by the University of Thuyloi. The authors would like to thank ROOM Research Group at the University of Thuyloifor their support during the research.

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