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Research Article

Photocatalytic Degradation of Anthracene in Closed System Reactor

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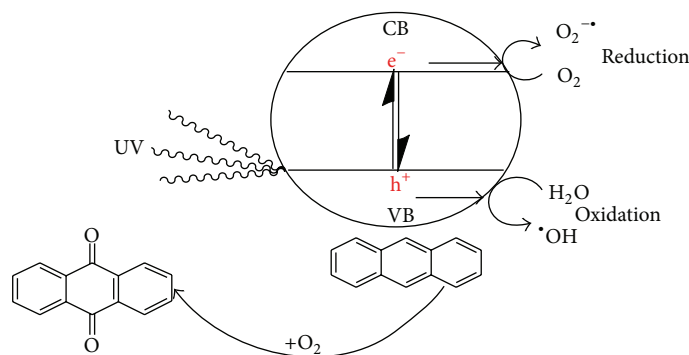
Polycyclic aromatic hydrocarbons (PAHs) represent a large class of persistent organic pollutants in an environment of special concern because they have carcinogenic and mutagenic activity. In this paper, we focus on and discuss the effect of different parameters, for instance, initial concentration of Anthracene, temperature, and light intensity, on the degradation rate. These parameters were adjusted at pH 6.8 in the presence of the semiconductor materials (TiO_2) as photocatalysts over UV light. The main product of Anthracene photodegradation is 9,10-Anthraquinone which is identified and compared with the standard compound by GC-MS. Our results indicate that the optimum conditions for the best rate of degradation are 25 ppm concentration of Anthracene, regulating the reaction vessel at 308.15 K and 2.5 mW/cm^2 of light intensity at 175 mg/100 mL of titanium dioxide (P25).

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute an important and hazardous group of priority contaminants [1]. Several researchers determined the concentrations of these compounds by different chromatographic techniques, for instance, HPLC [2–4], GC-MS/MS in [5], and GC-MS in [6, 7]. The main processes that successfully eliminated PAHs from the environment included the microbiological transformation and degradation, bioaccumulation, biological uptake volatilization, photooxidation, and chemical oxidation [8]. Photolysis and ozonation are the most important methods for transformation for most PAHs adsorbed on natural substances in an environment [9]. Photolysis of PAHs led to the formation of photodimers and photooxidation products [10]. In recent years, the release of toxic and organic contaminants into aquatic environment as a result of human activities has drawn much attention and is considering a baffling problem facing researchers today [11]. Zinc oxide and titanium dioxide are universally considered as the most important photocatalysts due to their lower cost and their

considerably low band gap energy ($\sim 3.2 \text{ eV}$) [12]. Nanoparticles of titanium dioxide were considered to be more efficient than bulk powder in photocatalytic field [13]. Several previous works used titanium dioxide as catalyst for degradation of different organic pollutants [14–16].

Semiconductors have been used for pollutants degradation in water to be less harmful inorganic material. Both catalysts titanium dioxide and zinc oxide have photocatalytic properties which made these catalysts the best for photodegradation of water pollutants [17]. Attention has been focused in the past decade on using nanocrystalline TiO_2 as a photocatalyst for the organic pollutants degradation. TiO_2 semiconductor has a wide band gap about 3.2 eV , which corresponds to the UV-range radiation. The formation of an electron hole pair occurs within the conduction and valence bands of TiO_2 semiconductor after absorption in UV range. Water molecules can be oxidized to hydroxyl radical by positive hole. Scheme 1 shows the mechanism diagram for photodegradation of Anthracene. The hydroxyl is a radical, frequent, and powerful oxidant. The oxidation of organic pollutants seems to be mediated by a series of

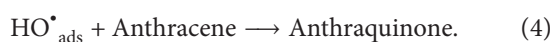
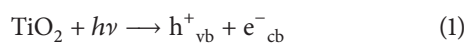


SCHEME 1: Mechanism diagram of photocatalytic degradation for Anthracene.

reactions started by hydroxyl radical on the TiO₂ surface. Recombination for the produced hole from valance band and separated electron from conductive band it can appear either in the volume or on the surface of the semiconductor particle accompanied with heat releasing. To this end, both UV light source and TiO₂ are necessary for photooxidation reaction to occur [18]. The photodegradation of PAHs compounds in water using TiO₂ catalyst has proved high efficiency in [19].

Furthermore, many researchers dealt with the PAHs in water by photocatalytic degradation for TiO₂. Woo et al. in [20] investigated photocatalytically oxidation using TiO₂ of 5 selected PAHs, namely, naphthalene, acenaphthylene, phenanthrene, Anthracene, and benzo[a]anthracene. Gu et al. in [21] studied degradation of phenanthrene on soil surfaces photocatalytically with the addition of nanoparticulate anatase TiO₂ under UV-irradiation. Vela et al. in [22] discussed photocatalytic processes using semiconductor materials (ZnO and TiO₂) to remove the residual concentrations of several PAHs from groundwater. Theurich et al. in [23] reported themechanism of the photocatalytic transformation of naphthalene and Anthracene qualitatively in aqueous suspensions of titanium dioxide. Indeed, catalyst TiO₂ can play as efficient photocatalyst in the oxidation of PAHs and convert it to safer compounds especially with Anthracene, Fluorene, and Naphthalene by artificial or sunlight illumination [19, 24]. To this end, our aim in the present paper is to study the effect of photocatalytic reactions on the degradation of Anthracene using titanium dioxide under different experimental conditions.

UV illumination of TiO₂ yields valence band holes and conduction band electrons (1), which interact with the surface adsorbed molecular oxygen to give superoxide radical anions, O₂^{•-} (2), and finally, the water produces radicals of HO[•] (3) [25]. These radicals oxidize target molecule (Anthracene) to Anthraquinone (4):



2. Experimental Procedure

2.1. Chemicals and Reagents. Anthracene was purchased from Sigma Aldrich, Germany, and used without further purification. Acetonitrile (anhydrous, ≥99.98%), Dichloromethane (anhydrous, ≥99.98%), Acetone, ethyl acetate (anhydrous, ≥99.98%), and methanol HPLC-gradient grade were purchased also from Sigma Aldrich, Germany. Titanium dioxide particles were purchased from Degussa (P25), anhydrous Na₂SO₄ (extra pure Allied Signal, Riedel-de—Germany).

2.2. Preparation of Stock Solution of Anthracene. A set of dilutions of Anthracene solution at the concentration of 100 mg/L were made in the following solvents: methanol, dichloromethane, acetonitrile, ethyl acetate, and acetone. Anthracene solutions in the above solvents were prepared and stored in room temperature (20 ± 2°C) in dark place to keep it from the light degradation. Calibration curve for Anthracene solution has been achieved by preparation several concentrations (0.1, 0.5, 1, 2, 4, 8, 16 and 30) mg/L. All glassware used for experiments was washed in chromic acid mixture for 12 h with methanol, deionized water, and acetone and then dried at 110°C for 3 h.

2.3. Solid Phase Extraction and Sample Preparation. Solid phase extraction (SPE) method was used to extract the Anthracene from the mixture (aqueous solution at different solvents) by Supelcoclean ENV-18 solid phase extraction tube. After passing the specific volume of aqueous solution through extraction column, the extract was treated with anhydrous Na₂SO₄ to remove all the water content from the extract and then it was concentrated by rotary evaporator (BUCHI-RE121-Switzerland made) in temperatures below 35°C by water bath (BUCHI 461 Metrohm/Swiss made) to be in volume 1 mL. Then samples were analyzed by GC 2010 (Shimadzu, Japan). The study revealed that the Anthracene level had no effect on the percent decrease of the compound during evaporation process for the solvent. The average recovery of analytes for every liquid media and corresponding relative standard deviations RSD ($n = 5$) were represented in Table 1. Chromatographic conditions are listed in Table 2.

TABLE 1: The average recovery of Anthracene and relative standard deviations RSD ($n = 5$).

Organic solvents	Recovery%	RSD%
Methanol	91	0.3
Dichloromethane	88	0.5
Acetonitrile	92	0.2
Ethyl acetate	81	0.4
Acetone	79	3.4

TABLE 2: Chromatographic conditions were used for determination Anthracene by GC.

Parameters	Details
Column	Type: Hp5 (60 m * 0.25 mm * 0.25 μ m)
Injection volume	1 μ L
Injector mode	Split less, temp. = 250°C
Carrier gas	High purity helium.
Detector	Type: FID, temp. = 310°C

2.4. *Photolysis Experiments.* The experiments were carried out in glass dual wall reactor closed system type, to keep the temperature constant using chiller (Julabo model EH/Germany) as temperature controller. Agitation of the reaction mixture was provided by a magnetic stirrer (Heidolph-Mr3001). The photoreactor operated in a batch mode. The study was carried out for selected compound Anthracene (Sigma Aldrich) without additional purification. The pH of the reaction solution adjusted about 6.8, pH by adding an exact volume of Sodium hydroxide or sulfuric acid.

2.5. *Kinetics of the Photocatalytic Process.* Kinetics of Anthracene degradation was calculated by the first-order equation:

$$C_t = C_0 \cdot e^{-kt} \quad (5)$$

or

$$\ln\left(\frac{C_0}{C_t}\right) = kt, \quad (6)$$

where C_0 , C_t are the PAH concentration at times (zero and t), respectively, and k is the rate constant. First-order degradation rate constants were determined by regression analysis.

3. Results and Discussion

Several parameters were studied to indicate the effect of these degradation rates as follows.

3.1. *Effect of the Initial Anthracene Concentrations.* The effect of initial Anthracene concentration on the reaction rate is the first parameter studied in this work. Figure 1 shows that Anthracene concentrations decrease with time increases. The rate of degradation increases as the initial concentration increases as well. For photochemical reactions the higher

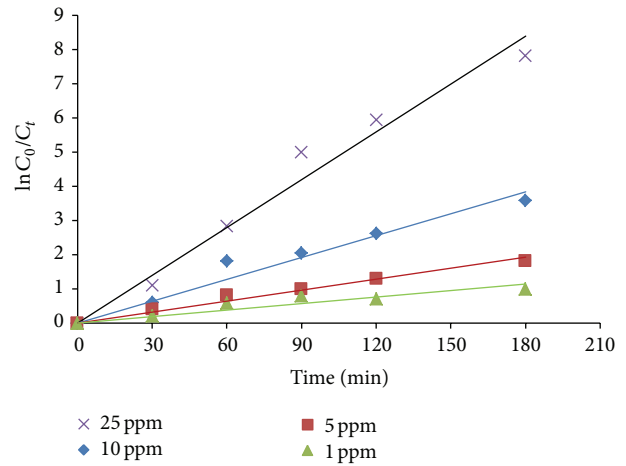
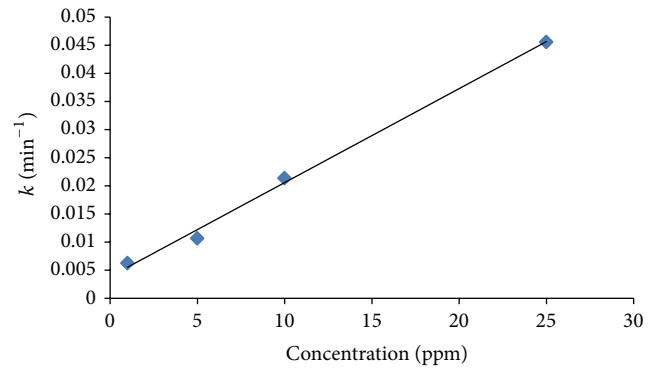
FIGURE 1: The changes of $\ln(C_0/C_t)$ with irradiation times on different Anthracene concentrations by TiO_2 .

FIGURE 2: Effects of initial Anthracene concentrations at a rate constant.

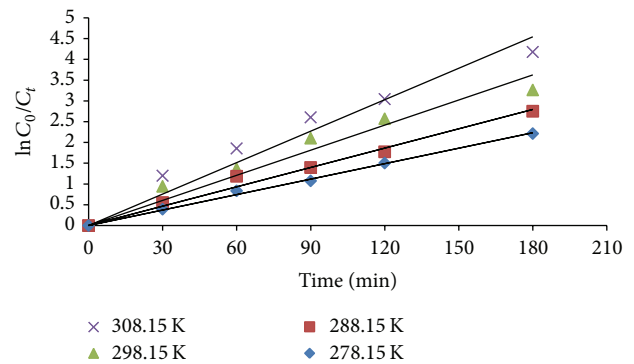


FIGURE 3: Effect of temperature on the degradation rate of Anthracene.

concentration causes a higher light absorption and consequently accelerates the degradation rate [26]. Figure 2 shows the relation between rate constant and initial concentrations of Anthracene.

3.2. *Effect of Temperature.* The oxidation of Anthracene molecule was studied at different temperatures, to indicate

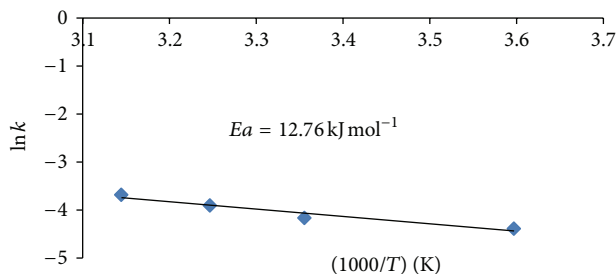


FIGURE 4: Arrhenius plot for photocatalytic degradation of Anthracene on TiO_2 at (278.15–308.15) K.

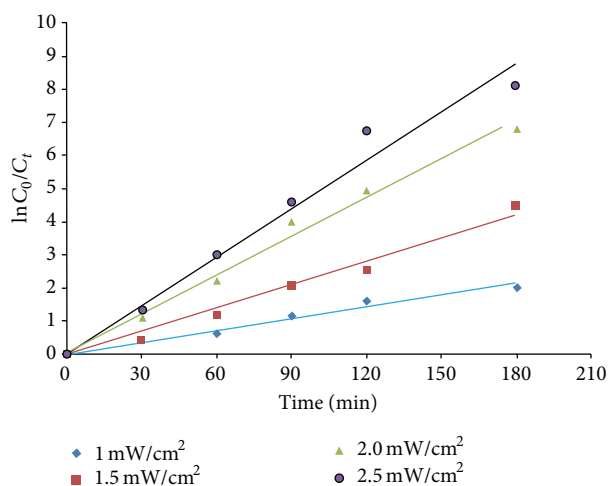


FIGURE 5: Effect of light intensity on the degradation rate of Anthracene.

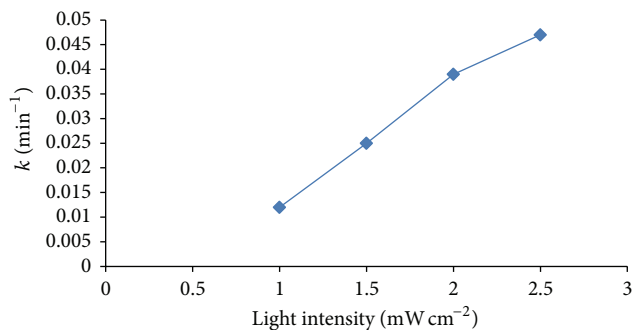


FIGURE 6: The effect of initial light intensity on the rate constant.

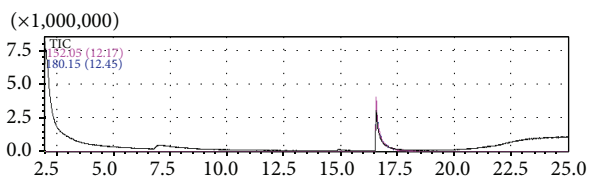


FIGURE 7: Chromatogram of GC-MS for standard 9,10-Antraquinone and produced by oxidation of Anthracene before exposure to UV light.

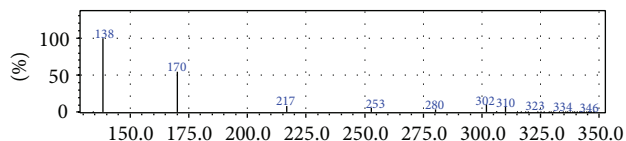


FIGURE 8: Mass spectra for standard 9,10-Antraquinone before exposure to UV light.

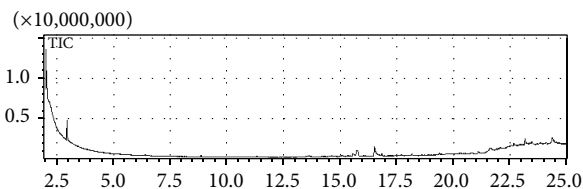


FIGURE 9: Chromatogram of GC-MS for standard 9,10-Antraquinone after exposure to UV light.

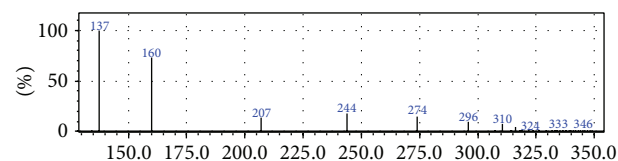


FIGURE 10: Mass spectra for standard 9,10-Antraquinone after exposure to UV light.

the best one at which the degradation rate is fastest. Figure 3 shows the effect of temperature on the concentration of Anthracene with time of reaction. Figure 4 illustrates the Arrhenius plot for the relation between $\ln k$ and $1/T$, activation energy calculated by Arrhenius equation.

The influence of temperature on the degradation rate is typical. The greatest increase of the rate of degradation about two times can be achieved after about 180 min at 308.15 K; initial rates within the first 30 min appear to increase with increasing the temperature. This phenomenon is related to the effect of temperature on the stability of Anthracene molecule. Luo et al. [27] reported that higher temperature slightly enhances the rate constant of Pyrene.

3.3. Effect of Light Intensity. UV light intensity has an important role in the process of photocatalytic degradation. Figure 5 shows effect of light intensity on the degradation rate of Anthracene molecule. This figure indicates that the reactions followed pseudo-first-order rate constant with increasing UV light intensity from 1–2.5 mW/cm^2 . The results indicate the perfect degradation at light value: 2.5 mW/cm^2 .

Therefore, when light intensity increases the number of photons increases which means that the formation of electrons and holes increases, and hence, electron-hole recombination is negligible. However, at the lower light intensity, electron and hole pair separation competes with recombination which in turn decreases the formation of free radicals [28], causing less effect on the rate of degradation of the Anthracene as shown in Figure 6.

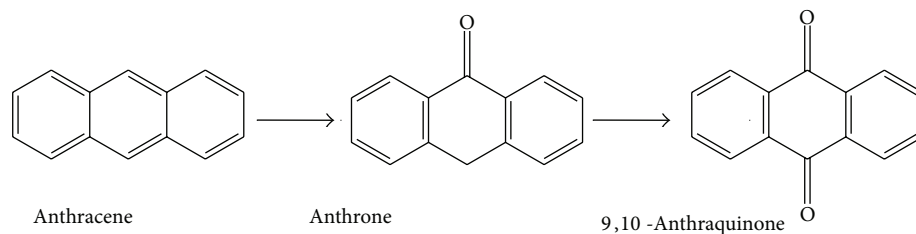


FIGURE 11: Proposed pathway degradation of Anthracene.

3.4. Photodegradation Products of Anthracene. The major product for photodegradation of Anthracene is 9,10-Anthraquinone. Anthraquinone is characterized by GC-MS (2010-SHIMADZU). Standard solution 25 ppm of 9,10-Anthraquinone (Sigma Aldrich) was prepared and compared with that produced by oxidation. Figures 7 and 8 illustrate that there are no differences between them. The proposed degradation pathway of Anthracene is as in Figure 11.

During the photocatalytic degradation experiments with Anthracene only 9,10-Anthraquinone was detected as an intermediate, in agreement with Theurich et al. [23]. Figures 9 and 10 show the GC chromatogram and mass spectra for 9,10-Anthraquinone after exposure to the light intensity in the same environment of perfect conditions for Anthracene degradation.

4. Conclusions

The photocatalytic degradation of Anthracene using artificial UV light has been achieved. The observations of these investigations demonstrate the importance of selecting the optimum parameters for degradation to obtain a high degradation rate, which is considered essential for any application of photocatalytic oxidation processes. The experimental work in controlled pH media at closed system reactor has found that the main product of oxidation of Anthracene is 9,10-Anthraquinone, which is safer for environment than Anthracene. The rate of photodegradation in present UV light has been found to be maximum in neutral medium with optimum concentration of 25 ppm of Anthracene. The optimum temperature for degradation is 308.15 K. The optimum light intensity is 2.5 mW/cm² at pH 6.8. The degradation of Anthracene increases with the increase of light intensity. Nevertheless, the increase of light intensity leads to the increase of the number of electron-hole pairs and increases the degradation of Anthracene.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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