



OPTIMAL CONDITIONS FOR SYNTHESIS OF 1, 4-NAPHTHAQUINONE BY PHOTOCATALYTIC OXIDATION OF NAPHTHALENE IN CLOSED SYSTEM REACTOR

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ABSTRACT

Naphthalene is one of the polycyclic aromatic hydrocarbons (PAHs). These compounds have been classified as carcinogenic. According to this fact, conversion of Naphthalene to safer compound represented by 1, 4-Naphthaquinone is studied in this work. The mechanism of photocatalytic degradation of Naphthalene has been predicted using titanium dioxide as catalyst in closed system reactor. The main initial product for this degradation was 9,10-Naphthaquinone in addition to other intermediate products. The optimum conditions for oxidation are: light intensity at 2.0 mW.cm^{-2} and pH value of the solution at 7 has the best percentage yield of production. Other experimental parameters such as initial concentration of naphthalene, temperature of solution and mass of catalyst are constant in all experiments.

Key words: Preparation of naphthaquinone, Oxidation of naphthalene, Photocatalytic of naphthalene.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are fused aromatic rings compounds. These compounds are consisting of carbon and hydrogen atoms only, arranged in several configuration structures, such as: linear, angular and cluster. The main sources of these compounds in an environment are generated from anthropogenic sources including uncompleted combustion of coal and oil¹, motor vehicle emission and waste incineration². Sixteen of PAHs compounds have been listed as priority environmental pollutants by United State Environmental Protection Agency (US-EPA) and by the European Community³. Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic pollutants and their low water solubility limits their degradation in aqueous solution⁴.

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Photocatalytic oxidation process is one of the many advanced oxidation processes, is based on generation of $\cdot\text{OH}$ by photo reaction in presence of catalysts like titanium dioxide to trigger oxidative degradation.

Naphthalene molecule is the smallest and most stable polycyclic aromatic hydrocarbons. This compound has a high vapor pressure at room temperature (0.2 mbar), making it relatively frequent for gaseous phase studies. Naphthalene molecule is water soluble about (20-30 mg/L) in ambient conditions. This compound has been very well experimented due to its role in interstellar chemistry and its environmental implications especially in the field of water pollution⁵. Naphthalene can be found in many anthropogenic fluxes, such as used oil combustion fumes and bilge water, which is exceedingly recalcitrant to degradation due to inhibitory nature⁶⁻⁸. Remove of naphthalene from water is possible via many techniques, such as: biofiltration⁹, microbial degradation^{10,11}, anaerobic degradation¹²⁻¹⁴, electron beam irradiation¹⁵, electrolytic aeration¹⁶ and photocatalysis¹⁷⁻¹⁹. Photocatalytic has been proposed as an alternative to degrade refractory organic compounds unquestionably due to the specificity of hydroxyl radical's generation, which represents high reaction rate and low selectivity²⁰⁻²³.

Furthermore, many researchers deal with the photocatalytic degradation for PAHs in water by TiO_2 . Woo et al.²⁴ investigated 5 selected PAHs, namely naphthalene, acenaphthylene, phenanthrene, anthracene and benzo[a]anthracene. Gu et al.²⁵ studied degradation of phenanthrene on soil surfaces in presence of nanoparticulate anatase TiO_2 under UV-irradiation. Vela et al.²⁶ used photocatalytic processes by semiconductor materials (ZnO and TiO_2) to remove the residual concentrations of several PAH compounds from groundwater. Indeed, catalyst TiO_2 can play as efficient photocatalyst in the oxidation of PAHs and convert it to safer compounds especially with Naphthalene, Anthracene and Fluorene by artificial or sunlight illumination²⁷⁻²⁹. This study aimed to investigate the optimal conditions for preparation of 1,4-Naphthaquinone from photo oxidation of naphthalene in closed system reactor.

EXPERIMENTAL

Chemicals and reagents

Naphthalene was purchased from Sigma Aldrich, Germany, and used without further purification. Acetonitrile (anhydrous, $\geq 99.98\%$) and Dichloromethane (anhydrous, $\geq 99.98\%$), Acetone, ethyl acetate (anhydrous, $\geq 99.98\%$), methanol HPLC-gradient grade were purchased also from Sigma Aldrich, Germany. Titanium dioxide particles were purchased from Degussa (P25), anhydrous Na_2SO_4 (extra pure Allied Signal, Riedel-de-Germany).

Preparation of stock solution of naphthalene

A set of dilution of naphthalene solution at the concentration of 100 mg/L made in the following solvents: acetone, dichloromethane, ethyl acetate, methanol and acetonitrile. Naphthalene solutions in the above solvents prepared and stored in room temperature ($20 \pm 2^\circ\text{C}$) in dark place to keep it from the light degradation. For quantitative, the calibration curves for all naphthalene solutions in different solvents was prepared basing the concentrations containing naphthalene at concentrations as 0.1, 0.5, 1, 2, 4, 8, 15 and 30 mg/L. All glassware used for experiments were washed in chromic acid mixture for 12 hr with methanol, deionized water, acetone and then dried at 110°C for 3 hr.

Solid phase extraction and sample preparation

Solid Phase Extraction (SPE) method was used to extract the Naphthalene from the mixture (aqueous solution at different solvents) by SupelcocleanTM ENV-18 solid phase extraction tube. After passing the specific volume of aqueous solution throw extraction column, the extract then treated with anhydrous Na_2SO_4 to remove all the water content from the extract and then it 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 Naphthalene 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 ($n = 5$) represents in Table 1.

Table 1: The average recovery of Naphthalene and relatively standard deviations RSD

Organic solvents	Recovery (%)	RSD (%)
Acetone	77	3.1
Dichloromethane	89	0.4
Ethyl acetate	84	0.7
Methanol	79	0.5
Acetonitrile	93	0.4

Synthesis of 1,4-naphthaquinone by photocatalysis oxidation experiments

The experiments carried out in glass dual wall reactor closed system type, to keep the temperature constant using chiller (Julabo model EH/Germany) as temperature controller at 298.15 K. Agitation of the reaction mixture provided by a magnetic stirrer (Heidolph-

Mr 3001) in presence of oxygen atmosphere. The study carried out for selected compound naphthalene without additional purification. The pH of the reaction solution adjusted by adding an exact volume of sodium hydroxide or sulfuric acid; several experiments were achieved for effect of light intensity by control the height of light source from the vessel of reaction; concentration of naphthalene solution was 25 ppm; temperature of reaction adjusted at 298.15 K and 175 mg of titanium dioxide (Degussa) was used as catalyst for this reaction. The time of reaction for all experiments was 150 min. The chromatographic conditions were used for determination of Naphthalene by GC: injector mode is splitless at temperature 250°C, sample injection 2 μ L in column type Hp5 (60 m*0.25 mm*0.25 μ m), carrier gas was helium and the detector type flame ionization detector at temperature 310°C.

RESULTS AND DISCUSSION

Effect of light intensities

UV light intensity is an important role in the process of photocatalytic oxidation. The effect of light intensity on the oxidation efficiency for naphthalene was examined at constant initial naphthalene concentration 25 ppm. It was found that the percentage of oxidation and photo oxidation for Naphthalene increases with increasing the light intensity as shown in Table 2. The light intensity was studied in the range (0.5-2.0) mW.cm^{-2} by changing the height and lowering the lamps. From these results, it was found that the degradation rate for naphthalene increases with increasing the light intensity. The explanations for this behavior that the UV light produce the required photons for the electron transfer from the valance band to the conduction band in titanium dioxide catalyst. The rate of oxidation for naphthalene increases when more light fall on the catalyst surface and hence more $\cdot\text{OH}$ radical is generated on catalyst surface³¹⁻³³. Fig. 1 shows the GC chromatograms for both Naphthalene and 1,4-Naphthaquinone at different exposure time for light.

Table 2: Effect of light intensities and pH value for percentage yield of 1,4-naphthaquinone

Effect of light intensity		Effect of pH value	
Light intensity (mW.cm^{-2})	Percentage yield	pH value	Yield (%)
0.5	20.9%	3	49.5%
1.0	43.6%	5	54.2%
1.5	51.4%	7	57.8%
2.0	56.8%	10	22.3%

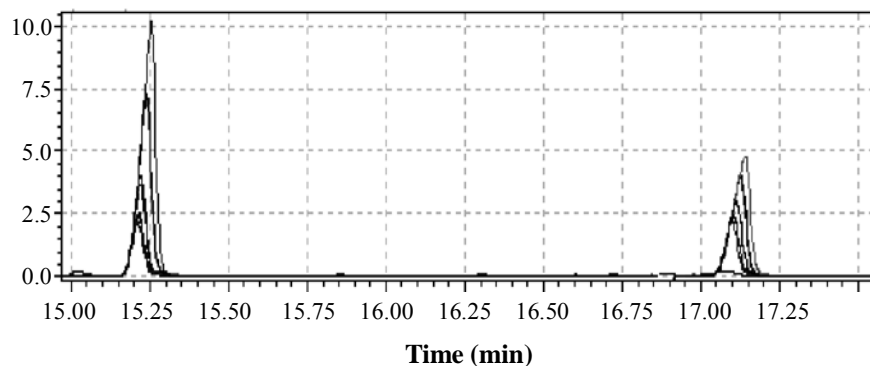


Fig. 1: GC chromatograms for both naphthalene and 1,4-naphthaquinone at different exposure time for light

Effect of pH value

The production of hydroxyl radicals considers as a function of pH³³⁻³⁵. Therefore, pH is an important parameter in photocatalytic oxidation and then on the yield percentage for 1,4-naphthaquinone. The zero point charge for this reaction was equal to 7.0 for titanium dioxide catalyst. The semiconductor surface will remain negatively charged in alkaline medium and positively charged in acidic medium, due to ionization state of the surface of semiconductor according to the following reactions in equations 1 and 2.



Investigation of 1,4-Naphthaquinone by FTIR

Following the main production of Naphthalene oxidation, 1,4-naphthaquinone was studied by comparing this standard compound with those produced by the degradation of Naphthalene. These investigations were compared by using the FTIR charts and GC-MS chromatograms for both compounds. Fig. 2 shows the FTIR chart for 1,4-naphthaquinone compound.

Investigation of 1,4-Naphthaquinone by GC-MS

Several samples were analysed by GC during this part of work in same conditions, such as; initial concentrations of naphthalene, the temperature of the reactor, the pH of the solution and the light intensity of the UV light. Figs. 3 and 4 show the GC chromatogram

and mass spectra for the Naphthalene and 1, 4-naphthaquinone after exposure to the UV light under the following conditions: a concentration of the compound of 25 ppm, a titanium dioxide concentration of 175 mg/100 mL, the temperature of the reactor equal to 298.15 K, a pH of 7, and light intensity equal to $2.0 \text{ mW}\cdot\text{cm}^{-2}$.

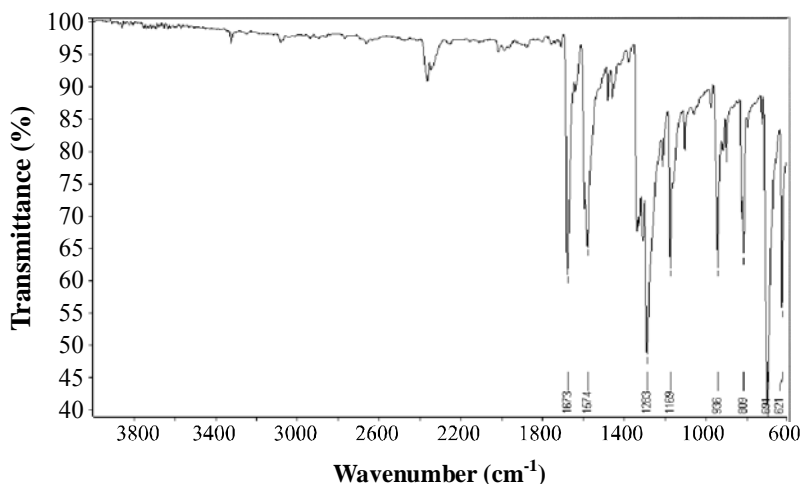


Fig. 2: FTIR spectrum for 1,4-Naphthaquinone

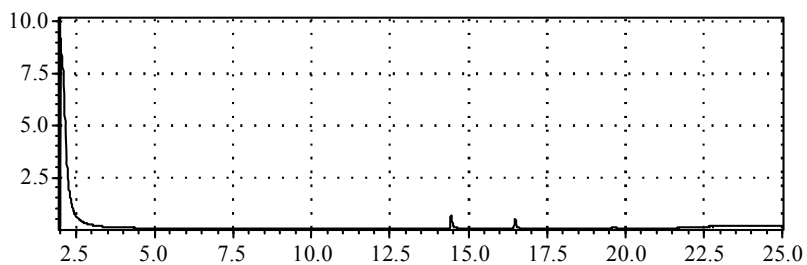


Fig. 3: GC chromatogram for naphthalene and 1,4-naphthaquinone after oxidation process

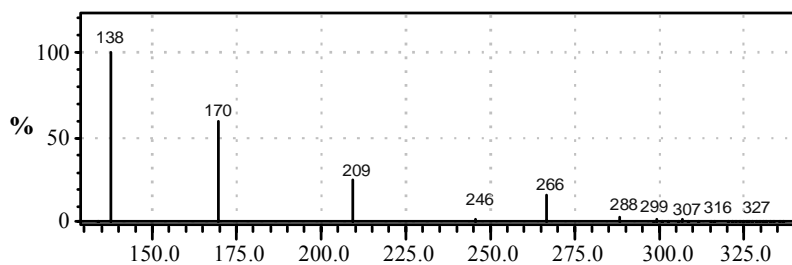
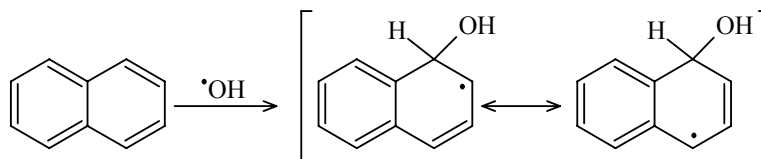


Fig. 4: Mass spectrum for 1,4-Naphthaquinone

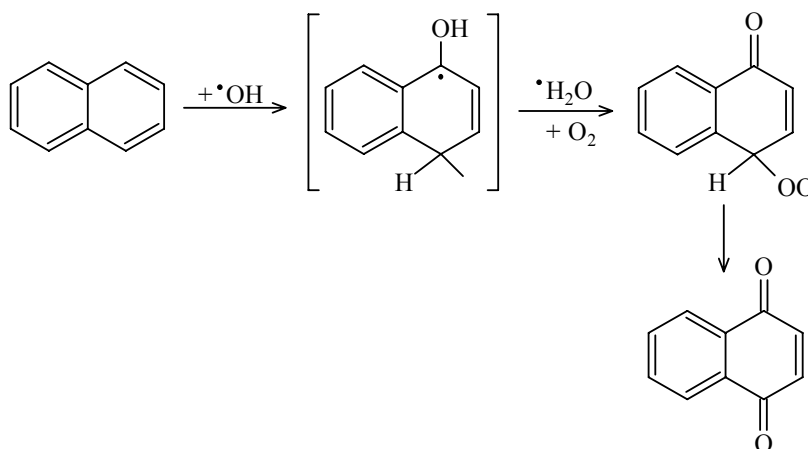
Mechanism

The mechanism suggested by Theurich and Bahnemann³⁰, for transformation of Naphthalene is start by attack of a photocatalytically generated free radical hydroxyl at alpha position, leading to formation hydroxylated Naphthalene radical as shown in **Scheme 1**.



Scheme 1: Attack of radical hydroxyl at alpha position of Naphthalene

The second supposed strategy is attack of free radical hydroxyl at alpha position with present the electron at same position, after loss of water molecule in presence of oxygen another oxygen molecule substitution will appear as shown in **Scheme 2**.



Scheme 2: Mechanism steps of photocatalytic oxidation for Naphthalene

CONCLUSION

The optimum conditions of photocatalytic oxidation of naphthalene are: 2.0 mW.cm⁻² of light intensity and 7.0 of pH with percentage yield 56.8% and 57.8%, respectively. In the presence of initial concentration 25 ppm of naphthalene; temperature 298.15 K and mass of titanium dioxide 175 mg as catalyst. The investigation about the main product of oxidation of naphthalene was appeared that 1,4-naphthaquinone using FTIR and GC-MS.

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