



Photooxidative Removal of Phenazopyridine by UV/H₂O₂ Process in a Batch Re-circulated Annular Photoreactor: Influence of Operational Parameters

SOUDABEH SAEID and MOHAMMAD A. BEHNAJADY*

Department of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran.

*Corresponding author E-mail: behnajady@iaut.ac.ir, behnajady@gmail.com

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ABSTRACT

In this work, efficiency of UV/H₂O₂ process in the removal of Phenazopyridine (PhP) as a model contaminant from pharmaceutical compounds was investigated. For this purpose, a suitable batch re-circulated annular photoreactor with a replaceable UV-C lamp in the center of photoreactor was used. Effect of operational parameters such as initial PhP concentration, H₂O₂ concentration, UV-light source power and pH of the solution was investigated. Results indicate UV/H₂O₂ process is a powerful method for removal of PhP from aqueous solutions so that a considerable removal of this contaminant has been obtained in the short irradiation time.

Key words: Advanced Oxidation Processes (AOPs), UV/H₂O₂, Phenazopyridine, Batch re-circulated annular photoreactor

INTRODUCTION

Development of ecologically clean and safe chemical technologies, processes and materials is vital for maintaining and controlling the environmental pollution¹. Such techniques are getting significant attention in academic and industrial researches due to the shortage in clean and natural resources. Beside many other pollutants of natural water resources, waste pharmaceutical compounds as a result of conventional disposal of these chemicals through sewer or incineration are

very serious pollutants^{2,3}. Because of extreme diversity of such chemicals, their elimination and disposal is a very important and challenging effort. Two main approaches undertaken to tackle with this problem include: applying suitable treatments before disposal of waste drugs in to the sewage system and adoption of refinement techniques for elimination of these compounds. However, despite the widespread utilization of these techniques, they do not help the complete removal of drugs from polluted waters. In order to fully eliminate such compounds and purify the contaminated water, new

approaches needed to be invented^{4,5}. Advanced oxidation processes (AOPs) are introduced as destructive techniques for water treatment by removal of organic contaminants through oxidative degradation procedures. In general, AOPs involve oxidation of chemicals through ultraviolet radiation in the presence of H_2O_2 , O_3 , Fenton, or TiO_2 which results in an efficient production of hydroxyl radicals⁶⁻⁸. These radicals are highly reactive oxidant with a short life cycle and non-selectively attack to contaminants⁸⁻¹⁰. Application of hydrogen peroxide in AOPs seems to be more promising among other approaches due to some of its advantages over others such as: its complete miscibility with water as well as its commercially availability. Moreover, the process can be done in ambient conditions and a whole mineralization of organic carbon into CO_2 may take place. In this process, hydroxyl radicals are generated by photolysis of H_2O_2 through direct absorption of UV light by H_2O_2 in a photoreactor. The maximum hydroxyl radical yields are obtained by using short-wave ultraviolet radiations (200–280 nm)¹¹.

In this work, the efficiency of UV/ H_2O_2 process in the removal of a Phenazopyridine (PhP) as a model contaminant from pharmaceutical compounds was investigated in a batch re-circulated annular photoreactor. The effect of operational parameters such as initial concentration of PhP, concentration of H_2O_2 , power of light source and pH were studied.

MATERIALS AND METHODS

Materials

Hydrogen peroxide (37%, w/w) was purchased from Merck (Germany). Phenazopyridine (PhP) with structural formula shown in Fig. 1, is a commonly used drug, and is chosen here as a model drug contaminant. PhP was prepared from Tehran pharmaceutical company (Iran). The presence of the azo group makes PhP as a refractory pollutant^{12,13}.

Photoreactor and Procedure

All experiments were performed in a batch re-circulated annular photoreactor (Fig. 2). The radiation source at annular photoreactor was UV-C lamp (4, 6 and 13 W, $\lambda_{max} = 254$ nm, Philips, Holland).

In each experiment 500 mL of the PhP and H_2O_2 solution was transferred to the photoreactor. Then the lamp was switched on to initiate the reaction. During irradiation, the solution was agitated in a constant rate and was transferred with peristaltic pump through annular photoreactor with volumetric flow rate of 140 mL min^{-1} . At certain reaction intervals, 5 mL of sample was withdrawn and the concentration of PhP was determined by means of a spectrophotometer (Shimadzu UV mini-1240).

RESULTS AND DISCUSSION

Effect of the initial concentration of PhP

The effect of initial PhP concentration ranging between $20 - 50 \text{ mg L}^{-1}$ on the removal of PhP was investigated. Figure 3 illustrates the result of the experiment with different initial PhP concentrations and fixed amount of hydrogen peroxide. Based on these results, efficiency of PhP removal decreases with increasing the initial PhP concentration. This may be due to the fact that in the higher PhP concentration a stronger inner filter effect makes the solution more impermeable to UV radiation. Hence, efficiency of photooxidative removal of PhP decreases¹⁴.

Effect of the initial concentration of H_2O_2

Figure 4 illustrates the effect of initial concentration of H_2O_2 ranging between $50 - 600 \text{ mg L}^{-1}$ on the removal of PhP. In general, increasing the initial H_2O_2 concentration increases the efficiency of the UV/ H_2O_2 process. A significant increase in the removal is observed in the range of $50 - 500 \text{ mg L}^{-1}$

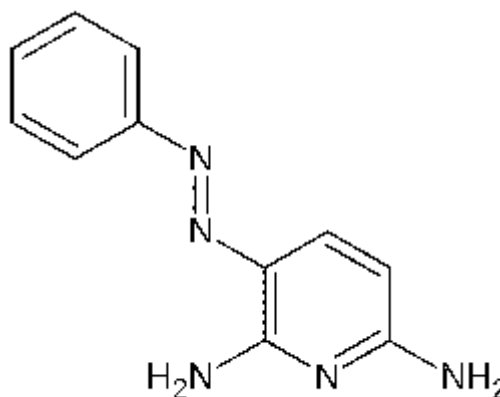


Fig. 1: Structural formula of PhP

from H_2O_2 and further increasing of the initial H_2O_2 concentration shows a decrease in the PhP removal percent. In the range of 50 - 500 $mg L^{-1}$ more available hydroxyl radicals ($\cdot OH$) in the solution justifies a dramatic increase in the PhP removal percent (Eq. 1). Whereas, further increasing of the H_2O_2

concentration, lead to produce of $HO_2\cdot$ as a result of H_2O_2 reaction with $\cdot OH$ (Eq. 2) which is less reactive than $\cdot OH$. Also $\cdot OH$ reacts with $HO_2\cdot$ or dimerize to H_2O_2 (Eqs. 3, 4) that has negative effects on the PhP removal efficiency^{14,15}.

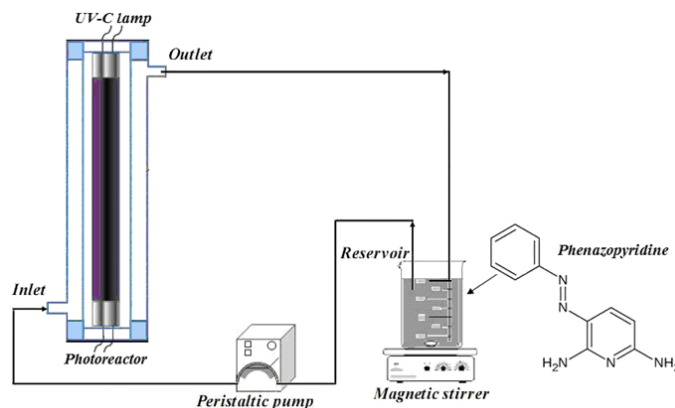


Fig. 2: Scheme of batch re-circulated annular photoreactor

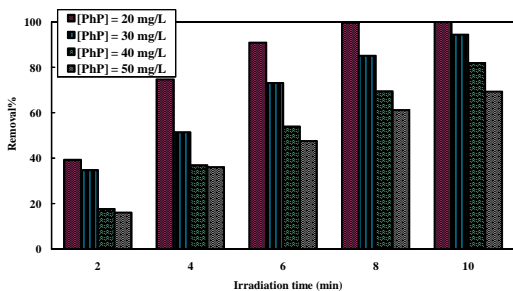


Fig. 3: Effect of initial concentration of PhP on the photooxidative removal of PhP.

P = 6 W, pH = natural, $[H_2O_2] = 500 mg L^{-1}$

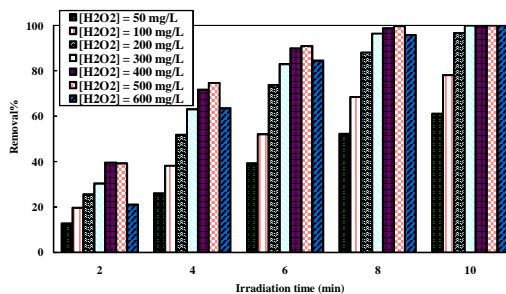


Fig. 4: Effect of the initial concentration of H_2O_2 on the photooxidative removal of PhP.

$[PhP] = 20 mg L^{-1}$, P = 6 W, pH = natural

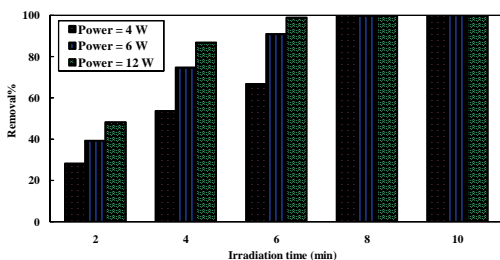


Fig. 5: Effect of UV light source power on the photooxidative removal of PhP. $[PhP] = 20 mg L^{-1}$, $[H_2O_2] = 500 mg L^{-1}$, pH = natural

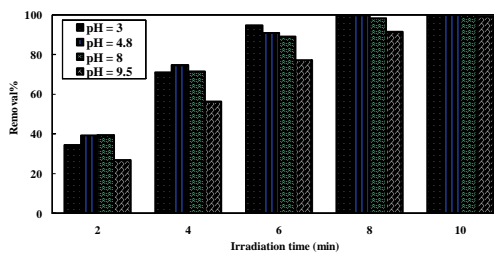
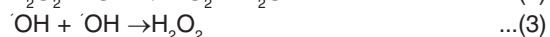


Fig. 6: Effect of pH on the photooxidative removal of PhP. $[PhP] = 20 mg L^{-1}$, P = 6 W, $[H_2O_2] = 500 mg L^{-1}$



in the alkaline pH ¹⁶.



Effect of light source power

As shown in Fig. 5 the removal percent of PhP increases with increasing power of light source from 4 to 12 W. This is justified with higher production rate of $\cdot\text{OH}$ at higher UV-light power and thus, an increase in reaction efficiency. According to Eq. (1) higher $\cdot\text{OH}$ produces when stronger light source uses in the photoreactor.

Effect of pH

The effect of pH ranging from 3–9.5 on the photooxidative removal of PhP was investigated as shown in Fig. 6. It was observed that the efficiency of the UV/ H_2O_2 process in the removal of PhP was lower in the pH = 9.5. This can be due to dissociation of H_2O_2 to the HO_2^- and H^+ at pH = 9.5 according to the Eq. 5. Hence, a decline in the process is rational

CONCLUSIONS

In this work, efficiency of the UV/ H_2O_2 process using a batch re-circulated photoreactor has been studied in the removal of PhP from aqueous solution. The effects of operational parameters such as, initial PhP concentration, H_2O_2 concentration, UV-light source power and pH have been investigated on the efficiency of the process. According to the results, H_2O_2 concentration has a critical effect in the removal of PhP and highest removal percent can be obtained by 500 mg L^{-1} from H_2O_2 concentration. Also, efficiency of the process in the removal of PhP is higher in the range of 3 - 8 for pH. UV-light source power has also positive effect on the efficiency of reactor and stronger light source causes higher removal percent.

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