

Research Article

Photocatalytic Degradation of Phenolic Compounds using Halogen/H₂O₂/TiO₂ Process in Aqueous Solution

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Abstract

Photocatalytic degradation of phenol (P) and 4-nitrophenol (4-NP) in aqueous solutions by different individual as well as combined sources (halogen light, H₂O₂, TiO₂) were studied. The influences of various operating parameters including the initial pollutant concentration (100–1000 mg/l), solution pH (3–11), and reaction time (1–6 h). The removal efficiency of halogen, H₂O₂/sunlight, halogen/H₂O₂, TiO₂, TiO₂/halogen, TiO₂/halogen/H₂O₂ photocatalytic degradation systems with various operation conditions had 24% 30% 39%, 46%, 53% and 64%; 33%, 49%, 62%, 70%, 79% and 87% for P and 4-NP, respectively. It is found that maximum removal of P and 4NP were obtained at pH 11, C₀ =100 mg/l, 4h reaction time. Combined halogen/H₂O₂/TiO₂ process may be applied as an effective process for removal of P and 4NP from aqueous solution such as industrial wastewater and polluted water resources.

Key words: Photocatalytic degradation, phenol, 4-nitrophenol, halogen, TiO₂, H₂O₂.

1. Introduction

Phenol compounds are widely used and have become common pollutants in water bodies (Suresh et al., 2011). These compounds are highly toxicity and bio refractory product which can cause adverse effects on the aquatic ecosystems and human health. To reduce its influence directly or indirectly effective and economic methods have to develop. There are many traditional wastewater treatment techniques for phenol removals were electrocoagulation (Suresh et al., 2013) activated carbon adsorption, chemical oxidation and biological digestion (Suresh et al., 2012 a-b; Suresh and Keshav, 2013). However, each technique has some limitations and disadvantages (Wang et al., 1999; Zhao et al., 2010). Photocatalysis is an oxidation process which is used for degradation of various pollutants. Among various semiconductor photocatalysts, titanium dioxide (TiO₂) is the most suitable material for prevalent environmental applications. However its wide band gap, high recombination rate of the generated charge carriers, and the slow transfer rate of electrons to oxygen limit the efficiency of this photocatalyst (Maicu et al., 2011). The present work deals to study of P and 4NP in the presence of halogen lamp, H₂O₂, TiO₂. The role of main factors that affecting the process was also examined.

2. Materials and methods

2.1. Materials

All chemicals used in the experimental work were Analytical grade. P and 4NP were purchased from Ranbaxy fine chemicals, New Delhi, India. TiO₂ and H₂O₂ were purchased from central drug house (P) Ltd., New Delhi, India. Stock solutions of P and 4NP were prepared by dissolving a weighed amount of P and 4-NP in double distilled water according our requirement respectively. The experimental test solutions were prepared by diluting the respective stock solution of P, 4NP. For HPLC purpose, HPLC Grade water (Central drug house (P) Ltd., New Delhi, India) was used in the analysis of P and 4NP.

2.2. Methods

Solution of P and 4NP were prepared for experiment such as 100 mg/l, 250 mg/l, 500 mg/l and 1000 mg/l. At end of experiments, these phenolic compounds were analyzed through HPLC (Waters Pvt. Ltd., India). The symmetry C₁₈ column was used (4.6 x 150 mm). A mixture of 40% methanol, 1% acetic acid and rest HPLC Grade water obtained were used as a solvent. Flow rate of solvent in the column and the wavelength were fixed at 1 ml/min and 280 nm respectively. At the end, concentration of P and 4NP are obtained from calibration curve of P and 4NP. In this way, the degradation of phenolic compounds (P and 4NP) was examined.

2.3. Photoreactor Setup

Photocatalytic process was performed batch wise to examine the rate of degradation of P and 4-NP at various conditions. The photoreactor setup was shown in Fig.1. A

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halogen lamp (500 W) and sunlight was used as light source. The photoreactor is made of plex glass in a rectangular shape (32" x 8 " x 8") the top surface is open. The inner surface of photoreactor was coated with black polished media, to improve the intensity of light which focused in the pollutants.

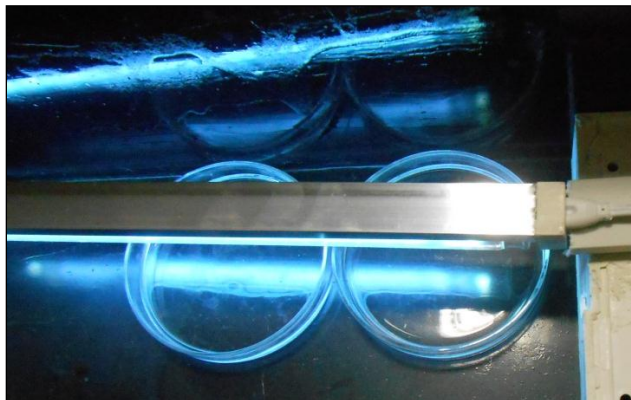


Figure 1 Experimental Setup of batch photoreactor

3. Result and Discussions

3.1. Effect of initial concentration of P and 4NP

The degradation of P and 4NP have been studied by varying initial concentration of pollutants in the range of 100-1000 mg/l at constant conditions (pH= 11, TiO₂ =0.2 g, H₂O₂ = 5 ml and 4h reaction time). The optimum values of TiO₂ and H₂O₂ were observed from literature (Zhao et al., 2010; Rahmani et al., 2008). The result was shown in Figs. 2-3.

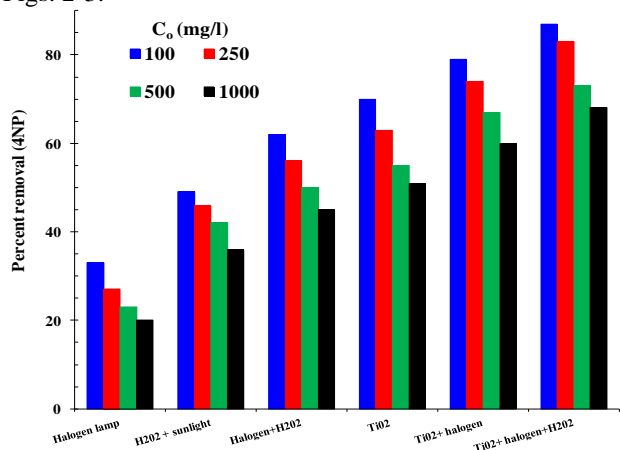


Figure 2 Effect of initial concentration of 4NP on efficiency of process (TiO₂=0.2g/l, pH=11)

The removal efficiency of P and 4NP increased with increasing the concentration upto 250 mg/l. for higher concentration no. significant addition improvement was observed at all the photo degradation system. For 100 mg/l of P and 4NP, the maximum removal were obtained as follows 24% 30% 39%, 46%, 53% and 64%, 33%, 49%, 62%, 70%, 79% and 87% for halogen, H₂O₂/sunlight, halogen/H₂O₂, TiO₂, TiO₂ /halogen, TiO₂ /halogen/H₂O₂, respectively.

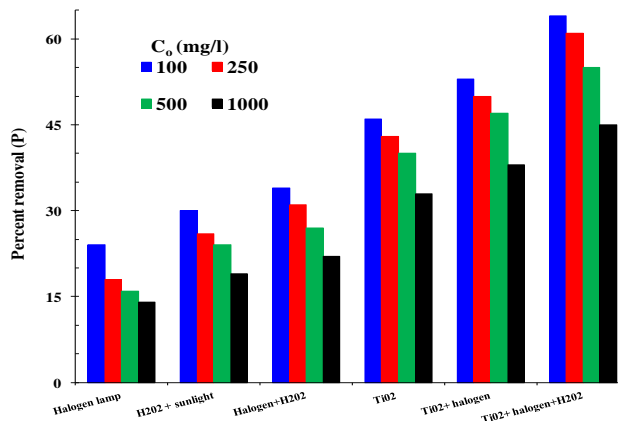


Figure 3 Effect of initial concentration of P on efficiency of process (TiO₂=0.2g/l, pH=11)

3.2. Effect of solution pH

The influence of pH of P and 4NP solution on the various processes efficiency were studied by using various initial pH value (3,6,8 and 11) without changing or checking them throughout all the process. The result was shown in Figs. 4-5. The degradation efficiency increases rapidly with increasing the pH value due to hydroxyions. The degradation increases in given order pH3 < pH 6 < pH 8 < pH < 11. Possessing materials was solute in water with alkali pH. It was converted to phenoxide ion that more degradable than P. Conversely in acid pH, phenol has a little degradability. Yang and Lee (2006) and llier et al. (2002) reported that the increase of pH increased the removal efficiency of humic acid and P in aqueous solutions. P and 4NP was more effectively eliminated by using combined. Halogen/H₂O₂/TiO₂ condition than either than. Halogen or H₂O₂ or TiO₂ separately or combined of both. Lee et al. (2003) reported similar results for the removal of organic compounds with UV/TiO₂ process.

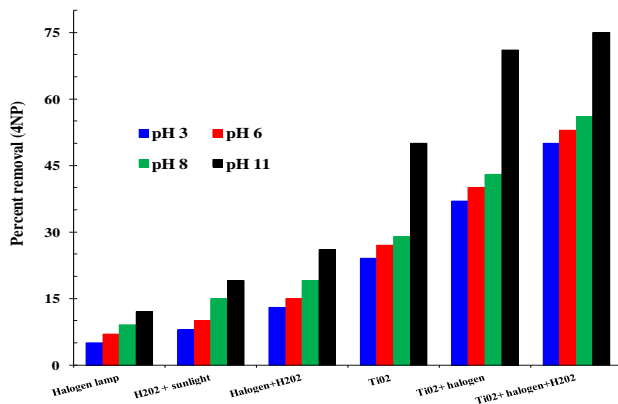


Figure 4 Effect of pH on 4NP degradation process (TiO₂=0.2g/l, initial conc. (4NP) = 100 mg/l)

The results show that degradation rate in a 4 h period with pH= 3, 7, 8 and 11 has been 50%, 53%, 56% and 75 % respectively for 4-NP and obtained 44%, 47%, 51% and 64% respectively for P at same condition. In addition, the extent of decreased degradation is more significant for P compared to 4-NP. This is because P is a stronger

competitor. Beside, the hydroxyl ion is released during the photo degradation of P.

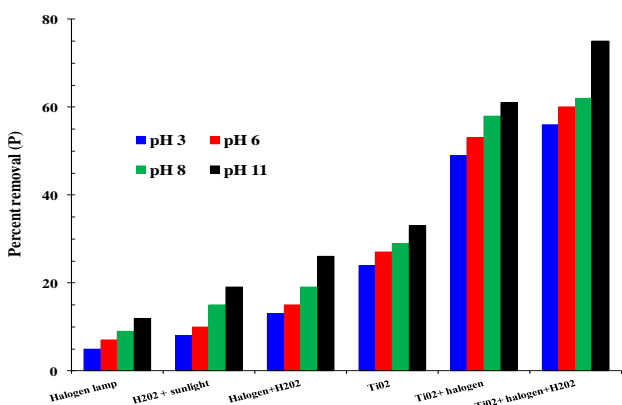


Figure 5 Effect of pH on P degradation process (TiO₂ =0.2g/l, initial conc. (P) = 100 mg/l)

3.3. Effect of Reaction time

TiO₂ particles and phenolic compounds, when comes contact to each other then pollutants get adsorbs on TiO₂ particles surface in the molecular forms. Due to this affinity, the rate of adsorption of phenolic compounds on active surface will be more and finally reacts with TiO₂ and enhance the photo degradation. The H₂O₂ is another way to get hydroxyl radicals peroxide. It favors generation of •HO₂ to carry reaction, while the amount of •HO increases. Therefore, the successive reactions and hydroxyl radical production enhanced since hydroxyl radical is likely the dominant oxidizing species in the photo degradation process (Mogyorosi et al. 2002).

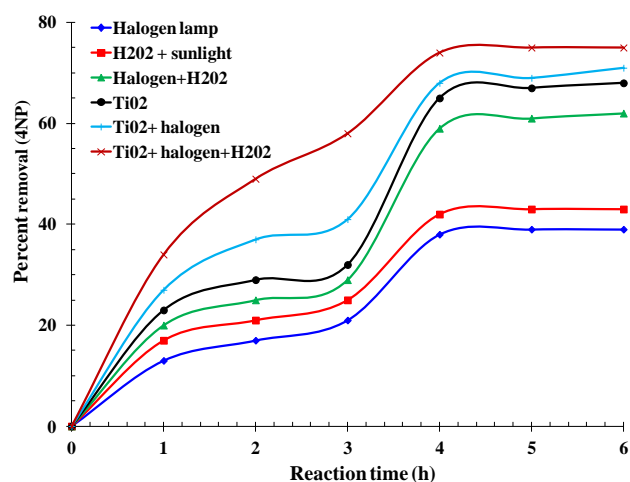


Figure 6 Effect of reaction time on 4NP degradation process (TiO₂ =0.2g/l, C₀ (4-NP) = 100 mg/l)

Effect of reaction time on degradation of P and 4NP at TiO₂ (0.2g/l) C₀ = 100 mg/l, pH =11 and shown in Figs. 6-7. By increasing the reaction time, efficiency of P and 4NP is raised. It can be observed that the removal efficiency increased by increasing the reaction time up to 4 h and the removal efficiency was nearly constant from 4-6 h and so on.

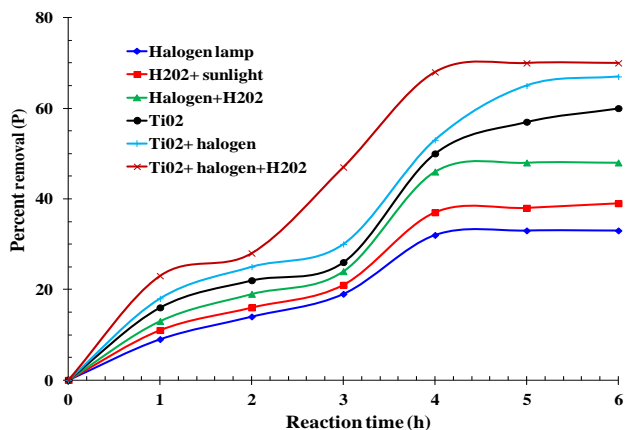


Figure 7 Effect of reaction time on P degradation process (TiO₂ =0.2g/l, C₀ (P) = 100 mg/l)

Conclusion

Halogen/H₂O₂/TiO₂ can be efficiently process to degradation of P and 4NP, under constant condition (H₂O₂ = 5ml; TiO₂ =0.2 g/l; pH=11). The reaction rates of photodegradation of 4 and 4NP were influenced by pH value. Degradation is more than the phenol because of the rate of adsorption on active sites and producing of free radicals oxidant are more. 4NP and P have maximum 75 % and 64 % respectively at constant mass loading (TiO₂ =0.2 g/l) and pH= 11. Finally, it observed the combination of TiO₂/H₂O₂ and halogen gives better result than other combined system. Photodegradation can be alternative treatment method for those contaminants resistant to conventional methods. Combined process for P and 4NP degradation is compatible with environment.

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