

Investigation of the Efficiency of ZnO Photocatalyst in the Removal of p-Nitrophenol from Contaminated Water

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ABSTRACT: *In the present study, photocatalytic removal of p-nitrophenol has been carried out in the presence of ZnO by using a batch reactor with a UV-C lamp (15 W). The effects of applied ZnO concentration and UV light intensity have been studied. The increase of initial pollutant concentration decreases the removal rate, and the results indicate that the apparent reaction rate constant in the UV/ZnO process is a function of ZnO concentration. The kinetics of removal follow pseudo- first order. The influence of pollutant assisting chemicals such as NaCl, NaHCO₃ and Na₂CO₃ on photocatalytic removal has been investigated. Addition of these chemicals reduces the removal rate. HPLC results showed that some intermediates appeared in the reaction course and were removed with increasing irradiation time. Therefore the results reveal that the mineralization of (p-NP) at optimum condition occurs and COD reduction of 80.0 % takes place after 150 min of irradiation.*

KEY WORDS: *Advanced oxidation processes, Photocatalysis, p-nitrophenol, ZnO.*

INTRODUCTION

The pollution of drinking water reservoirs and aquatic environment by chemicals has been a serious problem of these last years. Important organic contaminants in industrial wastewaters are phenols and its compounds. They are released into the environment, from effluents discharged by industries such as petroleum refining, coal tar, steel, dyestuff, synthetic resins, coal gasification and surface runoff from coal mines, by-products of agricultural chemicals, paper and pulp mills, tanning fiberboard production and paint stripping operations [1]. Nitrophenols are some of the most refractory substance present in industrial wastewaters because of their high stability and solubility in water.

They are considered priority toxic pollutants by the United States Environmental Protection Agency [2] and the maximum allowed concentration range is from 1 to 20 ppb [3]. Nitrophenols are involved in the synthesis of many products and appear in the degradation of pesticides like parathion and nitrofen [4, 5]. The treatment of wastewaters contaminated with these pollutants is very difficult since they are resistant to the traditional treatment techniques and long periods of incubation is required for the microbial degradation of p-nitrophenol [6].

Therefore in recent years an alternative to conventional methods, "advanced oxidation processes" (AOP_s), based on the generation of very reactive species

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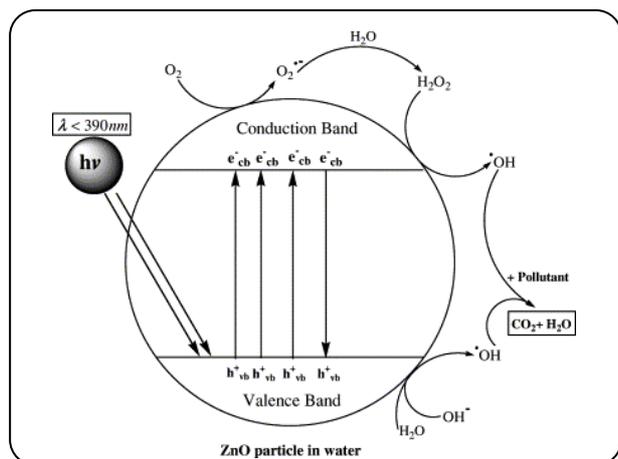
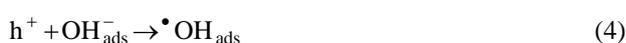
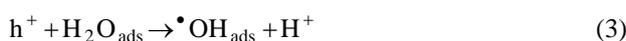


Fig. 1: General mechanism of the photocatalysis [11].

such as hydroxyl radicals, which could oxidize a broad range of organic pollutants quickly and non-selectively were developed [7, 8].

AOPs include photocatalysis systems such as combination of a semiconductor (TiO_2 , ZnO , etc) and UV light. Electronic structure of the metal atoms in semiconductors is characterized by an empty conduction band and a filled valence band. Valence band electrons are promoted to the conduction band under irradiation, which leaves a hole behind [9]. Electron-hole pairs can either interact distinctly or recombine with other molecules, as shown below:



Furthermore, indirect oxidation by hydroxyl radicals requires hydroxide ions on the surface in order to form

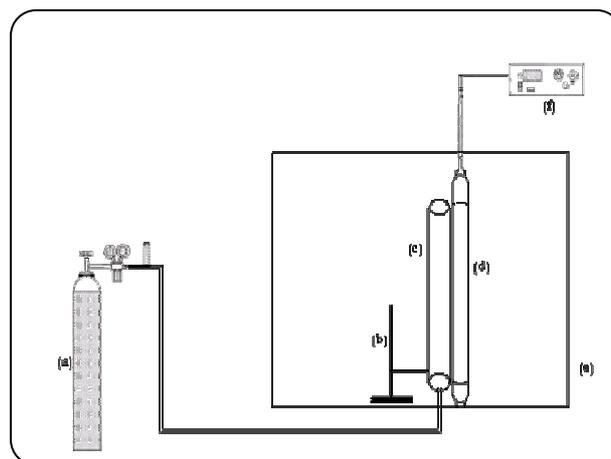


Fig. 2: Schematic diagram of slurry photocatalytic reactor: (a) O_2 cylinder, (b) clamp, (c) quartz tube reactor, (d) UV lamp, (e) shield and (f) power supply.

hydroxyl radicals or the adsorption of water [6], as shown in Fig. 1 [10].

The aim of the present work was to investigate the efficiency of ZnO photocatalyst in removal of p-nitrophenol from contaminated water. And also the effect of different parameters in removing p-nitrophenol such as UV light intensity, different amounts of ZnO , initial concentration of p-nitrophenol and the effect of H_2O_2 concentration were examined.

EXPERIMENTAL

Materials

p-nitrophenol (p-NP) was obtained from Fluka (Switzerland). ZnO , NaCl , Na_2CO_3 , NaHCO_3 and $\text{Na}_2\text{B}_2\text{O}_6$ were purchased from Merck (Germany) and used without further purification.

Solutions were prepared by dissolving requisite quantity of p-NP in double distilled water before each experiment. The pH of the solutions was adjusted to 9.0 by using dilute solution of $\text{Na}_2\text{B}_2\text{O}_6$.

Photoreactor and light source

For UV/ ZnO process, irradiation was performed in a batch quartz photoreactor of 100 mL volume with UV lamp (15 W, UV-C, $\lambda_{\text{max}} = 254 \text{ nm}$, manufactured by Philips, Holland) in vertical array, which was placed in front of the quartz tube reactor. There was not any distance between UV lamp and quartz tube reactor. So when the light intensity was measured by Lux-UV-IR meter (Leybold Co), maximum intensity was observed

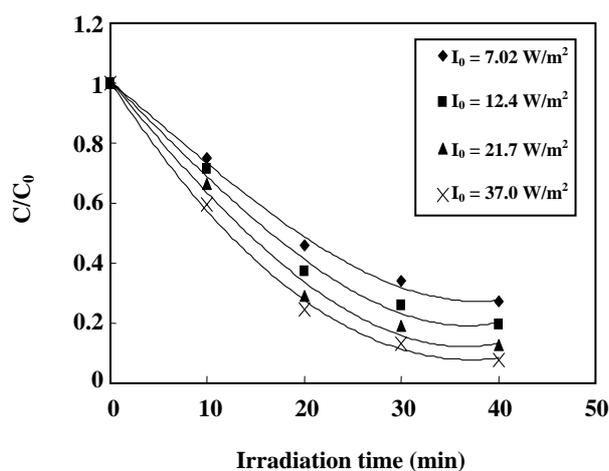


Fig. 3: The effect of UV light intensity. $\text{pH} = 9$, $[\text{ZnO}] = 400 \text{ mg L}^{-1}$, $[\text{p-NP}]_0 = 20 \text{ mg L}^{-1}$.

and when the distance between the lamp and the quartz tube reactor was increased, the light intensity decreased. A schematic diagram has been shown in Fig. 2.

Procedures

In the photocatalytic removal of p-NP, a solution which contains p-NP and ZnO was prepared and placed for 60 min in the darkness, then 100 mL of the above suspension was transferred to the quartz tube reactor and then O_2 was led through the reactor.

The pH was adjusted to 9.0 by using dilute solution of $\text{Na}_2\text{B}_2\text{O}_6$. At this pH, p-NP is predominantly in the deprotonated form, which has an absorption maximum at 400 nm, whereas the protonated form weakly absorbs visible light [12].

The reaction was initiated when the lamp was switched on during irradiation, O_2 flow was maintained in the quartz tube reactor to keep the suspension homogeneous, then at certain reaction intervals, 5 mL of sample was withdrawn, centrifuged and the concentration of p-NP was determined by means of a UV-vis spectrophotometer (Ultrospec 2000, England) at 400 nm. Chemical oxygen demand (COD) was monitored by the dichromate reflux method. Based on Beer-Lambert's law a calibration plot was established by relating absorbances to the concentrations.

The changes in the absorption spectra of p-NP at different irradiation times were recorded on a double-beam UV-vis spectrophotometer (Shimadzu 1700) with wavelength range from 190 to 550 nm.

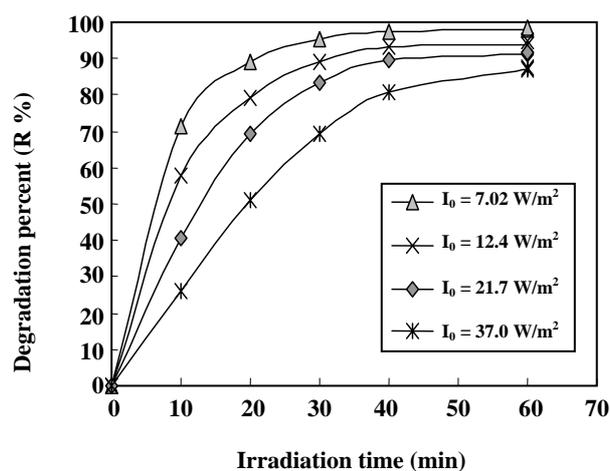


Fig. 4: The effect of initial p-NP concentration. $\text{pH} = 9$, $[\text{ZnO}] = 400 \text{ mg L}^{-1}$, $I_0 = 37 \text{ W m}^{-2}$.

RESULTS AND DISCUSSION

The effect of UV light intensity

The effect of UV light intensity on the removal of p-NP has been examined and it is quite evident that the removal rate steadily increases with increasing irradiation period with ZnO concentration of 400 mg L^{-1} and p-NP concentration of 20 mg L^{-1} as shown in Fig. 3.

The UV irradiation produces the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst, and the energy of the photon is dependent on the light intensity, and also as the more radiations fall on the catalyst surface and the rate of removal increases, the more hydroxyl radicals are produced. The enhancement of removal rate is due to increase in hydroxyl radical concentration, hence the increase in the light intensity, increases the removal at the time of 40 min. It appears that the UV light intensity employed in our study lies within the linear range and therefore all the photons provided were effectively used [13].

The effect of initial p-NP concentration

The effect of the initial concentration of p-NP solution on its removal was illustrated in Fig. 4. With varying p-NP concentration from 5 mg L^{-1} to 30 mg L^{-1} . The results showed that the removal rate decreased with increasing initial p-NP concentration. It can be seen that as initial p-NP concentration increases, the amount of adsorption of organic substances on the surface of ZnO increases, therefore, the generation of hydroxyl radicals

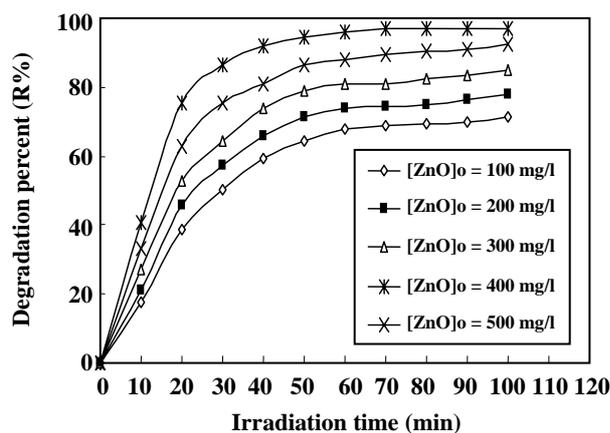


Fig. 5: The effect of catalyst concentration. $pH = 9$, $[p-NP]_0 = 20 \text{ mg L}^{-1}$, $I_0 = 37 \text{ W m}^{-2}$.

will be reduced, because of fewer active sites for adsorption of hydroxyl ions and generation of hydroxyl radicals. Furthermore, with increasing p-NP concentration, the adsorption of photons are decreased by the catalyst, as a result, the removal percent is reduced [14].

The effect of catalyst concentration

The effect of catalyst concentration using p-NP solutions at concentration of 20 mg L^{-1} was studied. As shown in Fig. 5 photocatalytic removal efficiency increases with an increase in ZnO concentration up to 400 mg L^{-1} , and then decreases with an increased catalyst loading. In a set of runs the percent of removal increased from 67.67 to 96.13 %. After that the increase in catalyst loading did not affect the removal significantly. This observation can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension [11].

The total active surface area increases with increasing catalyst dosage, which in turn increases the number of hydroxyl, and superoxide radicals. At the same time, due to an increase in the turbidity of the suspension, there is a decrease in UV light penetration as a result of increased scattering effect and hence the photoactivated volume of suspension decreases [12]. Since the most effective decomposition of p-NP was observed with 400 mg L^{-1} of ZnO, therefore this is considered an optimum concentration.

The effect of hydrogen peroxide concentration

Limitation to the rate of photocatalytic removal has been attributed by most researches to the recombination

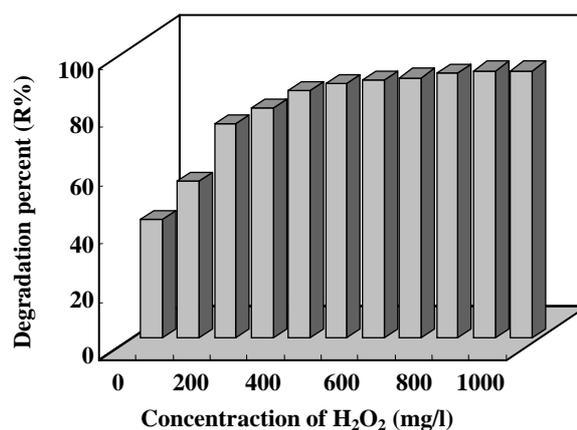


Fig. 6: The effect of hydrogen peroxide concentration. $[ZnO] = 400 \text{ mg L}^{-1}$, $[p-NP]_0 = 20 \text{ mg L}^{-1}$, $I_0 = 37 \text{ W m}^{-2}$, Irradiation time = 10 min.

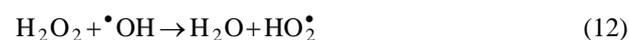
of photogenerated hole-electron pairs [13]. The rate of photocatalytic removal of organic compounds is significantly improved either in the presence of oxygen or by addition of hydrogen peroxide. The photocatalytic removal of p-NP has been studied at different hydrogen peroxide concentrations as shown in Fig. 6.

The removal rate of p-NP increased with increasing H_2O_2 concentrations. The higher reaction rates after addition of H_2O_2 were attributed to the increase in the concentration of hydroxyl radicals. According to Eq. (10), low concentration of hydrogen peroxide inhibits the hole-electron recombination. Since hydrogen peroxide is a better electron acceptor than molecular oxygen it could act as an alternative electron acceptor to oxygen [14].

Hydrogen peroxide may also split photocatalytically to produce hydroxyl radicals directly, as cited in the studies of homogeneous photooxidation using UV/ZnO.



By addition of excess H_2O_2 , it acts as hydroxyl radicals or hole scavenger by producing perhydroxyl radicals which is a much weaker oxidant than hydroxyl radicals [15].



Therefore, the proper addition of hydrogen peroxide could accelerate the photocatalytic removal rate of p-NP.

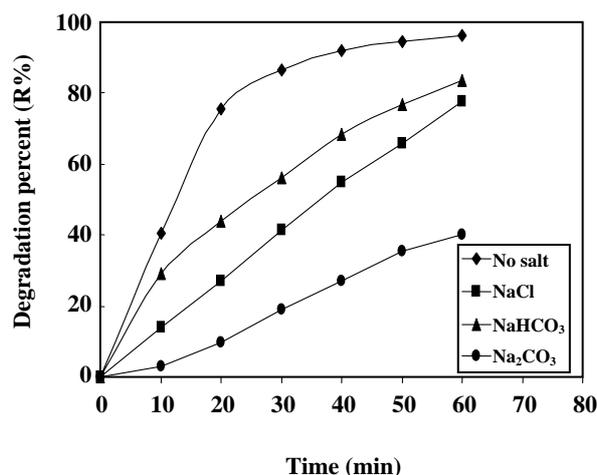


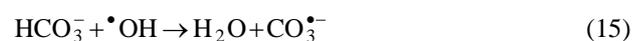
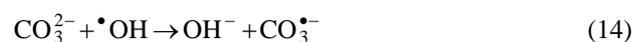
Fig. 7: The effect of salts. $[ZnO] = 400 \text{ mg L}^{-1}$, $[p\text{-NP}]_0 = 20 \text{ mg L}^{-1}$, $I_0 = 37 \text{ W m}^{-2}$, $\text{pH} = 9$.

However, in order to maintain the efficiency of the added hydrogen peroxide, it was necessary to choose the proper dosage of it.

The effect of salts

The effects of addition of salts such as NaCl and Na_2CO_3 (1000 mg L^{-1}) on the photocatalytic removal are given in Fig. 7. As can be seen, by increasing the concentration of CO_3^{2-} and Cl^- the removal percent significantly decreases [16].

Na_2CO_3 and NaHCO_3 strongly retard the removal rate and the strong retardation effect is due to the hydroxyl radical scavenging effect of carbonate and bicarbonate ions, respectively (Eqs. (14), (15)).



Like carbonate, addition of NaCl also affects the removal rate, but it doesn't decrease as strongly as Na_2CO_3 . The small decrease in the removal efficiency is due to the hydroxyl radical scavenging effect of chloride ion (Eqs. (16), (17)). Similar retardation by the addition of Na_2CO_3 and NaCl has been reported in the UV- H_2O_2 process [17].

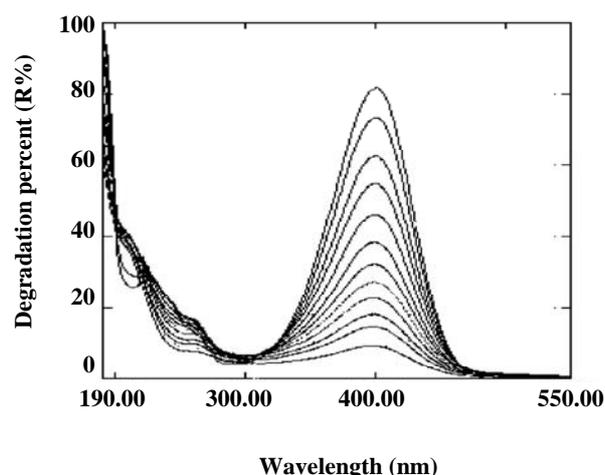


Fig. 8: The UV-vis spectra of p-NP. $[ZnO] = 400 \text{ mg L}^{-1}$, $[p\text{-NP}]_0 = 20 \text{ mg L}^{-1}$, $I_0 = 37 \text{ W m}^{-2}$, $\text{pH} = 9$.

The spectral changes of p-NP during photocatalytic removal

Fig. 8 shows the changes in absorption spectra under operational conditions of p-NP at different irradiation times. The decrease in the absorption peak of p-NP at wavelength of 400 nm reveals a significant removal of the starting material.

Fig. 9 also shows the HPLC chromatograms of p-NP at different time intervals and it is clear that main p-NP peaks are being disappeared when the irradiation time is increased while intermediates start to grow up to 10 min and then being to disintegrate.

CONCLUSIONS

The results presented in this paper indicate that UV/ZnO process could be efficiently used to degrade the p-NP. ZnO and UV light had a negligible effect when they were used independently. The results indicate that the degree of removal of p-NP was obviously affected by illumination time, concentration of p-NP and photocatalyst quantity and also optimal amount of photocatalyst was 400 mg L^{-1} , at p-NP concentration of 20 mg L^{-1} . The complete removal of p-NP, after selection of optimal operational parameters, could be achieved in about 1 h of radiation.

The results indicate that the apparent first order rate constant for photodegradation of p-NP in the presence of different concentration of ZnO could be deduced. The proper addition of hydrogen peroxide could improve the

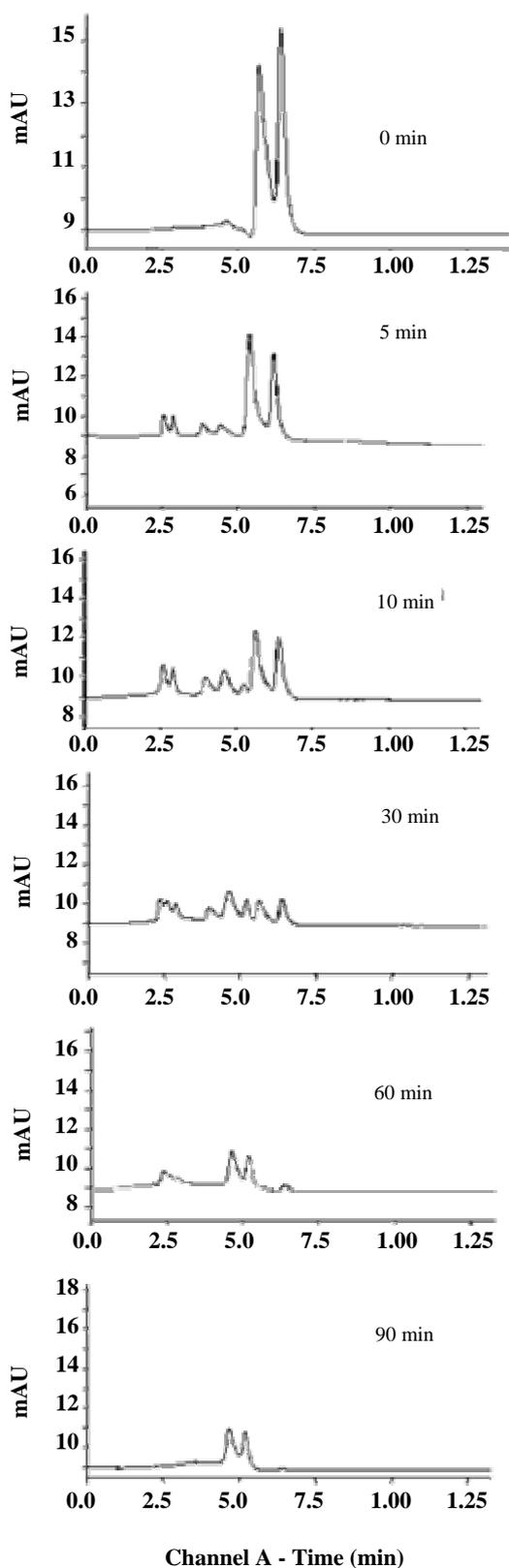


Fig. 9: The HPLC chromatograms of p-NP.

photocatalytic removal rate, but it was inhibited by salts. It was concluded that hydroxyl radicals were the main reactive species, but positive holes were probably also involved.

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