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Degradation of aqueous solution of 4-Chloro-2-Nitrophenol in nano-TiO₂/H₂O₂ system

ABSTRACT

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The present work is focused on the degradation of 4-chloro-2-nitrophenol in aqueous solution containing nano titanium dioxide, hydrogen peroxide and the combination of nano-TiO₂/H₂O₂. The effect of experimental parameters, such as the amount of nano- TiO₂ concentration of H₂O₂, initial concentration of 4-chloro-2-nitrophenol and pH on the reaction was investigated. Experimental data obtained under different conditions describe the dependency of degradation rate on the above mentioned parameters. The optimum conditions of the degradation treatment were: [H₂O₂]=100 mg/L; [nano- TiO₂]=0.004 g/250 mL; initial pH=10 and initial 4-chloro-2-nitrophenol concentration=15 mg/L. Consequently, kinetic parameters were experimentally determined and a pseudo-first-order kinetic was observed.

Keywords: 4-Chloro-2-Nitrophenol; Nano-TiO₂; H₂O₂; Kinetic; Degradation.

INTRODUCTION

Phenols are well known for their bio-recalcitrant and acute toxicity. Phenols are being continuously introduced into the aquatic environment through various industries effluents. The presence of toxic organic compounds in waste water effluent is still a major problem [1]. Further, their variety, toxicity and persistence can directly impact the health of ecosystem and present a threat to humans through contamination of drinking water supplies e.g surface and ground water. Consequently, considerable efforts have been devoted to developing a suitable purification method that can easily destroy these bio-recalcitrant organic contaminants. Despite their low concentration, these contaminants have raised substantial concern in the public due to their extremely high toxicity [2]. One of the most promising routes is to degradation of phenolic compounds using Advanced Oxidation Processes (AOPs). Advanced oxidation processes (AOPs) are technologies based on the intermediary of hydroxyl and other radicals to oxidize recalcitrant, toxic and non-biodegradable compounds.

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Among the emerging technologies in wastewater treatment processes, AOPs have emerged as potentially powerful methods that are capable of transforming the pollutants into harmless substances [3]. There are currently a wide range of AOPs being extensively researched and developed for the treatment of aqueous wastewaters such as ozonation, UV, Fenton processes, hydrogen peroxide and catalysts such as TiO₂ and combinations of them[4,5]. The environmental applications of AOPs are numerous, including water and wastewater treatment (i.e. removal of organic and inorganic pollutants), air pollution reduction and etc. They offer a high degree of process flexibility and the ability to degrade pollutants and concentration levels than the treatment processes like physical & biological treatment. These processes include a number of emergent methodologies viewing production of free hydroxyl radical, a highly reactive and nonselective oxidizing agent capable of destroying recalcitrant pollutants [6]. Heterogeneous catalytic oxidation process is one of AOPs methods. In the catalytic oxidation process, organic pollutants are destroyed in the presence of catalysts (e.g., TiO₂, ZnO) and an oxidizing agent such as oxygen or air. This process is largely dependent on the in-situ generation of hydroxyl radicals under ambient conditions which are capable of converting a wide range of toxic organic compounds into relatively less toxic compounds. Information from various investigations suggest that catalytic degradation of pesticides, phenols and dyes is largely dependent on the solution pH, types of catalyst and composition, organic substrate type and concentration, catalyst loading, ionic composition of waste water, oxidant concentration, and temperature[7,8]. In this work, the efficiency of H₂O₂ and nano TiO₂ for the degradation of the 4-chloro-2-nitrophenol is examined. The effect of variation in pH, H₂O₂ and nano TiO₂ concentration and 4C2NP concentration are carried out to optimize the oxidation rates in aqueous medium. Also, kinetic of reaction is studied, too.

EXPERIMENTAL

Materials

4-Chloro-2-nitrophenol was purchased from Fluka Company. All organic solvents were

HPLC grade from Merck. P-25 TiO₂ powder (80% anatase, average diameter 200 nm and surface area ~50 m²/g) was prepared from Degussa, Germany. H₂O₂ (30%, reagent grade) was from Merck company, too.

Methods

The experiments were conducted with an erlyn meyer filled with 250 mL of aqueous solutions of known concentration of 4C2NP with an initial concentration ranging between 5-30 mg/L. Nano TiO₂ concentration was varied from 0.001 to 0.005mg/250mL, the H₂O₂ concentration was ranged from 10 to 150 mg/L and pH from 3 to 10 adjusted by adding HCl and NaOH. The pH of Solution was 4.7. The samples are stirred on a magnetic stirrer for a period of 30 min. The samples were immediately analyzed for percentage of degradation. Suspensions were centrifuged and the 4C2NP concentrations were measured using a UV-Vis spectrophotometer (HACH-DR5000) at wavelength corresponding to maximum absorption (220 and 233 nm in acidic and basic solutions, respectively).

The removal percentage (%), was calculated from the following equation

$$\% \text{Removal} = \frac{C_0 - C_t}{C_0} \times 100$$

RESULTS AND DISCUSSION

Influences of four variables –H₂O₂ concentration, nano TiO₂ concentration, pH and 4C2NP concentration were studied. The effect of alone H₂O₂ and nano TiO₂ concentrations on degradation of 4C2NP was carried out, individually. The optimum concentrations of H₂O₂ and nano TiO₂ is obtained 50 mg/L and 0.004 g/250 mL, respectively (not shown here).

Therefore, all of the experiments were done by 50 mg/L of H₂O₂ and 0.004 g/250 mL of nano TiO₂.

Effect of H₂O₂ concentration in H₂O₂ /nano-TiO₂ system

The effect of initial H₂O₂ concentration on the degradation of 4C2NP in H₂O₂ /nano-TiO₂ system is illustrated in Figure 1. Hydrogen

peroxide doses are varied from 10 -150 mg/L. In the presence of H_2O_2 the 4C2NP degradation increased at low initial H_2O_2 concentrations and then decreased. However, increasing the initial hydrogen peroxide concentration decreased the 4C2NP oxidation. From the experiments it is concluded that the optimum H_2O_2 concentration is 100 mg/L at which maximum percentage removal of the 4C2NP is in maximum of 30 min reaction time. The higher the hydrogen peroxide concentration, the larger the amount of hydroxyl radicals produced, thus favoring 4C2NP oxidation [9]. Further addition of H_2O_2 did not improve the degradation rate due to self-decomposition of H_2O_2 [10]. Moreover, at higher concentrations, hydrogen peroxide acted as a free-radical scavenger itself and to form oxygen radicals [11], thereby decreasing the hydroxyl radical concentration and reducing compound removal efficiency.

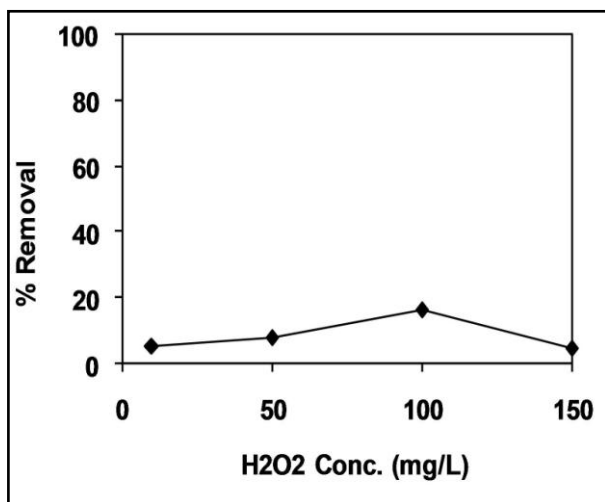


Fig. 1. Effect of H_2O_2 concentration on the degradation of 4C2NP.
[4C2NP] = 20 mg/L; [nano-TiO₂] = 0.004 g/250mL; pH = 4.7

Effect of nano- TiO₂ dosage

To study the effect of nano-TiO₂ concentration on heterogeneous AOPs (H_2O_2 /nano-TiO₂), the experiments were carried out by varying the nano- TiO₂ concentration from 0.001 g/250mL to 0.005 g/250mL with fixed reaction time i.e. maximum of 30 min. This experiment results shown in Figure 2 reveal that at 0.004 g/250mL of nano-TiO₂ concentration the maximum of 12.91% removal was achieved in H_2O_2 /nano-TiO₂ system. However, at higher nano/ TiO₂ dosage the

percentage removal is decreased due to the nano-TiO₂ tendency toward agglomeration, resulting in a reduction in degradation [12].

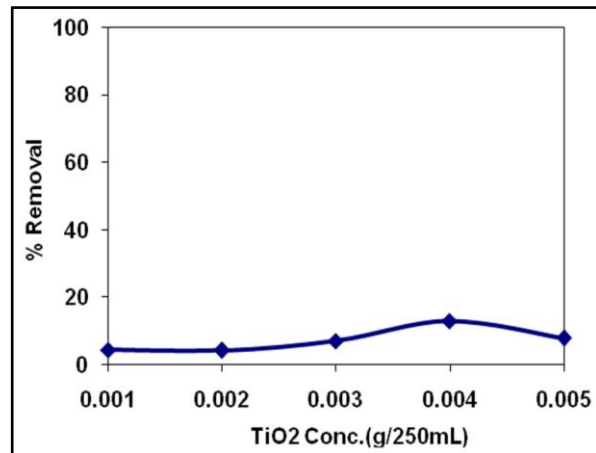


Fig. 2. Effect of nano- TiO₂ concentration on the degradation of 4C2NP.
[4C2NP] 20 mg/L; [H₂O₂] = 50 mg/L; pH = 4.7

Effect of pH

In order to study the effect of initial pH on 4C2NP degradation, a series of experiments are carried at pHs of 3, 7 and 10 and results are shown in Figure 3. As shown, the maximum degradation was achieved at pH 10 in heterogeneous H_2O_2 /nano-TiO₂ experiment. 4C2NP was efficiently removed at pH 10 due to the abundance of OH⁻ radicals in the particle surfaces as well as in the reaction medium [12].

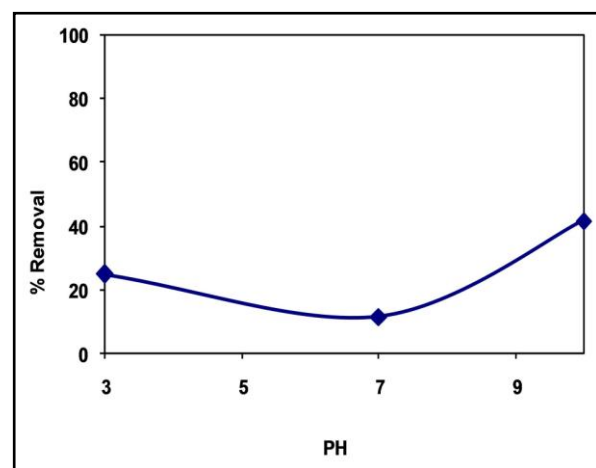


Fig. 3. Effect of pH on the degradation of 4C2NP.
[4C2NP] = 20 mg/L; [H₂O₂] = 50 mg/L; [Nano- TiO₂] = 0.004 g/250 mL

Effect of 4C2NP Concentration

It is important to study the dependence of the reaction rate on the substrate concentration.

Figure 4 shows the effect of 4C2NP initial concentration on removal of 4C2NP. As shown the degradation rate increases with increase in 4C2NP concentration to a certain level and a further increase in 4C2NP concentration leads to decrease the degradation rate of the 4C2NP. The initial 4C2NP concentration provides an important driving force to overcome all mass transfer resistance of 4C2NP between aqueous and solid phase [13]. The rate of degradation relates to the probability of •OH radicals formation on the nano-TiO₂ surface and to the probability of •OH radicals reacting with 4C2NP molecules. As the initial concentrations of the 4C2NP, increase the probability of reaction between 4C2NP molecules and oxidizing species also increases, leading to an enhancement in the degradation rate. On the contrary, the degradation efficiency of the 4C2NP decreases as the 4C2NP concentration increases further. The presumed reason is that at high 4C2NP concentrations the generation of •OH radicals on the surface of catalyst are reduced since the active sites are covered by 4C2NP[14].

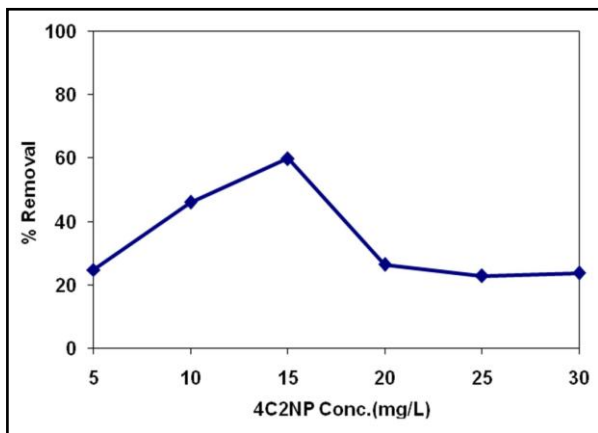


Fig. 4. Effect of 4C2NP concentration on the degradation of 4C2NP. [H₂O₂]= 50 mg/L; [Nano- TiO₂]=0.004 g/250 mL; pH= 4.7

Kinetic Study

The aqueous solutions of 4C2NP with known concentration are reacted in the presence of hydrogen peroxide and nanocrystalline TiO₂. The plots of the logarithm of 4C2NP concentrations and residence time were obtained to determine the

reaction order of 4C2NP compound as shown in Figure 5.

In the Table 1 the rate constant for 4C2NP degradation in H₂O₂/nano TiO₂ system is given.

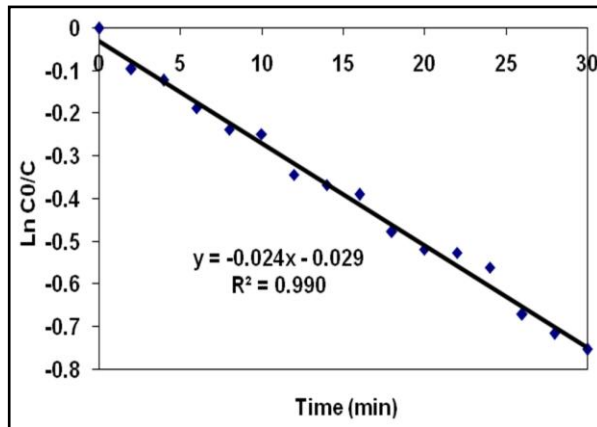


Fig. 5. Pseudo first order kinetic plot for degradation of 4C2NP

Table 1. Rate constant for 4C2NP degradation in H₂O₂/nanoTiO₂ system

k	R ²
0.024 min ⁻¹	0.990

CONCLUSIONS

The degradation of 4C2NP was investigated with heterogeneous (H₂O₂/nano-TiO₂)AOPs. The influence of pH, dosage of nano TiO₂, H₂O₂ concentration and 4C2NP concentration on the rate of degradation of 4C2NP was studied. The experimental results reveal that:

- (1) The optimum H₂O₂ concentration is 100 mg/L at which maximum removal of the 4C2NP is achieved in maximum of 30 min reaction time.
- (2) The maximum removal achieved with 0.004 g/mL of TiO₂ dosage in heterogeneous processes
- (3) The maximum degradation was achieved at pH 10 in H₂O₂/nano- TiO₂ system.
- (4) The degradation kinetic of aqueous solutions of 4C2NP in H₂O₂/nano- TiO₂ system followed pseudo-first-order model.

REFERENCES

- [1] Mahmoodi, N. M., Armani, M., Lymaee, N.Y., & Gharanjig, K. (2007). Photocatalytic degradation of agricultural N-heterocyclic organic pollutants using immobilized nanoparticles of titania. *J. Hazard. Mater.*, 145, 65-71.
- [2] Arques, A., Amat, A.M., Garcíya-Ripoll, A., & Vicente, R. (2007). Detoxification and/or increase of the biodegradability of aqueous solutions of dimethoate by means of solar photocatalysis. *J. Hazard. Mater.*, 146, 447-452.
- [3] Legrini, O., Oliveros, E., & Braun, A. M. (1993). Photochemical processes for water treatment. *Chem. Rev.*, 93, 671-698.
- [4] Majcen-Le Marechal, A., Slokar Y. M., & Taufer, T. (1997). Decolourisation of chlorotriazine reactive azo dyes with H₂O₂/UV. *Dyes Pigments*, 33, 281-298.
- [5] Arslan, I., & Balcioglu. I. A. (1999). Degradation of commercial reactive dyestuffs by heterogeneous and homogenous advanced oxidation processes: A comparative study. *Dyes Pigments*, 43, 95-108.
- [6] Alaton, I. A., & Balcioglu, I. A. (2001). Photochemical and heterogeneous photocatalytic degradation of waste vinylsulphone dyes: a case study with hydrolyzed Reactive Black 5. *J. Photoch. Photobio. A*, 141, 247-254.
- [7] Shakthivel, S., Janczarek, M. & Kisch, H. (2004). Visible light activity and photoelectrochemical properties of Nitrogen-doped TiO₂. *J. Phys. Chem. B*, 108, 19384-19387.
- [8] Byrappa, K., Subramania, A. K., Ananda, S., Rai, K. M. L., Dinesh, r., & Yushimura, M. (2006). Photocatalytic degradation of Rodamine B dye using hydrothermally synthesized ZnO. *Bulletin Mater. Sci.*, 29, 433-438.
- [9] Neamtu, M., Siminiceanu, I., Yediler, A., & Kettrup, A. (2002). Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H₂O₂ oxidation, *Dyes Pigments*, 53,93-99.
- [10] Kumar, B. N., Anjaneyulu, Y., & Himabindu, V. (2011). Comparative studies of degradation of dye intermediate (H-acid) using TiO₂/UV/H₂O₂ and Photo-Fenton process. *J. Chem. Pharm. Res.*, 3, 718-731
- [11] Aleboyeh, A., Aleboyeh, H., & Moussa. Y. (2003). Critical effect of hydrogen peroxide in photochemical oxidative decolorization of dyes: Acid Orange 8, Acid Blue 74 and Methyl Orange. *Dyes Pigments*, 57, 67-75.
- [12] Ahmed, S., Rasul, M. G., Martens, W. N., Brown, R., & Hashib, M. A. (2011). Advances in heterogeneous photocatalytic degradation of phenols and dyes in wastewater : a review. *Water, Air, & Soil Poll.*, 215, 3-29.
- [13] Shahryari, Z., Goharrizi, A. S., & Azadi, M. (2010). Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes. *Inter. J. Water Resour. Environ. Engin.*, 2, 16-28.
- [14] Konstantinou, I. K., & Albanis, T. A. (2004). TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. *Appl. Catal. B- Environ.*, 49, 1-14.

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