



ORIGINAL ARTICLE

Advanced Oxidation Process for Phenol Degradation By UV/TiO₂ In Aqueous Solutions

¹Suraiya Jabeen*, ¹Ramzan Ali, ¹Omme Hany, ¹Mudassir Amir, ¹Muhammad Anas Khan

¹Institute of Environmental Studies, University of Karachi, Karachi, Pakistan

*Corresponding author: sujabeen@uok.edu.pk

ABSTRACT

Phenolic compounds are widely used in industries and other daily life for various purposes and enter in the industrial effluent and ultimately the final disposal of this effluent which contain phenol compounds are different water bodies which may get contaminated through the continuous disposal of the these effluents. Highly toxicity and carcinogenicity of these compounds can cause considerable effects on the aquatic ecosystem and human health. The main focus of this research is to study the efficiency of photocatalytic degradation of phenolic compounds in aquatic solution by using UV and combination of UV/TiO₂; this is one of the Advanced Oxidation Processes (AOPs), which are techniques for the degradation of detrimental organic pollutants resistant to traditional treatment methods. In this experimental research the phenol concentration used was 30mg/L (constant) and contact time, pH and amount of TiO₂ were considered in photocatalytic system as the basic variables affecting the removal efficiencies. Phenol concentrations before and after the treatment were determined spectrophotometrically at 500 nm. The removal efficiencies of phenol by only UV exposure is negligible, combination of UV and TiO₂ can cause higher efficiencies of phenol removal. By UV exposure only 7, 6 & 4 % of phenol was degraded although the UV/TiO₂ degrades 17, 13 & 30 % of phenol in 2 hours at pH 3, 7 & 11 respectively. It was found that increasing the value of variables in the experiment can maximally remove the phenol therefore combined UV/TiO₂ process may be applied as an effective process for the removal of phenol from aquatic clarification such as industrial wastewaters and polluted water resources.

Keywords: Advanced Oxidation Process, TiO₂, UV ray, Photocatalysis

Received 12.08.2014

Revised 18.09.2014

Accepted 26.10.2014

INTRODUCTION

Environmental regulations and their applications have become stricter because of increased cognizance of the human health and ecological menace fraternized with environmental pollutants. Increasing living standards steered to setting up of different treatment plants which endowed surprisingly to the wastewater quantities. In recent years various treatment processes are revealed on waste minimization and water conservation. Photo catalytic degradation as part of the chemical treatment oxidizes harmful environment pollutants and converts it into innocuous substances [1,2]. Phenolic compounds are extensively used in industrial and domestic life, therefore they are common contaminants in aquatic bodies, and some of the compounds are highly toxic, persistent and have adverse effect on aquatic ecosystem and human health, most organic compounds are resistant to conventional chemical and biological treatments. For this reason, other methods are being studied as an alternative to biological and classical physico-chemical processes. Therefore use of a proficient and remunerative method for the elimination of phenol in water solutions has been a crucial need [3,4].

AOPs depend on in situ production of extremely reactive radical specie such as OH that breakdown a number of organic compounds without being selective [5,6,7] using chemical or light energy. The method employing a semiconductor activated by UV or visible light to degrade aquatic or atmospheric contaminants is termed photocatalysis which results in partial or complete mineralization of the organic compounds into CO₂, water and mineral acids [8, 9, 10, and 11]. However each method has some restrictions and disadvantages [3, 4]. The application of photo catalysis in the treatment of phenol in wastewater is a provocative alternative and is the widget of a great interest over the last years by myriad researchers. [12]. This particular research envisages towards a substitution technique where the

contaminants are degraded by irradiation suspension of metal oxide semiconductor particles such as TiO₂ or ZnO. TiO₂ is selected for photodegradation recognized as an excellent photo catalyst for complete mineralization of phenol in water and wastewater. It is nontoxic, insoluble in water and consonantly low cost. Titanium dioxide (TiO₂), a metal oxide semiconductor has been found to be one of the most effective photo catalysts due to its high efficiency and stability. TiO₂ (anatase) has a band gap of 3.2 eV that allows UV light to excite the valance electrons and inject these into the conduction band leaving holes in the valance band [13] it triggers by near UV light with wavelengths up to 388 nm in form of photons. It excites the electrons on the surface of titanium atoms suspended in the contaminated water, moving them from the valance band to the conductance band. This absorption corresponds to between 3 to 4 percent of the solar spectrum. The result of this energy change is the formation of holes in the surface of titanium atom, and free electrons, which are now available to form hydroxide (OH) or other radicals, which can oxidize organic chemicals. In entire cases, the degradation process primarily involved the formation of hydroxyl radicals [14, 15], though this is a small fraction of the spectrum, many studies have been carried out to develop an efficient method for using natural solar radiation to destroy toxic organic compounds. The main objective of this research was to study of photo catalytic oxidation of phenol in the presence of UV ray, UV/TiO₂

METHOD

Instruments for analysis:

1. UV/VIS Spectrophotometer model (SHIMADZU 1240) for phenol measurement, 2. Shaking water bath model OLS 200 (Grant) for shaking sampling, 3. Ultraviolet tube light fixed in a wood chamber, 4. pH meter model WTW 330i, 5. Digital balance model Libror AEG-120 (SHIMADZU).

Chemicals:

All chemicals including Phenol, potassiumferricyanide, ammonium chloride, ammonium hydroxide, 4-amino antipyrine, sodium hydroxide, hydrochloric acid, titanium dioxide were obtained from Merck Chemical Company.

Reactor description:

The treatment system consisted of a UV-tube light of 42cm fixed inside the top lid of a wood chamber of 17×10×9 inches and this UV-chamber is attached with a shaking water bath of the same size of chamber. The samples are taken inside the shaking water bath Grant Model Type SS30 for continuously shaking and in the meantime the UV-tube light turned on to provide the irradiation to the shaking samples. The samples are shaken at the room temperature 30°C and 130 rpm in shaking water bath.

Experimental methodology:

Phenol solution was prepared in 30mg/L concentrations. The concentration of phenol was measured at 500nm by a spectrophotometer. TiO₂ was used anatase, pH adjustment in the samples was done by using 1N HCl and 1N NaOH. A UV-tube light of 42cm in length which was fixed 20cm above the samples surface in the reactor and the light intensity was 306 lux measured by lux meter model LX-101 (LUTRON).

Experimental setup and measurements:

In this research, the photochemical cell consisted of five 250 ml beakers in the shaking part of the reactor to shake the sample in the presence of UV irradiation, the shaking speed of the samples were adjusted at 130 rpm and the temperature of reactor was controlled at 30°C. In the first phase, the beakers were filled with 200 ml of phenol solution (30mg/L) and in separate stages were contacted with UV and combination of UV/TiO₂. Also the effects of various parameters including contact time (1 to 5 hrs. for UV, 1 to 2 hrs. for UV/TiO₂), pH (7 for only UV treatment and 3, 7 and 11 for UV/TiO₂) and amount of TiO₂ (0.5 and 1.0 gr/L) in the removal efficiency of phenol were investigated. The treatment experiment of UV/TiO₂ has done in three runs. In the first run the six 250 ml beakers containing 200 ml of phenol solution (30 mg/L) were treated in the reactor, pH of the samples were adjusted at 11, and the detention time of three beakers were 1hr in which one is a blank and two beakers containing TiO₂ of 0.1 gr (0.5 gr/L) and 0.2 gr (1 gr/L), similarly the detention time for other three beakers was 2hours which contain the same concentration of TiO₂ in the two beakers and a blank one. In the second run all the measurements are same but the pH of the samples were controlled at pH 7 and the same case in the third run but the pH of the samples in the this run is quite acidic i.e. 3. The acidic and basic pH of the samples were maintained by using 1N HCl and 1N NaOH.

The samples were withdrawn from the beakers with the pipette (10 ml) before and after the photochemical reaction and the residual phenol was measured. Before phenol measurement, the samples containing TiO₂ were centrifuged at 5000 rpm for 10 min, and then the upper liquid layers were sucked. Then concentrations of phenol in the prepared samples were measured by [16]. All experiments were conducted at lab temperature 30°C.

RESULTS

The results obtained from (Phase 1) the experiment in which phenol solutions were only treated with the UV-irradiation without any catalyst, the pH of the sample was neutral. It has been seen that only a very small or negligible amount of phenol was degraded. The detention time for this experiment was from 1 to 5 hours for five beakers. The % of phenol which was degraded is shown in figure 1.

The results obtained from (Phase 2) the experiment in which phenol solutions were treated with catalyst TiO₂ in the presence of UV-irradiation at three different pH are interesting. It is found that the efficiency of the concentration of phenol in terms of % is affected by TiO₂ concentration, pH of the solutions and the exposure time to UV-irradiation. The results show that degradation yields in 2 hours period with pH 3, 7 and 11 has been 17%, 13% and 30%, respectively.

TABLE: 1 (% DEGRADATION OF PHENOL AT pH= 3 WITHIN A GIVEN TIME)

pH 3			
Time (hour)	OD_{500nm}		% of Phenol Degraded
1	UV	1.94	7
	TiO₂(0.1gr)	1.85	11
	TiO₂(0.2gr)	1.79	14
2	UV	1.91	8
	TiO₂(0.1gr)	1.82	13
	TiO₂(0.2gr)	1.76	17

TABLE: 2 (% DEGRADATION OF PHENOL AT pH= 7 WITHIN A GIVEN TIME)

pH 7			
Time (hour)	OD_{500nm}		% of Phenol Degraded
1	UV	1.96	6
	TiO₂(0.1gr)	1.88	9
	TiO₂(0.2gr)	1.80	13
2	UV	1.93	7
	TiO₂(0.1gr)	1.84	11
	TiO₂(0.2gr)	1.87	14

TABLE: 3 (% DEGRADATION OF PHENOL AT pH= 11 WITHIN A GIVEN TIME)

pH 11			
Time (hour)	OD_{500nm}		% of Phenol Degraded
1	UV	1.98	4
	TiO₂(0.1gr)	1.80	13
	TiO₂(0.2gr)	1.71	17
2	UV	1.91	8
	TiO₂(0.1gr)	1.63	21
	TiO₂(0.2gr)	1.49	28

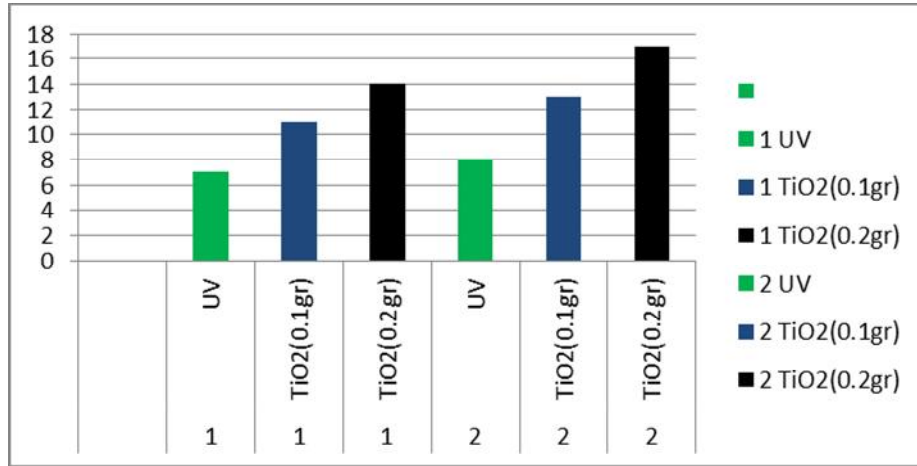


Figure 1: Removal Efficiency of Phenol at pH 3

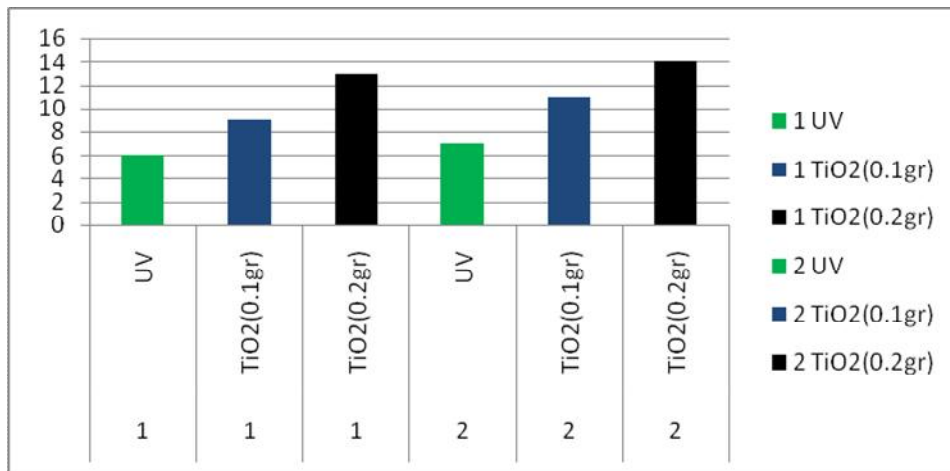


Figure 2: Removal Efficiency of Phenol at pH 7

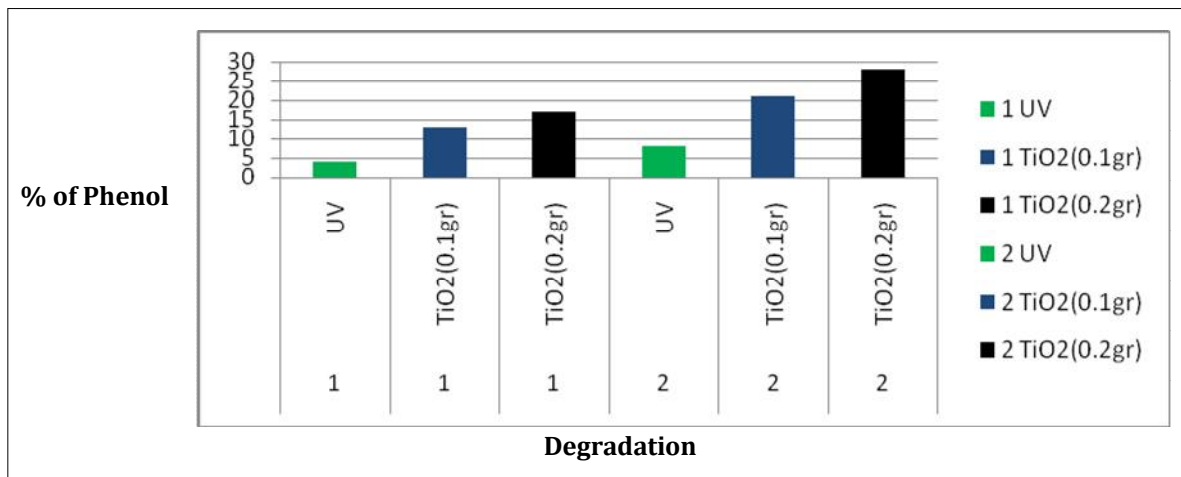


Figure 3: Removal Efficiency of Phenol at pH 11

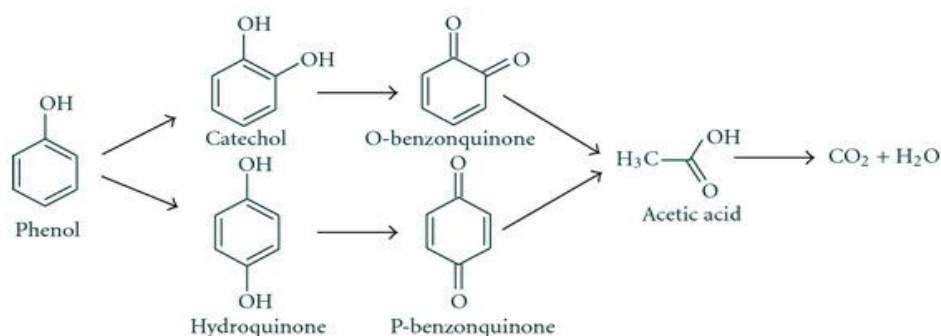


Fig.4 Proposed photocatalytic degradation pathway of Phenol under UV irradiation (Tao *et al*, 2013).

DISCUSSION

One of the leading sources for the water crisis is water contamination. On average, two million tons of human excrement as well as toxic industrial wastes are carelessly discarded daily and thus contaminating terrestrial and aquatic bodies [17, 18]. Industrial effluents including phenols, chlorophenols, oils and organic dyes, disposed off from the fabric, paint, tannery and food industries, constitute one of the major sources of water pollution (19).

The photocatalytic degradation of toxic organic compounds has been recommended as a practicable method to decontaminate aquatic solutions. Irradiating semi-conductors like TiO₂ in suspension or fixed to various supports in aqueous solutions containing organic contaminants, and able to abolish these pollutants. Photocatalytic mineralization of organic water pollutants has a strong potential in the industrial compounds in water as this has been widely validated in recent years, and the applications and target compounds are abundant.

Phenolic compounds are considered one of the most common pollutants of water resources. Photocatalytic oxidation of phenol by using TiO₂ as a catalyst and UV ray is one of the developing methods. In this study, photocatalytic removal of phenol was investigated by stressing on contact time, pH and initial phenol concentrations. The results from examinations in pH 3, 7 and 11 as the function of exposure time in the experimental processes are shown that phenol degradation efficacy is affected by TiO₂ concentration, UV irradiation and pH of the solution. By escalating the contact time, efficiency of phenol degradation is enhanced. The most observed vintage is related to pH 11 and pH 7. The UV ray alone has less ability to degrade phenol. Oxidant concentration in these processes influences the rate of photocatalytic oxidation, with increase in concentration, the percentage degradation increased, it bizarrely encourages elimination efficiency. Phenol was more effectively eliminated by using combined UV/TiO₂ condition than using UV alone. With the synergistic effect of UV and TiO₂, pH has a focal effect. As a result, increasing pH leads to decreasing the process time. The process efficiency in pH 11, during 1 hour was 17%, it was then 28% in next hour and by increasing contact time the yield would be little increased this is because of reason that the reaction rate is related to phenol concentration. Thus, when phenol present as solute in water bodies with alkaline pH, it was converted to phenoxide ion that more degradable than phenol, solubility helps in dilution and ultimately in degradation. On the other hand, in acidic pH, phenol has a little degradability. TiO₂ used in this study, as an advanced oxidative, is a recoverable photocatalyst, UV/TiO₂ process for phenol degradation is benign to the environment. Most organic compounds are resistant to traditional chemical and biological treatments.

CONCLUSION

Photocatalysis part of green technology with prospective applications in various disciplines, such as environmental technologies, in this research, photocatalytic degradation of phenol in aqueous solution was studied using TiO₂ photocatalyst in a UV irradiated reactor, it was seen that degradation was influenced by pH values and contact time. Photodegradation can be an alternative treatment method for those contaminants resistant to conventional methods. Photodegradation can be used for complete mineralization of phenol. Since TiO₂ that was used in this study, is a recoverable photocatalyst, UV/TiO₂ process for phenol degradation is compatible with the environmental. For this reason, other methods are being studied as an alternative to biological and classical physico-chemical processes. Therefore use of an effective and economic method of photocatalysis for the elimination of phenol in water solutions would be an urgent demand.

REFERENCES

1. D. Abhilasha., M. A.K., Chakraborty.M., (2010). Photochemical Oxidation of Phenol and Chlorophenol by UV/H₂O₂/TiO₂ Process : A Kinetic Study. *International Journal of Chemical Engineering Applications*,(1) No.3, 247-250
2. H. Choi, S.R.Al-Abed, D.D.Dionysiou, E. Stathatos and P. Lianos,(2010).“TiO₂ Based Advanced Oxidation Nanotechnologies for Water Purification and Reuse”, *Sustainability Science and Engineering*, 2010 (1.2) pp.229-254.
3. Rehmani.A.R., Samdani M.T., Enayati Moafagh A.,(2008). Investigation of Photocatalytic Degradation of Phenol by UV/TiO₂ Process in Aquatic Solutions. *J Res Health Sci*, (8) 55-60.
4. Wang KH, Hsieh YH, Chou MY, Chang CY. (1999). Photo catalytic degradation of 2- chloro and 2 nitrophenol by titanium dioxide suspensions in aqueous solution. *Applied Catalysis B: Environmental* ., (21) 1-8.
5. T. Kudo, Y. Nakamura, and A. Ruike, (2003). “The design of highly active rectangular column-structured titanium oxide photocatalysts and their application in purification systems,” *Journal of Catalysis Today*, (122) pp. 14–19.
6. G. Zayani, L. Bousselmi, F. Mhenni, and A. Ghrabi,(2009). “Solar photocatalytic degradation of commercial textile azo dyes: performance of pilot plant scale thin film fixed-bed reactor,”*Journal of Desalination*, (246), no. 1–3, pp. 344–352.
7. U. I. Gaya and A. H. Abdullah, (2008). “Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide,”*Journal of Photochemistry and Photobiology C*, (9) no. 1, pp.1–12.
8. C.S.Turchi and D.E.Ollis, (1999). Photocatalytic degradation of organic water contaminants: mechanism involving hydroxyl radical attack, *Journal of Catalysis*, (122) no.1, pp. 178-192
9. Y. Tao, Z.L.Cheng, K.E.Ting, and X.J.Yin, Photocatalytic Degradation of Phenol Using a Nanocatalyst: The Mechanism and Kinetics, *Journal of Catalysts*, 2013, 1-6.
10. C. Guillard, J. Disdier, J.-M. Herrmann, (1999). “Comparison of various titania samples of industrial origin in the solar photocatalytic detoxification of water containing 4-chlorophenol,”*Journal of Catalysis Today*,(54) no. 2-3, pp. 217–228.
11. W. A. Zeltner and D. T. Tompkin, Ashrae (2005). *Transactions vol.III, vol. 2*, American Society of Heating and Air-Conditioning Engineers, Atlanta, Ga, USA.
12. Akbal F, Nur Onar A. (2003). Photocatalytic degradation of phenol.,*Environ MonitAssess.*; 83(3): 295-302.
13. C. Kormann, D. W. Bahnemann, and M. R. Hoffmann,(1988). “Preparation and characterization of quantum-size titanium dioxide,” *Journal of Physical Chemistry*, (92) no. 18, pp. 5196–5201.
14. Yu, J.C.; Yu, J.; Ho, W.; Jiang, Z.; Zhang, L., (2002). Effects of F-doping on the photocatalytic activity and microstructures of nanocrystalline TiO₂ powders. *J. Chem. Mater.* (14) 3808-3816.
15. Anpo, M.; Takeuchi, M., The design and development of highly reactive titanium oxide photocatalysts operating under visible light irradiation., *J. Catal.*,2003,(216) 505-516.
16. Yang R.D., Humphery A.E. (1975). Dynamic and steady state studies of phenol Biodegradation in pure and mixed cultures. *Biotechnol.Bioeng.* (17),1211-1235.
17. Weber, E. J.; Adams, R. L., Chemical- and Sediment-Mediated Reduction of the Azo Dye Disperse Blue 79,*Envir. Sci. Tech.*1995 (29) 1163-1165.
18. Jung, K. Y.; Park, S. B., 2001, Effect of calcination temperature and addition of silica, zirconia, alumina on the photocatalytic activity of titania, *Chem. Eng. J.* 2001,(18) 879-888.
19. Ollis, D. F., Contaminant degradation in water ,*Envir. Sci. Tech.*,1985 (19) 480-48

CITATION OF THIS ARTICLE

Suraiya J, Ramzan A, Omme H, Mudassir A, Muhammad A K .Advanced Oxidation Process for Phenol Degradation By UV/TiO₂ In Aqueous Solutions. *Bull. Env. Pharmacol. Life Sci.*, Vol 3 [12] November 2014: 143-148