IOP Conf. Series: Earth and Environmental Science **78** (2017) 012007 doi:10.1088/1755-1315/78/1/012007

Study on Photocatalytic Degradation of Endocrine Disrupting Compound

Bhagwan Pralhad Parihar, Smita Gupta, Mousumi Chakraborty*

Department of Chemical Engineering, Sardar Vallabhbhai National Institute of Technology Surat – 395 007, Gujarat, India
Email: mch@ched.svnit.ac.in, mousumi_chakra@yahoo.com

Abstract. Propylparaben (PP) is catagorized as endocrine disrupting compounds and is found to be present in urban wastewater comparatively at high concentrations. In the present work, propylparaben was degraded photo-catalytically by optimizing different process parameters such as initial concentration of propylparaben (25mgL^{-1} to 100 mgL^{-1}), pH of the feed phase and concentration of photocatalyst TiO_2 (50 mgL^{-1} to 200 mgL^{-1}). Finally PP degraded and converted to CO_2 and H_2O and the degradation was found to follow the first order kinetics.

1. Introduction

The most common techniques are to treat wastewater containing organic dyes, pigments and pharmaceutical compounds are classifiable into three main categories i.e. physical (adsorption, filtration, and flotation), chemical (coagulation, oxidation, reduction, electrolysis) and biological (aerobic, anaerobic degradation). However, due to the complexity and variety of organic compounds, it has become rather difficult to find a unique treatment procedure that covers the actual elimination of all toxic organic compounds. Particularly, biochemical oxidation suffers from significant limitations since most organic compounds found in the commercial market have been intentionally designed to struggle aerobic microbial degradation. Physical processes also have some limitation therefore the chemical process should be treated by alternative advanced processes. Photocatalytic degradation process is also one of the important advanced oxidation methods. This results in complete mineralization of wide range of the recalcitrant or hazardous organic compounds. Recently, it is found that parabens are frequently released in urban wastewater comparatively at high concentrations and, even with considerably removal of them using conventional treatment methods; they have been still identified in river water samples [1]. Hence, the U.S. Environmental Protection Agency has considered these compounds as emerging environmental pollutants [2]. From literature it is found that numerous articles are available on photocatalytic degradation of different endocrine disrupting compounds (Table 1) but very few have studied the photocatalytic degradation of PP using UV/TiO_2 system and that too at lower pollutant concentration.

So in this study, photocatalytic degradation of PP have been examined by varying the process parameters such as initial concentration of propylparaben (25 mgL^{-1} to 100 mgL^{-1}), pH of the feed phase and concentration of photocatalyst TiO_2 (50 mgL^{-1} to 200 mgL^{-1}) and kinetic study is also performed.

Table 1. Literature review on photocatalytic degradation of endocrine disrupting compounds

Author	pollutant	Oxidation condition	Remark

Alaton and Balcioglu (2001)	Reactive Black 5	H_2O_2=10Mm, H_2O_2/UV-A; pH=4;	COD 62%; TOC 75% in 2h[3]
Watanabe et al.(2002)	Bisphenol A	pH=3 ; TiO_2	90% degradation of BPA[4].
Katsumata et al.(2003)	Bisphenol A	pH=4; Fe(II)=$4*10^{-5}$ mol/L; H_2O_2 $4*10^{-4}$ mol/L	90% degradation in 36 h[5].
Li et al. (2007)	Bisphenol A	pH 3-4;Oxalate ; iron oxide	84% removal in 40 min[6].
Yamazaki et al.(2008)	4 tert-octyl phenol	$K_2S_2O_8$=$2*10^{-2}$mol dm^{-3}; TiO_2 peroxy disulphate	83.2% degradation in 6 h[7].
Bledzka et al.(2010)	n-butyl paraben &4 tert-octyl phenol	pH=7; H_2O_2=0.01M; H_2O_2/UV	90% degradation [8]
Yanlin et al.(2012)	4 tert-octyl phenol	pH=4.5; TiO_2 precursor sol 13.6% ; TiO2	90% degradation in 30 min[9].
Huange et al.(2012)	Bisphenol A	Neutral pH; Fe(III)- ethylene diamine N,N'-di succinic acid (EDDS) =0.1mM with 1mM of H_2O_2;	Complete degradation in oxygen saturated solution[10].
Yanlin et al.(2013)	4 tertoctyl phenol	pH=3.5; Fe(III)=$3*10^{-4}$ mol/L	80%degradation in 60 min[11].
Osarumwense et al. (2015)	Phenol in aqueous solution	Periwinkle shell ash (PSA) as photocatalyst.	90% degradation[12]
Hurtado et al. (2016)	phenol and 4-chlorophenol (4-CP)	coupled electro-oxidation/ozonation > electro-Fenton-like process > photo-Fenton process > heterogeneous photocatalysis	Comparison of different treatment processes[13]

2. Experimental Procedure

2.1. Materials and Method

Propylparaben (LOBA Chemie), silver nitrate (Sigma Aldrich) and TiO_2 (Finar) were purchased and used without further purification. All other chemicals HCl, NaOH, H_2O_2 used were of analytical grade. All the solutions were prepared in demineralized water. Calibration curve was plotted using 2 to 10 mg/L propylparaben (at 256 nm wavelength) solution on the UV-Vis spectrophotometer (HACH, Germany) to determine the rate of the degradation

2.2. Experimental Procedure

All experiments were performed in a batch reactor. The reactor was cylindrical with 150 ml volume and made of quartz glass for the transfer of the radiation. Irradiation was achieved by using UV lamp of 125 W (medium pressure lamp) which was immersed in the glass tube surrounded by cooling water jacket to maintain reactor temperature. The reaction chamber, between the reactor walls and UV lamp, was filled with the reaction mixture. Mixing was accomplished using air bubbler to keep the photocatalyst in suspension.

2.3. Mechanism of Photocatalytic Reaction

TiO_2 is used as photocatalyst to make the degradation process faster as TiO_2 is a semiconductor and act as an oxidizing agent. There are many oxidizing agents like hydrogen peroxide, magnesium peroxide, fluorine, potassium bromide etc. but in most of the research work, TiO_2 was used as photocatalyst because it produces of $OH^•$ at a faster rate than other photocatalysts. When photo catalyst TiO_2 captures UV radiation from sunlight or illuminated light source (fluorescent lamps), the electron of the valance band of TiO_2 becomes excited. The excess energy of this excited electron of TiO_2 promotes the electron from valence band to the conduction band. So negative electron and positive hole are formed. The energy difference between valence band and conduction band is known as band gap energy. The positive hole of TiO_2 breaks apart the hydrogen molecule to form hydrogen gas and hydroxyl radical. The negative electron reacts with oxygen molecule to form super oxide anion. This cycle continues until sunlight or illuminated light source is available [14].
Photocatalytic reaction with TiO_2 photocatalyst occurs as follows [15]
On the TiO_2 oxidizing agent absorption of photon energy in the form of UV light occurs and then electron-hole pair formation takes placed.

$$TiO_2 + hv \rightarrow TiO_2^- + OH^• \text{ (Or } TiO_2^+)$$

Produce extremely reactive but short lived hydroxyl radical ($OH^•$) by hole trapping.

$$H^+ + H_2O \rightarrow OH^• + H^+$$

Surface reaction i.e. oxidation reaction of the pollutant molecules under UV light to produce carbon dioxide and water.

$$OH^• + O_2 + C_xO_yH_{(2x-2y+2)} \rightarrow xCO_2 + (x\text{-}y\text{+}1)\ H_2O$$

Radical recombination (energized holes and electrons can recombine)

$$TiO_2^- + OH^• + H^+ \rightarrow TiO_2 + H_2O \text{ (recombination)}$$

3. Results and Discussions

3.1. Effect of pH on Feed Phase

The photocatalytic degradation of PP was carried out at different pH at 4, 6, 8 and 10. Maximum degradation was observed at pH 8. It was observed that the slight basic pH of feed phase was favourable for degradation of propylparaben while the acidic pH was not favourable. Figure 1, shows degradation rate decreased at acidic pH because, in acidic phase, the formation of $OH^•$ radicals may be too fast. It is noticed that the optimum results was found out at pH 8. Thus, all the remaining experiments were conducted at pH 8 and further evaluation were considered on same basis.

3.2. Effect of TiO_2 loading

The photocatalytic degradation of PP was carried out at different concentration of TiO_2 (50-200 mg/L). Concentration of PP was kept 100 mg/L in the feed solution (Figure 2). Maximum degradation (58.39%) was observed at 50 mg/L of TiO_2. It might be due to UV light falls on the solution resulting into generation of sufficient number photons and electrons by UV light during the degradation reaction but thereafter with further increase in catalyst loading the degradation rate starts declining due to the screening effect of suspended TiO_2 present in the feed solution.

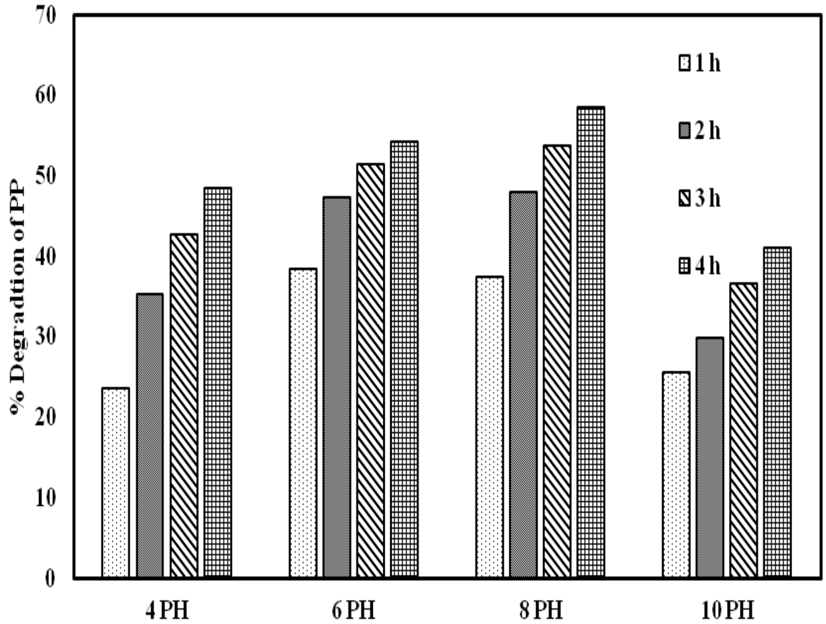

Figure 1. Effect of feed phase pH

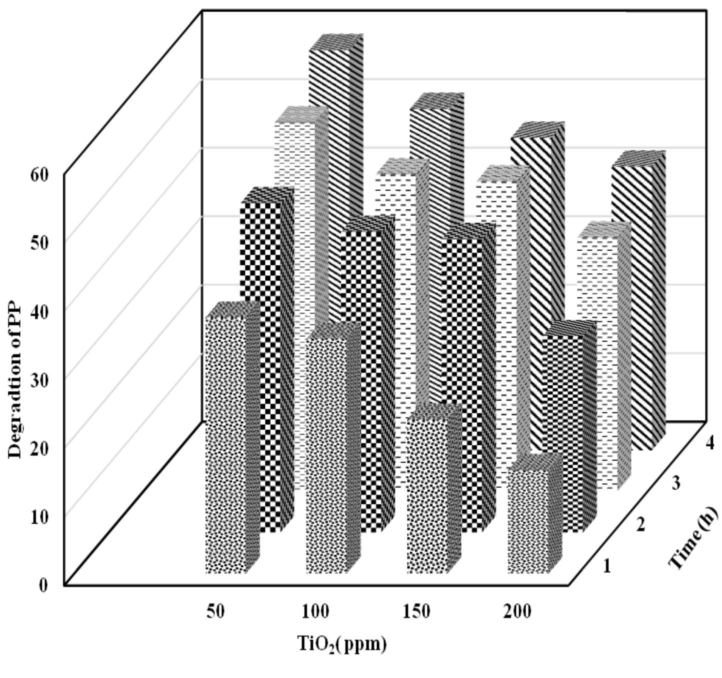

Figure 2. Effect of TiO_2 concentration

3.3. Effect of initial concentration of PP in feed phase

The degradation of PP was studied at 25, 50, 75 and 100 mg/L. It is found that as concentration of propylparaben solution increases, the rate of degradation decreases and 25 ppm of PP solution showed maximum 85.2 % degradation in 4h whereas degradation of 100 ppm solution was only 58.39%. Actually there was not enough dosage of TiO_2 to provide active radicals for the degradation of PP at higher initial concentration which also led to formation of more by- products, which might absorb some photons or consumed additional active radicals and decreased degradation rate.

3.4. Kinetic Study

Degradation kinetics was studied using 50 ppm TiO_2 concentration and 25 ppm PP solution as feed.

$$\ln (C/C_0) = - kt$$

Plot of ln (C/C_0) vs. time was plotted (not shown). It was observed that degradation followed first order kinetics and average rate constant value was found to be $k = 3.31 \times 10^{-4}\ s^{-1}$.

3.5. Energy Consumption

Major cost of degradation process is the electrical and chemical cost. For photocatalytic degradation energy consumption was calculated by this equation

$$\text{Daily consumption (kWh)} = \text{Wattage x hours used per day}/1000$$

The evaluation of energy consumption was calculated for 100% degradation. Time taken for 100% degradation was substituted in the above equation to calculate daily consumption of the power, which was found to be 2-3 kWh, quite cheaper than other advanced treatment technique

4. Conclusion

This study showed that photocatalytic degradation process was strongly pH dependent. Process efficiency of photocatalytic degradation also depends on feed concentration, dosing amount of the TiO_2 photocatalyst. Using 50 ppm TiO_2 photocatalyst, 25 ppm of PP showed maximum 85.2 % degradation in 4h whereas degradation of 100 ppm solution was only 58.39%. Comparing energy consumption with other advanced treatment technique, it was observed that photocatalytic degradation is more economical than other processes.

5. References

[1] I. Gonzalez-Marino, J. Quintana, I. Rodrıguez, R. Cela, Evaluation of the occurrence and biodegradation of parabens and halogenated by-products in wastewater by accurate-mass liquid chromatography-quadrupole-time-of-flight-mass-spectrometry, Water Res, 45 (2011) 6770-6780.

[2] Y. Lin, C. Ferronato, N. Deng, J. Chovelon, A. Catal., Study of benzylparaben photocatalytic degradation by TiO_2, Appl Catal Environ,104 (2011)353-360.

[3] I. Alaton, I. Balcioglu, Photochemical and heterogeneous photocatalytic degradation of waste vinylsulphone dyes a case study with hydrolysed Reactive Black 5, J. Photochem Photobiol A, 141 (2001) 247-254.

[4] N. Watanbe, S. Horikoshi, H. Kawabe, Y. Sugie, J. Zhao, H. Hidaka, Photo degradation mechanism for bisphenol A at the TiO_2/H_2O interfaces, Chemosphere, 52 (2003) 851-859.

[5] H. Katsumata, S. Kawabe, S. Kaneco, T. Suzuki, K. Ohta, Degradation of Bisphenol A in water by photo-Fenton reaction, J Photoch Photobio A Chem, 162 (2004) 297-305.

[6] F. Li, X. Li, X. Li, T. Liu, J. Dong, Heterogeneous photo degradation of bisphenol A with iron oxides and oxalate in aqueous solution, J. Colloid Interface Sci, 311 (2007) 481-490.

[7] S. Yamazaki, T. Mori, T. Katou, M. Sugihara, A. Saeki, T. Tanimura, Photocatalytic degradation of 4-tert-octylphenol in water and the effect of peroxydisulfate as additives, J Photochem Photobiol A Chem, 199 (2008) 330-335.

[8] D. Bledzka, D. Gryglik, M. Olak, J. Gebicki, J. Miller, Degradation of n-butyl paraben and 4-tert-octylphenol in H_2O_2/UV system, Radiant Phys Chem, 79 (2010) 409-416.

[9] Y. Wu, H. Yaun, X. Jiang, G. Wei, C. Li, W. Dong, Photocatalytic degradation of 4-tert-octylphenol in a spiral photo reactor system, J Environ Sci, 24 (2012) 1679-1685.

[10] W. Huange, M. Brigante, F. Wu, K. Hanna, G. Mailhot, Development of new homogeneous photo-Fenton process using Fe (III)-EDDS complexes. J Photochem Photobiol A Chem, 239 (2012) 17-23.
[11] Y. Wu, H. Yuan, G. Wei, S. Zhang, H. Li, W. Dong, Photo degradation of 4-tert-octylphenol in aqueous solution prompted by Fe(III). Environ Sci Pollut Res, 20 (2013) 3-9.
[12] J. O. Osarumwense, N. A. Amenaghawon, F. Aisien, Heterogeneous, photocatalytic degradation of phenol in aqueous suspension of periwinkle shell ash catalyst in the presence of UV from sunlight, J Eng Technol, 10 (2015) 1525-1539.
[13] L.Hurtado, D.Amado-Piña, G. Roa-Morales, E. Peralta-Reyes, E. M. Campo and R. Natividad, Comparison of AOPs Efficiencies on phenolic compounds degradation, J Chem (2016), Article ID 4108587, 8 pages
[14] M. Hoffmann, S. Martin, W. Choi, D. Bahnemann, Environmental applications of semiconductor photo catalysis, Chem Rev,95 (1995) 69-96.
[15] G. Puma, A. Bono, D. Krishnaiah, J. Collin, Preparation of titanium dioxide photo catalyst loaded onto activated carbon support using chemical vapor deposition a review paper. J. Hazard Mater, 157 (2008) 209-219.