Photocatalytic Degradation of Paracetamol Using Degussa Tio_2 Photocatalyst

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ABSTRACT

Huge amounts of commercial pharmaceuticals are used worldwide for medical purposes. Paracetamol (PARA) is a medication widely used to reduce fever and pain. It is also combined with other drugs in some prescription pain medications. A current environmental issue is the effects of pharmaceuticals and personal care products on human and environment is a major concern. In the present paper , detail studies on the photocatalytic degradation of paracetamol using Degussa P-25 TiO_2 photocatalyst and artificial UV irradiation was investigated. The effect of various operating parameters such as catalyst loading, pH of solution, initial concentration of PARA on the photocatalytic degradation of PARA have been studied and optimized.

Keywords: Photocatalysis, Paracetamol, TiO_2 Degussa P-25.

Introduction

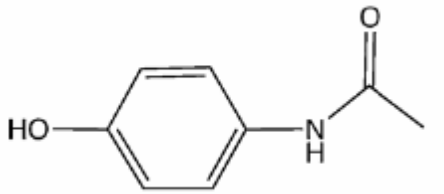
Industrialization growths are likely to keep increasing the quantity of wastewater discharged. Also, considering the fast development of pharmaceutical industry and the general aging of population, it can be assumed that greater quantities and a more diverse array of pharmaceutically active compounds will be consumed, with development of new compounds that have unknown effects on the environment [1-3]. The pharmaceutical manufacturing industry produces a wide range of products to be used as human and animal medications [4]. In the pharmaceutical industry various types of processes are involved in the manufacture of pharmaceutical products such as research and development, chemical synthesis, natural product extraction and formulation [5-7]. Research and development a wide range of chemical and biological laboratory wastes are produced. The most common chemical wastes produced from research and development department includes halogenated and non-halogenated solvents, photographic chemicals, radionuclide, bases, and oxidizers [8]. In chemical synthesis, manufacturers use a large group of solvents listed as priority pollutants and these are used for product recovery, purification, and as reaction media. At the end of whole process equipment is thoroughly cleaned. Natural product extraction is the production of pharmaceuticals from natural material sources such as roots, leaves, barks and animal glands [9-13]. Wastes from natural product extraction include spent raw materials such as leaves and roots,

water-soluble solvents, solvent vapours and waste waters. Pharmaceutical formulation is the preparation of various dosage forms such as tablets, capsules, liquids, parenteral and creams and ointments etc. persistent bio-accumulative toxicants (PBTs) or persistent organic pollutants (POPs) such as lead, mercury, and dioxin, and they have highly detrimental effects over long periods of time [12].

Pharmaceuticals have been detected in wastewater treatment plant effluents, surface water, ground water, and drinking water [13-15]. Worldwide detection of waste pharmaceuticals in the environment causes a risk associated with their introduction into wildlife habitats and is becoming a serious issue for both regulators and the pharmaceutical industry. Pharmaceuticals plants generate a large amount of wastes during manufacturing, housekeeping and maintenance operations [16-20]. Typical waste streams include spent fermentation broths, process liquors, solvents, and equipment wash waters, spilled materials, and used processing aids. Different classes of drug have been documented as environmental pollutants such as analgesics, antibiotics, antiepileptic, antihypertensive, antiseptics, beta-blocker heart drugs, contraceptives, hormones, and psychotherapeutics.

Paracetamol is an acylated aromatic amide, which was firstly introduced into medicine as an antipyretic/analgesic by Von Mering in 1893 and has been in use as an analgesic for home medication for over 30 years and is accepted as a very effective treatment for the relief of pain and fever in adults and children [21]. It is the most used medicine after acetylsalicylic acid in many countries as an alternative to aspirin and phenacetin. Paracetamol (fig. 1) is also known as acetaminophen (N-acetyl-paminophenol, 4-acetamidophenol); it is a major ingredient in numerous cold and flu medications and many prescription analgesics.

Figure 1 : Structure of paracetamol



Paracetamol is a common analgesicand antipyretic drug for human beings. At therapeutic doses, paracetamol isconsidered a safe drug [22]. So in most countries, it can be purchased inretail stores as an over-the-counter preparation and it is currentlythe most widely used drug worldwide. Due to the huge production and usingquantity, paracetamol has been found frequently in the environment, especiallyin the aquatic environment with 0.01–0.3 mg/LIn fact, paracetamol is not an absolutely safe drug. It can cause hepatic necrosis, nephrotoxicity, extra hepatic lesions, and even death in humans and experimental animals when taken in overdoses [23-24]. Lower than 0.5mM paracetamol can be metabolized together with

cytochrome P450, which introduces N-acetyl-p-benzoquinone imine (NAPQI) in to the body's system. NAPQI is an active chemical compoundand its structures indicate that it is capable of taking part in freeradical reactions. Consequently, paracetamol can lead to a number of unfavourable consequences on the target or nontarget species. And its structures indicate that it is capable of taking part in freeradical reactions. Consequently, paracetamol can lead to a number of unfavourable consequences on the target or nontarget species.

Various advanced oxidation processes such as electrochemical, ozonation, H_2O_2/UV oxidation, Fenton and electro-Fenton has been used for removal of PARA from water. The removal of PARA using adsorbent such as activated carbon has been attempted. Membrane bioreactor is also used to remove paracetamol. A.S. Mestre et al. [25] prepared sisal-based activated carbons with K_2CO_3 have suitable properties to remove paracetamol from liquid phase.The degradation of paracetamol in the Fenton and electro-Fenton processes in an aerator reactor shown by C.C. Su et al [26].

Heterogeneous photocatalysis has been a broadly studied field in the last decades, in which the main applications analyzed were those correlated to the use of light and a solid catalyst, irradiated by light with an appropriate wavelength, in order to degrade liquid and gas-phase pollutants [27, 28]. Photocatalytic degradation has proven to be a promising technology for degrading various organic compounds. Compared with other conventional chemical oxidation methods, photocatalysis may be more effective because semiconductors are inexpensive and capable of mineralizing various refractory compounds [29].

TiO_2 has been the most widely studied and used in many applications because of its strong oxidizing abilities for the decomposition of organic pollutants, super hydrophilicity, chemical stability, long durability, nontoxicity and low cost [30-33]. TiO_2 is a wide band semiconductor material with a gap of 3.2 eV. The photocatalytic properties of TiO_2 are derived from the formation of photogenerated charge carriers (hole and electron) which occurs upon the absorption of ultraviolet (UV) light corresponding to the band gap [34]. The photogenerated holes in the valence band diffuse to the TiO_2 surface and react with adsorbed water molecules, forming hydroxyl radicals (•OH). The photogenerated holes and the hydroxyl radicals oxidize nearby organic molecules on the TiO_2 surface. Meanwhile, electrons in the conduction band typically participate in reduction processes, which are typically react with molecular oxygen in the air to produce superoxide radical anions (O_2•−).

$$TiO_2 + hv \rightarrow e^- + h^+ \quad (1)$$

Materials and Methods

Materials

Aqueous paracetamol solutions were prepared in Milli Qwater.TiO_2 Degussa P-25 was used as photocatalyst. Disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4),

tetrabutylammonium hydroxide (TBAOH), methanol andDe-ionized water (DI Water) was used for analysis of sample.

Analytical procedure

The concentration of paracetamol in the samples was monitored by high performance liquid chromatography fitted with a UV detector and a C-8 column. The mobile phase was 0.7 L DI water, 0.3 L methanol, 6.6 g disodium hydrogen phosphate and 2.8 g sodium dihydrogen phosphate, 1.15 tetrabutylammonium hydroxide (TBAOH). Flow rate of mobile phase was 1.5 ml/min. Column temperature was 35 ^{o}C.

Photocatalytic oxidation experiment

Photooxidation of paracetamol was conducted in a batch process. This unit is configured with an annular cylindrical reactor (Fig. 2) witha quartz tube at the centre of the reactor to house 80W UV light (λ_{max}= 365nm) source, jacket was provide for cooling purpose. Cooling media (water) was circulated by chillier (Julabo). For each set of experiments, 0.1 g/L solution of paracetamol was prepared. In prepared paracetamol solution TiO_2 catalysts was suspended. This suspension was mixed with a magnetic stirrer for 15 min. This mixture was charge into reactor for photooxidation. Air was bubbled through the reaction mixture at a constant rate of 16.66 ml/sec at bottom of reactor. Samples were periodically withdrawn, centrifuged and analysed by High Performance Liquid Chromatography (HPLC) equipped with a C-8 column.

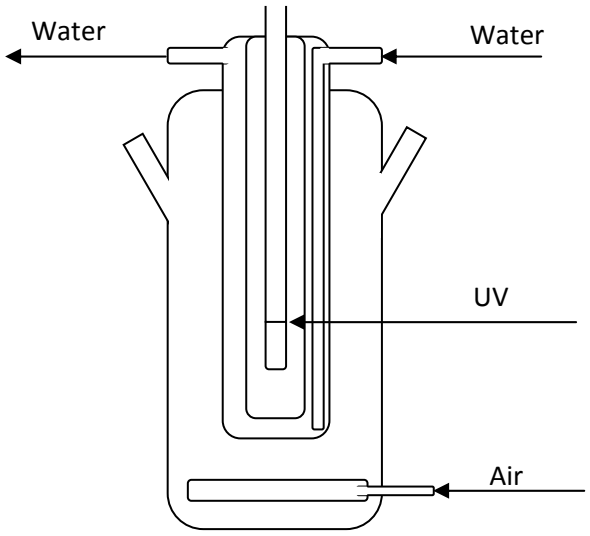


Figure 2: Photocatalytic reactor

Results and Discussions

Effect of Catalyst Loading

Photocatalytic treatments using TiO_2 in suspension were performed to know its influence on paracetamol degradation. Main goals chased in this case were the comparison of catalyst loading. In Fig.

3, the paracetamol decay curves are shown for TiO_2 dosage, varying from 1 to 4 g/L. Degradation of paracetamol increased with increasing TiO_2 loading in the range 1 to 4 g/L.Catalyst loading of 1 g/L TiO_2 showed slow degradation of paracetamol. Catalyst loading of 2 g/L and 3 g/L TiO_2 had similar degradation. After 180 min, degradation of paracetamol in case of 2 g/L catalyst loading was more than 3 g/L. The 2 g/L TiO_2 catalyst loading showed remarkable degradation as compared to 4 g/L.

Based on the results, the optimum titanium dioxide concentration for degradation of paracetamol in aqueous solution is 2 g/L. Degussa P25 TiO_2 is a highly photoreactive catalyst among many different kinds of TiO_2 (Anatase and rutile), which is generally ascribed to have a slow electron-hole recombination rate. When TiO_2 concentration increases, more photons are absorbed by catalyst, which in turn leads to higher concentrations of hydroxyl radicals and other reactive species which accelerate the degradation process. The increase in photodegradation with an increase in the catalyst concentration approaches a limiting value at high TiO_2 concentrations, and this limit depends on the total illumination of the TiO_2 particles; when the catalyst concentration is very high, turbidity hinders further penetration of light into the reactor.

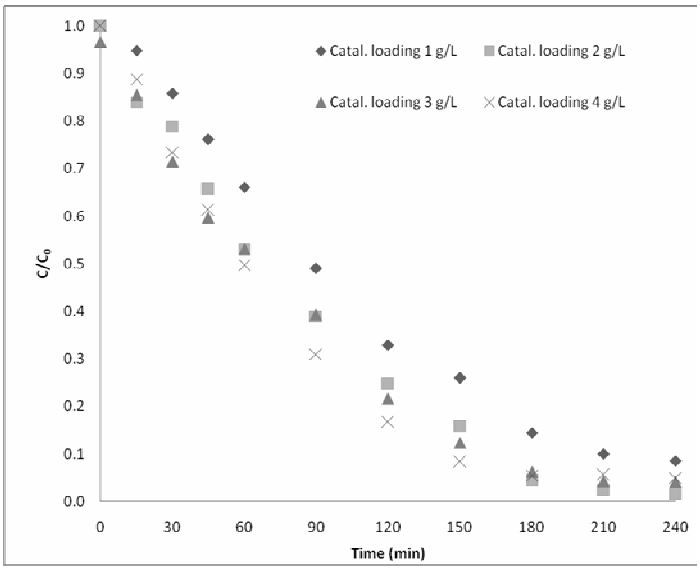


Figure 3: Effect of catalyst loading

Effect of Initial Concentrations of PARA

Fig. 4 shows the effect of initial PARA concentration on degradation at 2 g/L Degussa P25 TiO_2. The degradation of PARA at different initial concentration of 50 mg/L, 100 mg/L, 200 mg/L and 500 mg/L were studied. It was observed that complete degradation of 50 mg/L of PARA achieved at 90 min. The degradation rate depends on initial concentration of PARA it decreases with increases in initial

concentration of PARA. The degradation of PARA were found 100% 80% and 50% at initial concentration of PARA 100, 200, and 500 mg/L respectively at 240 min. It was reported in the literature, that the photocatalytic reaction occurs between the adsorbed substrate (PARA) and $OH^{\bullet}$ generated on TiO_2 surface. The concentration of adsorbed PARA increases with increase in feed PARA concentration. However, for constant light intensity, TiO_2 loading and dissolved oxygen concentration, the concentration of $OH^{\bullet}$ remains practically same. Thus although adsorbed PARA concentration increases, the rate of photocatalytic degradation decreases due to a lower $OH^{\bullet}$/PARA ratio.

Effect of Initial pH Value

Pharmaceutical industrial effluent water has different pH. pH of effluent water plays an important in degradation of pollutant, so effect of pH on degradation was studied. The pHs of PARA solution were changed from 3, 5, 7, 9 and 11. Fig. 5 shows the degradation of PARA at different pH with respect to time. In the alkaline range, the pH was varied using aqueous NaOH, whereas in the acidic range, pH was varied using $HClO_4$. Initial PARA concentration of 100 mg/L and catalyst loading of 0.20% (w/vol of solution) were used in all these experiments. It is observed that as the pH decreases from alkaline to acidic the rate of photocatalytic degradation of PARA increases.

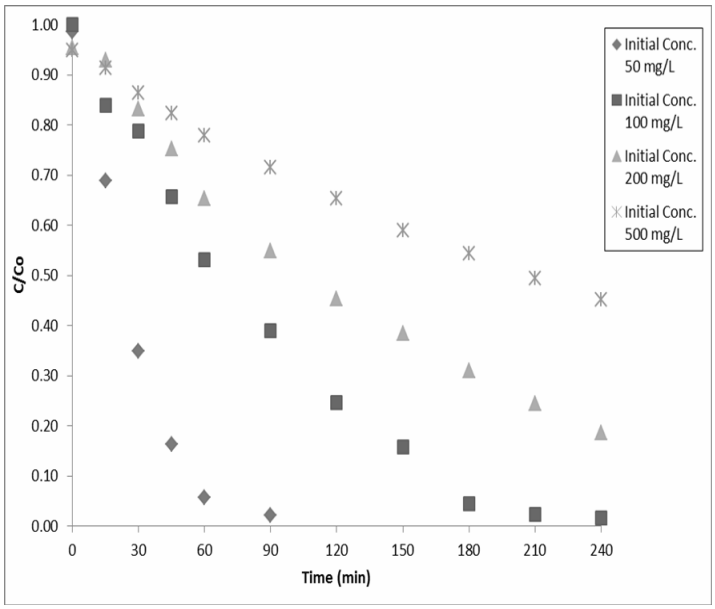


Figure 4: Effect of initial concentrations of PARA

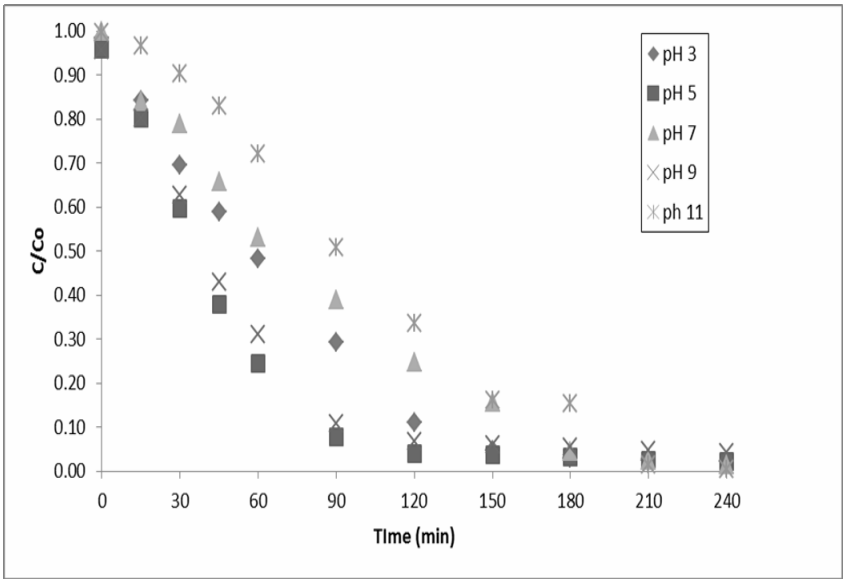


Figure 5: Effect of pH on degradation of PARA

Conclusions

Various advanced oxidation processes such as electrochemical, ozonation, H_2O_2/UV oxidation, Fenton and electro-Fenton has been studied for removal of paracetamol from wastewater. In this study, photocatalytic process (TiO2/ UV radiation) technique was employed for degradation of paracetamol. The completed degradation of paracetamol was achieved using Degussa P-25 TiO_2 catalyst and UV radiation. The influences of dosage TiO_2 on paracetamol degradation investigated. The selection of an optimal catalyst loading is of paramount importance in order to avoid excess of catalyst and to ensure a total absorption of efficient photons. The PARA degradation was found optimum catalyst loading at 2 g/L. For the initial concentration of PARA, degradation of PARA decreased with decreased concentration of PARA. It is observed that as the pH decreases from alkaline to acidic the rate of photocatalytic degradation of PARA increases.

References

1 J. Radjenovic, M. Petrovic, D. Barcelo, Trends in Analytical Chemistry, 2007, 26, 1132-1144.

2 K. Shalini, Z. Anwer, P. Sharma, V. Garg, N. Kumar, International Journal of Pharm Tech. Research, 2010, 2, 2265-2270.

3 A. M. Deegan, B. Shaik, K. Nolan, K. Urell, M. Oelgemoller, J. Tobin, A. Morrissey, International Journal Environment Science Technology, 2011, 8, 649-666.

4 J. Zhou, Z. Zhang, E. Banks, D. Grover, J. Jiang, J. Zhou, Z. Zhang, E. Banks, D. Grover, J. Jiang, Pharmaceutical residues in wastewater treatment works effluents and their impact on

receiving river water, Journal of Hazardous Materials, 2009, 166, 655–661.

5 J. An, Q. Zhou, F. Sun, L. Zhang, Journal of Hazardous Materials, 2009, 169, 751–757.

6 C. Su, A. Chang, L. Bellotindos, M. Lu, Separation and Purification Technology, 2012, 99, 8–13.

7 I. Penatea, C. Lebiguea, U. Hazac, A. Wilhelma, H. Delmasa, Journal of Hazardous Materials, 2012, 221, 131– 138.

8 E. Brillas, I. Sires, C. Arias, P. Cabot, F. Centellas, R. Rodriguez, J. Garrido, Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode, Chemosphere, 58 (2005) 399–406.

9 A. Trovo, S. Melo, R. Nogueira, Journal of Photochemistry and Photobiology A: Chemistry, 2008, 198, 215–220.

. 10 Q. Isariebel, J. Carine, J. Javier, W. Marie, D. Henri, Ultrasonics Sonochemistry, 2009, 16, 610–616.

. 11 M. Jagannathan, F. Grieser, M. Ashokkumar, Separation and Purification Technology,2013, 103, 114–118.

. 12 L. Martinez, S. Torres, V. Likodimos, J. Figueiredo, J. Faria, Applied Catalysis B: Environmental, 2012, 123, 241– 256.

. 13 Y.Lina, C. Ferronatob, N. Dengc, Applied Catalysis B: Environmental, 2011, 104, 353–360.

. 14 M. Sousa, C. Gonçalves, J. Vilar,A. Boaventura, M. Alpendurada, Chemical Engineering Journal, 2012, 198, 301–309.

. 15 H. Son, G. Ko, K. Zoh, Journal of Hazardous Materials, 2009, 166, 954–960.

. 16 L. Rodriguez, S. Cuevas, I. Ollera, A. Aguera, Journal of Hazardous Materials, 2012, 211, 131–137.

. 17 S. Yurdakal, V. Loddo, V. Augugliaro, H. Berber, G. Palmisano, L. Palmisano, Catalysis Today, 2007, 129, 9–15.

. 18 L. Martineza, J. Fariaa, J. Rodriguezb, C. Rodriguezb, A. Silva , Applied Catalysis B: Environmental, 2012, 113, 221– 227.

. 19 M. Bosch, A. Sanchez, F. Rojas, C. Ojeda, Journal of Pharmaceutical and Biomedical Analysis, 2006, 42, 291–321.

. 20 J. Radjenovic, C. Sirtori , M. Petrovic, D. Barcelo, S. Malato, Applied Catalysis B: Environmental, 2009, 89, 255–264.

. 21 A. Mestre, A. Bexiga, M. Proença, M. Andrade, M. Pinto, I. Matos, I. Fonseca, A. Carvalho, Bioresource Technology, 2011, 102, 8253–8260.

. 22 C. Sirtori, P. Altvater, A. Freitas, G. Zamora, Journal of Hazardous Materials, 2006, 129, 110–

115.

. 23 R. Molinari, F. Pirillo, V. Loddo, L. Palmisano, Catalysis Today, 2006, 118, 205–213.

. 24 L. Chuang, C. Luo, C. Lin, Procedia Engineering, 2011, 15, 5133 – 5137.

. 25 T. Paul, P. Miller, T. Strathmann, Environmental Science & Technology, 2007, 41, 4720-4727.

. 26 L. Yin, Z. Shen, J. Niu, J. Chen, Y. Duan, Environ. Sci. Technol., 2010, 44, 9117–9122.

. 27 N. Quici, M. Morgada, G. Piperata, P. Babay, R. Gettar, M. Litter, Catalysis Today, 2005, 101, 253–260.

. 28 T. Doll, F. Frimmel, Catalysis Today, 2005, 101, 195–202.

. 29 A. Bernabeu, R. Vercher, L. Santos-Juanes, P. Simon, C. Lardin, M. Martinez, J. Vicente, R. Gonzalez, C. Llosa, A. Arques, A. Amat, Catalysis Today, 2011, 161, 235–240.

. 30 R. Wang, C. Yu, Ultrasonics Sonochemistry, 2013, 20, 553–564.

. 31 W. Adams, C. Impellitteri, Journal of Photochemistry and Photobiology A: Chemistry, 2009, 202, 28–32.

. 32 L. Estrad, M. Maldonado, W. Gernjak, A. Aguera, A. Fernandez, M. Ballesteros, S. Malato, Catalysis Today, 2005, 101, 219–226.

. 33 C. Reyes, J. Fernandez, J. Freer, M. Mondac, C. Zaror, S. Malato, H. Mansilla, Journal of Photochemistry and Photobiology A: Chemistry, 2006, 184, 141–146.