

PHOTOCATALYTIC DEGRADATION OF ACETAMINOPHEN BY USING NANOPARTICLES – A REVIEW

K.Dhivya¹, R.Bhuvaneshwari²

¹P.G Scholar, Coimbatore

²Assistant professor, Coimbatore

^{1,2}Dept. of Environmental Engineering, Government college of Technology, Tamilnadu, India

Abstract - Over recent years, the appearance of pharmaceutical waste in the environment has become a major worldwide issue. Pharmaceutical compounds are chemical compounds that are used to diagnose, cure, and prevent the occurrence of diseases. But the disposal of pharmaceutical waste in our country is not proper and because of this the environment is very badly affected. In this study, the most commonly used drug acetaminophen pain relief drug, was taken for degradation by using visible light along with nanocatalyst. The most suitable method of degradation of Acetaminophen is "PHOTOCATALYTIC DEGRADATION". The Titanium Dioxide is an important semiconductor material for wide range of solar Energy Conversion Applications. The synthesis of TiO₂ from the plant or flower Extract is the feasible and Eco-friendly. The Carbon doped TiO₂ gives high Degradation Efficiency of 94%.

Key Words: Acetaminophen, Flower Extract, Photocatalytic Degradation, Nanoparticles

1. INTRODUCTION

Nanomaterials are being highly attracted by researchers to exploit their excellent properties for various Application. Pharmaceuticals and personal care products such as therapeutic drugs, hormones, skincare products have attracted global environment. Among the various pharmaceutical Acetaminophen is one of the widely used pain relief drugs. The method included in this study of degradation of Acetaminophen is "Photocatalytic Degradation". Photocatalytic Degradation is mainly adopted in degradation of Acetaminophen by using Nanoparticles. Pharmaceutical wastes are potentially generated through a wide variety of activities in the health care system, including syringes, and are not limited to intravenous (IV) preparation. Global awareness of ACT as an emergent hazardous material and the requirements of technologies for its efficient control have been increasing rapidly [1]. Titanium dioxide is the most popular photocatalyst in various degrading techniques for emerging contaminants, owing to its highly stable chemical structure, relatively low cost, non-toxicity, and highly oxidizing photo-generated holes [2]. Number of works have been carried out to extend the absorption wavelengths of TiO₂ from UV to the visible region by doping with various element [3,4]. Compared the photocatalytic degradation of methylene blue by visible light using carbon (C-TiO₂), nitrogen (N-TiO₂), and co-doped (C-N-TiO₂) nanoparticles that had been prepared by sol-gel methods. C-TiO₂ was more active than N-TiO₂ [5]. Additionally, doping with carbon may form carbonaceous species at the surface of TiO₂, which facilitate further degradation under visible light [6]. Synthesized C-TiO₂ using sol-gel method, as a photocatalyst under visible light, and they found that carbon doping was maximal when the calcination temperature was 200 to 250 °C [7]. The addition of dopants such as C, N, and S favors the transformation of anatase to rutile in TiO₂, while a synergistic effect between the anatase and rutile forms reportedly increases the photocatalytic activity of such mixture [7]. Several modified TiO₂ materials were prepared following a hydrothermal method and a further thermal treatment in different atmospheres (air or nitrogen) [7]. Among the different photocatalysts, TiO₂ is still the most widely used due to its well-known advantages: low cost, non-toxicity and chemical stability [7]. The use of environmental friendly materials like extracts of plant (leave, flower, bark, seed, and peels), bacteria, fungi and enzymes for synthesis of titanium dioxide nano particles offers eco-friendliness and non-toxic nature of material [8]. Green synthesis provides advantages over chemical and physical methods because it is not only cost-effective but also environment-friendly and easily scalable for large scale production. Also this method does not require costly equipments, high pressures, temperatures and not even small doses of toxic chemicals [9]. Hibiscus rosa sinensis possesses anticomplementary, antidiarrhetic and antiphlogistic activity, the flower possesses antispermatogenic, androgenic, antitumour and anticonvulsant activities. The leaves and flowers have been observed to promote hair growth [10].

2. Green Synthesis of TiO₂ Nanoparticle

2.1 TiO₂ Nanoparticle using Hibiscus Flower Extract: [11]

To synthesis the TiO₂ nanoparticles, dissolve 1.0 N of titanium isopropoxide (TTIP) in 100 ml of Millipore water. Added flower extract drop wise under constant stirring up to achieve pH of solution became 7. The mixture was subjected to stirring for 3 hours continuously. In this process nano particles were formed, afterwards separate this nanoparticles using whatman filter paper and washed the materials with water repeatedly to remove the by-products. The nanoparticles were dried at 100°C for overnight and calcined at 500°C for 4 hours. The TiO₂ nanoparticles were successfully synthesised using green synthesis method. From XRD analysis average crystallite size of the sample was obtained 24.89 nm. It observed that Tetragonal structure was formed. The average particle size was estimated 43.3 nm from particle size analyzer. The optical properties were studied by UV-Visible Spectroscopy it infers that the wavelength was 354 nm and Energy band gap was 3.503 eV. The weight loss was measured by



FIG 2.1

TG-DTA curve as 3.9%. The above results showed that the prepared TiO₂ particle in the Nano-range.

2.2 TiO₂ Nanoparticle aloe vera Extract: [12]

The leaves of Aloe Vera were separated from plant, which were thoroughly washed and cut into small pieces. Take 25g of the leaves into 100ml distilled water boiled for 2hrs at 90°C. The extract was filtered using what man filter paper. The filtrate was stored for the synthesis of nanoparticles. To synthesis the TiO₂ nanoparticles, dissolve 1.0 N of Titanium Chloride (TiCl₄) in 100 ml of Millipore water. Added leaves extract drop wise under constant stirring up to achieve pH of solution became 7. The mixture was subjected to stirring for 4 hours continuously. In this process nano particles were formed, afterwards separate this nanoparticles using what man filter paper and washed the materials with water repeatedly to remove the by-products. The nanoparticles were dried at 100°C for overnight and calcined at 500°C for 4 hours.



FIG 2.2

2.3 TiO₂ NANOPARTICLE USING ORANGE FRUIT WASTE: [13]

Orange peel was collected from left over material of eaten orange fruit in the lab, make it into small pieces. Orange peel was collected from left over material of eaten orange fruit in the lab, make it into small pieces. A 50 g of orange peel was directly taken into the beaker and extracted with 150 ml of water for 2 hrs at 90°C. The extract was filtered using what man filter paper. The filtrate was stored for the further synthesis of nanoparticles. The filtrate was stored for the further synthesis of nanoparticles. Dissolve 1.5 N of titanium tetra iso propoxide in 100 ml of distilled water for synthesis of TiO₂ Nanoparticles. Add extract dropwise under constant stirring upto achieve pH of solution comes to 7. The mixture was subjected to constant stirring for 3 hours continuously at room temperature. In this process formation of nanoparticles were occurred, separate this nanoparticles using what man filter paper and washed the materials with distilled water repeatedly to remove the by-products. The obtained wet nanoparticles were dried at 80°C for overnight. Finally particles were calcined at 600°C for 3 hours for obtaining Rutile phase.



FIG 2.3

3. PHOTOCATALYTIC DGRADATION OF ACETAMINOPHEN BY USING NANOPARTICLES

3.1 PHOTOCATALYTIC DEGRADATION:

The rate of photocatalytic degradation of certain pollutant depends on its nature, concentration and other existing compounds in water matrix. A number of studies have reported the dependency of the TiO₂ reaction rate on the concentration of contaminants in water.

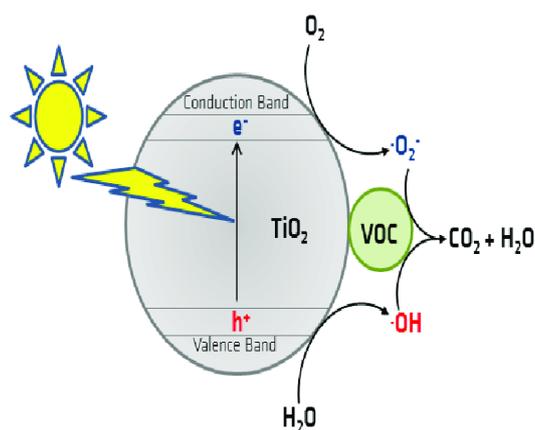


FIG 3.1

3.2 Photocatalytic oxidation of Acetaminophen using carbon self-doped titanium dioxide[14]

A new carbon self-doped (C-doped) TiO₂ photocatalyst was synthesized by solegel method, in which titanium butoxide was utilized because of its dual functions as a titanium precursor and a carbon source. The effects of calcination temperature from 200 to 600 °C on the photocatalytic activity towards acetaminophen (ACT, which was used as a model persistent organic pollutant) under visible light were examined. Photocatalytic activity increased as the calcinations temperature initially increased from 200 to 300 °C but it decreased as the calcinations temperature further increased from 400 to 600 °C. C-doped TiO₂ was synthesized using titanium butoxide, ethanol and deionized water in a simple solegel method and was found effective to degrade ACT under visible light. This work also verifies that the calcination temperature of the C-doped TiO₂ affects its photocatalytic

activity. The results revealed that the photocatalytic activity increased with calcinations temperature from 200 to 300 °C and then decreased as the calcination temperature was further increased from 300 to 600 °C. Calcination temperature also affected the crystalline phase and size of the synthesized TiO₂. Amorphous TiO₂ was formed at 200 °C; the anatase phase was formed at 300 °C and above, and the rutile phase was formed at 600 °C. Lower calcination temperatures produced smaller crystals. The Cdoped TiO₂ that was calcined at 300 °C exhibited the highest photocatalytic activity for the degradation of ACT, efficiency of 94%.

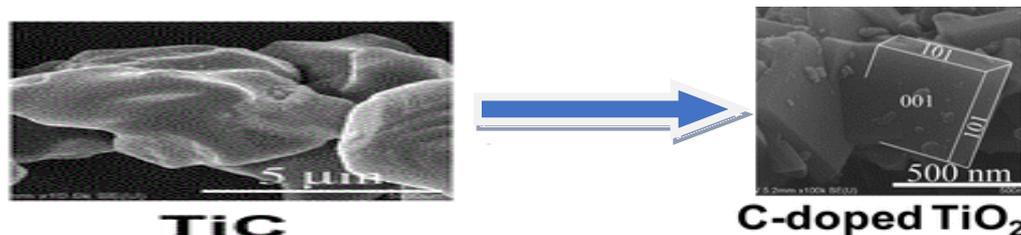


FIG 3.2

3.3 Photocatalytic degradation of acetaminophen using C-modified TiO₂[15]

The current study deals with the hydrothermal synthesis of C-modified TiO₂ photocatalysts using lignin as carbonaceous precursor. The C-modified TiO₂ photocatalysts have been tested for the degradation of a model pharmaceutical (acetaminophen) in water under solar irradiation. Novel C-modified TiO₂ photocatalysts were prepared by hydrothermal process. Lignin was used as carbonaceous precursor. The photocatalysts were tested for the degradation of acetaminophen. C-modified TiO₂ showed a higher degradation rate than non-modified TiO₂. The photocatalysts showed good stability upon four successive cycles.

3.4 Photocatalytic Degradation of Acetaminophen using silver doped TiO₂ Nanoparticle[16]

Nanoparticles of silver deposited on TiO₂ have been tested as catalysts for the removal three organic molecules with photocatalysis treatments. The photocatalysis is an efficient treatment for the removal of numerous organic compounds; however, when the catalyst is modified by the addition of metal particles as silver, its efficiency can be increased and even be activated in visible light. It was shown that titanium–silver catalysts doped with the photodeposition method show changes in physical and chemical properties which make them attractive for their use as supported catalysts. According to the results, it was observed that the solids have absorption in the region of the plasmon of 400 to 600 nm that corresponds to the region of the visible reason why the solids have potential to be used with natural light. The fundamental aspects that define the photocatalytic efficiency of the catalysts are in function of their method of synthesis and in the organic molecule that is treated; in this study, the behavior of a common drug acetaminophen was shown which showed conversion rates higher than 80%



FIG 3.3

3.5 Photocatalytic Degradation of Acetaminophen using Fe/TiO₂ Nanoparticle[17]

This work was aimed to prepare Fe doped TiO₂ on an ionic liquid template so that nanoparticles (IL-Fe/TiO₂(Ar)) could be formed to degrade acetaminophen (ACE) using the photocatalytic process. A novel Fe doped TiO₂ was successfully prepared on

1-octadecyl-3-methylimidazolium bromide template. Characteristic analyses like XRD studies showed a pure anatase crystal structure with the presence of Fe impurities. In addition, FT-IR confirmed existence of F-O, C=C, C=N and hydroxyl groups, which are critical for better visible light responses and photocatalytic activity performance.

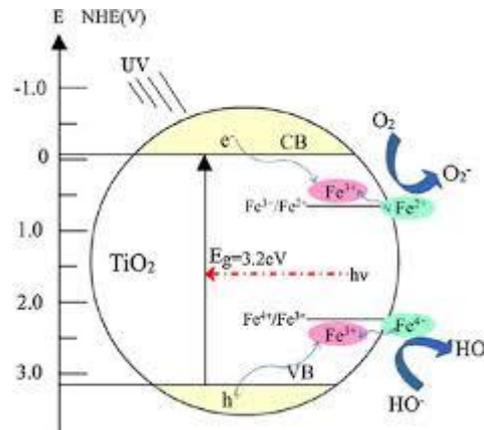


FIG 3.4

3.6 Photocatalytic Degradation of Acetaminophen using Au, Ag, Pt loaded TiO₂ Nanoparticle [18]

The sustainability and feasibility of using solar irradiation instead of UV light in photocatalysis is a promising approach for water remediation. In this study, photocatalytic degradation (PCD) of a widely used analgesic and antipyretic drug, acetaminophen (AP), with noble metal loaded TiO₂ photocatalysts (Ag/TiO₂, Au/TiO₂ and Pt/TiO₂) was investigated in aqueous suspension using solar light. Three nanosized noble metal loaded TiO₂ photocatalysts (Ag/TiO₂, Au/TiO₂ and Pt/TiO₂) were fabricated, characterized and employed for photocatalytic degradation of AP under solar light and compared with UV light. The metal loaded TiO₂ photocatalysts showed enhanced solar photocatalytic degradation of AP in a wide pH range of 4.2–8.0 as well as in the presence of other interferences such as surfactants, and drug excipients and binding materials. The highest photocatalytic activity observed with Pt/TiO₂, which was ascribed to the fact that Pt is a better trapping site for photoelectron than Ag and Au. The results demonstrated that the degradation products are dependent upon light energy, irradiation time as well as the type of photocatalyst. Photocatalysis with solar light could be implemented as a feasible and environmentally benign method for effective degradation of AP using noble metal loaded TiO₂ photocatalyst.

4. CONCLUSION

From the above study it is concluded that the Green Synthesis of TiO₂ by using the Hibiscus Flower, Aloe vera and Orange fruit waste Extract are Eco-friendly, feasible and Cost effective compared to the chemically synthesized Nanoparticles of TiO₂. And the Characteristics of the Extract are Similar to that of Nanoparticles. The photocatalytic Degradation of Acetaminophen by using Carbon doped Nanoparticles gives high Efficiency of degradation in 94% at Ph range of 7. The photocatalytic Activity is dependent on Calcination Temperature. As if the Calcination temperature increases the catalytic activity of Nanoparticle gets decreased based on study. The Calcination temperature of CTiO₂ is at 200 - 300°C. The Photocatalytic Degradation performed under solar light is Efficient.

REFERENCES

- [1]. EFPIA. The Pharmaceutical Industry in Figures. Brussels, Belgium: European Federation of Pharmaceutical Industries and Associations; 2014.
- [2]. Roberts PH, Thomas KV. The occurrence of selected pharmaceuticals in wastewater effluent and surface waters of the lower Tyne catchment. *Sci Total Environ* 2006.
- [3]. Kumar SG, Devi LG. Review on modified TiO₂ photocatalysis under UV/Visible light: selected results and related mechanisms on interfacial charge carrier transfer dynamics.
- [4]. Daghrrir R, Drogui P, Robert D. Modified TiO₂ for environmental photocatalytic applications: a review. *Ind Eng Chem*.
- [5]. Chen DM, Jiang ZY, Geng JQ, Wang Q, Yang D. Carbon and nitrogen co-doped TiO₂ with enhanced visible-light Photocatalytic Activity. *Ind Eng Chem*.

- [6]. Park Y, Kim W, Park H, Tachikawa T, Majima T, Choi W. Carbon-doped TiO₂ photocatalyst synthesized without using an external carbon precursor and the visible light activity. *Appl Catal B- Environ*.
- [7]. A. Gómez-Avilés*, M. Peñas-Garzón, J. Bedia, J.J. Rodriguez, C. Belder C-modified TiO₂ using lignin as carbon precursor for the solar photocatalytic degradation of acetaminophen.
- [8]. Vijaylaxmee Mishra, Richa Sharma, Nakuleshawar Dut Jasuja and Deepak Kumar Gupta, "A Review on Green Synthesis of Nanoparticles and Evaluation of Antimicrobial Activity," *International Journal of Green and Herbal Chemistry*, Vol.3(1), pp.081-094, February- 2014.
- [9]. Rameshwar Rao, CH. Shilpa Chakra and K. Venkateswara Rao, "Eco-friendly Synthesis of Silver Nanoparticles Using Carica Papaya Extract for Anti Bacterial Applications," *Advanced Materials Research* Vol. 629, pp. 279-283, 2013.
- [10]. Sangeetha Arullappan, Shamsul Muhamad and Zubaidah Zakaria, "Cytotoxic Activity of the Leaf and Stem Extracts of Hibiscus rosa sinensis (Malvaceae) against Leukaemic Cell Line (K-562)," *Tropical Journal of Pharmaceutical Research*, vol. 12(5), pp. 743-746, October 2013.
- [11]. K. Ganapathi Rao Ch. Ashok K. Venkateswara Rao Ch. Shilpa Chakra V. Rajendar, Green Synthesis of TiO₂ Nanoparticles Using Hibiscus Flower Extract, 2014
- [12]. K. Ganapathi Rao, CH. Ashok, K. Venkateswara Rao*, CH. Shilpa Chakra, Pavani Tambur, Green Synthesis of TiO₂ Nanoparticles Using Aloe Vera Extract, 2015.
- [13]. K. Ganapathirao, CH. Ashok.k Venkateswara Nanoparticle from orange fruit waste, 2015, rao, CH. Shilpa chakra, V. Rajendar Synthesis of TiO₂, 2016
- [14]. Mark Daniel G. de Luna, Justin Chun-Te Lin, Mary Jane N. Gotostos, Ming-Chun Lu, Photocatalytic oxidation of Acetaminophen using self-doped Titanium-di-oxide, 2016
- [15]. A. Gómez-Avilés, M. Peñas-Garzón, J. Bedia, J.J. Rodriguez, C. Belder C-modified acetaminophen using lignin as carbon precursor for the solar photocatalytic degradation of acetaminophen, 2018.
- [16]. C. A. Aguilar¹ · C. Montalvo¹ · B.B. Zermeño² · R. M. Cerón¹ · J. G. Cerón¹ · F. Anguebes¹ · M. A. Ramírez¹ Photocatalytic degradation of acetaminophen, tergitol and nonylphenol with catalysts TiO₂/ Ag under UV and Vis light, 2018.
- [17]. Amir Mohammad Sheikh Asadi¹ · Mohammad Malakootian^{1,2} Preparation and characterization of Fe/TiO₂ in the presence of ionic liquid to optimize the photocatalytic degradation of acetaminophen using the response surface methodology, 2019.
- [18]. Osama Nasra, Omima Mohameda, Al-Sayed Al-Shirbinib, Aboel-Magd Abdel-Wahaba, Photocatalytic degradation of acetaminophen over Ag, Au and Pt loaded TiO₂ using solar light. 2019.