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Research Article

**PHOTOCATALYTIC DEGRADATION OF PHARMACEUTICAL  
COMPOUNDS IN WASTEWATER USING Mn NANOPARTICLE**Kavitha J<sup>1</sup>, Sakthi Kumar L<sup>2</sup><sup>1</sup>Department of Chemistry, V.V.Vanniaperumal College for Women, Virudhunagar, (affiliated to Madurai Kamaraj University, Madurai), Tamilnadu, India<sup>2</sup>Department of Chemistry, Saiva Bhanu Kshatriya College, Aruppukottai, (affiliated to Madurai Kamaraj University, Madurai), Tamilnadu, India**Article Received:** July 2022**Accepted:** August 2022**Published:** September 2022**Abstract:**

*Now a days, the current research develops on the field of early diagnosis and therapeutic applications. They focused on the orientation of target molecule and the active site of the drug design. The drug molecule synthesized by various industries and utilization in every health centres. For each production of the drug molecules, the solid waste and the effluent wastes were directly discharged into the water bodies. The above limitation of the level leads to the mutation in the protein and the DNA. The significance of the work focused on the treatment of pharmaceutical effluents by photocatalytic degradation using manganese nanoparticle. The synthesis of Mn nanoparticle was synthesized by the chemical reduction method and it was characterized by UV-Visible spectroscopy, X-ray diffraction and the morphology of the material was seen by field emission microscope. The photocatalytic activity of the pharmaceutical product was studied by normal and the photocatalytic condition. The photocatalytic study was carried by varying the catalyst loading and the time of degradation. The real sample was studied in real pharmaceutical products.*

**Keywords:** Treatment of pharmaceutical effluents, Photocatalytic degradation, Mn Nanoparticle, real sample analysis.

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**INTRODUCTION:**

World's population increases along with the expected economic development, are major challenges water and energy consumption. However, nowadays 800 million people do not have access to drinking water. Thus, all strategies that enable to maximize water reuse, and contribute to the preservation of water resources, as well as those promoting more efficient use of renewable energies, are essential to help in minimizing water scarcity and energy demand.<sup>[1]</sup> Water treatment technologies upgrade is the key to face current water quality challenges. The utmost challenge for drinking water and wastewater treatment, as well as water reuse, is linked to the presence of natural organic matter and micro pollutants in raw water, the latter often related to pharmaceutical compounds. Several Pharmaceutical compounds partially or totally resist to conventional treatments. So it is crucial to upgrade the design and operation conditions of wastewater treatment plants, and water treatment plants with innovative, cost- and resource- effective solutions to achieve high- quality water standards.

Water pollution is a globally pressing ecological problem and has adverse impacts on both natural ecosystems and human daily life. The growth of industry along with the unprecedented increase in the human population have led to a high demand for water resources, whereas at the same time large amounts of various wastewaters are generated and threaten the quality of these resources Food and energy security sustainable development, human and ecosystems health rely on water availability and quality.<sup>[1-5]</sup> Therefore, it is of utmost importance to make sure that industrial wastewaters are adequately treated prior to their disposal so as to minimize the impact on the human health and environment.

Although by means of conventional methods and especially of biological processes, 80-90% of all pollutants are usually removed, it has been found that hazardous organic pollutants may escape these processes. Chlorophenols constitute a group of organic compounds that is widely used in the dye manufacture, petroleum refineries, herbicide production and pharmaceutical industry. They can be found in the environment through the release of polluted water from these industries. They are

harmful to humans and ecosystem and considered as potential carcinogenics. Moreover, they are known to exhibit a bio-resistant nature. Advanced oxidation processes can be utilized to eliminate such toxic organic pollutants in wastewaters by converting them into water and carbon dioxide.<sup>[6]</sup>

Active pharmaceutical metabolites and unmetabolized components are excreted from the human body and aquatic life. For example the steroid hormone 17 ethinylestradiol, affect the reproduction of fish and induce structural rupture in kidneys and intestines of fish. Most pharmaceutical drugs have been shown to be potent beyond their expiry dates. Some analgesics and antibiotics have been shown to still contain concentrations of at least 90% of their compounds. Therefore pharmaceuticals need to be removed from water because humans are not safe from negative effects of continuous exposure to pharmaceutical drugs in water.<sup>[7]</sup>

As a result a gradual growth pharmaceutical components is observed in water environment. However, it is impossible to separate pharmaceutical compounds i.e. antibiotics, hormones, steroids, etc. through wastewater treatment and cannot be degraded by means of biological treatment. Several groups of researcher have adopted photocatalysis in presence of nanoparticle, one of the main categories of advanced oxidation process to eliminate effects of pharmaceutical compounds. Some of pharmaceutical compounds resist conventional treatments and are also highly resistant to photolysis and adsorption onto solid matter leading to their high persistence in the aquatic environment. Consequently, tertiary treatments are fundamental to assure the removal of these pharmaceutical compounds. These treatments cover a large range of technologies: UV disinfection, ozone, or chloride, and advanced water treatment technologies.<sup>[8,9]</sup>

Pharmaceutically active compounds have been detected in sewage treatment plant, surface water and even drinking water. Traditional wastewater treatment plant cannot remove all the pollutant compound due to its trace concentration and biology degradation. So advanced oxidation processes can be successfully used in the field of wastewater, underground water and gas treatment, to convert

toxic and bio contaminants into biodegradable by-products, to remove color or to reach the complete degradation of organic pollutants.<sup>[10]</sup>

There are the huge number of harmful pharmaceutical drugs detected in environmental waters that badly affects human health and animals. Many oxidation techniques are reported for the elimination of organic micro contaminants found in environmental waters. The complete elimination of pharmaceutical compounds is not possible by ordinary methods. Chlorination is commonly used technique to remove bacteria and germs. But this methods are harmful to human health. Metal oxide is the best source to degrade this pharmaceutical waste products in water.<sup>[11-16]</sup> Advanced oxidation process is an efficient process to remove harmful pharmaceutical compounds into non-toxic compounds, Carbon di oxide and water compare to another techniques like; adsorption, coagulation, sedimentation, bio-filtration etc., Advanced oxidation process can be achieved by direct ozonolysis, catalytic oxidation, with the more recent advances in photocatalytic degradation method. The photocatalytic degradation actively degrade the effluent products and decomposed into unharmed substances. For the active process of degradation, the manganese nanoparticles were utilized. Because the Mn nanoparticles is an half-filled stable transition metal and actively involved in various applications which include calorimetric sensor, electrochemical application which are supercapacitor, sensors and solar cell application.

### MnO<sub>2</sub>

MnO<sub>2</sub> is an inexpensive and environmentally friendly multi-functional material, which has been used in numerous applications<sup>[17]</sup>. Crystallographically, MnO<sub>2</sub> can have many polymorphic forms, such as  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ - MnO<sub>2</sub><sup>[18]</sup>, which are made of the basic structure unit [MnO<sub>6</sub>] octahedron with different connectivity. According to different [MnO<sub>6</sub>] octahedron links, the MnO<sub>2</sub> structures can be divided into chain-like tunnel structures and sheet or layered structures<sup>[19]</sup>. The polymorphs have distinctive atomic arrangements that result in various types of pores or tunnels within the crystal structure. Due to the distinctive crystal structure, the selectivity toward different ions or electron transfer kinetics is immense<sup>[20]</sup>.

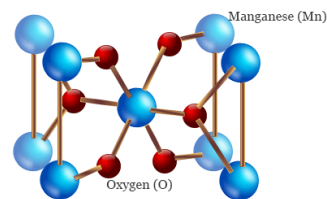


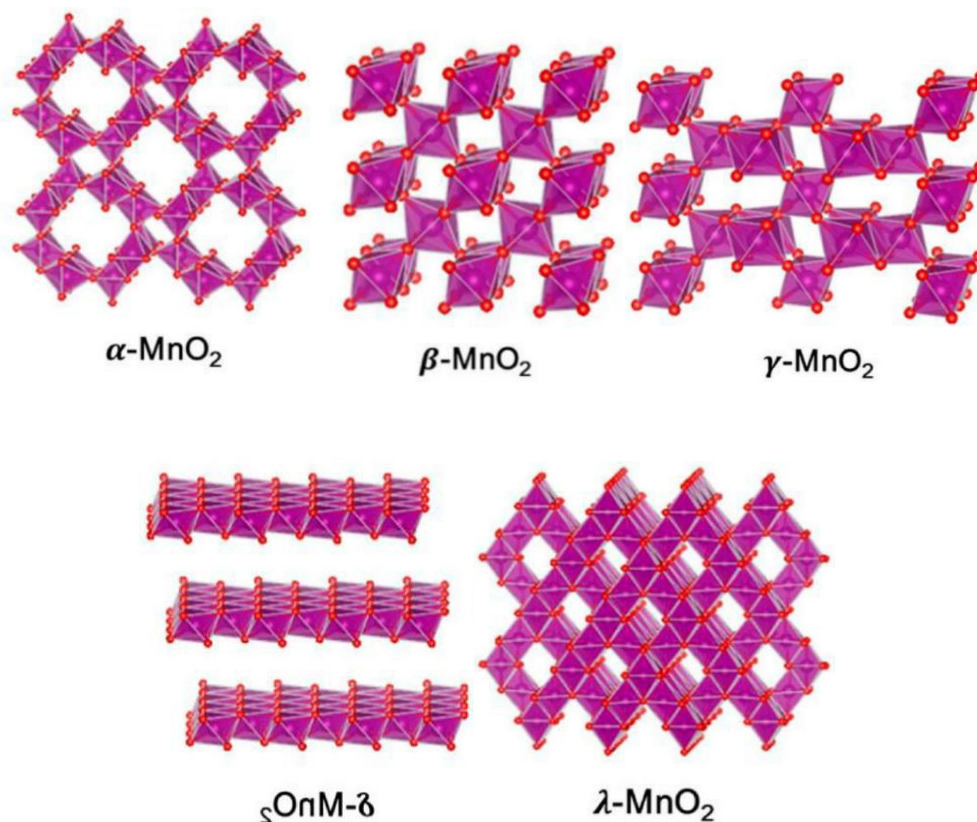
Fig. 1. Crystallographic unit cell arrangement in MnO<sub>2</sub>

**$\alpha$ -MnO<sub>2</sub>:** The **Fig. 2(a)**  $\alpha$ -MnO<sub>2</sub> consists of interlinking double chains of MnO<sub>6</sub> octahedra and an interstitial space composed of 1D tunnels with relative dimensions 2 2 and 1 1 that extend along the c-axis of the tetragonal unit cell. The continuous extension of MnO<sub>6</sub> octahedra along the c-axis direction can lead to the preferred growth of MnO<sub>2</sub> along with the [001] direction. 1D MnO<sub>2</sub> includes nanorods, nanofibers, nanoneedles, nanotubes, and nanowires. The attractive properties of 1D MnO<sub>2</sub> are efficient electron transportation and excitation along the longitudinal pathway with outstanding mechanical strength. Hence, 1D nanostructure has been widely used in the field of electrical, optical, sensor, and photocatalysis<sup>[21-35]</sup>

**$\beta$ - MnO<sub>2</sub>:** It is composed of a single strand of edge-sharing MnO<sub>6</sub> octahedral to form a 1D (1×1) tunnel **Fig. 2(b)**. And it is found that  $\beta$ -MnO<sub>2</sub> is one of the metal oxides which are easier to be present as nanowires.

**$\gamma$ - MnO<sub>2</sub>:** It is a random intergrowth of ramsdellite an orthorhombic manganese dioxide mineral, usually found in deposits containing other manganese oxide crystals (1×2) and pyrolusite a common manganese mineral that constitutes an important ore, it is black amorphous and often granular, fibrous, found as reniform crusts or in columnar structure, (1×1) domains **Fig. 2(c)**.

**$\delta$ -MnO<sub>2</sub>:** This has a layer structure, with sheets made from manganese-oxygen octahedra, separated by alkali or other ions, and water. It has a ~7 Å interlayer separation and it is a 2D compound **Fig. 2(d)**<sup>[20]</sup>.



**Fig. 2:** Structures of (a)  $\alpha\text{-MnO}_2$ , (b)  $\beta\text{-MnO}_2$ , (c)  $\gamma\text{-MnO}_2$ , (d)  $\delta\text{-MnO}_2$ , (e)  $\lambda\text{-MnO}_2$ . Pink and red spheres represent Mn, and O atoms, respectively[22].

In the comparative study of oxidation over  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ -  $\text{MnO}_2$ , it was found that the oxidation activity of catalysts decreased in the order of  $\alpha\text{-MnO}_2 > \delta\text{-MnO}_2 > \gamma\text{-MnO}_2 > \beta\text{-MnO}_2$  [23]. Among all the transition metal oxides,  $\text{MnO}_2$  has a relatively high catalytic activity in the catalytic decomposition of organic compounds by oxidation [23].  $\text{MnO}_2$  has many uses, including the manufacture of batteries, beverage cans, agricultural pesticides and fungicides, and electronic circuitry[24].

In this article, first time we report the treatment of pharmaceutical effluents by photocatalytic degradation method. For the active participation of removal process Mn nanoparticles were used. The nanoparticle was synthesized by the chemical reduction method and it was characterized by various confirmation techniques. The optimization techniques were carried out by different steps and the active sample was studied by known vitamin C tablet. And the real sample was studied by photocatalytic degradation method and the results produced were appreciable for the future analysis.

## REVIEW OF LITERATURE

1. In 2009, M. A, Rauf et al., The photocatalytic degradation in Advanced oxidation process used in the dye degradation in aqueous suspension using  $\text{TiO}_2$  as a catalyst. Since Advanced oxidation process rely on the generation and subsequent reaction of highly reactive oxygen radical with dye. There are many factors that can affect the efficiency of this process. To summarize and highlight the effect of a variety of condition on  $\text{TiO}_2$  photocatalytic decolouration of dye. Such as the amount of catalyst reaction  $\text{pH}$ , light intensity, concentration of organic dye, presence of ions. The azo dyes are under the degradation with some of the intermediate that are during their degradation. Finally a survey is presented the various classes of dye and their relative of degradation by Advanced oxidation process. [1]
2. In 2014, Nadia Riaz et al., The Bimetallic Cu-Ni/ $\text{TiO}_2$  photocatalysts were synthesized using wet impregnation method with  $\text{TiO}_2$  as support and

- calcinated at different temperature (180°, 200° and 300°) for photodegradation of diisopropanolamine and visible light. The photocatalyst were characterized using thermal gravimetric analysis, UV-Visible, FESEM, diffuse reflectance spectroscopy, FTIR spectroscopy and temperature programmed reduction. The result from the photo degradation experiments revealed that the Cu-Ni/TiO<sub>2</sub> photocatalysts exhibited much higher photocatalytic activities compared to bare TiO<sub>2</sub>. [2]
- In 2001, C. Hachem et al., The photocatalytic degradation of various dyes has been studied using P<sub>25</sub> Degree as catalyst. All dye solution under wet a decolourisation. The Kinetic were found to be zero (or) first order with respect to dyes and compared to adsorption properties. The effect to the addition of hydrogen peroxide studied that the rate of observed all cases he order to respect to additive almost zero. It is difficult to give a general picture of kinetics using very difficult dye but process effective for the decolourisation of textile waste water. [3]
  - In 2010, Saber Ahmed et al., The heterogeneous photocatalytic water purification process indegradation and mineralizing the organic compounds as well as the possibility of utilizing the solar UV and Visible spectrum. The photocatalytic degradation of phenol and substituted phenols are presented. Extensive research has focused on the enhancements of photocatalytic by modification of TiO<sub>2</sub> emptying metal, non-metal and ion doping. Recent development in TiO<sub>2</sub> photocatalytic for degradation of various phenol and substituted phenol are also reviewed. [4]
  - In 2003, A. Di Paola et al., The photocatalytic degradation of 2-3-and 4-nitrophenol has been oxygenated aqueous suspensions containing TiO<sub>2</sub>. The organic reaction intermediate have determined by high performance liquid chromatography. The results of complete the substrates and forming of nitrate and ammonium ions. The degradation involving a rapid opening aromatic ring followed by slower oxidation of aliphatic compounds. The ring hydroxylation of attack by the nitrophenol formation of dihydroxynitrobenzenes. The position activated by the contemporaneous presence of phenolic and nitro group. [5]
  - In 2018 M. Akkari et al., The photocatalysts based the ZnO nanoparticles the surface of sepiolite fibrous clay mineral can be modified by treatment with acetyl-trimethyl ammonium bromide and tetramethoxyortosilicate. The photo activity of the resulting material has been tested solar light irradiation for the degradation of emerging pollutants, such as ibuprofen, acetaminophen and antipyrine. The resulting ZnO/sep hetrostructure exhibit photocatalytic compared to ZnO/SiO<sub>2</sub>-sep and ZnS/Fe<sub>3</sub>O<sub>4</sub>-sep material. Ibuprofen higher degradation rates than the other target compounds. The use of ZnO/Fe<sub>3</sub>O<sub>4</sub>-sep photocatalyst the simultaneous features of super magnetic character and photocatalytic activity, recovery by application of an external magnetic field. [7]
  - In 2017 Mehdi Ahmadi et al., The photocatalytic degradation of tetracycline using Multi walled carbon nanotube /TiO<sub>2</sub> nano composite was investigated under UV-C irradiation. The effective operational parameters include P<sup>H</sup>, irradiation time, photocatalytic dosage weight ratio to MWCNT to TiO<sub>2</sub> ratio of 1.5 (W/W %), P<sup>H</sup> 5, photocatalytic dosage of 0.2g/L pseudo-first order kinetic mode was fitted he experimental results (R<sup>2</sup>=0.9-0.98 for different concentration) . The real pharmaceutical waste water the COD concentration of decreased. [8]
  - In 2020 Kiran S.Varma et al., The water pollutant is a serious concern in heavily industrialized countries. The waste water treatment for effective removal of pollutants especially pharmaceutical and pesticide compounds (PPCs). Doped TiO<sub>2</sub> nanomaterial of photocatalytic degradation of waste water in complex organic pollutants. Improvement of doped TiO<sub>2</sub> nanomaterial of resultants in the effective utilization of visible light and solar light as light source. In this context doped TiO<sub>2</sub> nanomaterial mediated waste water treatment process role in water energy. [9]
  - In 2016 Sara Teixeira et al., The waste water treatment plant in the conventional treatment are ineffective in their removal, new method should be semiconductor photocatalysis. The degradation of pollutants for the degradation of pharmaceutical in real water. The heterogenous photocatalytic degradation of pharmaceutical with initial concentration present in a waste water treatment pollutant effluent. The UVA irradiation of TiO<sub>2</sub> P<sub>25</sub> or ZnO nanoparticles to



- degradation of the analyzed pharmaceutical. This system ZnO present faster the degradation of the waste water.[10]
10. In 2001, Ammar Houas et al., The  $\text{TiO}_2/\text{UV}$  photocatalytic degradation of methylene blue in aqueous heterogeneous suspension. To removal of the color  $\text{TiO}_2/\text{UV}$ - based photocatalytic was to oxidize the dye with almost completely mineralization of carbon and nitrogen and sulfur heteroatom into  $\text{CO}_2$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^-$ . The result of  $\text{TiO}_2/\text{UV}$  photocatalytic may be envisaged as a method for treatment of dilute waste water in textile industries.[6]
  11. In 2021, A. Chatzimpaloglou et al, focused on the photolytic and photocatalytic degradation of the antineoplastic drug irinotecan in aqueous solution. Photocatalytic was carried out using commercial  $\text{TiO}_2$ . Significant photolytic degradation of IRI was observed at neutral and basic pH. Quantum yield of IRI for photolytic degradation were calculating using different methods, ranging from 0.00022 to 0.00499  $\text{molEinstein}^{-1}$ . DOC and toxicity values reduced much slower than IRI, possibly due to the subsequent production of TPs that are not easily degraded and remain in the solution as DOC. [11]
  12. In 2008, Fabiola Mendez-Arriaga et al, investigated the heterogeneous photocatalytic degradation of Naproxen using  $\text{TiO}_2$  as photocatalyst. Effect of  $\text{TiO}_2$  loading, temperature, volumetric flow and dissolved oxygen concentration as operational parameters were studied. Identification of by products has shown that demethylation and decarboxylation are the principal initial processes in the degradation of NPX. [12]
  13. In 2017, Alaa Salma et al, studied Nebivolol is one of the top-sold prescription drug belonging to the third generation of beta blockers. Within this study Nebivolol has been found for the first time in effluent samples of wastewater treatment plants in Germany with an average concentration of  $13\text{mg L}^{-1}$ . Nebivolol degradation during UV-B and UV-C treatment followed pseudo first order reaction kinetics with highest removal rate treatment in pure water. The photo oxidation involves reactive oxygen species such as superoxide and singlet oxygen. These oxidative species may be formed upon reaction of photo-excited Nebivolol with oxygen. [13]
  14. In 2020, Si Li et al, were investigated that photolytic degradation of Tetracycline in mono and binary solute systems of  $\text{Ca(II)}$  and Humic acid under UVA light emitting diode light irradiation. Absorbance and fluorescence measurements revealed that the strong complexation between TC and Largest reduction of 32.5% in rate constants was observed with the highest  $\text{Ca(II)}$  concentration. Scavenger studies revealed that TC could undergo direct photolysis and self-sensitization by  $\text{O}_2$ . These results suggested that the coexistence of HA and  $\text{Ca(II)}$  greatly influences the fate of TC in natural waters. [14]
  15. In 2008, Zhongliang Chen et al, studied that the formation of 2,8 -dichlorobenzo-p-dioxin (2,8-DCDD) in the photolytic degradation of triclosan has evoked a great concern for its safety and environmental fate. The photochemical behavior of triclosan in daily used chemical products in which triclosan is present in relatively high concentrations and coexists with surfactants, was however addressed less frequently. Based on the analysis of photoproduct, hemolytic scission of ether bond, dechlorination, ring closure and photopolymerisation were proposed as the main routes of triclosan photodegradation. [15]
  16. In 2016, Fariba Mahmoudkhani et al, The degradation of benzene, a carcinogenic air pollutant, was studied in a gas-phase photochemical reactor with an amalgam lamp emitting ultraviolet light at 185 & 254 nm. A comprehensive mechanistic simulation model was developed incorporating a chemical kinetics mode. The model successfully predicted the efficiency of the reactor, generally within 20%, which indicates that the model is sound, and can be used for feasibility studies. The prediction of the reactor efficiency in the presence of ozone was less successful, with systematically overestimated efficiency. [16]
  17. In 2019, Ana S. Mestre et al, The literature data on the photocatalytic removal of carbamazepine, diclofenac, and sulfamethoxazole by semiconductor materials was critically revised to highlight the role of the carbon in the enhanced semiconductor performance under solar irradiation. Carbon was added as a dopant or as a support or doping materials (i.e., nonporous

carbons, carbon nanotubes, grapheme and biochars) and in the large majority. In cases,  $\text{TiO}_2$  was the semiconductor tested. The removal and mineralization rates, as well as degradation pathways. [20]

18. In 2021 T. Velempini et al, In recent years, metal oxide semiconductors have been explored as photocatalysts for the degradation of the organic contaminants in wastewaters. The uniqueness of these oxide materials is in their ability to harness energy in the UV range, their relative ease of synthesis, low cost, and their general high environment surface ratio to, mass, etc. In this article, pharmaceutical drugs abatement from water via photocatalysis process using oxide-based advanced metals such and toxicity of the treated solutions were also critically analyzed, as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{WO}_6$  and  $\text{Bi}_2\text{WO}_6$  is discussed. Finally, a short preview of degradation of pharmaceuticals pilot scales is also highlighted. [18]
19. In 2015, Santanu Sarkar et al, In recent years disposal of pharmaceutical wastes has become a major problem globally. The heterogeneous photocatalysis process becomes lucrative method for reduction of detrimental effects of pharmaceutical compounds. The main disadvantage of the process is the reuse of photocatalysis is a tedious job. The degradation of aqueous solution of chlorhexidinedigluconate, an antibiotic drug, by heterogeneous photocatalysis was study using  $\text{TiO}_2$  nanoparticle. The major concern of this study is to bring down the limitations of suspension mode heterogeneous photocatalysis by implementation of immobilized  $\text{TiO}_2$  with help of calcium alginate beads. [19]
20. In 2004, Qialin Yang et al, investigated the photolytic degradation of 2-chlorophenol, 4-chlorophenol etc., room temperature ionic liquids has been using UV radiation of 253.7 nm. At low concentrations chlorinated phenols could be degraded in these RTILs following pseudo-first order kinetics. Purification of RTILs using activated carbon enhanced the photo degradation rates. The impurities could at same extend, protect the ionic liquid from photolysis and enhance the stability of the solvent [17].

### MATERIAL AND METHODOLOGY:

Manganese chloride, Sodium hydroxide and ascorbic acid are purchased from SRL, India. For the electrochemical studies done with the three-electrode system – Electrochemical workstation (Model: CHI-760E) - USA. The material was confirmed via UV-Visible spectroscopy (UV-Vis) transition of  $\text{MnO}_2$  nanocomposite recorded with 2000c nanodrop spectrophotometer, Nanodrop technologies – USA. All the experiments were done at room temperature ( $25 \pm 0.2^\circ\text{C}$ ). The surface morphology of GNR was examined by High-Resolution Transmission Electron Microscope (HR-TEM) 2100 plus Electron microscope (JEOL, Japan). The coating of  $\text{MnO}_2$  dispersion on the copper grid and dried at vacuum at room temperature for analysis. All the experiments were carried out using double distilled water at room temperature.

### Experimental section

Using the chemical reduction method, the  $\text{MnO}_2$  nanoparticle was synthesized using the manganese chloride as the salt precursor. And it has been reduced using the chemical reduction method. Initially, the 0.5 g of manganese chloride was dissolved in water, it has been reduced using the reducing agent sodium hydroxide. The change of color from pink to brown color solution was appeared. After one hour of the continuous stirring at 700 rpm, the brown color solid was precipitated. After completion of the reaction, the brown precipitate was centrifuged and collected. The precipitate was dried at the temperature of  $60^\circ\text{C}$  for whole day and got the fine powdered products.

### Photocatalytic study

About 0.1 g of the prepared  $\text{MnO}_2$  was dispersed in  $\text{H}_2\text{O}$  using low frequency waterbath sonication. The UV-Visible spectrum was recorded in the normal light and after the degradation using photocatalytic study. For the treatment of pharmaceutical effluent process, the ascorbic acid was taken. The study of degradation was studied under the normal and the UV-Light process.

### RESULTS AND DISCUSSION:

Fig.3 shows the photographic image for the  $\text{MnO}_2$  nanoparticle. After the chemical reduction of manganese chloride, the sodium hydroxide reduces the size of the metal atom and increase the conductivity property of the nanosized metal atom. The prepared  $\text{MnO}_2$  nanopowder was dispersion was used for the characterization of material and the application of photocatalytic studies.



Fig.3 shows the photographic image for the preparation of powdered MnO<sub>2</sub>

#### UV-Visible study

The MnO<sub>2</sub> was dispersed using low frequency water bath sonication for 10 minutes and checked the UV-Visible spectroscopy. The prepared MnO<sub>2</sub> showed the two transition peak was appeared at 284 and 380 nm which are related to the d-d metal transition of MnO<sub>2</sub> nanoparticle. Those appeared corresponding transition peaks confirms the formation of MnO<sub>2</sub> nanoparticle.

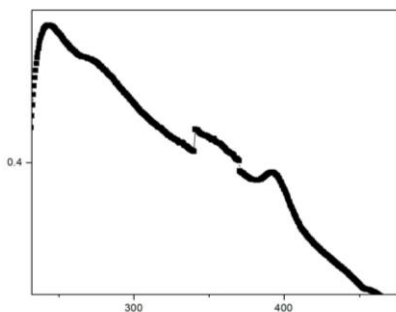


Fig.4 Illustrates the UV-Visible spectrum of MnO<sub>2</sub> nanoparticle

#### XRD Spectroscopy

For the confirmation analysis the MnO<sub>2</sub> was studied by XRD technique. The typical MnO<sub>2</sub> showed the 2 $\theta$  values were obtained at 18, 28.6, 36.7, 38.6, 41.9, 49.7, 56.4, 60.2, 65.4, 69.6 and 72.9° corresponds to (200), (310), (400), (211), (420), (301), (600), (521), (002), (541) and 312 planes shown in **fig.5** The obtained diffractional angle and the planes were corresponds to the  $\alpha$ -MnO<sub>2</sub> nanoparticle

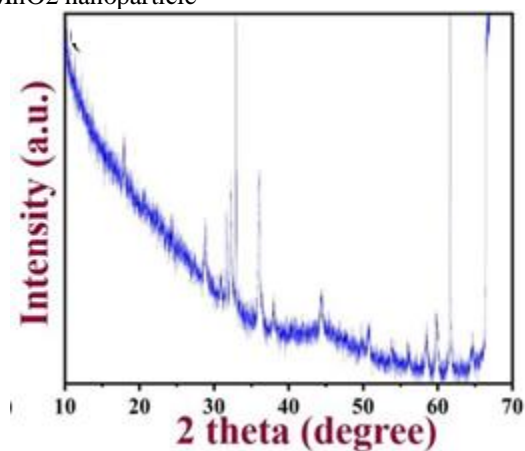
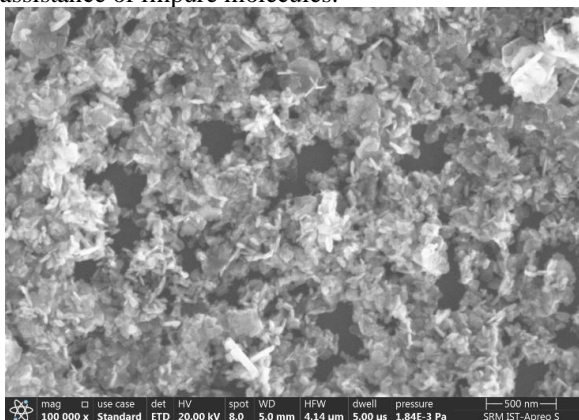


Fig.5 The XRD spectrum of MnO<sub>2</sub> nanoparticle



### FE-SEM Analysis

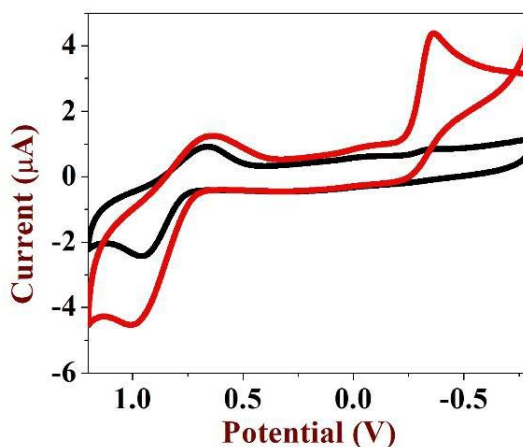
The prepared MnO<sub>2</sub> dispersion morphology was seen by FE-SEM analysis. The sample shows the nanoplate morphology. The elemental analysis of MnO<sub>2</sub> dispersion showed the presence of Mn and oxygen only. It confirms the MnO<sub>2</sub> was formed without the assistance of impure molecules.



**Fig:6 FE-SEM**

### Electrochemical behavior of MnO<sub>2</sub> nanoparticle

The GCE was modified with the prepared MnO<sub>2</sub> catalyst was studied by cyclic voltammetry. The CVS showed the Figure 4 (black curve) the notable catalyst MnO<sub>2</sub> showed the corresponding redox peak was appeared at (0.65 and 0.95 V) with high catalytic current.



**Fig:7 Electrochemical behavior of MnO<sub>2</sub> nanoparticle**

### DEGRADAION PROCESS

- The product Manganese nano particle was dispersed by using ultra sonicator.
  - The ascorbic acid solution was prepared by dissolving 0.5g of ascorbic acid in 25ml of double distilled water.
  - Adding 300 microlitre of ascorbic acid solution at a time interval in the photo reactor.
  - In each addition the degrade solution is collected in a beaker.
- After the completion of reaction the solution was tested for UV spectrum.

### Photocatalytic degradation:

Photocatalytic degradation of pharmaceutical waste water product is promising technology due to its advantage of degradation on pollutants instead of their transfer under ambient condition.

### Degradation process under various time interval:

The degradation process was carried out by using ascorbic acid in the presence of Manganese oxide nanoparticle at different time interval. After the process the solution were tested for UV-Visible spectrum, the degradation curve appear at a wavelength of different region 425nm, 423nm, 418nm, 416nm, 404nm, 402nm.

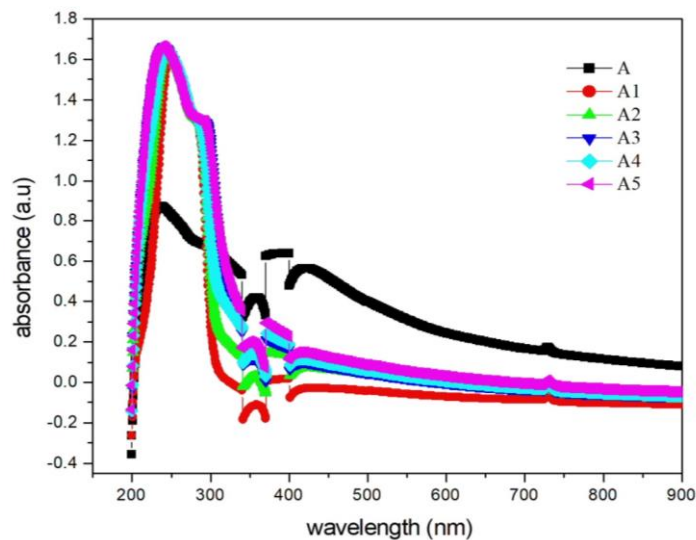


Figure 8. UV-Visible spectrum of degradation process under different time interval

### Degradation process under various concentration:

Again the degradation process was carried out by using ascorbic acid at different concentration of the solution. After completion of process, the solution were tested for UV-Visible spectroscopy. The degradation process under various concentration of the spectrum give a cure appear at a range of 244nm, 246nm, 282nm, 284nm, 286nm, 282nm, 295nm.

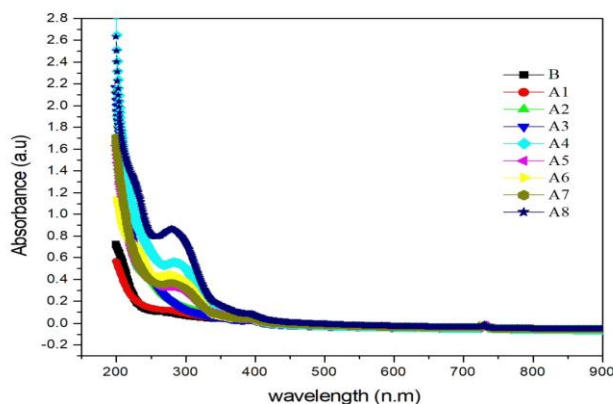


Figure.9.UV-Visible spectrum degradation under the various concentration

### CONCLUSION

Photocatalytic degradation of pharmaceutical in waste water can be part of treatment technologies in

the future. Clean water is the most important source of human population. The benefits of using the photocatalytic method with metal oxides as catalyst is

that this method can also be successfully used to effectively treat contaminated water. In this article in terms of metal oxide photocatalyst selection for the degradation of pharmaceutical waste. Therefore photocatalyst should disperse very well in aqueous solution and have the ability to adsorb pharmaceutical on their surfaces. Experimental results conclude that Manganese nanoparticle is a very efficient. Photocatalyst for the photo degradation of pharmaceutical waste water.

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