Approaching the pharmaceutical water pollution issue using nanosized efficient compounds *via* photocatalytic degradation

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ABSTRACT

In this work, pharmaceutical waste product in water via photocatalytic degradation using MnO_2 nanoparticles were studied. The removal of waste product as well as degradation pathway and toxicity of the treated solution were also critically analyzed under normal and UV light radiation. The product has been investigated using UV spectroscopy. The degradation product of the pharmaceutical water pollutant product, ascorbic acid was studied by UV-Visible spectroscopy by different interval of time, and different concentration of solution. In future study, the optimum catalyst loading, different concentration study will be analyzed.

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

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. [1-5]

Water treatment technologies upgrade is the key to face current water quality challenges. The upmost 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.[6-12]

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 unprecedentedincrease 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.[13-16]

Therefore, it is of outmost 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.[17-23]

Active pharmaceutical metabolites and metabolized components are excreted from the human body and aquatic life. For example the steroid hormone 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. [24-27]

As a result a gradual growth pharmaceutical component 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 photo catalysis in presence of nanoparticle, one of the main categories of advanced oxidation process to eliminate effects of pharmaceutical compounds. [28-30]

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.

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.

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 method is harmful to human health. Metal oxide is the best source to degrade these pharmaceutical waste products in water.

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.

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 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 Tio_2photocatalyticdecolouration of dye. Such as the amount of catalyst reaction P^H, 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.

2. In 2014, Nadia Riaz et al., The Bimetallic Cu-Ni/Tio_2photocatalyts were synthesized using wet impregnation method with 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 reveated that the Cu-Ni/Tio_2photocatalaysts exhibited much higher photocatalystic activities compared to bare TiO_2.

3. In 2001, C. Hachem et al., The photocatalytic degradation of various dyes has been studied using P_{25} Degree as catalyst. All dye solution under wet a decolourisation. The Kinetic were found to be zero (or) firs 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.

4. 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_2 emptying metal, non-metal and ion doping. Recent development in Tio_2photocatalytic for degradation of various phenol and substituted phenol are also reviewed.

5. In 2003, A. Di Paola et al., The photocatalytic degradation of 2-3-and 4-nitrophenol has been oxygenated aqueous suspensions containing Tio_2. 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 .

6. 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/sephetrostructure exhibit photocatalytic compared to Zno/Sio_2-sep and ZnS/Fe_3O_4-sep material. Ibuprofen higher degradation rates than the other target compounds. The use of Zno/Fe_3O_4-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 photocatalyic degradation of tetracycline using Multi walled carbon nanotube /TiO_2nano composite was investigated under UV-C irradiation. The effective operational parameters include P^H, irradiation time, photocatalytic dosage weight ratio to MWCNT to TiO_2 ratio of 1.5 (W/W %), P^H 5, photocatalyic dosage of 0.2g/L pseudo-first order kinetic mode wad fitted he experimental results (R^2=0.9-098 for different concentration) . The real pharmaceutical waste water the COD concentration of decreased.
8. In 2020 KiranS.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_2 nanomaterial of photocatalyticdegradationof waste water in complex organic pollutants. Improvement of doped Tio_2 nanomaterial of resultants in the effective utilization of visible light and solar light as light source. In this context doped Tio_2 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 heterogenousphotocatalytic degradation of pharmaceutical with initial concentration present in a waste water treatment pollutant effluent. The UVA irradiation of Tio_2 P_{25} or ZnO nanoparticles to degradation of the analyzed pharmaceutical. This systemZnO present faster the degradation of the waste water.

10. In 2001, AmmarHouas et al., The Tio_2/UV photocatalytic degradation of methylene blue in aqueous hetrogenous suspension. To removal of the color Tio_2/UV- based photocaalytic was to oxidize the dye with almost completely mineralization of carbon and nitrogen and sulfur heteroatom into CO_2, NH_4^+, $NO_3^-$and SO_4^-. The result of Tio_2/UV photocatalytic may be envisaged as a method for treatment of dilute waste water in textile industries.

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 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 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.

12. In 2008, Fabiola Mendez-Arriaga et al, investicated the heterogeneous photocatalytic degradation of Naproxen using TiO_2 as photocatalyst. Effect of 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.

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 Nebivololhas been found

for the first time in effluent samples of wastewater treatment plants in Germany with an average concentration of 13mg L^{-1}. Nebivolol degradation during UV-B and UV-C treatment followed pseudofirst 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.

14. In 2020, Si Li et al, were investicated that photolytic degradation of Tetracycline in mono and binary solute systems of 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 Ca(II) concentration.

Scavenger studies revealed that TC could undergo direct photolysis and self-sensitization by O_2. These results suggested that the coexistence of HA and Ca (II) greatly influences the fate of TC in natural waters.

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 photo-polymerisation were proposed as the main routes of triclosanphotodegradation.

16. In 2016, FaribaMahmoudkhani 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.

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.,nonoporous carbons, carbon nanotubes, grapheme and biochars) and in the large majority. In cases, TiO_2 was the semiconductor tested. The removal and mineralization rates, as well as degradation pathways.

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 TiO_2, ZnO, Fe_2O_3, WO_6 and Bi_2WO_6 is dicussed. Finally, a short preview of degradation of pharmaceuticals pilot scales is also highlighted.

19. In 2015, SantanuSarkar et al, In recent years deposal 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 TiO_2 nanoparticle. The major concern of this study is to bring down the limitations of suspension mode heterogeneous photocatalysis by implementation of immobilized TiO_2 with help of calcium alginate beads.

20. n 2004, Qialin Yang et al, investicated 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.

OBJECTIVE

The main goal of the project is to design a well suitable remedy for the pharmaceutical water pollution.
The objectives of the project are,

- To understand the global-pharmaceutical pollution issues and the impact by pharmaceutical.
- To study the mechanism of action of various drugs in the human body upon pharma exposure and also the extend of the health risk in human due to pharmaceutical pollution using previous literature.
- To review the previous reports on the same issue with various remediation and finding out their demerits.
- To involve the photo catalytic degradation of selective pharmaceutical with various catalyt
- To observe the photocatalyticevaluation results and find a suitable catalyst.

MATERIAL AND METHODLOGY

Chemical required:

Manganese chloride-0.5g
Sodium hydroxide-2g

- About 0.5g of $MnCl_2$ is dissolved in 20 ml of double distilled water and the solution was placed in a magnetic stirrer for 30 minutes.
- Then 2g of NaOH was dissolved in 30 ml of double distilled water in another beaker and also placed in a magnetic stirrer for 30 minutes.
- The NaOH solution was added drop wise in a $MnCl_2$ solution beaker in a stirrer.

- The NaOHsolution was added until the color changes to brown color, and maintain the solution in a magnetic stirrer for 2 hours.
- After 2 hours the solution was centrifuged to collect the precipitate.
- The precipitate was dried in oven at 60^0c until it get powdered form.

PRODUCT OF MnO_2

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.

RESULTS AND DISCUISSION

UV-VISIBLE SPECTROSCOPY:

UV-Visible spectroscopy is one of the most widely used technique for structural characterization of the compounds. The formation of Manganese nano particle is confirmed by UV-Visible spectroscopy in the range of wavelength from 200nm to 900nm. The absorption spectrum of Manganese nanoparticle give the peak of 395nm in the wavelength region.

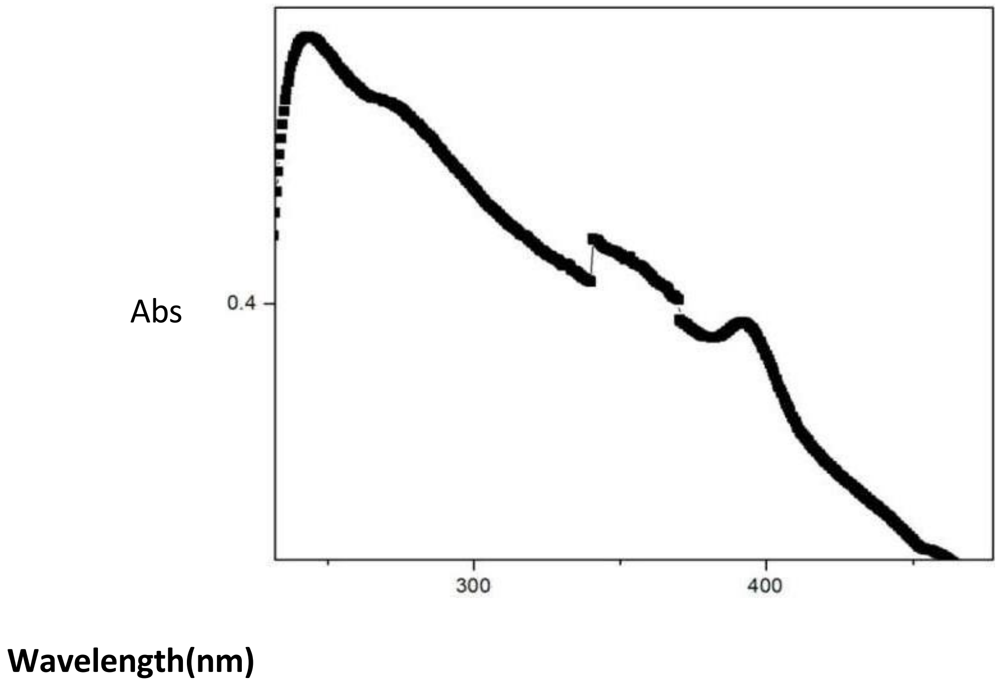


Figure.1. UV-Visible spectrum of Manganese oxide nanoparticle

Photocatalytic degradation:

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

Degradation process under various time internal:

The degradation process was carried out by using ascorpic 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.

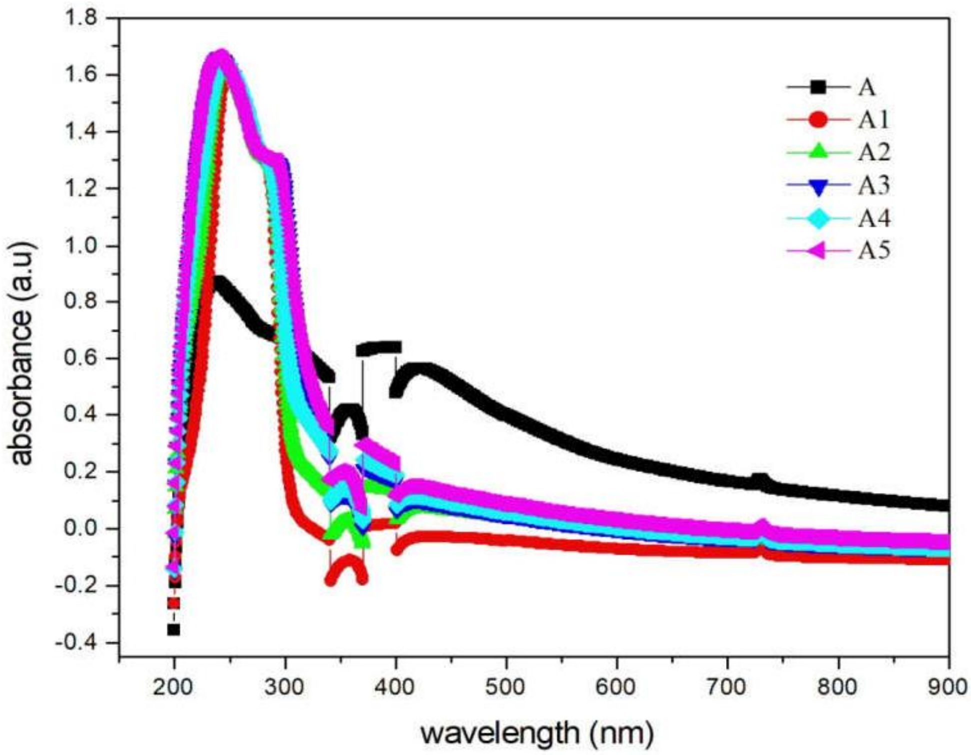


Figure.2. UV-Visible spectrum of degradation process under different time interval

Degradation process under various concentration:

Again the degradation process was carried out by using ascorpic 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.

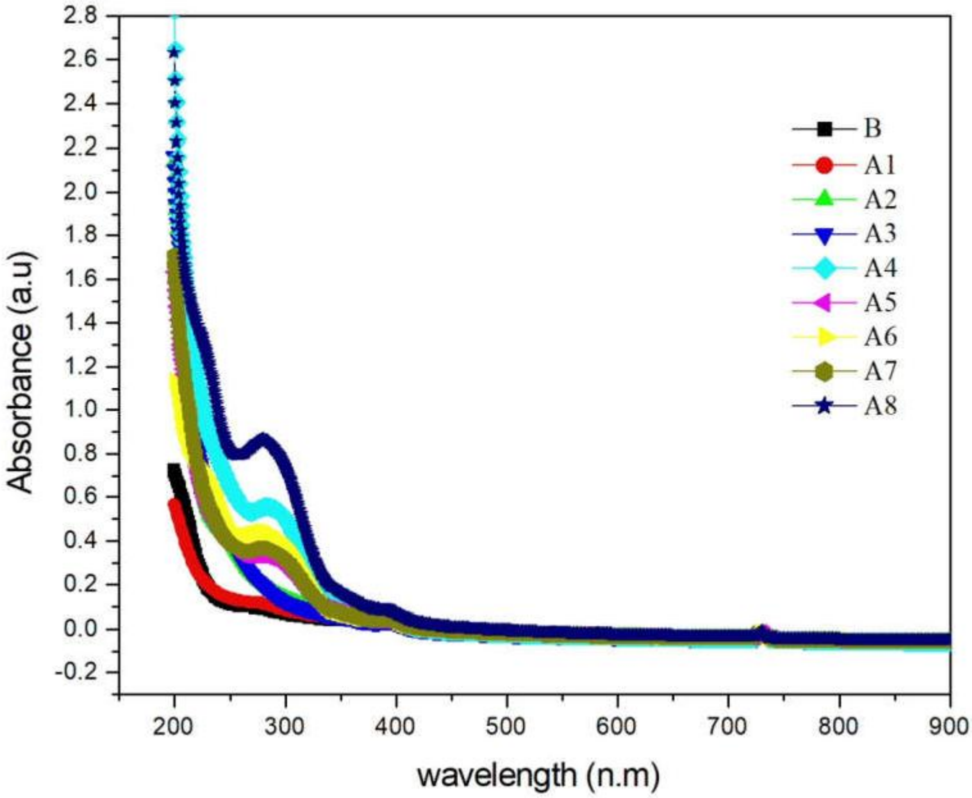
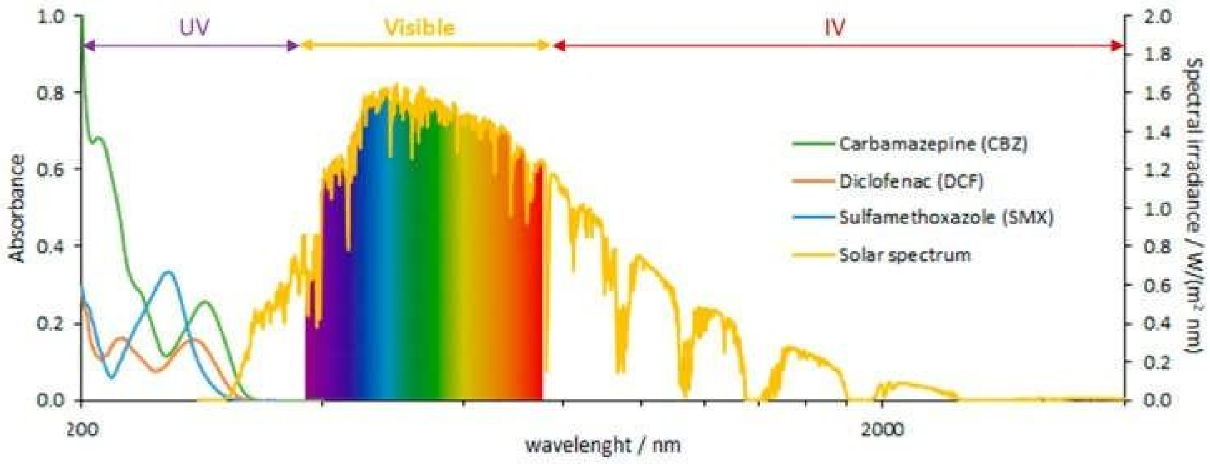


Figure.3.UV-Visible spectrum degradation under the various concentration



UV absorption spectra of CBZ, DCF, and SMX (5 mg/L solutions in inorganic matrix at pH 7.1) versus sunlight spectrum at sea level

Conclusion

Photocatalytic degradation of pharmaceuticl 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 photocatalyic 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 o adsorb pharmaceutical on heir surfaces. Experimental results conclude that Manganese nanoparticle is a very efficient. Photocatalyst for the photo degradation of pharmaceutical waste water.

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