STUDIES ON PHOTOCATALYTIC DEGRADATION OF DICLOFENAC USING NANO AMORPHOUS MnO_2 AS A PHOTOCATALYST AN OVERVIEW

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Abstract: ***The increasing use of various drugs, recently their production goes up and along with that the problem of disposal of the unused drugs and effluents produced during production has creating an environmental problem. The adverse effects of these pollutant drugs and their organic effluents in water bodies have been the issue of concern for ecology of living system. As these chemical materials gets accumulated in the water bodies and decomposes slowly by consuming the dissolved oxygen from the aqueous medium and increases the chemical oxygen demand. So, in this regard various methods have been developed to control the amount of such material in water bodies such as chemical oxidation and irradiation by UV-light and microwave. However, that is not sufficient to reduce the solid effluent in the industrial production which releases in the normal water bodies. In this context the development of photo-sensitive catalyst for degradation of these pollutants is a promising solution for water treatment. A Nano amorphous MnO_2 photocatalyst for degradation of diclofenac has been used and studied for various conditions of the aqueous medium. It was found to be a cheap and easy way to decompose the diclofenac and similar pollutants in the aqueous medium and could be used for treatment of waste water.***

Keywords: Photocatalysis, Diclofenac, Nano MnO_2, Manganese Dioxide, Photocatalyst, Degradation.

I. INTRODUCTION:

The environmental pollution by chemicals such as medicinal drugs has become a serious problem and a severe threat to the ecosystem. Many organic drugs and pesticides like BHC (hexachlorebenzene), dicofol and cypermethrin are well known for their toxicity and biological accumulation. These drugs disposed when unused and the effluents produced during their production causes environmental problem. These materials get accumulated in the water bodies and decomposes slowly by consuming dissolved oxygen by increasing chemical oxygen demand and solid waste material.

By considering the adverse effects of these drugs and load of organic effluents in water bodies, many methods have been developed to protect water resources. In this regard, various techniques have been developed to degrade the drugs in water bodies such as chemical oxidation methods, non-classical method like sonolysis or irradiation with UV-light and microwave [1].

Effluent treatment is one of the key processes in industrial production. Because of inadequate techniques of waste treatments and waste management there is increased solid load of effluent.

In this context, development of a visible light-responsive photocatalyst for degradation of pollutants is a suitable solution for water treatment. Efforts have been made on the development of visible light responsive TiO_2 [2].

Advanced oxidation-reduction processes have been considered as an effective way to degrade wide variety of contaminants such as pharmaceuticals. Efficiency of these processes mainly depends upon the ability of the oxidant to form free radicals and it is possible with the help of photocatalyts. Photocatalytic oxidation would be a promising way for degradation of organic pollutants in waste water treatment [3].

With the onset of the environmental crisis, several researches were conducted to improve the technologies to terminate the pollutants. One of those technologies which have shown potential is the use of photocatalyst TiO_2 to decompose the organic pollutants in wastewater. Along with TiO_2 the MnO_2 photocatalyst also shows remarkable capability of decomposing pollutants such as acid orange II under visible light. But simple MnO_2 suffers rapid capacity fade during cycling process. So, developing and studying nano structured or doped MnO_2 as a photocatalyst would be a better option [4].

Non-biodegradable compounds present in wastewater are of concern all over the world. Pharmaceutical industries dispose drugs and other intermediates in the water bodies like river, creek or sea. High E-factor of these processes also makes the pharmaceutical waste an issue of concern in terms of environmental regulations and norms. Even though the quantity of these drugs in the environment water is less, their continuous addition and accumulation may result in a potential risk in future about their degradation and removal.

Diclofenac (DCF), 2-[2, 6-(dichlorophenyl) amino]phenylacetic acid, is a non-steroidal anti-inflammatory drug (NSAD) most commonly used to treat inflammatory pains associated with different rheumatic and non-rheumatic diseases. It is one of the most popular antiphlogistics drugs which produced worldwide. It has been found that these drugs are ubiquitously present in aquatic environment as they are non-biodegradable. In aquatic environment like river and surface waters, diclofenac is one of the most frequently detected pharmaceutical drugs. Even at low concentrations, this drug has adverse effect on aquatic life [5].

Photocatalysis is a promising way for the degradation of various organic molecules like pesticides, drugs, dyes etc. Photocatalysis does not require any expensive oxidizing material and the catalysts are generally non-hazardous and need very small quantity. Photocatalysis process requires UV/Visible light and the oxidation is sure and indiscriminate leading to the mineralization of the majority of organic pollutants present in wastewater. The limitation of the rate of photocatalytic degradation is mainly due to the recombination of photogenerated electron-hole (e^--h^+) pairs. Several methodologies have been used to reduce the e^--h^+ recombination in photocatalytic processes. It can be achieved by doping metal ions into the lattice of the commonly used photocatalysts such as TiO_2 [6, 7].

This article is an overview of the studies on photocatalytic degradation of diclofenac using nano amorphous MnO_2 as a photocatalyst in aqueous solution.

II. EXPERIMENTAL:

2.1 Procedure:

In the experimental procedure, a stock solution of diclofenac (50 ppm) was prepared with distilled water which was diluted to the desired concentrations. The experimental setup was simple handmade assembly consists of a 100 ml glass immersion photoreactor fitted with a magnetic stirrer and an UV fluorescent tube (16 W) as the light source. Known weight of catalysts is added to the solution and mixture is sonicated for 10 minutes in order to disperse catalyst in solution uniformly. The solution of diclofenac to be degraded was stirred in the dark for 30 minutes to establish the adsorption equilibrium. This concentration was recorded as the zero-time value and the solution was irradiated. Aliquots were taken at regular intervals, centrifuged and filtered through 0.45 μm membrane filter to analyse the percent degradation of the drug.

2.2 Formula:

% degradation of a diclofenac is calculated by using following equation (Equation no. 1)

$$\% \text{ Degradation} = \frac{(\text{Initial Concentration-Final Concentration})}{(\text{Initial Concentration})} \times 100$$

Equation 1: Calculation of percent degradation

2.3 Calibration Curve:

To calculate percentage degradation in various experimental conditions; calibration curve for absorbance vs. concentration was plotted (Figure no. 1). Various solutions (10, 20, 30 and 40 ppm) of diclofenac were prepared from stock solution (50 ppm).

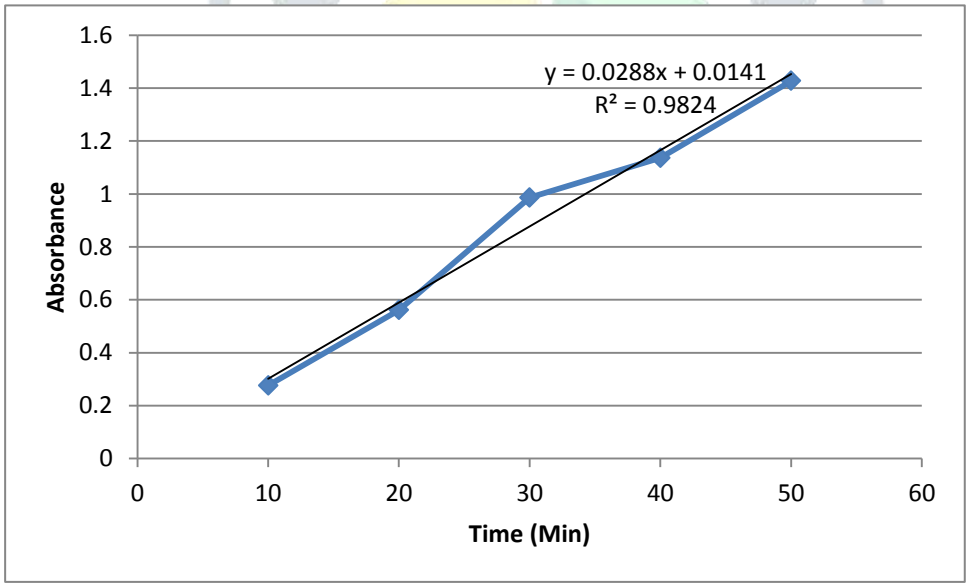

Figure 1: Calibration curve

R^2 value is calculated from MS-Excell which is 0.9824 (nearly equal to 1) and the equation obtained y = 0.0288 x + 0.0141 is used for the calculating concentrations.

III. RESULT AND DISCUSSION:

3.1 Effect of initial concentration of the diclofenac on photocatalytic degradation:

The photocatalytic degradation of diclofenac was carried out at different initial concentrations (30ppm – 50ppm). A graph of concentration v/s time is plotted. It has been observed from the graph that percentage degradation increases with increase in time (Figure no. 2).

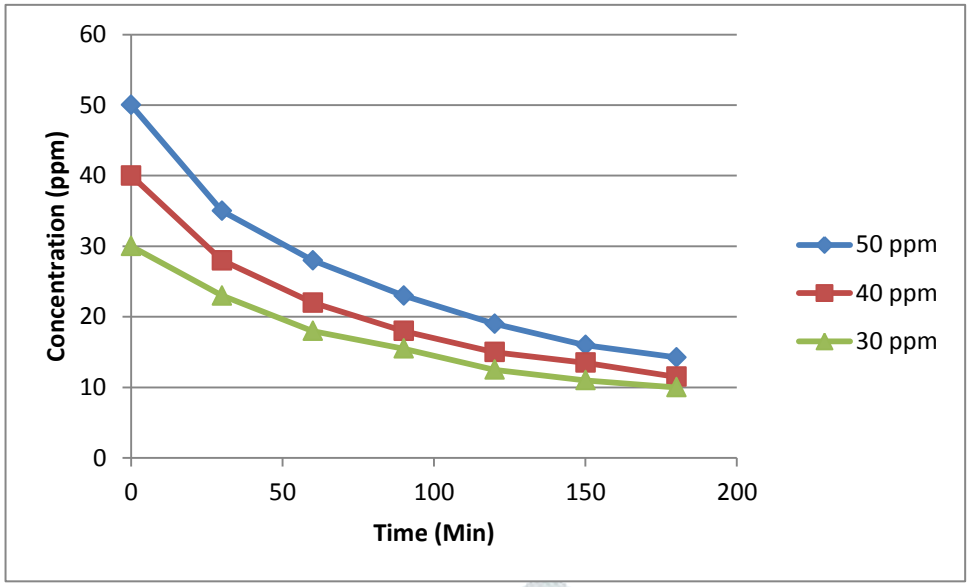

Figure 2: Effect of initial concentration on the degradation of diclofenac

From the graphs, it can be seen that as there is no such change in percentage degradation with various solutions, 50 ppm solution was used for the further studies. For initial concentration studies, no oxidants were used and it was carried out by using 0.1g of nano amorphous MnO_2 ($ANMnO_2$) catalyst.

3.2 Effect of catalyst loading on photocatalytic degradation of diclofenac:

In order to study effect of catalyst loading, photocatalytic degradation of diclofenac was carried out by using 0.1, 0.2 and 0.3g/l of catalyst. It was observed that with increase in catalysis loading, percentage degradation increases (Figure no. 3).

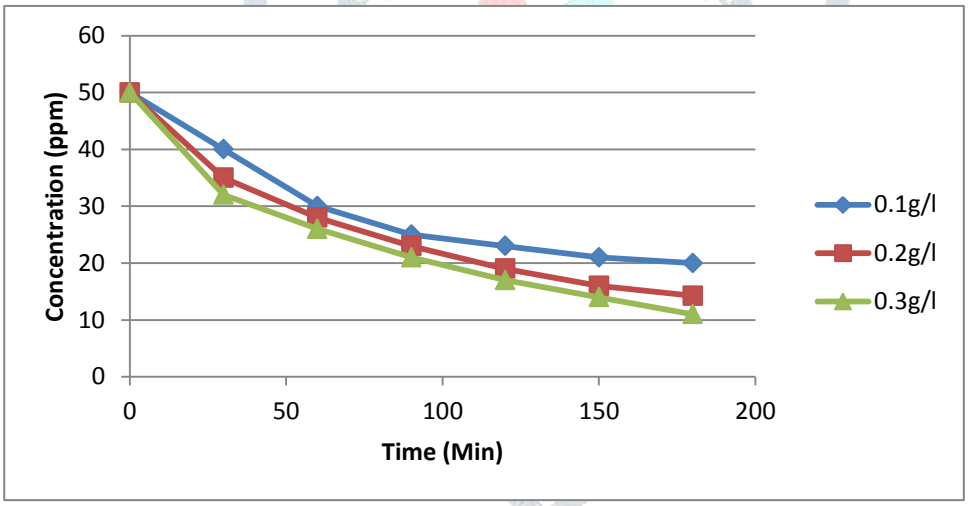

Figure 3: Effect of catalyst loading on % degradation of diclofenac

0.3g/l showed maximum degradation and because of this optimum amount is used for the further degradation studies.

3.3 Effect of oxidant on photocatalytic degradation of diclofenac:

Effect of oxidant always has profound effect on photocatalytic degradation. So, hydrogen peroxide and TBHP (Ter-Butyl Hydro-Peroxide) were used as oxidants for degradation. Manganese dioxide decomposes hydrogen peroxide to water and oxygen. It is well known from the literature that aerated aqueous solution having dissolved oxygen helps photocatalytic oxidation (Figure no. 4).

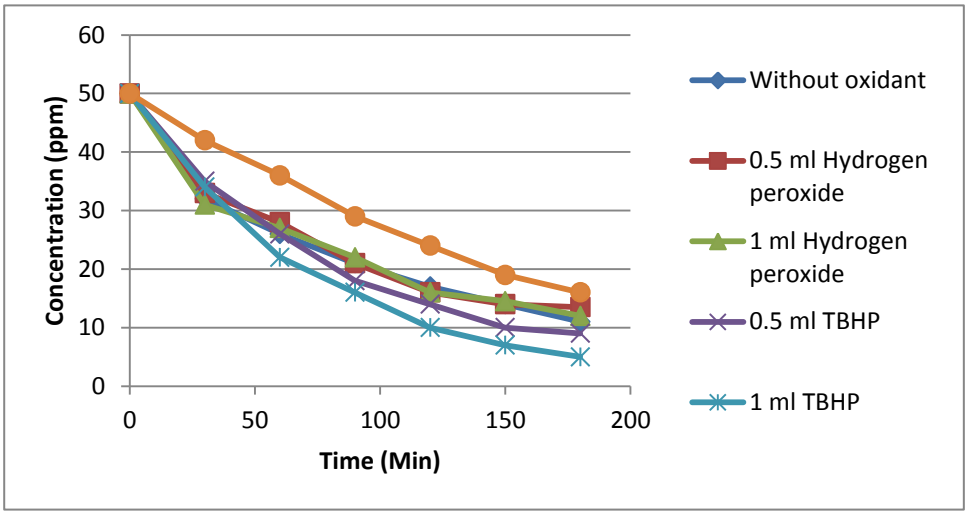

Figure 4: Effect of oxidant on photocatalytic degradation of diclofenac

When hydrogen peroxide was used as oxidant (0.5ml, 1 ml), with increase in its amount, % degradation increased in some amount. TBHP when used as oxidant, degradation of diclofenac was comparatively more than in H_2O_2. It may because of presence of more hydroxyl radical in solution.

IV. CONCLUSIONS:

Photocatalytic degradation of diclofenac shows appreciable results with nano amorphous MnO_2 as a photocatalyst in aqueous medium.

TBHP suitable oxidant for photocatalytic degradation process. It is cheap and makes the process easy.

A small quantity of the catalyst (0.3g) is enough for the degradation of diclofenac and it may be reusable.

V. ACKNOWLEDGEMENT:

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VI. REFERENCES:

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