

Degradation of Pesticide from Aqueous Solution Using Photocatalytic Composite

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Abstract: Due to an increase in pesticide usage in agriculture worldwide, there exists a need for the development of an effective pollutant removal process for pesticides in agricultural run-off water. It is advantageous for the treatment to not require the addition of treatment chemicals which could potentially have a harmful effect on the environment. A reactor utilizes a photocatalyst Titanium Dioxide (TiO₂) with the exposure to UV-light for treatment of insecticide chlorpyrifos. The catalyst was characterized with XRD (X-ray Diffraction) and SEM (Scanning Electron Microscope). The peaks appeared at 2θ value indicates the formation of anatase phase of TiO₂. At the higher calcination temperatures, the larger particle size with spherical morphology is obtained. Grain boundaries are observed in the SEM micrographs of the samples. Energy Dispersive X-ray shows the chemical constituents of Ti and O present in the samples. And there was no impurity peak is in the EDAX spectra. Photocatalytic degradation of Chlorpyrifos in aqueous phase in the presence of artificial UV-light by using photocatalyst TiO₂ is observed. The degradation of insecticide (chlorpyrifos) was investigated in terms of reduction in COD. The effect of the catalyst in the dark was nearly 20% i.e., in the absence of UV light. Experiments were performed in the presence of UV light at optimized condition. The effect of catalyst loading and pH was determined. In this case the concentration of the catalyst was optimized at 4g/L and pH value at 6, where around 61% degradation of the insecticide was observed.

Keywords: Titanium Dioxide; Ultraviolet light; X-ray diffraction; Scanning electron microscope; Insecticide; Chlorpyrifos

1. Introduction

A pesticide is any substance used to kill, repel, or control certain forms of plant or animal life that are considered to be pests [1]. Most pesticides are non-selective; they are also harmful to ecological systems as well [2]. Most pesticides are resistant to chemical and/or photochemical degradation under typical environmental conditions [3]. Pesticides are designed to control pests, but they can also be toxic (poisonous) to desirable plants and animals, including human. These plant protecting agents called pesticides are environmentally harmful waste [4]. The possibility of entry of pesticides into water sources are follows: (i) industrial waste or effluents discharged directly into water (ii) seepage from buried toxic wastes into water supplies and (iii) contamination of surface and groundwater directly or from runoff during spraying operations. They are also major sources for water pollution [5]. They can enter into the environment by several routes such as spraying, soil and storage, as well as wastewater discharge. Moreover, these compounds can contaminate surface and groundwater, posing a risk to wildlife and human health, due to the potential toxicity of these compounds.

The amount of pesticides routinely applied to agricultural commodities has dramatically increased in recent years which have led to serious concerns about the increasing risks to human health. The use and production of several organic pesticides has continuously increased since introduction of DDT in the early 1940s, giving as a result a great family of organo chlorine pesticides [5,6].

Chlorpyrifos is one of the world's most widely used organophosphorus insecticide in agriculture [7]. It was introduced in 1965 by Dow Chemical Company and is known by many trade names, including Dursban and

Lorsban. It acts on the nervous system of insects by inhibiting acetylcholinesterase [8].

Chlorpyrifos is moderately toxic to humans, and exposure has been linked to neurological effects, persistent developmental disorders, and autoimmune disorders. Exposure during pregnancy retards the mental development of children. In agriculture, it remains "one of the most widely used organophosphate insecticides", according to the United States Environmental Protection Agency (EPA) [9]. Chlorpyrifos (CP) is a crystalline organophosphate insecticide that is widely used to control pests. As a result of crop and non-crop usage, chlorpyrifos residues may be present in a variety of environmental matrices, e.g., crops and crop products, air, soil and water [10].

2. Methods

2.1 Chemicals

One of the most commonly used pesticides is chlorpyrifos, or *O,O*-diethyl *O*-3,5,6-trichloropyridin-2-yl phosphorothioate (Figure 1) which is moderately toxic to humans, but cumulative exposure can produce typical symptoms of acute poisoning by organophosphates, affecting the central nervous, cardiovascular and respiratory systems [47].

Chlorpyrifos (IUPAC name: *O,O*-diethyl *O*-3,5,6-trichloropyridin-2-yl phosphorothioate) is a crystalline organophosphate insecticide [7]. Chlorpyrifos – 1.5% D.P was purchased from Arumugam Agro Agency, West Tambaram. The prepared stock solution was used throughout the experiment. Chlorpyrifos is a complex molecule containing chlorine, nitrogen, phosphorous, sulfur, oxygen, hydrogen, and carbon.

Empirical formula - $C_9H_{11}Cl_3NO_3PS$

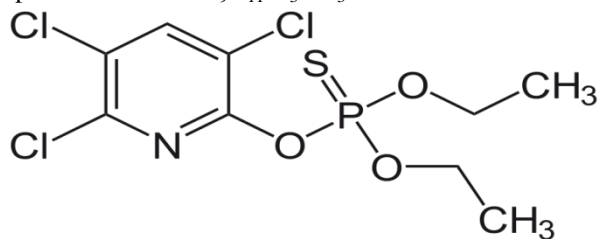


Figure 1: Chlorpyrifos molecular structure.

2.2 Photocatalyst

A catalyst TiO_2 was synthesised using different chemicals Commercial Activated Carbon(CAC), Ferrous Nitrate[$Fe(NO_3)_3 \cdot 9H_2O$], Ethanol, Ethylene Glycol, Titanium Isopropoxide, 2-propanol, Distilled Water and with different apparatus Grinder, Sieve (300 μm), Oven, Muffle furnace, Sonicator, Micro pipette. The prepared catalyst was characterized using X-ray Powder Diffraction(XRD) and Scanning Electron

Microscope(SEM). The peaks appeared at 2θ value ranging the diffraction peak at 2θ with 11.07° , 12.33° , 12.73° , 25.34° , 37.61° , 48.00° corresponds to the crystal planes of (71), (67), (62), (100), (28) and (31) respectively, indicates the formation of anatase phase of TiO_2 . The average size of the particles was calculated using Debye-Scherrer's formula:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

The crystallite size of a catalyst ranges between 0.34nm to 7.4nm. At the higher calcination temperatures, the larger particle size with spherical morphology is obtained. Grain boundaries are clearly observed in the SEM micrographs of the samples. Energy Dispersive X ray shows the chemical constituents of Ti and O present in the samples. And it shows that there was no impurity peak is in the EDAX spectra.

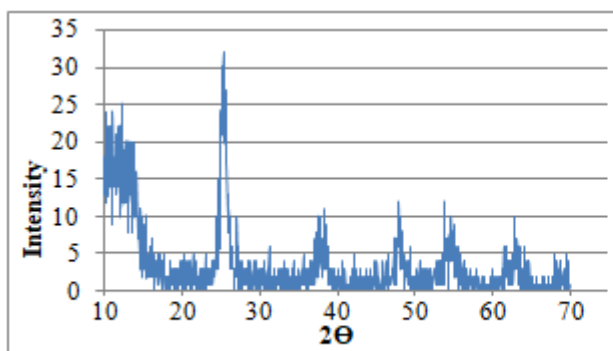


Figure 2(a): X-ray diffraction graph of TiO_2

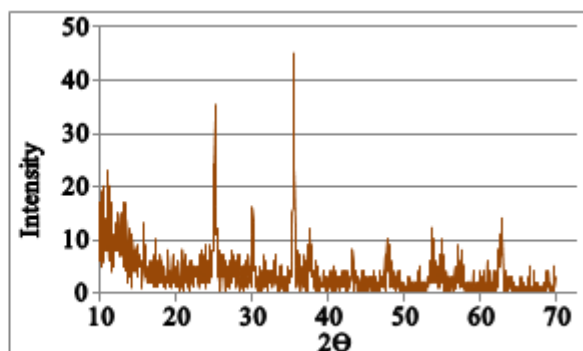
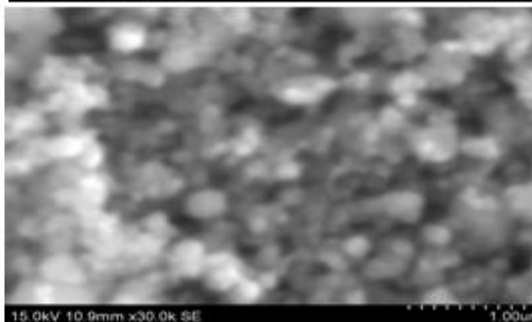
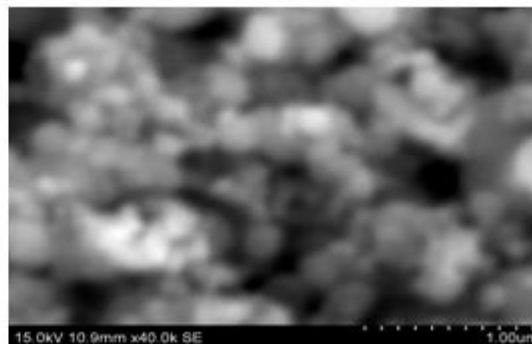
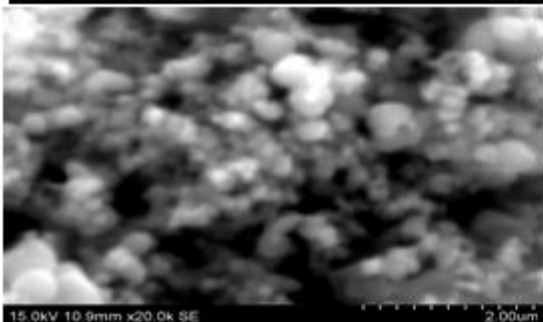
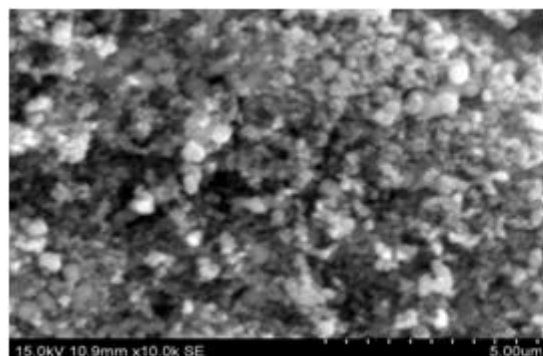


Figure 2(b): X-ray diffraction graph of Fe-C/ TiO_2



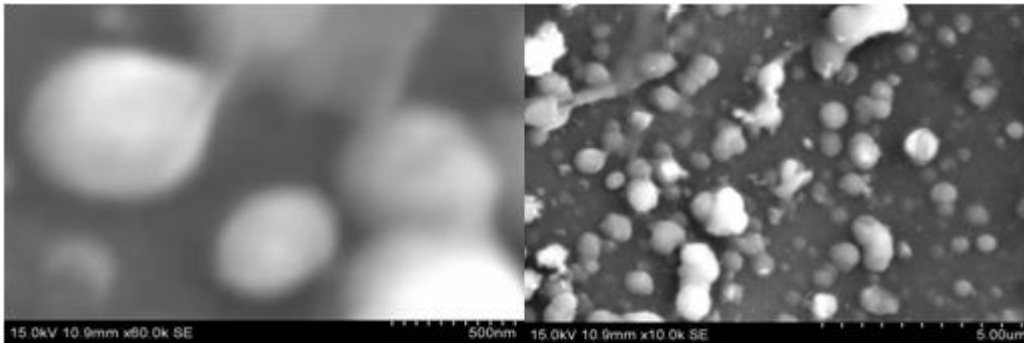


Figure 3(a): SEM images for Catalyst I, TiO₂

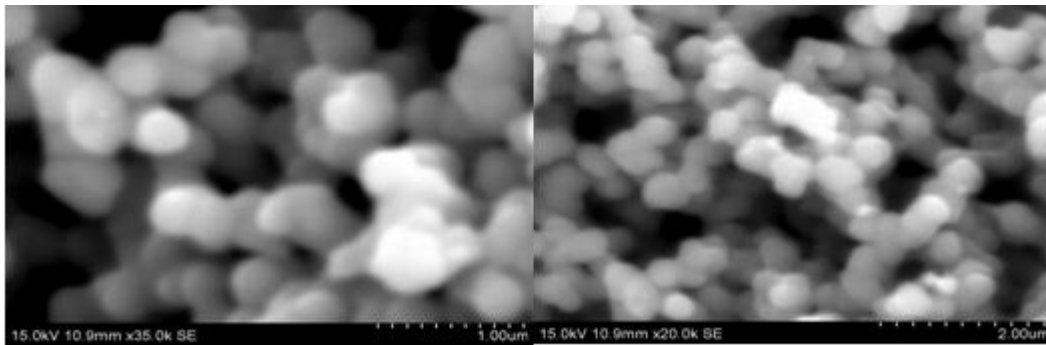


Figure 3(b): SEM images for Catalyst II, Fe-C/TiO₂

The morphology and structure of the particles were investigated using field emission scanning electron microscopy. It was observed that, at the higher calcination temperatures, the larger particle size with spherical morphology is obtained. Grain boundaries are clearly

observed in the SEM micrographs of the samples calcined at the high temperatures. Agglomeration was evident in all samples, with larger, more consolidated agglomerates.

EDAX Analysis

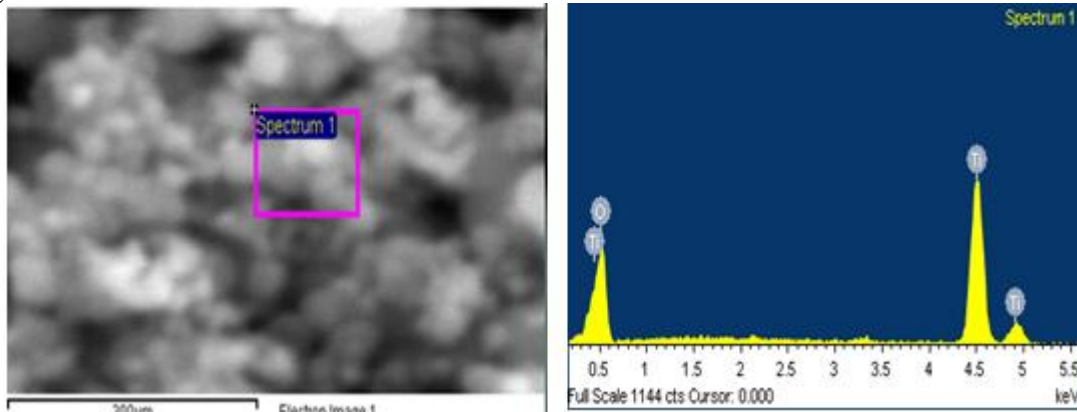


Figure 4(a): EDAX spectrum 1 of Catalyst I, TiO₂

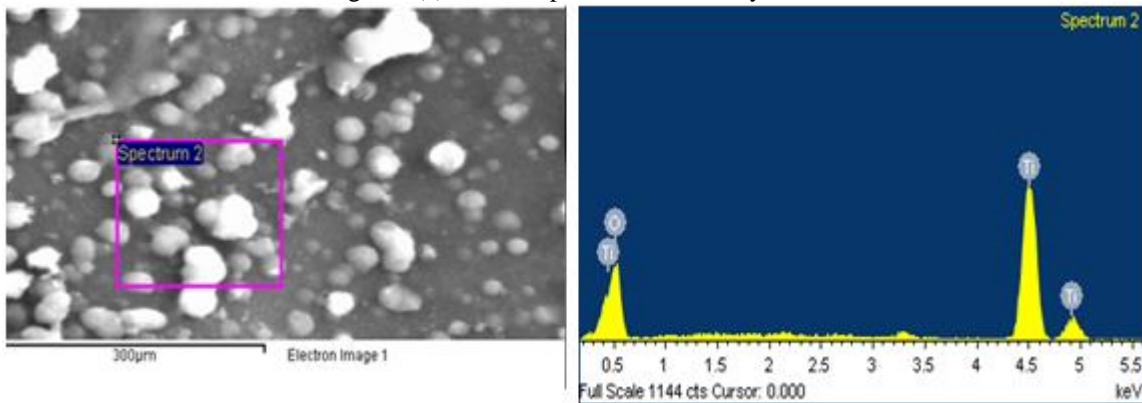


Figure 4(b): EDAX spectrum 2 of Catalyst II, TiO₂

EDAX or EDX or EDS, Electron dispersive X ray spectroscopy is an analytical technique used for elemental analysis or chemical characterization of the sample. It relies on an interaction of some source of Xray excitation.

Figure 4(a) and figure 4(b) shows the EDAX spectrum of as prepared nano TiO₂. The spectrum shows the chemical constituents of Ti and O present in the samples. There is no impurity peak is observed in the EDAX spectra. This confirms that the prepared samples are in pure form.

SEM image displayed the uniform morphology in the form of nano clusters. EDAX spectra confirm the samples are in pure form.

2.3 Photoreactor

The photocatalytic experiments was equipped with TL 6W BLB UV tubes (Philips) attached inside the quartz envelope having a wavelength less than 400nm. The reactor having 70mm diameter and 360mm in height made up of borosil glass was placed inside the chamber. The reactor has a beaker of capacity 500ml. The aerator and the UV lamp is connected to the power switch, in such a way that it can be controlled(off/on) manually. The aerator supply air into the beaker at a constant rate. The aerator is used for the circulation of the sample and the catalyst inside the glass beaker. It is covered with a box painted in black inside and outside, so that the light is trap inside.

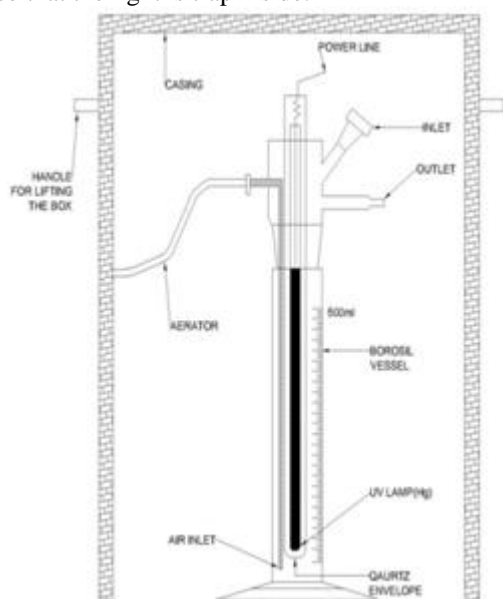


Figure 5: Experimental setup of: UV Chamber, Reactor, UV Lamps, Aerator.

3. Results and Discussions

3.1 Initial value

The pH of the prepared sample solution pesticide (chlorpyrifos) was measured using the pH paper and the pH meter. The pH paper reads the value of 7.0 and using the pH meter the stock solution has value of 6.78. The initial COD value of the synthesized stock solutions was measured using COD digestion apparatus and titrating it. The initial COD of the stock solution(chlorpyrifos) is 312 mg/l.

3.2 Preliminary Studies

The insecticide was stirred with a catalyst dose of 1g/L in the dark i.e., sample was stirred without the presence of UV light radiations. The sample was taken out at an interval of 1 hour for COD analysis. The sample was analysed to estimate the percentage of COD reduction and it was found to be nearly 20%(Figure 3). Addition of catalyst TiO₂ leads to monolayer formation on the surface. As soon as catalyst was added, insecticide from solution was adsorbed on the surface, thus leads to decrease in COD values in the solution. After monolayer formation, no free active sites were available for further adsorption so no further reduction in COD was observed. Thus decrease in COD was due to the adsorption of pesticide(chlorpyrifos).

The stock solution was taken in reactor beaker and was exposed under UV light in a closed container. At regular interval of time the sample was tested for COD. From the figure 3, we found that the degradation of the insecticide using TiO₂ with UV light showed the reduction in COD. As the duration of sample solution exposed increases the effect of the catalyst TiO₂ and the light increases. The degradation of the insecticide using TiO₂ with UV light showed nearly 35% reduction in COD, thus assuming that adsorption-desorption of substrate and reaction intermediate is relatively slow as compared to the formation of electron/hole pairs.

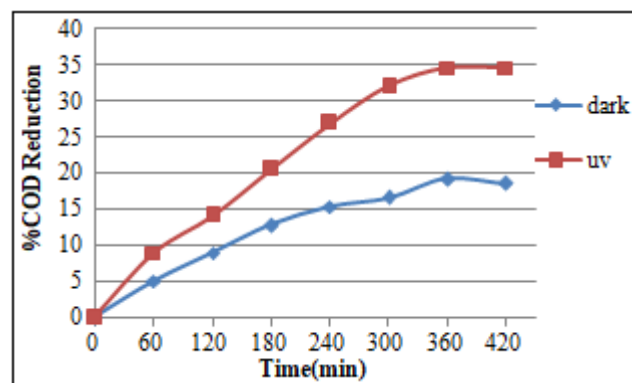


Figure 6: Comparison between the presence and absence of UV light

3.3 Effect of Catalyst

The effect of catalyst dose on the degradation of insecticide(chlorpyrifos), TiO₂ was varied from 1.0 g/L to 7.0 g/L. UV light was introduced in this process. It was observed that the degradation rate of pesticide increases with increased in catalyst concentration and it comes to constant at a certain level as shown in Figure 4 and then decreased after one particular optimum dose. This is due to the number of photons adsorbed in UV light and the number of pollutants molecules absorbed on the surface of catalyst are increased owing to increase in rate of photocatalytic reaction.

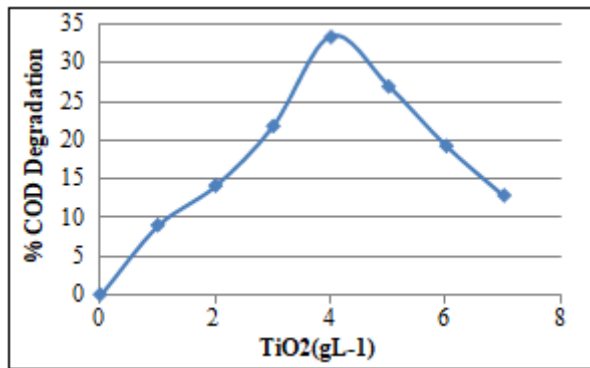


Figure 7: Effect of Catalyst Concentration on pesticide(chlorpyrifos)

The decrease in degradation is due to the decrease in the surface area of catalyst due to aggregation of TiO₂. The highest COD reduction was observed at the catalyst dose of 4 g/L, after this the COD reduction decreased substantially.

3.4 Effect of pH

Experiments were carried out at different pH values i.e., 1 to 8 for studying the photodegradation rate shown in the figure 5. At optimum dose of catalyst, the degradation rate of the insecticide reaches nearly 61% at a pH value of 6. The pH value is adjusted with the help of 0.1N H₂SO₄ and 0.1N NaOH. The initial pH value increases from 1.0 to 6.0 and decreases thereafter in basic medium. This is due to the fact that TiO₂ shows an amphoteric character so that either positive or a negative charge can be developed on its surface.

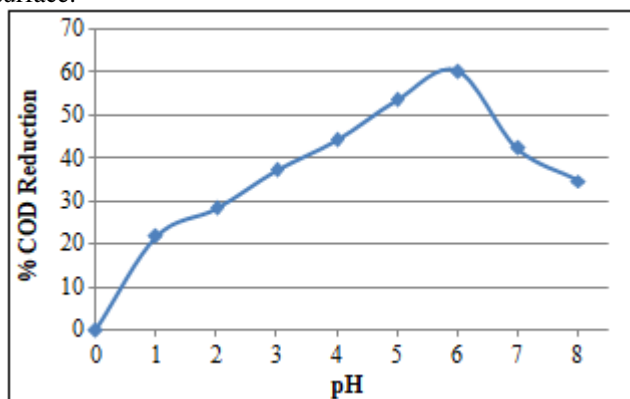


Figure 8: Effect of pH on pesticide(chlorpyrifos)

From the above figure, it was observed that degradation of insecticide increases to some certain point or pH i.e., 6 and then decreases substantially.

4. Conclusions

The formation of the TiO₂ nanoparticles was confirmed by powder X-ray diffraction (XRD). The peaks appeared at 2θ value showed the crystalline nature, the diffraction peak at 2θ with corresponds to the intensity indicates the presence or formation of anatase phase of TiO₂. The size and morphology of the samples were characterized using scanning electron microscopy (SEM). The spherical shaped particles were confirmed through the SEM analysis. Agglomeration was evident in the samples, with large, consolidated agglomerates. The chemicals of Ti and O were found in the

samples. There is no impurity peak was observed in the EDAX spectra. This confirms that the prepared samples are in pure form.

The initial COD value of the sample was found 312mg/l and pH value 6.78. The degradation of insecticide using TiO₂ in the dark (without UV light) was found at 20% COD reduction and degradation using TiO₂ with UV light showed nearly 35% reduction in COD. The catalyst loading was observed and the optimum dosage was found to be at 4g/L. The effect of the pH was observed at an optimum dose of catalyst. The pH value of the sample was varied/adjusted using 0.1N H₂SO₄ and 0.1N NaOH and the rate of degradation was nearly 61% at a pH of 6 and at a catalyst dose of 4g/L.

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