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PHOTODEGRADATION OF DIRECT YELLOW 50 DYE USING THE PHOTOCATALYST ZINC OXIDES UNDER ULTRA-VIOLET LIGHT

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Abstract

In this research photodegradation of direct yellow dye using zinc oxide as catalyst under ultra-violet light has been investigated. The concentration of photocatalyst has been found to be 0.003 M, while the results reveal that, the best amount H2O2 can be used as 10 ml, furthermore, pH to run the reaction of photodegradation was observed at acidic media. It has been found that the direct yellow dye can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band, the cleavage of N=N leads to break down the dye.

Keywords: Photocatalytic Degradation; Direct Yellow 50 Dyes; Zinc Oxide Catalyst.

1. Introduction

The photocatalytic degradation process has emerged as powerful technique to generate clean environment, it has been found that it is the most efficient process for the degradation of dyes, because of the ability of this method to completely mineralize the target pollutants [1-3]. Heterogeneous photocatalysis reactions are activated by absorption of a photon with sufficient energy (equals or higher than the band-gap energy (E_{bg}) of the catalyst).The absorption process leads to promotion of an electron (e^-) from the valence band of the semiconductor photocatalyst to the conduction band, thus generating a hole (h^+) in the valence band.[4-7] (the schematic diagram of the process is presented in Scheme 1 [8].
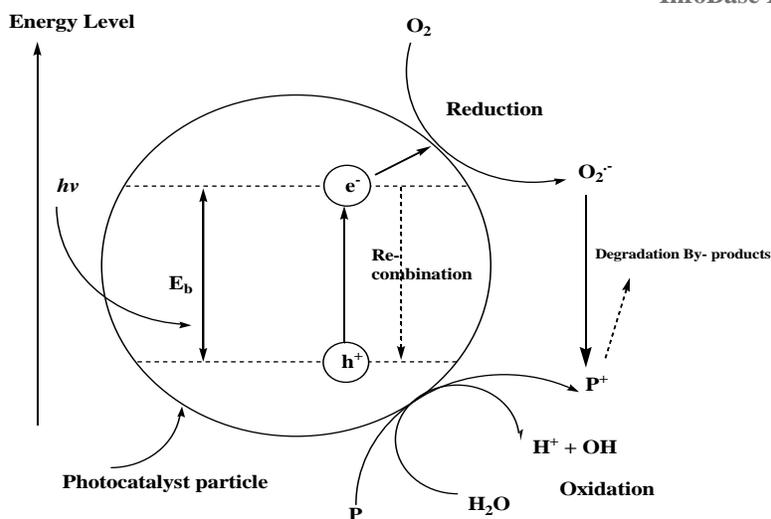
Scheme 1: Mechanism of electron-hole pair formation in a photocatalyst particle in the presence of dye in water [8].

It has been found that the recombination of the electron and the hole must be prevented as much as possible if a photocatalyzed reaction must be favored. The ultimate goal of the process is to proceed an electron towards the acceptor molecules such as O_2 adsorbed on the photocatalyst-surface or dissolved in water, reducing it to superoxide radical anion $O_2^{-\bullet}$ to produce a reduced product, whereas positive photoholes are transferred to donor molecules to produce an oxidized product. The photogenerated holes can oxidize the organic molecule to form R^+, or react with OH^- or H_2O oxidizing them into $OH^\bullet$ radicals. It has been reported that the resulting $^\bullet OH$ radical, being a very strong oxidizing agent (standard redox potential +2.8 V) can oxidize most azo dyes to the mineral end-products [9]. This work studies the photodegradation process to break down the azo dye Direct Yellow 50, which is widely used in textile industries for colouring of cotton and synthetic fabric materials.

Furthermore, the aim of this work to degradation the Direct yellow 50 dye using the photocatalyst ZnO. The photocatalytic degradation of Direct Yellow has been studied using $CaZnO_2$ nanoparticle [10], TiO_2 and Fe^{3+}-doped TiO_2 nanoparticles [11] while G. E. A. Mahmoud et al. studied degradation of the dye by Fenton and photo-Fenton processes [12]. In addition, K. Diouri et al studied the adsorption of the dye onto Marble powder sorbents [13].

2. Materials and Methods

1) Photolytic cylindrical pyrex cell volume 75 ml fitted with water jacked for temperature control. The cell window was made from quartz and the cell supplied with two opens of 0.5 cm in diameter used for gas purging and sampling processes.
2) The ultraviolet light source was deuterium lamp, 1Ampir, from England.
3) pH meter type Philips PW 9420.
4) Centrifuge type (REMI R&C Laboratory centrifuge), England.
5) UV-Visible spectrophotometer type Shimadzu 1650, Japan.
6) Analytical balance type (Sartorius BL 210 S).

2.1. Dye Solution

Direct Yellow 50 (DY50)) was obtained from Ciba-Geigy (Fig. 1). 50 ppm stock solution of dye was prepared by dissolving 50 mg of the dye in 1000 ml deionized water. Other further dilute solutions are prepared by dilution of stock solution.
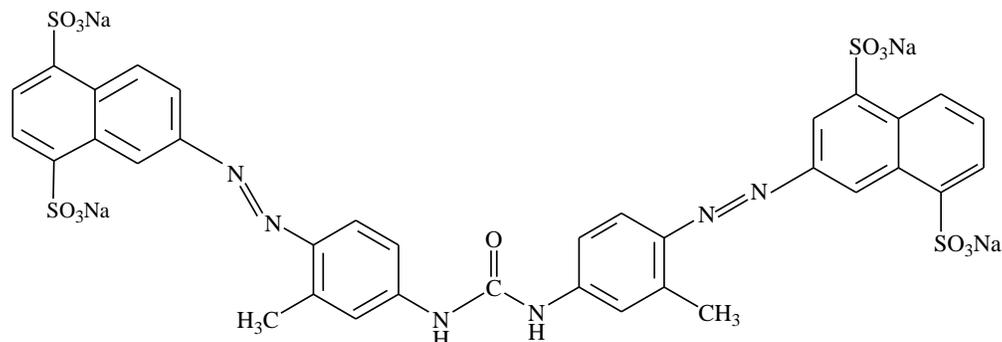

Figure 1: Structure of Direct yellow 50

2.2. Procedure

The photolysis experiments were carried out in a photolytic cylindrical Pyrex cell (volume 75ml) which is diagrammatically fitted with water jacket for temperature control. The cell is supplied with two openings of (0.5 cm) in diameter and these were used for gas purging and sampling processes.

Zinc Oxide powder was added to an aqueous solution of known concentration of direct yellow 50 dye solution mixture. Magnetically, stirred reaction mixture in photo reactor was irradiated with deuterium lamp. Five milliliter samples were taken at various irradiation time intervals. The Zinc oxide was removed from the samples by using centrifuge. Photodegradation products were identified by UV. Visible- spectrophotometer. The temperature of reaction was at 25˚C. The estimation of decolorization degree (D %) was done according to the following equation :

$$\%D = \frac{C_0 - C_t}{C_0} \times 100$$

Where %D: The percentage degradation, C_0: The initial concentration (mg/l) at zero time, C_t: The final concentration (mg/l) at any time.

3.   Results and Discussion

3.1. Absorption Spectrum of Dye

Fig. 2 shows the absorption spectrum of Direct Yellow dye, Ʌ max has been determined from the spectrum at 298 nm at 25 ˚C.
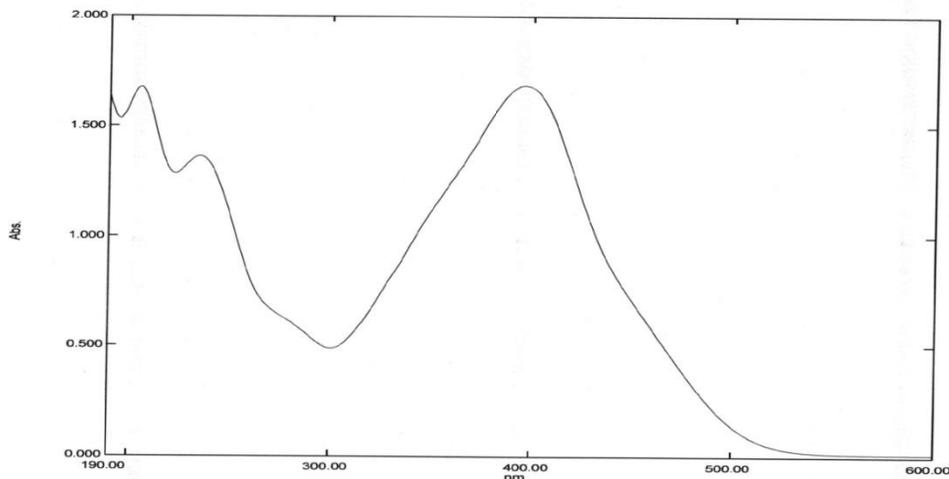
Figure 2: Absorption spectrum of direct yellow 50 in distilled water

3.2. Calibration Curve

Calibration curve has been done by measuring the absorbance of dye at different concentrations; table 1 shows the values of absorbance at 398 nm for different prepared concentrations of dye. It has been found that the concentration at 50 ppm is the best concentration to use in latter experiments, as greater this concentration, deviation in straight line which can be produced from the plot of absorbance of dye against concentration, as shows in fig.3.

Table 1: values of absorbance of direct yellow dye at 398 nm of different concentrations

Con. ppm	5	10	15	20	25	30	35	40	45	50
Absorbance	0.130	0.283	0.463	0.665	0.790	0.936	1.082	1.27	1.463	1.688

In latter experiments, the absorbance values can be converted to the concentration by applying the equation which results from the relationship as mention above.
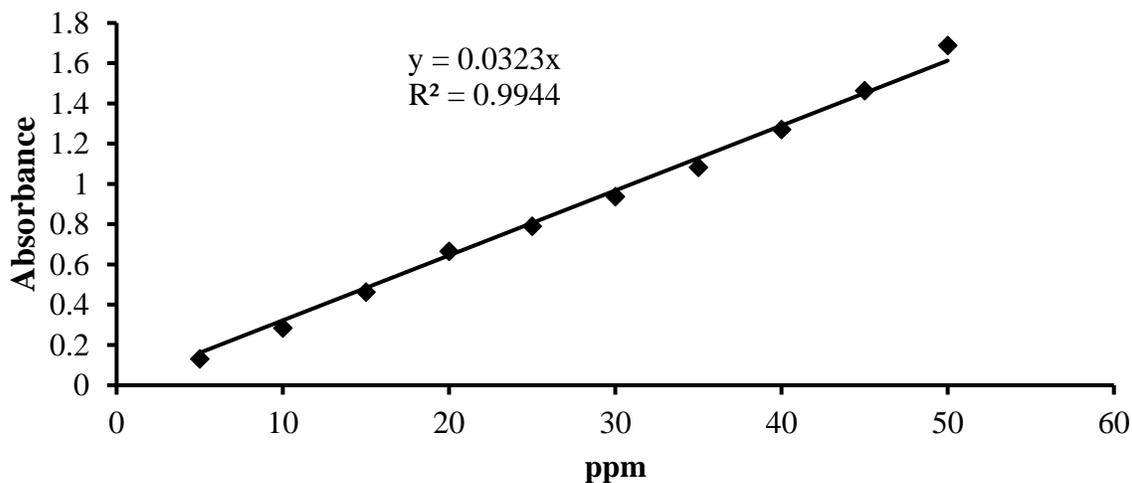

Figure 3: Calibration curve of concentration versus absorbance at 398nm

3.3. Effect of Catalyst Amount

Since the process of photodegradation of dye by using catalyst occurs on the surface of the catalyst, the effect of catalyst concentration on the photocatalytic degradation was conducted over a range of the catalyst amount from (0.001-0.005 g). As observed in fig.4 that the photodegradation of dye increased in different interval time, further increase in the catalyst concentration decreases the degradation, it is observed that the best concentration is (0.003 M) of the catalyst to use in the reaction of degradation so it fixed for subsequent experiments as shown in fig.4.
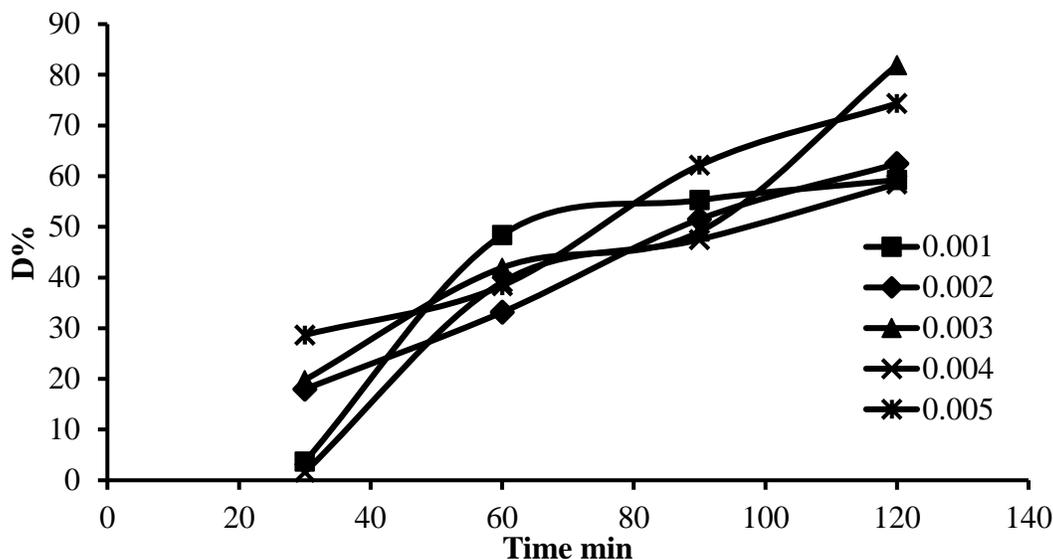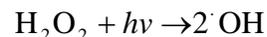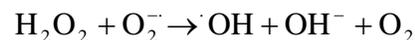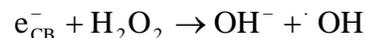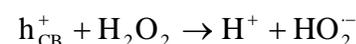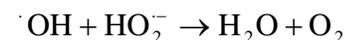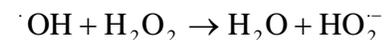

Figure 4: Relationship between the degradation percent of dye against time with using different amounts of catalyst ZnO

3.4. Effect of H_2O_2

The photodegradation process of dye 50 has been studied at different hydrogen peroxide (20 %) concentrations. for a fixed dye 50 and ZnO concentrations (50 ppm, 0.003 M) respectively , the following H_2O_2 concentration were tested: 2,4,6,8,10 ml (from 20% H_2O_2) , when the concentration increased from 2ml to 10 ml for interval range (30-120 min) the removal of dye color increased, which monitored by measuring the absorbance at 398 nm as it has been observed that the intensity band decreased as shown in the fig.5. [The figure shows values of concentrations of dye, which calculated from calibration curve equation] This could be explained that H_2O_2 increases the rate of hydroxyl radical formation by different ways: Firstly, it can be as an alternative electron acceptor to oxygen. Secondly; produce hydroxyl radical by the reduction of H_2O_2 at the conductance band or accepting an electron from superoxide. Thirdly; the self-decomposition by radiation will also results hydroxyl radical, thus inhibiting the electron-hole recombination at the semiconductor surface.

$$e_{CB}^{-} + H_2O_2 \rightarrow OH^{-} + ^{\cdot}OH$$

$$H_2O_2 + O_2^{\cdot -} \rightarrow ^{\cdot}OH + OH^{-} + O_2$$

$$H_2O_2 + hv \rightarrow 2^{\cdot}OH$$

At high concentration, the hydrogen peroxide adsorbed on the surface of the catalyst can effectively scavenge not only the photocatalytic formed hydroxyl radical but also the photogenerated holes (h_{CB}^{+}), which leads to inhibit the major way for generation of hydroxyl radical. [14-18]

$$^{\cdot}OH + H_2O_2 \rightarrow H_2O + HO_2^{\cdot -}$$

$$^{\cdot}OH + HO_2^{\cdot -} \rightarrow H_2O + O_2$$

$$h_{CB}^{+} + H_2O_2 \rightarrow H^{+} + HO_2^{\cdot -}$$

The results reveal that, the best H_2O_2 concentration can be taken as 10 ml as can see in the results shown in fig.5.
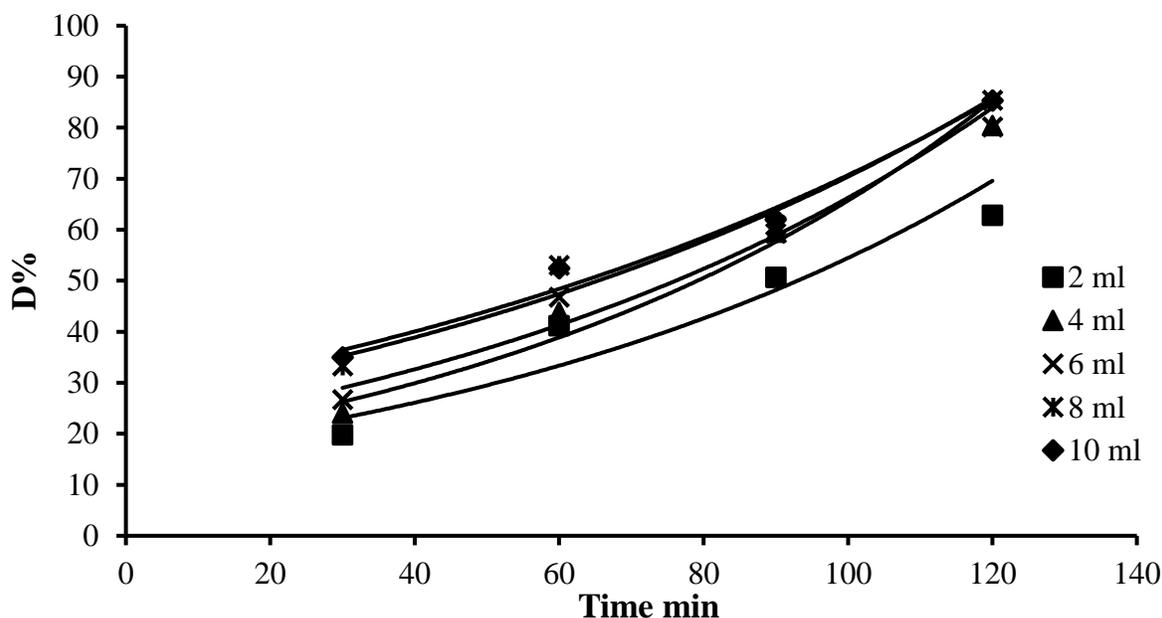
Figure 5: Relation between degradation percent of dye and time by using H_2O_2 as catalysts

3.5. Effect of pH

The photodegradation of dye 50 is conducted at different pH values (pH = 2-11) and the dye concentration 50 ppm, at catalyst loading of 0.003 M. the degradation of the dye at different pH media are shown in fig.6. The pH value influence the generation of hydroxyl radicals in photodegradation reaction of dye. At low pH value the photodegradation was higher than the degradation at high pH value. Solutions of 0.1M of sodium hydroxide (NaOH) and 0.1M HCl were used to adjust and maintain the pH levels. It has been found that the best result of

degradation of dye was observed at acidic media as can be shown in fig.6. The interpretation of pH effect on the efficiency of degradation of dye is a very difficult task because of its multiple roles. First, is belonged to the ionization state of the surface. The point of zero charge (pzc) for zinc oxide is at pH ~ 9.2 [19].

In acidic solution the pH is lower than pzc and hence the ZnO surface is positively charged.

$$pH \langle pzc : Zn - OH + H^+ \leftrightarrow ZnOH_2^+$$

In basic solution the surface is negatively charged as given in the following equation:

$$pH \rangle pzc : Zn - OH + OH^- \leftrightarrow ZnO^- + H_2O$$

In addition, the dye contain sulphonate group, so that hydrolyzed molecule behaves as anionic dye.

$$(dye - SO_3Na) \rightarrow (dye - SO_3)^- + Na^+$$

pH change can thus influence the adsorption of dye molecule onto the ZnO surface, an important step for the photocatalytic oxidation to take place. Second, hydroxyl radical can be formed by the reaction between hydroxide ions and positive holes. The positive holes are considered as the major oxidation species at low pH, while hydroxyl radical are considered as the predominant species at neutral or high pH levels.
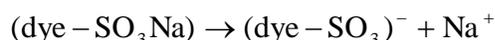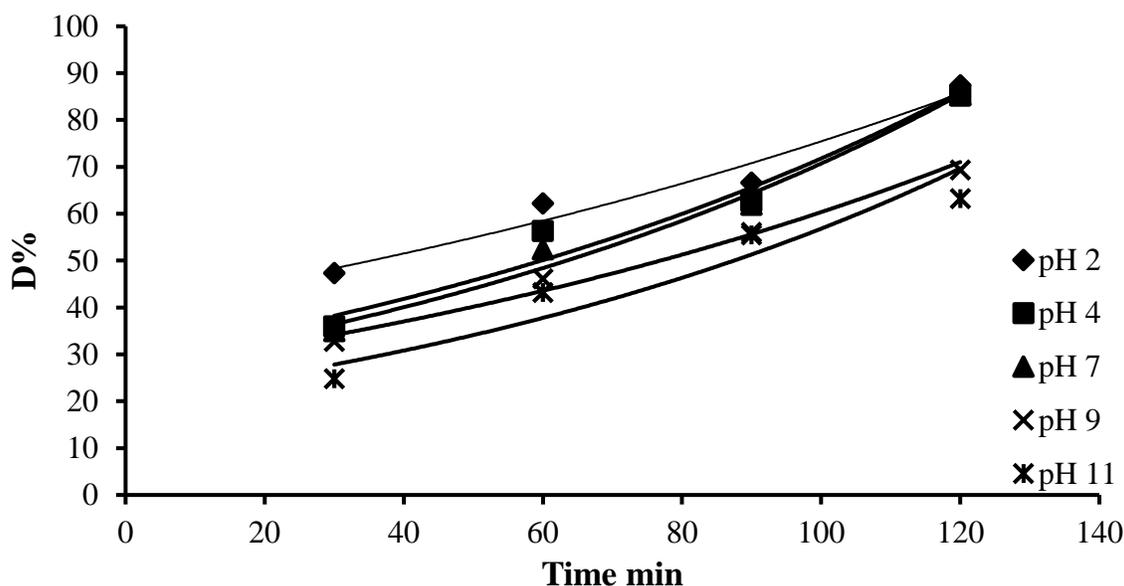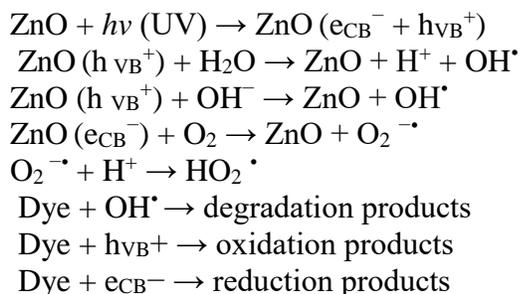

Figure 6: Relation between degradation percent of dye and time by using ZnO, H_2O_2 at different pH

3.6. Mechanism of Degradation

These experiments demonstrated that , UV-light and the photocatalyst ZnO influences the effective destruction of Direct yellow dye , because it is well known that, the photocatalyzed degradation of organic material in solution is initiated by formation of electron – hole pair on the surface of catalyst when the catalyst undergo to photo –excitation. Azo bonds are the most active bonds in direct yellow dye, which can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band, the cleavage of N=N leads to break down the dye ,from the results above the mechanics can be expressed as follows [10, 11]:

$$ZnO + hv \, (UV) \rightarrow ZnO \, (e_{CB}^{-} + h_{VB}^{+})$$
$$ZnO \, (h_{VB}^{+}) + H_2O \rightarrow ZnO + H^+ + OH^{\bullet}$$
$$ZnO \, (h_{VB}^{+}) + OH^- \rightarrow ZnO + OH^{\bullet}$$
$$ZnO \, (e_{CB}^{-}) + O_2 \rightarrow ZnO + O_2^{-\bullet}$$
$$O_2^{-\bullet} + H^+ \rightarrow HO_2^{\bullet}$$
$$Dye + OH^{\bullet} \rightarrow degradation \, products$$
$$Dye + h_{VB}+ \rightarrow oxidation \, products$$
$$Dye + e_{CB}- \rightarrow reduction \, products$$

4. Conclusion

The degradation of direct yellow dye has been studied in aqueous solutions, as the photoreaction has taken place on the surface of photocatalyst ZnO, the degradation has been examined at different pH values. The degradation has been identified by measuring the percentage of degradation at different interval time.

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