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Evaluation of the Photocatalytic Degradation of Eosin Red using Anatase Nano Titanium Dioxide – UV System

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ABSTRACT

Synthetic dyes are essential raw materials in numerous industrial processes, which include textile, food, cosmetic, and pharmaceutical industries. However, they constitute environmental pollutants when discharged as wastewater effluents without adequate treatment. This work is focused on the treatment of a dye, Eosin Red, through the photocatalytic degradation process using anatase nano titanium dioxide. The light source for this experiment is an 8 W monochromatic UV bulb, which provides wavelength of sufficient energy to overcome the anatase titanium dioxide band energy of 3.2 eV. Dye concentration reduction was determined using a UV/Vis Spectrophotometer, with 519 nm as the wavelength of maximum absorbance of Eosin Red dye. The result obtained showed a significant degree of ER photodegration and highlighted the dependence of the photodegradation process on some influencing parameters like initial concentration of dye, catalytic loading, contact time, and pH. The kinetic study in this research indicates that the photodegradation of Eosin red dye strongly follows pseudo-first-order kinetics, as is evident in the R^2 and k' values of 0.998 and 0.0115 min^{-1} respectively of 10ppm Eosin red.

INTRODUCTION

Over the years, innovative processes have been proposed for the treatment of polluted wastewater; these include technologies for the reduction, or even eradication, of toxicity in effluent water to meet environmental standards. This is necessary because contaminants from effluent waste pose serious environmental and health problems to flora and fauna. Untreated effluent may also contains dyes, especially in discharges from textile and fabric industries. Synthetic dyes has an adverse effect on all forms of life when discharged carelessly into the environment, therefore, there is need for the cleanup of such pollutants in wastewater through an efficient water treatment process. Some of these processes include biological treatment, adsorption on solid phase, ozonation, filtration, reverse osmosis, incineration, coagulation, etc. However, each of these processes is accompanied by their respective advantages and disadvantages. Recent findings have revealed that photocatalytic processes can also be used to achieve rapid and efficient destruction of environmental pollutants, whether organic or inorganic in nature (Gnanaprakasam, et al. 2015, Sobana, et al 2008, Rajabi, et al.2013). In contrast with other conventional methods in environmental cleanup, photocatalytic degradation involves the breakdown of the pollutants from complex molecules into simple and non-hazardous substances. Hence no residue is left and no sludge is produced from the process. Therefore, no secondary treatment is needed to process the sludge. Also, photocatalyst has the advantage of simultaneous removal of metals and organic pollutants.

This paper focuses on the degradation of a synthetic dye using a photocatalyst, while also considering some parameters influencing this process.

Among easily available photocatalyst, TiO_2 and ZnO have been widely applied as photocatalyst due to their high activity, nontoxicity, chemical stability, lower cost, optical and electrical properties, and environment friendly characteristics (Shifu et al; 2009). The photocatalyst of interest is nano sized anatase titanium dioxide while the dye under evaluation is eosin red. Eosin red is a xanthene dye with the chemical formular, $C_{20}H_6Br_2N_2Na_2O_9$ and structure shown below; Walthall and Stark, 1999 reported an acute and chronic toxicity of xanthenes dyes to *Daphnia pulex*. The 48h LC_{50} of fluorescein sodium salt and phloxine B was indicated as 337 mg/L and 0.423 mg/L respectively. Therefore, the treatment of wastewater polluted with xanthene dyes is necessary before discharging it into the environment.

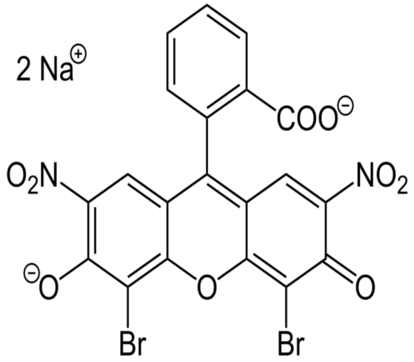

Fig 1. Eosin Red.

The mechanism of photocatalytical degradation is as follows: upon illumination of semiconductor electrolyte interface with light energy greater than the semiconductor band gap, electron-hole pairs (e^- /h^+) are formed in the conduction and valence band of the semiconductor, respectively.

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These charges which migrate to the semiconductor surface are capable of reducing or oxidizing species in solution having suitable redox potential.

- Photocatalyst is irradiated with photons of energy equal to or more than bang gap energy of PC, exiting electrons from valence band (VB) to conduction band (CB) with the simultaneous creation of holes in the VB as shown in fig 1.

$$PC + hv \rightarrow e_{CB}^- + h_{VB}^+$$

- The photoinduced holes in the VB are trapped by H_2O on the PC surface to give hydroxyl radical $OH^{\cdot}$

$$H_2O + h_{VB} \rightarrow \cdot OH + H^-$$

- The electrons generated in conduction band could be readily trapped by O_2 absorbed on the PC surface or the dissolved O_2 to give superoxide radicals- $O_2^{\cdot -}$

$$e_{CB}^- + O_2 \rightarrow O_2^-$$

- Consequently, $O_2^{\cdot -}$ could react with H_2O to produce hydroperoxy radical- $HO_2^{\cdot}$ And hydroxyl radical $OH^{\cdot}$ which are strong oxidizing agents to decompose the organic molecule

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

- The organic waste, R is oxidized to give carbon dioxide and water as shown below

$$h_{VB}^+ + R \rightarrow intermediates \rightarrow CO_2 + H_2O$$

$$\cdot OH + O_2 + R \rightarrow CO_2 + H_2O$$

- Adsorption of metal ion to the surface of TiO_2 is possible because the surface of PC is electron rich enabling it to attract the cationic metal ion through reduction of the metal ion.

$$M^+ + e^- \rightarrow M_{(s)}$$

- Finally, there is also the possibility of the rembination of VB hole and CB electron which could lead to a reduction in the photocalytic activity of the PC

$$e_{CB}^- + h_{VB}^+ \rightarrow PC$$

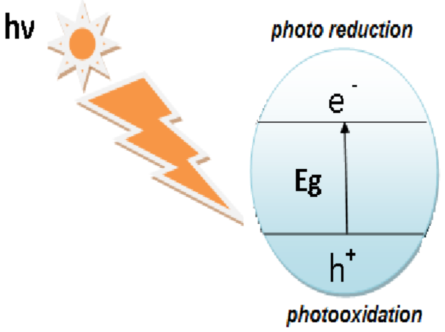

Fig 2. Showing to transfer of electrons from the valence band to the conduction band giving a hole in the valence band.

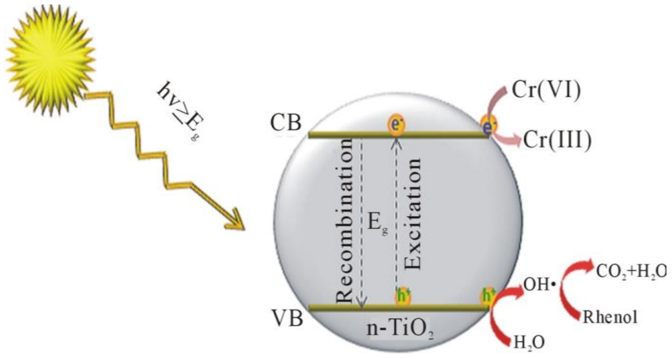

Fig 3. Showing the simultaneous mineralization of an organic pollutant reduction of an inorganic ion, Cr (VI) to Cr (III).

MATERIALS AND METHODS

Materials

Eosin Red dye was obtained from Labtech Chemicals and used without further purification. The maximum absorption (λmax) for ER is 519nm, this was confirmed using a spectrophotometer. Different concentration of dye was prepared by dissolving the requisite quantity of the dye in deionized water. The pure anatase form of titanium oxide (TiO_2) used in the experiment was also purchased from US nano inc.. The pure anatase TiO_2 were nano sized with a particle size < 20 nm, surface area of 200-240 $m^2\ g^{-1}$, and was used for all photocatalytic experiments without further treatment. Hydrochloric acid and sodium hydroxide used in this work (30% w/w) was obtained from Sigma and Aldrich. All reagents were of analytical grade and were used without further purification.

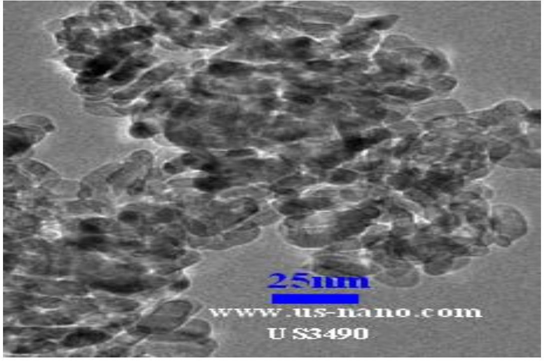

Fig 4. SEM image for anatase TiO_2.

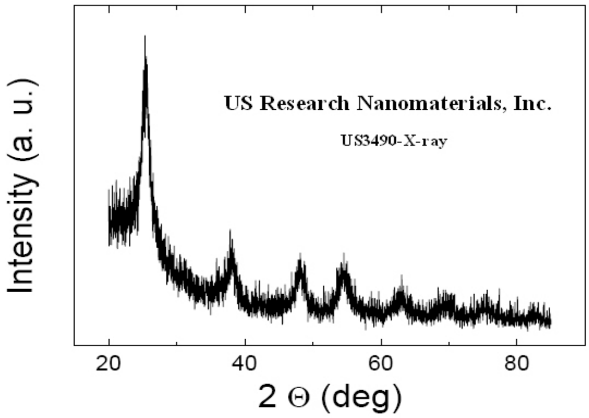

Fig 5. XRD pattern for anatase TiO_2.

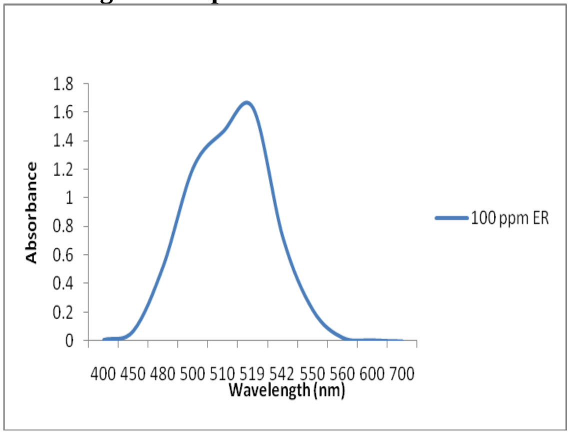

Fig 6. Absorbance curve of Eosine Red.

Photoreactor and light source

The reactor used in this research is a rectangular box measuring 25 × 70 × 50 cm^3, equipped with a magnetic stirrer, and an 8 W UV bulb (HM F8T5 GL). This light source provides sufficient energy to overcome the band width of anatase titanium dioxide (3 eV)

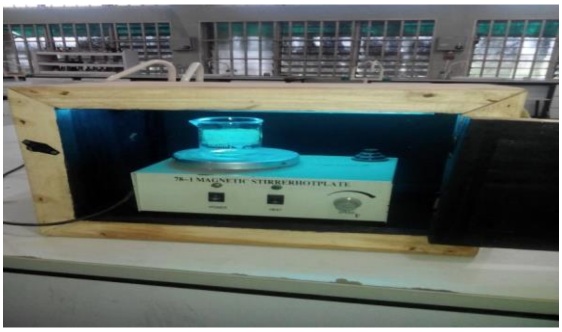

Fig 7. Showing the photoreactor and light source used in the research.

PROCEDURE

Photolysis test

This test is carried out to determine the degradation of the contaminants as a result of exposure to the UV light source alone (without the photocatalyst). Here, 50 ml of 50ppm of Eosin red is kept in the photoreactor for 1hr with constant stirring. After which, UV analysis for synthetic dye is carried out for evidence of photodegration.

Adsorption of the contaminants on the photocatalyst

This test is carried out to ascertain what fraction of contaminant disappearance can be attributed to its adsorption to the surface of photocatalyst. The process is as follows; 50 ml solution of 50ppm Eosin red is mixed with 0.2 g of TiO_2 and the suspension is mixed with a magnetic stirrer in the dark for 1 hr. The resultant solution is analysed for any change in concentration. The difference in concentration (if any) is attributed t the adsorption of the contaminants on the photocatalyst.

Photocatalytic degradation

The Eosin Red solution (50 ml) containing the appropriate quantity of TiO_2 was continuously stirred and irradiated by an 8 W UV lamp under ambient temperature in the photoreactor. Aliquots of the mixture was filtered and anlaysed periodically (0, 60, 80 and 200 mins), to study the effect of contact time. Also, the pH of the solution was adjusted using 0.1 M hydrochloric acid (HCl) and sodium hydroxide (NaOH), to investigate the effect of pH on photodegradaton. HCl was used to adjust the pH because it does not significantly affect the adsorption-surface properties of TiO_2 (Chen et al. 1997). Degradation of Eosin Red was monitored with a UV- Vis spectrophotometer (UV-160 A) at absorbance wavelength of 595 nm. Dye degradation is defined as the gradual decomposition of a dye into another substance and can be visibly observed a change or disappearance of the dye colour. The percentage degradation was calculated as follows:

$$Degradation\ (\%) = \frac{Co - Ct}{Co} \times 100,$$

C_O is the initial dye concentration, C_t is the final dye concentration at time, t.

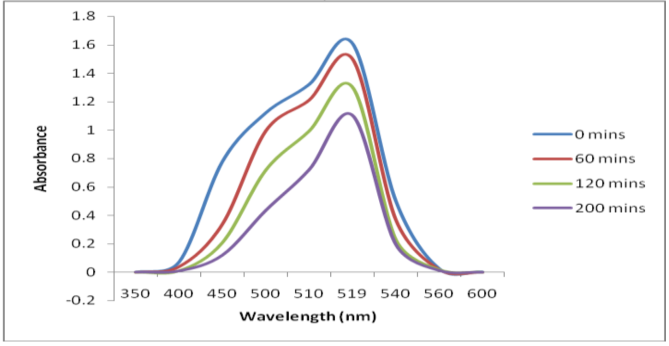

Fig. 8. Absorbance curve for the photodegradation of 50ppm ER. Reaction conditions: TiO2 = 2g/L; 8W UV light; pH = 6.67

RESULTS AND DISCUSSION

Effect of Initial Concentration

The initial dye concentrations evaluated were 10 ppm, 30 ppm and 50 ppm. Result obtained showed that the degradation efficiency of dyes after 60 minutes of irradiation is as follows: 10 ppm (73.8%), 30 ppm (52.3%) and 50 ppm (45%). At 120 mins, degradation efficiency of 10ppm Eosine red was increased further to 95%, 30ppm (61%) and 50ppm (53.9%). Figure 9 indicates that the initial concentration of Eosine Red has a significant effect on the degradation rate; the higher the initial concentration, the lower the photodegradation efficiency. These results correspond with the findings of Kaur and Singh, 2008, who worked on the photodegradation of reactive red 198 dye using TiO_2. The increase in Eosin red dye concentration reduces the number of photons penetrating the solution because they are absorbed before reaching the TiO_2 catalyst. This phenomenon leads to a decrease in the absorption of photons by the TiO_2 catalyst and therefore fewer electron- hole pairs are generation. Thus, fewer superoxide ions/hydroxyl radicals are generated and oxidation of the dye is hindered. Thus, larger amount of TiO_2 catalyst is required to provide greater surface area to degrade a more concentrated dye.

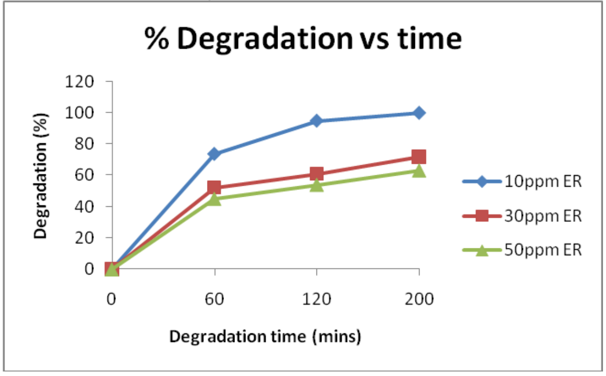

Fig 9. Influence of Initial Concentration on degradation efficiency. Reaction conditions: catalytic loading = 2g/L; 8W UV light, pH = 6.63.

Effect of pH

pH influences the surface charge of photocatalyst, and oxidation potential of the valence band (Sobana, et al. 2008). According to Mai, et al., 2008, when the surface of a photocatalyst is negatively charged at high pH value, it results in the increased adsorption of cationic molecules, while in the reverse situation it would adsorb anionic molecules very easily. Results in this research indicate that degradation efficiency increased at acidic Ph and decreased at basic Ph as shown on fig. 10. This corresponds with the findings of Sobana, et al., 2008 and Mai, et al., 2008. . Acidic and neutral pH values were found to be more effective for degradation of Eosin red dye than was basic pH using pure anatase nano-TiO_2. This outcome can be attributed to the point of zero net charge (PZC) of TiO_2, which is pH 6.8. In an acidic solution (pH<6.8), TiO_2 surface becomes positively charged, while Eosin red is negatively charged due to the presence of carboxylic group (COO^-) in its molecule. This situation favors the adsorption of the anionic dye onto the TiO_2 catalyst surface. As more dye molecules are absorbed on the active sites of TiO_2 photocatalyst, the degradation efficiency is enhanced. On the other hand, at higher pH, the surface of the TiO_2 photocatalyst becomes negatively charged, and lower amount of the dye molecule is attracted to it. At pH 3, degradation efficiency was 89.86% after 60 minutes of UV irradiation, pH 6.6 (45%) while the degradation efficiency at pH 11 was 25.4% after the same duration of light irradiation.

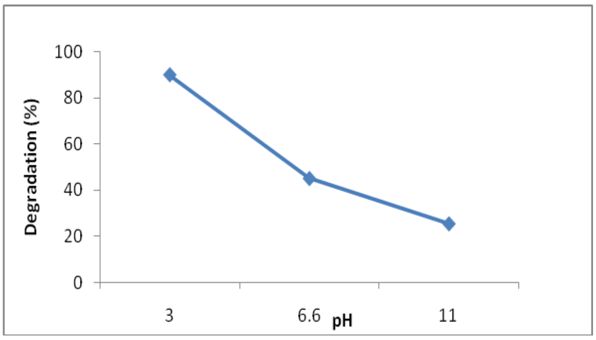

Fig 10. Effect of pH on degradation efficiency. Reaction conditions: Dye conc.= 50ppm; catalytic loading = 2g/L; reaction time = 60 mins; 8W UV bulb.

Effect of Contact time

Influence of photodegradation of Eosin Red on contact time can be clearly observed on fig 11. This indicates that concentration of the dye decreases with increasing contact time with the photocatalyst. Thus, the degradation of the dye is enhanced by increasing its contact time with TiO_2 in the presence of UV irradiation. 10ppm ER was completely degraded in 120 mins; the concentration of 30 ppm ER was reduced to 11.7ppm and 8.4ppm at 120 mins and 200 mins respectively. Degradation efficiency of 50ppm ER at was 63.1% (18.426 ppm) at 200 minutes. This result corresponds with the findings of Barka, et al., 2009 and Kaur and Singh, 2008, who stated that photodegradation efficiency of synthetic dyes is enhanced with increasing contact time with the photocatalyst.

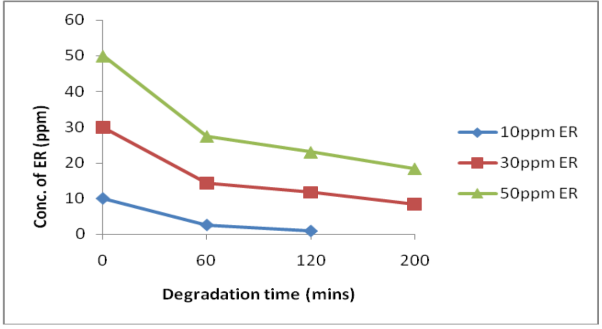

Fig 11. Effect of Contact time. Reaction condition: pH = 6.63; 8W UV bulb, catalytic loading = 2g/L.

Kinetic Study of Photodegradation

The degradation of Eosin red dye by pure anatase TiO_2 follows first-order kinetics. This finding correlates with Neppolian et al. (2002) who stated that the photodegradation of most organic compounds is described by pseudo-first-order kinetics. Thus the kinetics of the degradation of Eosin red can be represented as follows;

$$r = -\frac{d[ER]}{dt} = k'[ER] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$C_{ER} = C_o e^{-kt} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$In\left(\frac{[ER]_t}{[ER]_o}\right) = -k't \text{ or } In[ER]_t \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$= -k't + In[ER]_o$$

where k' is the first-order rate constant (min^{-1}), $[ER]_t$ and $[ER]_0$ are the concentration of the Eosine red dye at time t and t =0, respectively. The correlation coefficient of 0.99 in fig 13 for the photodegradation of 10ppm ER, indicates that the photodegradation strongly follows pseudo-first-order kinetics. The k values for the photodegradation of 10ppm, 30ppm and 50ppm ER is given as 0.0115 $mins^{-1}$, 0.008 $mins^{-1}$, and 0.00712 min^{-1} respectively. This is reflected on table 1, which shows the R and k values for the photodegradation of different concentration of ER. These values prove that the photodegradation of Eosin Red follows the pseudo-first-order kinetics

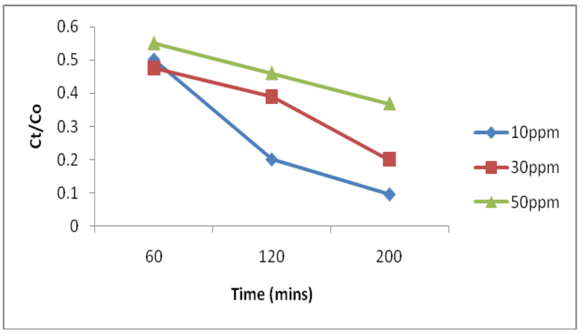

Fig 12. Kinetics of the degradation of Eosin red dye. Reaction conditions: pH = 6.63; 8W UV bulb, catalytic loading = 2g/L.

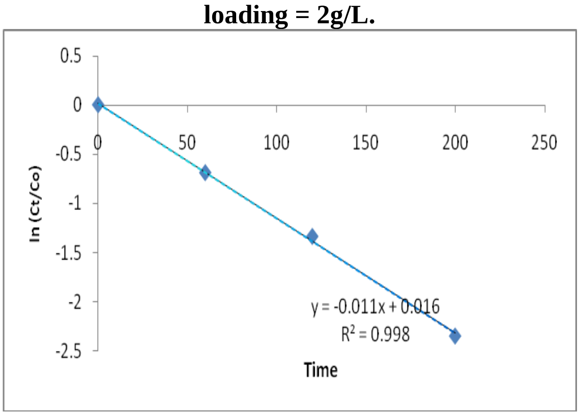

Fig 13. The pseudo-first order kinetics plot for photodegradation of 10ppm ER.

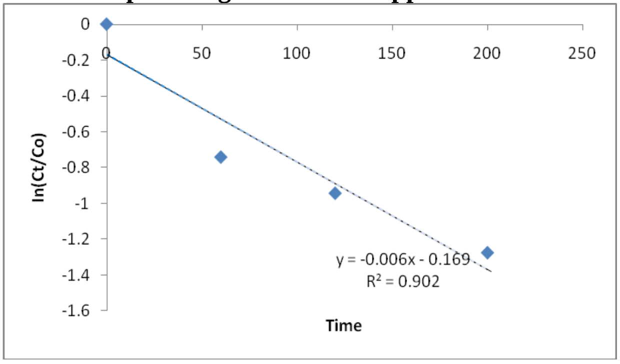

Fig 14. The pseudo-first order kinetics plot for photodegradation of 30ppm ER.

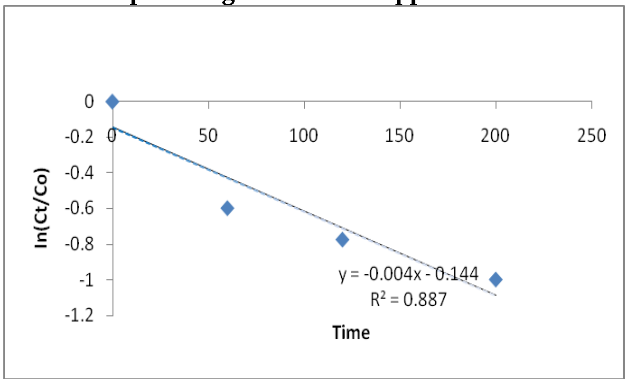

Fig 15. The pseudo-first order kinetics plot for photodegradation of 50ppm ER.

Table 1. showing rate constant values correlation values of photodegradation of different concentration of ER dye.

INITIAL CONC. (ppm)	K' (min^{-1})	R^2 values
10	0.0158	0.998
30	0.0088	0.902
50	0.00712	0.887

CONCLUSION

It is evident that nano sized anatase titanium dioxide can be used to breakdown eosin red dye molecules via photocatalytic reaction, when the system is irradiated with UV light. It has also been shown that influencing parameters in this process include; initial dye concentration, reaction time and pH of the reaction system. Finally, the kinetics of this photodegradation has been shown to obey the pseudo-first order kinetics, which is evident in the correlation values of the plot and the rate constant obtained. This study has indicated that lower concentration of eosin red gave higher degradation efficiency, and this has been attributed to an enhanced light penetration into the system, leading to an increase in the excitation of the photocatalyst.

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