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PHOTOCATALYTIC DEGRADATION OF EDTA BY USING TiO_2 SUSPENSION

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ABSTRACT

The photocatalytic degradation of an aqueous solution of ethylene diamminetetra-acetic acid (EDTA) has studied under different conditions in the presence of TiO_2 suspension. The effect of various parameters such as mass of titanium dioxide, EDTA concentration, light intensity, addition of H_2O_2 and flow rate of O_2 on the photocatalytic degradation were investigated. Results showed that, the photocatalytic degradation process was high at the beginning and then decreased with time. This process was well described by pseudo, first order kinetics according to the Langmuir-Hinshelwood model.

The results explained the photocatalytic degradation efficiency, which was increased by increasing catalyst loading from 1 g to 2 g. The degradation efficiency decreased with the increase in catalyst loading. Results also showed that the rate of photocatalytic degradation was increased with decreasing EDTA concentration.

The proper amount of hydrogen peroxide improved the rate of photocatalytic degradation of EDTA, while the excess hydrogen peroxide quenched that formation of hydroxyl radicals $^{\bullet}OH$, which caused reducing at the rate of photocatalytic degradation. The effect of dissolved oxygen level of bubbling pure oxygen gas into the solution has been found to enhance the photodegradation rate. Results indicated that the photocatalytic degradation was enhanced by increasing light intensity.

Key words: EDTA, Photocatalytic degradation, Titanium dioxide, Kinetic study, Light intensity.

INTRODUCTION

EDTA is used as a complexing agent and has wide applications in the pharmaceutical, agriculture and as a domestic cleaning of boilers. In recent years, EDTA was found in fresh water, sewage effluents and ground water, that paid much attention because its low bio-degradability and the capability for formation very stable complexes with heavy metals, which prevent theses complexes from re-dissolved again in water[1,2].

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Different methods were used for degradation of EDTA. Biological treatment had low efficiency and the treatment of chlorine had low scarcely. The best methods were the using of a different technique here used in AOPs, such as H_2O_2/UV, radiolysis, ozonation, photocatalysis, Fenton and solar-assisted oxidation[3,4].

Advanced oxidation processes (AOPs) concerned with the total oxidation of organic and inorganic materials by heterogeneous photocatalysis[5]. In photocatalytic oxidation the organic molecules were degradable in the presence of semiconductor, light and oxidizing agents such as air or oxygen. The heterogeneous photocatalytic degradation process by TiO_2 is a complex sequence step, which can be expressed in a set of simplified equations as shown below. When a semiconductor absorbs a photon of energy higher or equal to the band gap of semiconductor, an electron from the valence band (VB) is promoted to the conduction band (CB) with the simultaneous generation of positive hole (h^+) in valance band[6,7] –

$$TiO_2 \xrightarrow{hv} TiO_2(e^-_{CB} + h^+_{VB}) \quad \ldots(1)$$

In aqueous solutions the positive hole (h^+) in VB reacted with water molecule which adsorbed on the surface of semiconductors, or with hydroxide ion OH^-, or with any donor species:

$$h^+_{VB} + H_2O_{ads.} \longrightarrow {}^{\bullet}OH_{ads.} + H^+ \quad \ldots(2)$$

$$h^+_{VB} + OH^-_{ads.} \longrightarrow {}^{\bullet}OH_{ads.} \quad \ldots(3)$$

$$h^+_{VB} + D_{ads.} \longrightarrow D^+_{ads.} \quad \ldots(4)$$

The e^-_{CB} can react with adsorbed species to give anionic species:

$$e^-_{CB} + A_{ads.} \longrightarrow A^-_{ads.} \quad \ldots(5)$$

The anion $A^-_{ads.}$ may be a dissolved oxygen, which transformed to superoxide radical anion $O_2^{\bullet-}$.

This can lead to the formation of hydroxyl radical ${}^{\bullet}OH$:

$$e^-_{CB} + O_{2\,ads.} + H^+ \longrightarrow HO_2^{\bullet} \quad \ldots(6)$$

$$HO_2^{\bullet} \longrightarrow H^+ + O_2^{\bullet-} \quad \ldots(7)$$

$$2\,HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \quad \ldots(8)$$

$$H_2O_2 + O_2^{\bullet-} \longrightarrow {}^{\bullet}OH + O_2 + HO^- \quad \ldots(9)$$

Hydroxyl radicals could oxidize all organic species to CO_2, H_2O and other compounds depending on the structure of treated pollutants.

The aim of this paper is to focus on the kinetic studies by using different parameters for degradation of aqueous solution of EDTA in the existence of TiO_2.

EXPERIMENTAL

Titanium dioxide (Hombikate UV 100) was supplied by the Sachtleben Chemie GmbH, ethylene diaminetetraacetic acid (EDTA) was purchased from Scharlau Chemie S.A Barcelona, Spain, was used without further treatment. Photocatalytic degradation was carried out in an experimental setup consist of a homemade photoreactor. Irradiation source is Philips mercury lamp UV (A), contains six lamps of 15 W for each one (Germany).

Most experiments were carried out in a reactor containing 400 cm^3. The lamp was positioned perpendicularly above the radiation vessel and the distance was fixed for a chosen light intensity.

In all experiments, the required amount of the catalyst was suspended in 200 cm^3 of aqueous solutions of EDTA, by using a magnetic stirrer. At predominant times, 3 cm^3 of reaction mixture was collected and centrifuged (8000 rpm, 15 minutes) in a Hettich centrifuge. The supernatant was carefully collected in a syringe with a long pliable needle and centrifuged for a second time, at the same speed and for the same period of time. This second centrifugation was found necessary to remove the fine particles of TiO_2 that found effective on the result of analysis by UV-Visible spectrophotometer.

EDTA concentration was determined by Parkash et al.[8] at a wavelength 750 nm, by using UV-Visible spectrophotometer (Type Apel PD-303 UV). All experiments carried out under temperature 298 K.

RESULTS AND DISCUSSION

Effect of mass dosage

The influence of the photocatalyst concentration (1-3.5 g/L^{-1}) on the photocatalytic degradation of EDTA was investigated at an initial EDTA concentration of 2 mM, light intensity (0.94 μens. sec^{-1}), flow rate of O_2 (5 mL. min^{-1}) and buffer concentration of the suspension pH 5. The experimental data could be analyzed assume-first order kinetic as shown in Fig. 1.

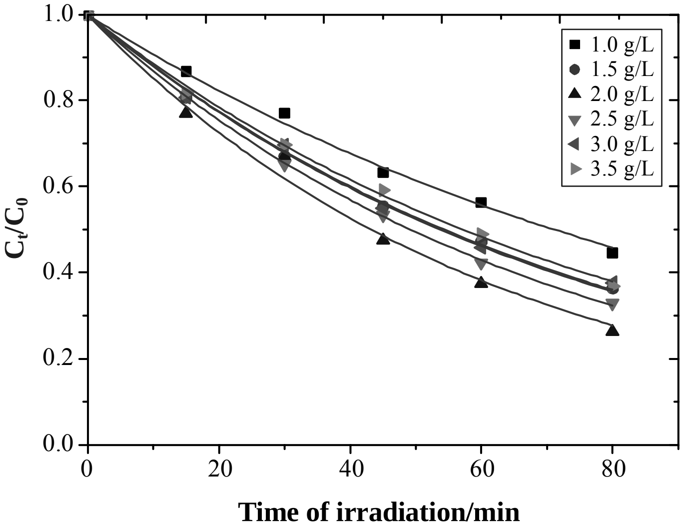

Fig. 1: EDTA concentration vs. time profiles at different photocatalyst concentrations

From Fig. 2, results indicates that the rate of photodegradation increases by increasing the amount of TiO_2 upto 2 g/L^{-1}. Furthermore 2 g/L^{-1}, the rate of photocatalytic degradation was taken a plateau region from 2-2.5 g/L^{-1}, then the rate of degradation decreased slightly with increase in mass dosage. Fig. 2 shows three regions.

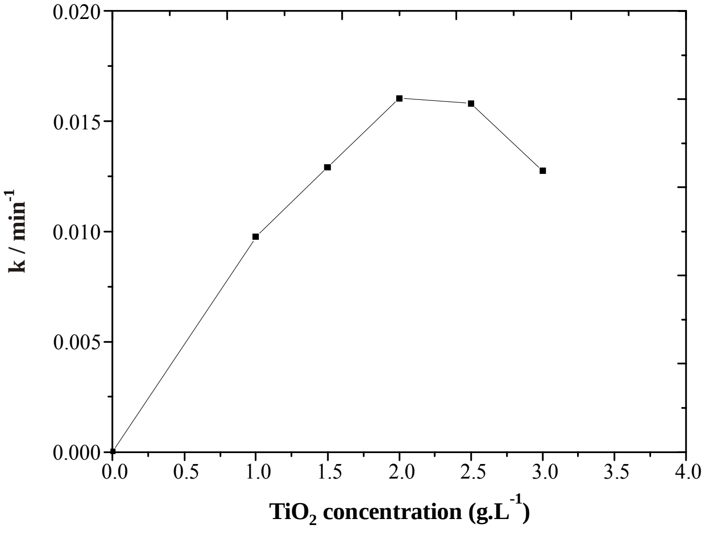

Fig. 2: Evaluation of photocatalytic degradation rate constant according to different mass concentrations of photocatalyst

In the region less than 2 g/L^{-1}, when the mass dosage were increased, the rate of degradation was increased because the number of active sites increased. In the region between 2-2.5 g/L^{-1}, shows an approximately plateau curve which indicates the numbers of active sites have an equilibrium between the numbers of photon induced that absorbed by the catalyst and a particle of EDTA adsorbed.

A region above catalyst concentration 2.5 g/L^{-1} shows a decrease in rate of degradation, with the increase of mass dosage. This behavior may be due to increasing of scattering of light and decreased in the penetrations of photon, losing in surface area by a phenomena particle – particle interactions[9-11], that caused to reduce of EDTA adsorption on the catalyst. Therefore 2 g/L^{-1} of TiO_2 was selected as an optimal mass for all experiments in this work.

Effect of substrate concentration

The effect of EDTA concentration has been investigated at pH 5, catalyst concentration 2 g/L^{-1}, light intensity 0.94 (μens.sec^{-1}), flow rate of O_2 (5 mL. min^{-1}) and EDTA concentrations (1, 1.5, 2, 2.5 and 3 mM). The experimental data could be analyzed to assume-first order kinetic as shown in Figure 3.

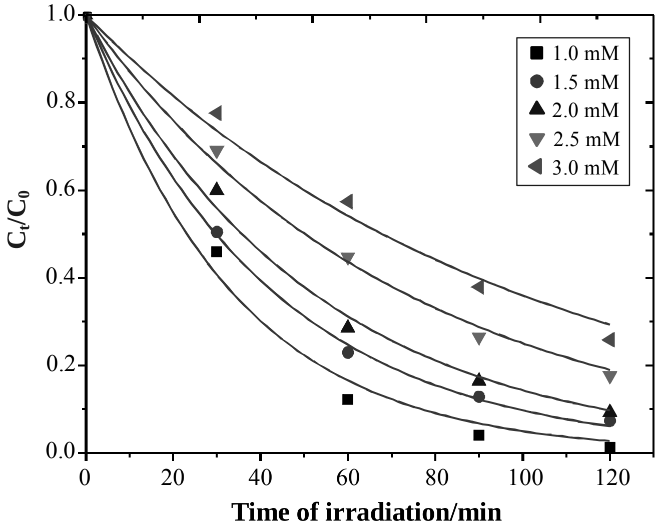

Fig. 3: Photocatalytic degradation of different EDTA concentrations vs. time profiles

Figure 4 shows that when the concentration was increased, the rate of photodegradation decreased, this occurs by either reduced of the holes or hydroxyl radical

$^{\bullet}$OH, because the active sites will complete coverage by EDTA molecules, or an increasing in the initial concentration caused to increased in the adsorption of EDTA molecules on the surface of the catalyst , which lead to reduce in the OH radical generation, because very low active site available as free on the surface of catalyst[12-14].

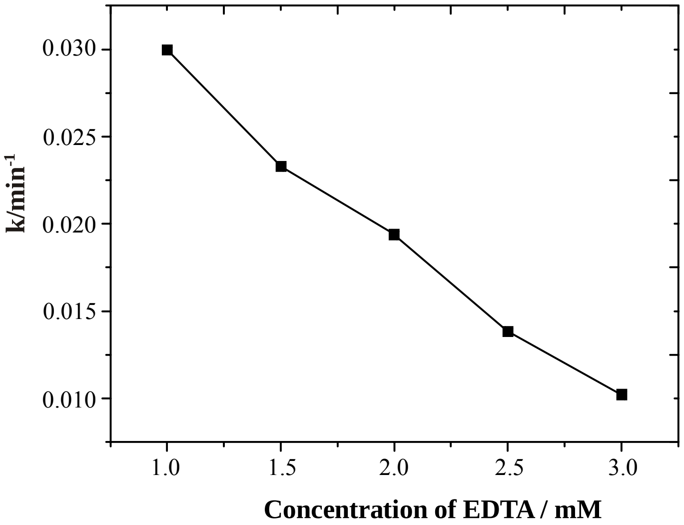

Fig 4: Evaluation of photocatalytic degradation rate constant according to different initial EDTA concentrations

The effect of oxygen flow rate

The effect of oxygen flow rate has been investigated at pH 5, EDTA concentration 2 mM, concentration of catalyst 2 g/L^{-1} and light intensity (0.94 μens. sec^{-1}). The experimental data could be analyzed to assume-first order kinetic as shown in Fig. 5.

Figure 6 shows that the photocatalytic degradation efficiency was increased with increase of flow rate upto 30 mL/min. Above 20 mL/min., the photocatalytic efficiency not affected because all coverage areas of the catalyst surface saturated with oxygen so the excess of oxygen left the catalyst surface and not affected on the photocatalytic degradation efficiency.

The molecular oxygen adsorbed on the surface of photocatalyst, working to prevent hole–electron pair recombination process[15,16]. The process of recombination decreased from the rate of photocatalytic degradation. It was found that the source of hydroxyl radicals is superoxide, formed by incident light on the molecular oxygen adsorbed on the surface of the catalyst.

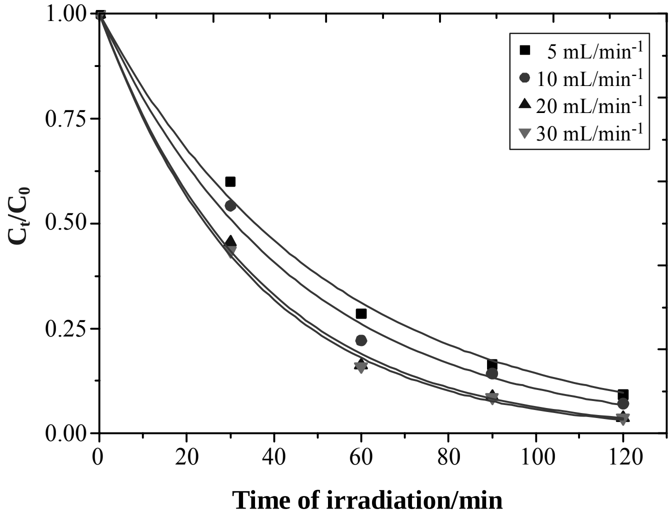

Fig. 5: EDTA concentrations vs. time profiles, at different oxygen flow rates

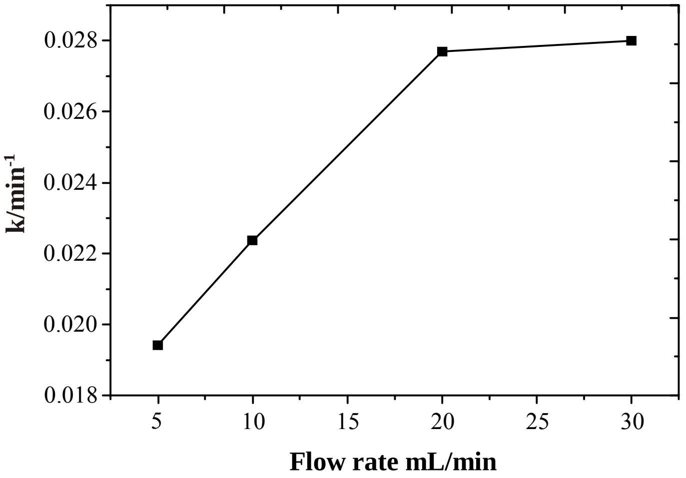

Fig. 6: Evaluation of photocatalytic degradation rate constant according to different flow rates of oxygen

The following equations explains formation of hydroxyl radical, which may be considered the significant species for organic molecules oxidations.

$$TiO_2 \xrightarrow{hv} TiO_2\,(e^-_{CB} + h^+_{VB}) \qquad \ldots(10)$$

$$e^-_{CB} + O_{2\,ads.} \longrightarrow O_2^{\bullet -} \qquad \ldots(11)$$

$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet}$ …(12)

$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$ …(13)

$HO_2^{\bullet} + O_2^{\bullet} \longrightarrow HO_2^- + O_2$ …(14)

$HO_2^- + H^+ \longrightarrow H_2O_2$ …(15)

$H_2O_2 \xrightarrow{hv} 2\,{}^{\bullet}OH$ …(16)

$O_2^{\bullet -} + H_2O_2 \longrightarrow {}^{\bullet}OH + {}^{-}OH + O_2$ …(17)

${}^{\bullet}OH + EDTA \longrightarrow$ Intermediates →→→ $CO_2 + H_2O$ + Oxides …(18)

Effect of addition of H_2O_2

The effect of addition of H_2O_2 on the rate of photocatalytic degradation of 1 mM EDTA was investigated at pH 5, flow rate (5 mL.min^{-1}), mass catalyst 2 g/L^{-1}, light intensity (0.94 µens. sec^{-1}) and H_2O_2 concentrations (2-10 mM). The experimental data could be analyzed to assume-first order kinetic as shown in Fig. 7.

The addition of H_2O_2 was regarded as a good parameter for enhancement of photocatalytic degradation process[17]. The result as shown in Fig. 8, indicate that the hydrogen peroxide had accelerated the photocatalytic degradation of EDTA. The photocatalytic degradation of EDTA increased when hydrogen peroxide concentration increased from 0 to 5 mM. This could be due to the increase in the ${}^{\bullet}OH$, where working to prevent electron- hole recombination, as in following equations[14].

$TiO_2\,(e^-) + H_2O_2 \longrightarrow TiO_2 + OH^- + {}^{\bullet}OH$ …(19)

$H_2O_2 + e^-_{CB} \longrightarrow OH^- + {}^{\bullet}OH$ …(20)

$H_2O_2 + O_2^{\bullet -} \longrightarrow OH^- + {}^{\bullet}OH + O_2$ …(21)

Moreover increasing of hydrogen peroxide concentration more than 5 mM decreased the rate of photocatalytic degradation that could be due to by scavenging effect.

$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + HO_2^{\bullet}$ …(22)

$HO_2^{\bullet} + {}^{\bullet}OH \longrightarrow H_2O + O_2$ …(23)

It is found from the experiments of addition of H_2O_2 to the system consist of UV/EDTA/TiO_2, the rate of photocatalytic degradation was increased more, than without the

H_2O_2 addition because H_2O_2 consider as trapping electron on the surface of the catalyst. As in following equations:

$$H_2O_{2\,\text{assorbed}} + e^-_{CB} \longrightarrow OH^- + {}^{\bullet}OH_{\text{adsorbed}} \qquad \ldots(24)$$

$$H_2O_2 + O_2^{\bullet-} \longrightarrow OH^- + {}^{\bullet}OH_{\text{adsorbed}} + O_2 \qquad \ldots(25)$$

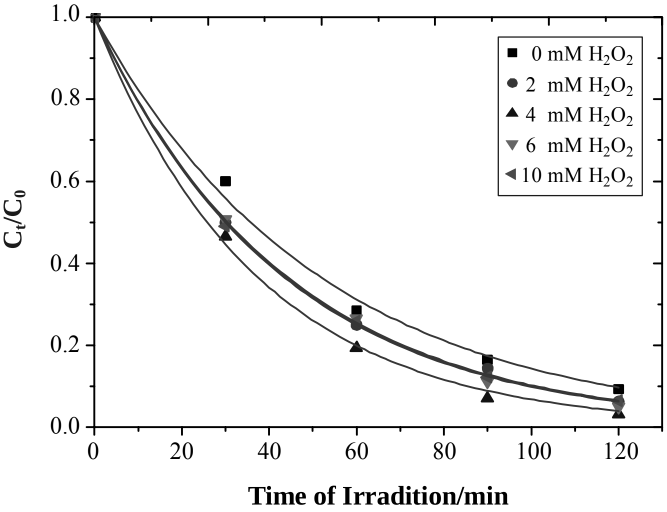

Fig. 7: EDTA concentrations vs. time profiles, at different H_2O_2 concentrations

Equations 24 and 25 suggeste that the electrons in the conduction band and superoxide could initiate radical formation from H_2O_2. The rate of photocatalytic degradation was decreased at higher concentration of H_2O_2, this negative effect of H_2O_2 at higher concentration may occur due to inhibition of ${}^{\bullet}OH$, because at high concentration of H_2O_2, the amount of ${}^{\bullet}OH$ formed on the surface was increased quickly and hence the annihilation ${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$ rate which consider faster than the degradation rate of EDTA. Also another reason H_2O_2 is sorbed on the surface of the catalyst can effectively as scavenging not for the surface of the catalyst that formed a radical but also for photogenerated holes h^+_{VB}, then inhibited the process of photocatalytic degradation, as in following reactions:

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + HO_2^{\bullet} \qquad \ldots(26)$$

$$H_2O_2 + h^+_{VB} \longrightarrow {}^{\bullet}OH + H^+ \qquad \ldots(27)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \longrightarrow H_2O + O_2 \qquad \ldots(28)$$

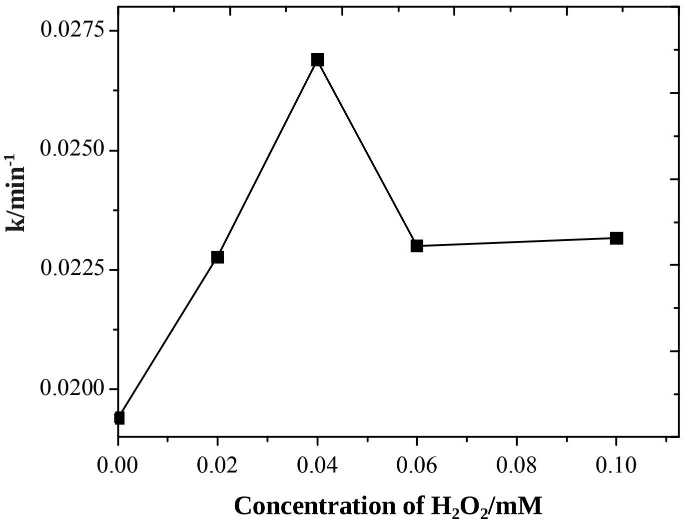

Fig. 8: Evaluation of photocatalytic degradation rate constant according to different H_2O_2 concentrations

Effect of light intensity

The effect of light intensity (0.23-1.1 μens. sec^{-1}) was observed by varying of distance between light source and exposed surface of the semiconductor. EDTA photodegradation by the effect of light intensity was studied in the presence of catalyst 2 g/L^{-1}, 2 mM EDTA, flow rate of oxygen 5 ML/min^{-1} and pH 5. It was found that all the reactions still follow the first-order kinetics as shown in Fig. 9.

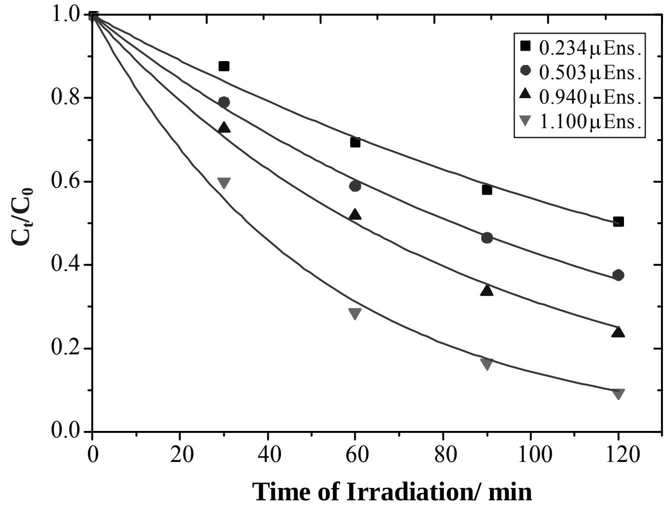

Fig. 9: EDTA concentrations vs. time profiles, at different light intensities

From results as shown in Fig. 10, an acceptably good linear correlation exists between the apparent first-order rate constant and light intensity ($R^2 = 0.9919$) under the ranges studied. So when light intensity was increased photodegradation efficiency was increased. It may be deduced, the high light intensity caused to excited particles of TiO_2 to generate hole- electron pairs[18,19]. Ollis et al.[20] reviewed the studies reported for the effect of light intensity on the kinetics of the photocatalysis process and stated that at low light intensities (0–20 mW.cm^{-2}), the rate would increase linearly with increasing light intensity (first order). This is likely because of low light intensity reactions involving electron–hole formation are predominant and electron–hole recombination is negligible[21].

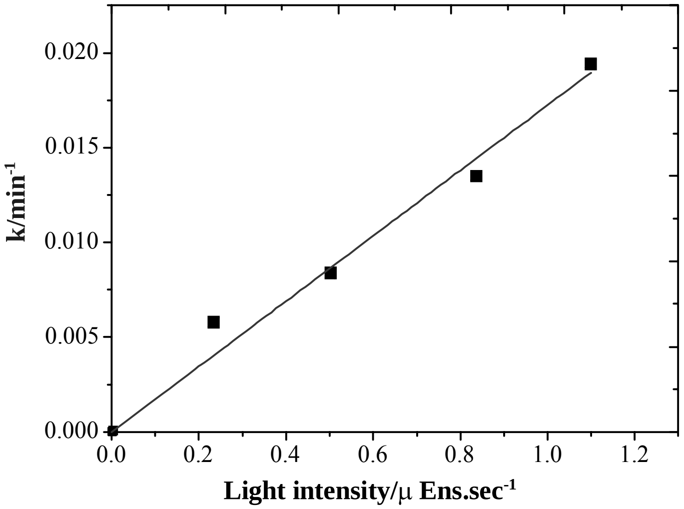

Fig. 10: Effect of light intensity on the rate constant of photocatalytic degradation of EDTA

CONCLUSION

(i) Control experiments showed exist of UV, catalyst TiO_2 and O_2 are essential for photocatalytic degradation of EDTA.

(ii) The photocatalytic degradation of EDTA by using TiO_2 photocatalyst strongly depends on the amount of catalyst and EDTA concentration.

(iii) The photocatalytic degradation found follow first order kinetics in all types of experiments conditions.

(iv) Addition of H_2O_2 is very important to increase the rate of photocatalytic degradation.

(v) Variation of light intensity caused to change in the results of photocatalytic degradation.

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