دراسة كفاءة التحويل الضوئي للمثيل الأحمر والرودامين B بوجود EDTA في أوساط حامضية مختلفة

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الخلاصة

تمَّ إجراء دراسة لفحص كفاءة التحويل الضوئي الحراري لأشعة الشمس للمحاليل المائية لصبغة المثيل الأحمر (Methyl Red) والرودامين B (Rhodamine B) بواسطة تعريضها إلى ضوء الشمس المباشر لمدّة ثمانية ساعات للمثيل الأحمر و7 ساعات للرودامين B في يومٍ مشمس وصافي ، حيث تمَّ قياس الفرق في درجات الحرارة بين محاليل الصبغة والماء باعتباره المذيب (المرجع) حيث اعتبر ΔT دالة مباشرة للتحويل الضوئي الحراري .

تمت دراسة تأثير تركيز الصبغة ضمن المدى $1 \times 10^{-5} - 1 \times 10^{-4}$ مولاري وكذلك تمت دراسة تأثير إضافة EDTA كواهب للإلكترونات ضمن مدى التركيز $1 \times 10^{-5} - 1 \times 10^{-4}$ مولاري ، وكذلك دُرِسَ تأثير pH ضمن المدى 3-12 .

من خلال نتائج الظروف المذكورة وجِدَ أن أفضل تحويل لمحاليل المثيل الأحمر (ΔT_{max}) تمَّ الحصول عليها عند وجود الصبغة و EDTA بتركيز 1×10^{-4} مولاري ودالة حامضية مقدارها 6 في حين كانت لصبغة الرودامين B 8×10^{-5} مولاري و 1×10^{-4} مولاري و pH=5 على التوالي . وُجِدَ أن أفضل قيم ΔT تمَّ بلوغها بعد خمس ساعات من فترة التشعيع وهي فترة الظهيرة .ووجد بصورة عامة بأن صبغة الرودامين B

اكثر ثباتا من المثيل الأحمر وكذلك استنتج بأن وجود واهب الإلكترونات EDTA قد ساعد في التقليل من سرعة انحدار تركيز الصبغتين.

Studying the efficiency of Photoconversion of Methyl Red and Rhodamine B in The Presence of EDTA in Different PH mediums

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Abstract

This study have been performed to investigate the efficiency of photoconversion of sun light by methyl red and rhodamine B dyes in aqueous solutions via exposing the solutions for limited period to direct solar radiation at sunny and clear day. The study included measuring the difference between dye solution and water (reference). So the ΔT values considered as a direct function of photoconversion efficiency.

The work involves the study of the effect of dye concentration (1 x 10-4 – 1 x 10-5 M) , EDTA as donor of electrons (1 x 10-4 – 1 x 10-5 M), and the effect of pH value (3-12). It has been found that the optimum conditions of photoconversion were : presence of dye (1 x 10-4 M), EDTA (1 x 10-4 M) and pH = 6 of methyl red and 8x10-5 M , 1x10-4 M and PH=5 for rhodamine B respectively.

Generally ,it has been found that the rhodamine B dye was more stable than methyl red , and the presence of EDTA increases the stability of the two dyes.

Introduction

The search for new and renewable sources of energy witnessed a huge expansion especially by using the sun light which supplies the earth with most of clean energy.The radiation from sun consists of a spectrum of a light with different wavelengths at different intensities which reaches 0.2µm -- 50µm, then it is reduce to0.3 --3 µm when it reaches the surface due to absorption of part of it by different atmospheric compounds such as ozone, oxygen, carbon dioxide, aerosols, steam, and clouds [1].The intensity of solar radiation that reaches the surface of earth has a power of about 1 KW/m^2 [2] The using of coloring materials involving organic dyes , pigments , inorganic salts in conversion and the storage of solar energy witnessed a considerable attention in past 25 years as a result of expecting consumption of classical sources of energy , but this subject suffers from some difficulties due to high cost and low efficiency of substituent systems used.

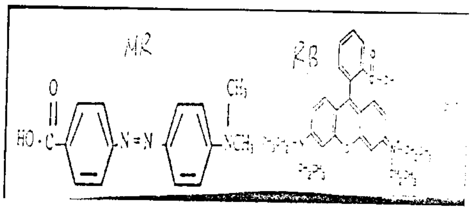
The coloring materials may be use as solution thin films in order to harvest of solar radiation energy. Some requirements must be available in solar energy collector systems; must absorb a wide range of solar spectrum , the materials must have a rigid structure to resist the thermal and photo dissociation.

The using of dye as absorbers in the liquid solar collector systems (LSCS)has been performed and investigated previously [3-6]. The solar energy may be directly converted to heat or used to storage as a chemical fuel such as generating of hydrogen gas by photocleavage of water [7,8,9] or produce of light hydrocarbones by photodegradation of heavy ones [10] by using suitable catalyst.

The recent studies [11,12] used the photoelectrochemical cells (PEC) such as dye sensitized solar cells (DYSC) as a media to collect and convert the solar energy heterogeneous systems by introduce of semiconductors such ZnO , TiO_2 , SnO_2 .... etc. The same system may be contain only the color material in solution [13] .

The present work aims to investigating the thermal performance of methyl red and rhodamine B (fig 1) solutions as solar collector which were used as a photosensitizer [14] and exhibited a low efficiency in photosensitization reaction due to degradation under irradiation with UV light. To increase the efficiency of above systems, new processes were performed such as the modification of semiconductors surfaces by adsorption of coloring materials [15,16] or adsorption of metals such as Ag, Au, Pt ....et as thin film [17,18].

Fig(1); structural formula of rhodamineB and methyl red dyes.



experimental,

Chemicals :

All chemicals obtained in the present work were used without further purification. Sodium hydroxide, methyl red, and standard pH buffer tablets (4,7) were supplied by BDH. EDTA , hydrochloric acid and rhodamine B were received from Fluka.

Instruments :

The electronic spectra of methyl red and rhodamine B solution were recorded by using Shemadza UV 160 spectrophotometer. The pH values were checked by PW 9420 pH meter supplied by Philips. The Beckman glass thermometer was used to measure the ΔT values.

Method :

Pyrex flasks of 1 liter have been used to prepare a dye solution in the range 1×10^{-5} – 1×10^{-4} M by dissolving the dye powder in water with stirring and slight heating to complete the dissolving, then those solution were exposed to direct sun light for 8 hours for methyl red and 7 hours for other dye in clear and sunny day.

The difference of temperatures between dye solutions and water (reference) has been recorded at one hour interval times. Other solutions containing optimum concentration of dye were prepared and EDTA was added in the range $1 \times 10^{-5} - 1 \times 10^{-4}$ M, also , ΔT values were measured.

The effect of pH (3-12) value was studied in the presence of optimum concentration of dye and EDTA and the solutions were exposing to sun light for the same time. The outer sides of vessels were cleaned after all the measurement.

The concentration of two dyes at the same interval time was measured spectrophotometery by reading the absorbancy at λmax of electronic spectrum of meaning dye, which is compared with calibration curve.

Results and Discussion

Solar insolation can be used as active source of heat as a result of high temperature which is generated by solar systems including photochemical absorbing processes which produce an excited state of absorber molecules, then a photoactivated moleculer excited state can drive either [19].

1 – photo dissociation (2) photoisomerisation (3) photoredex reactions :

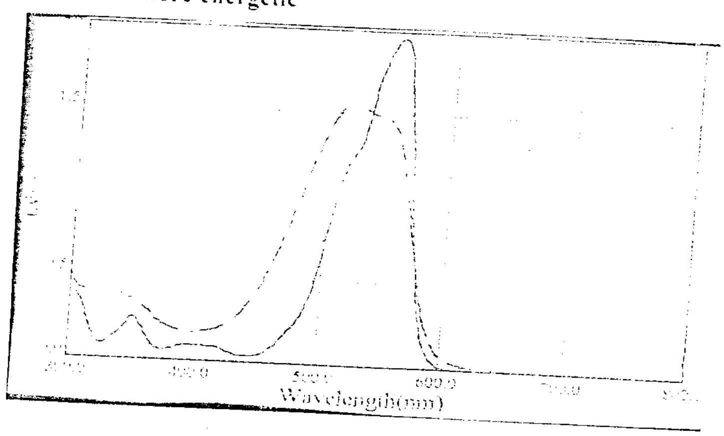
$A + h\upsilon \longrightarrow A^*$ excitation

$A^* \longrightarrow A^- + e^-$ oxidation

The solar activated photodissociation process involves the cleavage of simple excited molecules into two or more energetic species, but this process is limited by several factors such as limited absorption of solar insolation by absorber molecules, low quantum yield, rapid back reaction [20].

The dyes were widly used as absorbers in harvesting and collecting solar energy because of the ability to absorb the visible light by heterogeneous or homogeneous solution or by sensitized thin films.

The rhodamine B and methyl red dyes which are used in the present work have a maximum absorption 545 and 510nm and ε_{max} 33600 and 14500 $L.mol^{-1}.cm^{-1}$ respectively (Fig 2).



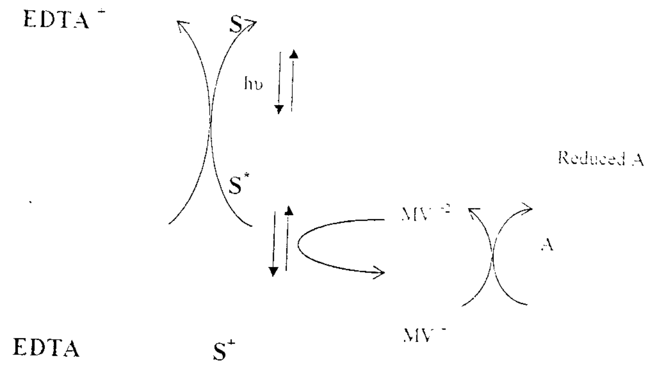
Fig(2);electronic spectra of rhodamine B(____) and methyl red(----) dyes.

This study involved the exposition of aqueous solutions of methyl red dye to direct sun light for 8 hours at different temperatures between dye solutions and the reference was measured . Figure (3) shows the relation of ΔT with time of exposing. It is clear that the ΔT values reach the maximum after 5 hours. The highest ΔT_{max} was 4.7C° for 6 x 10^{-5} M solution , but the solution 1 x 10^{-4} M has the most stable and highest ΔT_{max} values among the other solutions.

Fig (4) shows that the optimum value of ΔT_{max} in the presence of EDTA was 5.0 C° in 1x10^{-4} M methyl red, while ΔT_{max} approach 3.1 C° at PH=6 in the same concentration of EDTA and methyl red as fig (5) shows.

The Fig (6) shows the ΔT values of rhodamine B dye at different concentrations. It is clear the ΔT_{max} of all solutions were in the same time : 4 hours after starting the exposing, while the concentration 1x10^{-4} M recorded the best stability of conversion and best ΔT_{max} for concentration 1x10^{-4} M.

EDTA was used to enhance the efficiency of photoconversion which used succesfully in previous study [21]. Scheme(1) shows the mechanism of EDTA in the presence of photosensitizer. Fig (7) shows the effect of EDTA concentration, and the optimum ΔT_{max} was 4.4 C° in the presence of EDTA 1x10^{-4} M. Fig (8) shows that the best PH medium of rhodamine B was 5 with ΔT_{max} 3.4 C°.



Scheme(1) : Mechanism of EDTA in presence of photosensitizer (S : organic dye)

Figures (9) and (10) show the concentration gradiant of dyes under conditions studied,which showed that rhodamine B has the best stability when comparision with other dye due to the rhodamine B characters and the peculiarity of its rigid structure (fig1) . Figures (11) and(12) shows absorption spectra of rhodamine B and methyl red dyes at intervals of times, it is clear that the degradation of methyl red is faster than other dye, Also the presince of EDTA reduced the degradation of two dyes by reducting the oxidized molecules

Table (1), (2), and (3) summerize the highest values of photoconversion of two dyes at the studied conditions.

There are several forms to investigate the efficiency of thermal performance , all depend on the difference in temperature such as the following one [13] ; which applies to flet plate solar collector (continuous system) :

$$y = m \times C_p (T_o - T_i)/I \times A$$

T_i and T_o temperatures of inlet and outlet water from collector ; C_p heat capacity ; m mass flow rate ; A the area exposing to sun light ; I intensity of incident sun light. Also there is another form called figure of merit (FM) [4] ; which determines the thermal performance.

$$FM = \frac{\Delta T_{max}}{\bar{I} \cdot t\Delta t_{max}}$$

ΔT_{max} : the maximum difference of dye solution and water (reference) ; $t\Delta T_{max}$ the time required to reach ΔT_{max} ; $\bar{I}$ the average of sun light intensity within the same time. So, the above forms depend on ΔT i.e ΔT can be considered as a function of the thermal performance or thermal conversion.

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Table (1) : The highest values of photo conversion (ΔT) of MR and RB in neutral aqueous solutions of different concentrations(mol/l).

Conc. / Dye	$1x10^{-5}$	$2x10^{-5}$	$3x10^{-5}$	$4x10^{-5}$	$5x10^{-5}$	$6x10^{-5}$	$7x10^{-5}$	$8x10^{-5}$	$9x10^{-5}$	$1x10^{-4}$
RB	2.9	3.1	3.8	3.5	3.8	3.8	3.6	3.9	3.7	3.6
MR	2.5	2.7	3.2	3.7	4.2	4.3	4.1	4.1	4.0	4.7

Table(2): The highest values of photo conversion(ΔT) of RB ($1x10^{-4}$ M) and MR ($8x10^{-5}$M) in presence of EDTA of different concentrations(mol/l).

Conc. / Dye	$1x10^{-5}$	$2x10^{-5}$	$3x10^{-5}$	$4x10^{-5}$	$5x10^{-5}$	$6x10^{-5}$	$7x10^{-5}$	$8x10^{-5}$	$9x10^{-5}$	$1x10^{-4}$
RB	2.8	2.9	3.7	3.2	3.2	3.2	3.2	3.2	3.0	4.4
MR	2.9	2.4	2.4	3.5	4.3	3.6	4.4	4.7	4.4	5.0

Table (3) : The highest values of photoconversion(ΔT) for MR ($1x10^{-4}$ M) and RB ($8x10^{-5}$ M) in presence of EDTA ($1x10^{-4}$ M) at different PH values.

pH / Dye	3	4	5	6	7	8	9	10	11	12
RB	2.9	3.4	3.6	3.4	2.9	2.7	3.4	2.9	2.9	2.9
MR	2.6	3.2	2.6	3.2	2.6	2.6	2.4	2.6	2.5	2.7

Fig (4) : Relation of thermal conversion values of methyl red solutions (1×10^{-4} M) with time of exposing in presence of EDTA at different concentrations

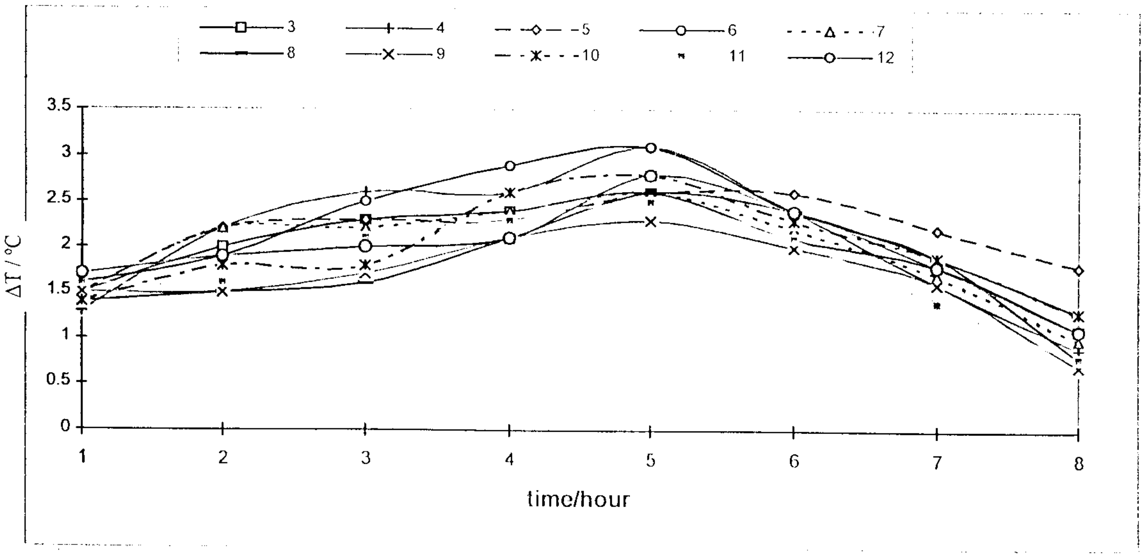


Fig: (6) Relation of thermal conversion values of aqueous solutions of rhodamineB dye with time of exposing in different Conc.

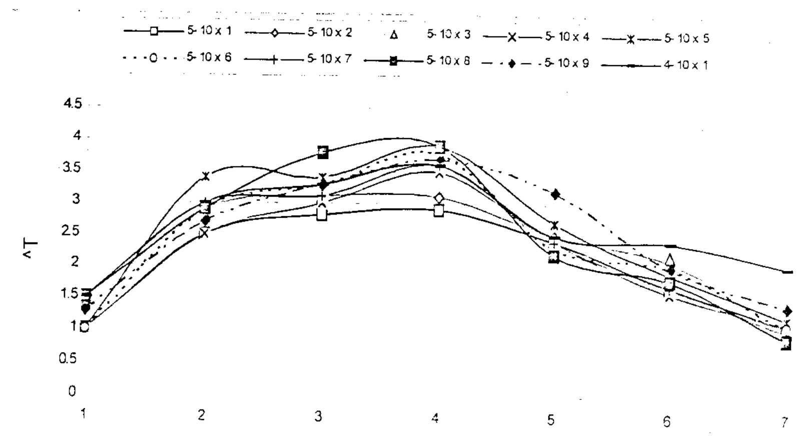
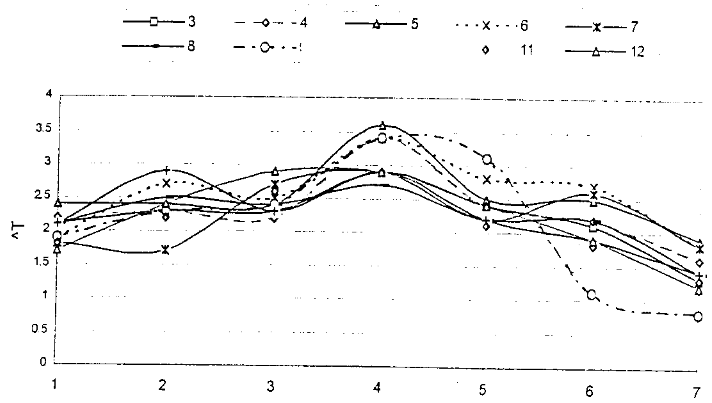


Fig: (7) Relation of thermal conversion values of rhodamine B solution (0.8 x 10^{-5} M) with time of exposing in presence of EDTA at different oncentration.



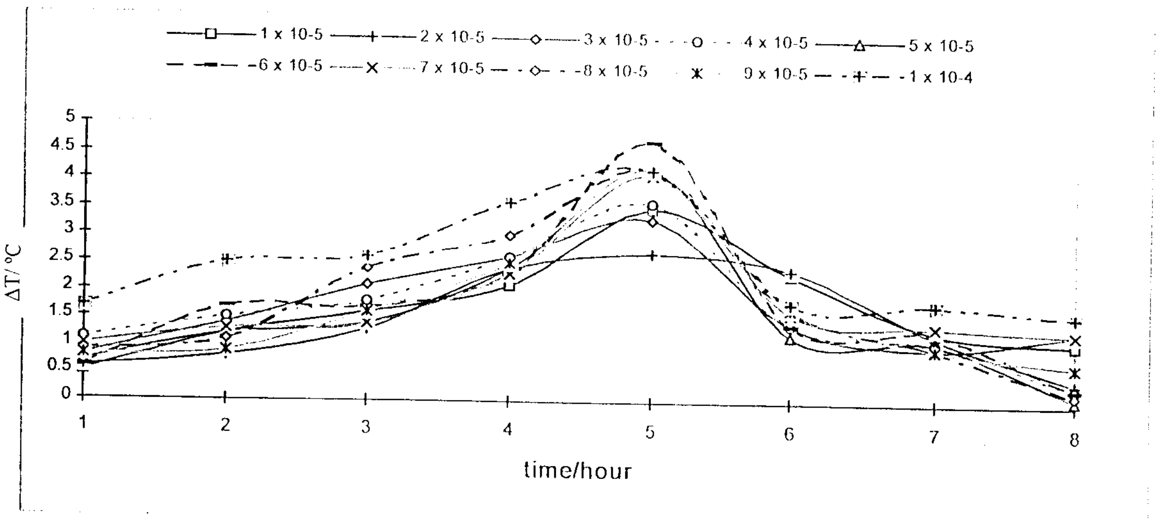


Fig (3) : Relation of thermal conversion values of aqueous solutions of methyl red dye with time of exposing in different Conc.

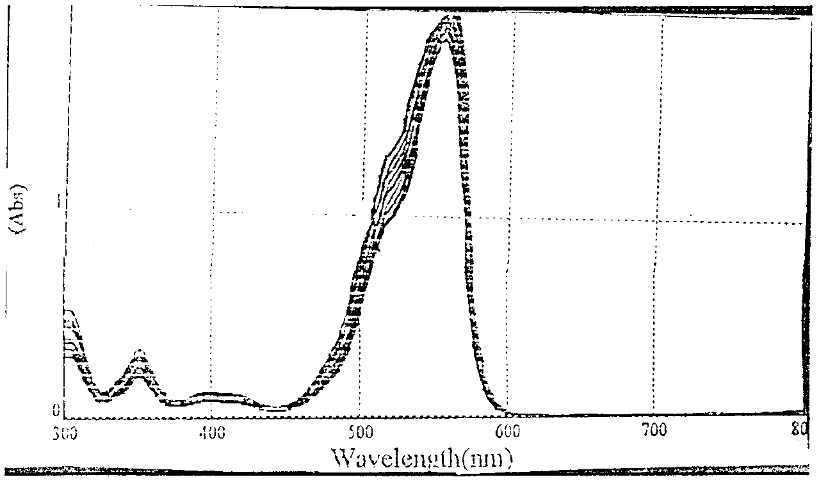
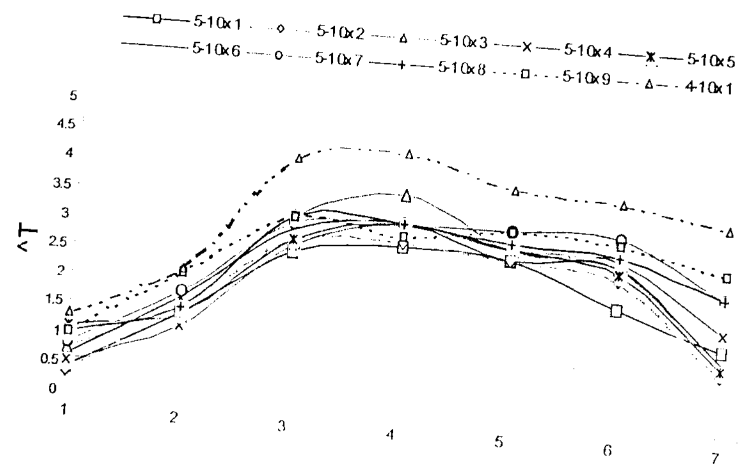


Figure (11): UV-visible spectra of rhodamine B dye (1x10^{-4} mol.l) at different times of irradiation under direct sun light

Fig(5) : Relation of thermal conversion value of methyl red solutions (1 x 10^{-4} M) with time of exposing at different PH in presence of EDTA (1 x 10^{-4} M).



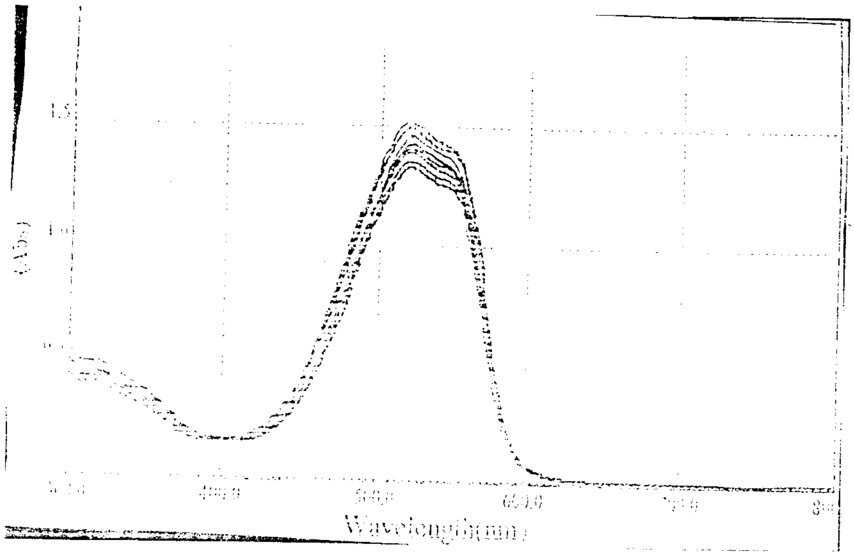
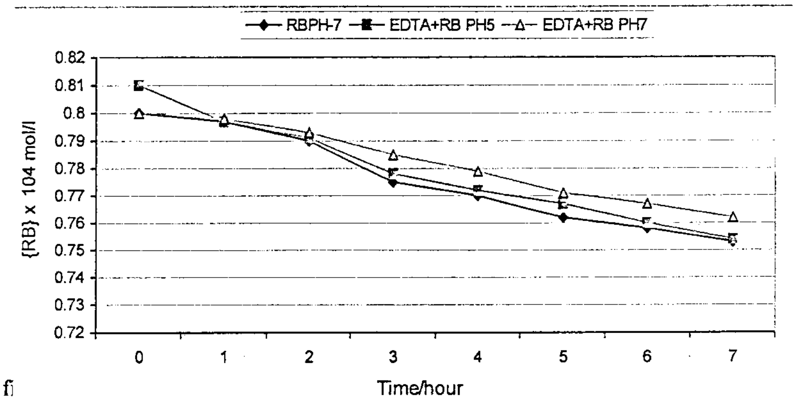


Figure (12): UV-visible spectra of methyl red dye ($1x10^{-4}$ mol.l) at different times of irradiation under direct sun light.

Fig (8) : Relation of thermal conversion value ofrhodamineB solutions (0.8 x 10^{-5} M) with time of exposing at different PH in presence of EDTA (1 x 10^{-4} M).



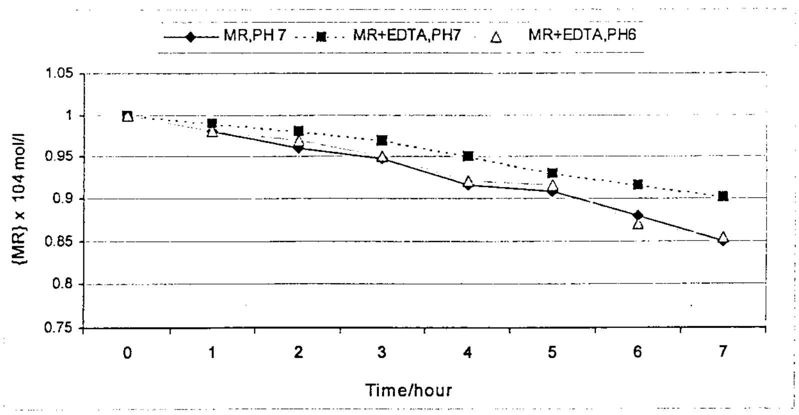


Fig (10): values of methyl red concentration at different times of irradiation.