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Photo Degradation of Methylene Blue in Aqueous Solution by Using Advanced Oxidation Process and Solar Irradiation

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Abstract

The work consists of two parts . The first including of photodegradation of Methylene Blue by using advanced oxidation processes at lab temperature in presence and absence of UV light . The second part consists of photocatalytic reaction of Methylene Blue has been carried out with sun light on ZnO powder. Advanced oxidation processes have proved to be highly effective in degradation of most pollutants in wastewaters. The photocatalytic bleaching of the dye was observed Spectrophotometer . The aim of this study was to show the some parameters such effect of initial dye concentration, pH , initial hydrogen peroxide dosage and catalyst ZnO on the oxidation of MB dye . Generally it has been found that the rates of photodegradation of MB dye was higher in presence of UV radiation . Also, photocatalytic ZnO showed the importance with sun light lead to enhance the generation of hydroxyl radicals which drive the photooxidation processes. It has been found the photodegradation reaction of dye under UV obeys the first order kinetics. The work was done on the roof of the laboratory building and the time of irradiation was between 1.00 am - 3.00 pm and the date of experiments was in July .

.Introduction1

The environmental risks by effluents of textile wastewater industry are the major source of water and ground water pollution. Textile industry is one of the most complicated industries among manufacturing industry(1). Various semiconductors have been used as photocatalysts for the removal of different dyes from their aqueous solutions. Photocatalytic and oxidative degradation of wastewater pollutants in the presence of TiO_2 was observed by Das et al.(2) . Major pollutants in textile wastewaters are high acidity, heat and other soluble substances main pollution in textile wastewater came from dyeing and finishing processes(3-4) . Photo-oxidation technique is one of the important techniques that is used in many fields which was high efficiency in the removal of the toxic effects of the environmental pollutants (5). The degradation of these synthised dyes have been extensively investigated by different technological and chemical processes such as photocatalytic degradation (SiO_2 ,TiO_2 , ZnO ,……) (6,8) , chemical methods: ozonation (9-10), chlorination (11-12) ,biodegradation(13), adsorption(14,16) and oxidation process(17). Many researches suggested that the potential exists for the use of highly concentrated sunlight in the removal of dyes from wastewater (18,20) . Heterogeneous photocatalysis by semiconductor particles is a promising technology for the reduction of global environmental pollution. MB has wide applications, which include colouring paper, dyeing cottons, wools and coating for paper stock. In some of the processes ZnO has been reported to be more economical for the treatment of industrial effluents and more efficient than TiO_2 (21). Carla and coworkers have been studies photo oxidation of cork manufacturing wastewater by different homogeneous (H_2O_2/UV-Vis and H_2O_2/Fe^{2+}/UV-Vis) and heterogeneous (TiO_2/UV-Vis) systems, with degradation performances being evaluated in terms of total organic carbon(TOC) removal (22). Generally , many studies show clearly that the efficiency of a photocatalytic for the degradation of organic and inorganic compounds is strongly dependent on their chemical nature of the dye (23- 25). Fig (1) shows the scheme structural .formula of dye

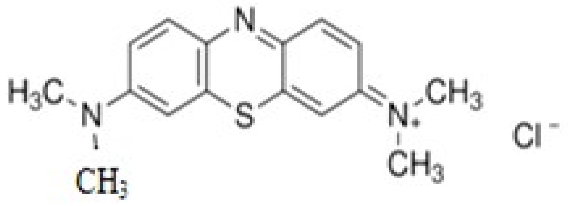


Fig (1): Structural formula of Methylene Blue dye.

2. Experimental

2.1. Materials

All chemicals were used without further purification. Hydrogen peroxide (H_2O_2 30% w/v), sodium hydroxide (NaOH) and hydrochloric acid(HCI) and sulphuric acid H_2SO_4 were supplied from BDH. Methylene Blue dye (product of USA.MSDS) was purchased from Omega. The photocatalyst ZnO was purchased from Merck (99% purity). All the other chemicals and solutions were prepared with double distilled water.

2.2.Experimental procedures.

The first part deals with dye solutions were irradiated for a period of 90 minutes (the primary experiments indicated that the most of dye molecules are degraded or become colorless at the time near to this period). Within this time samples were taken by syringe for measuring the dye absorption at λ_{max} =664nm and then determination of dye concentration by using the calibration curve shown in Fig(2), Fig(3) shows the UV-Visible absorption spectrum of dye. The pH was adjusted to the desired value using 0.1N of sodium hydroxide and hydrochloric acid(26). Control experiments were carried out under UV irradiation with H_2O_2 in the solutions and with H_2O_2 but no irradiation. In all experiment the lamp was warming on for 10 min prior to initiation of reaction. Aqueous ZnO suspensions were prepared by adding 0.80 gm of powder to 1L of ZnO aqueous dye solution (concentration of all dyes was $1X10^{-5}$ M). Then all solutions were placed in petridishes outside the laboratory building and directly exposed to natural sun light for 120 min at temperature range (35-41) º C in July 2013. At each time step, one petridish was wrapped with aluminum foil, and waited until all irradiations were finished, then samples were taken and pH was determination by used pH-meter (211- Instrument, Romania). In the same time the absorption was measured by using spectrophotometer (Shimadzu UV-Visible 1650 spectrophotometer) after removal the ZnO particles by centrifugation (CORP Triup International, Italy instruments) and filtration then recording the results and absorbance at λ_{max} which determine by used.

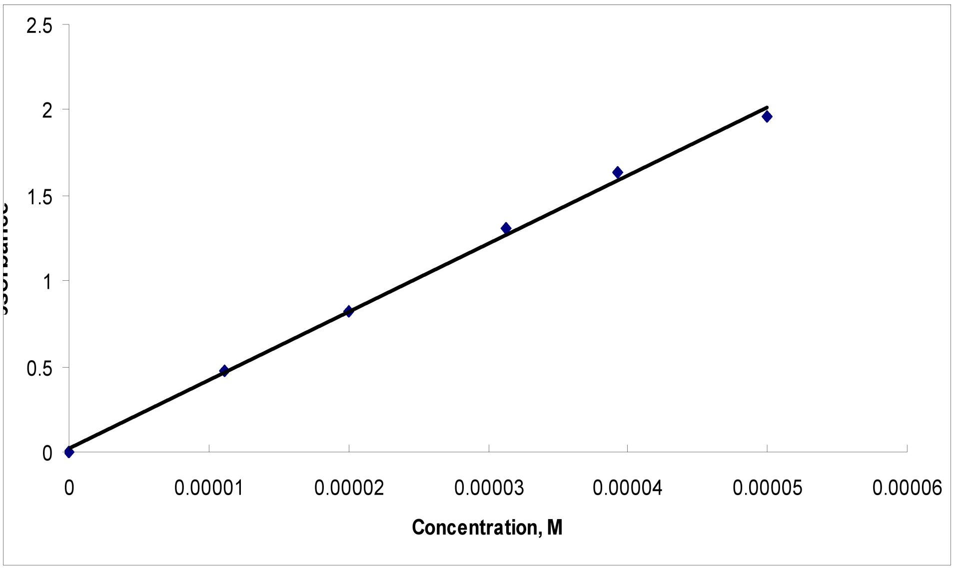


Fig (2):Calibration curve for Methylene Blue dye at pH=6,T=298K.

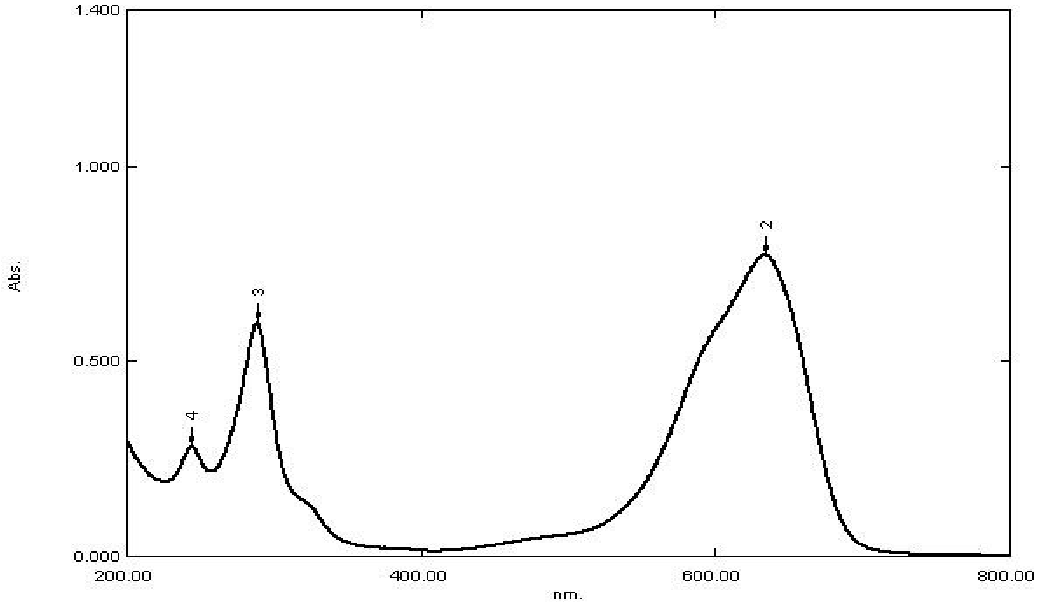


Fig (3): UV-Visible spectrum of aqueous solution of MB dye (1x10^{-5} M), pH=6, T=298K.

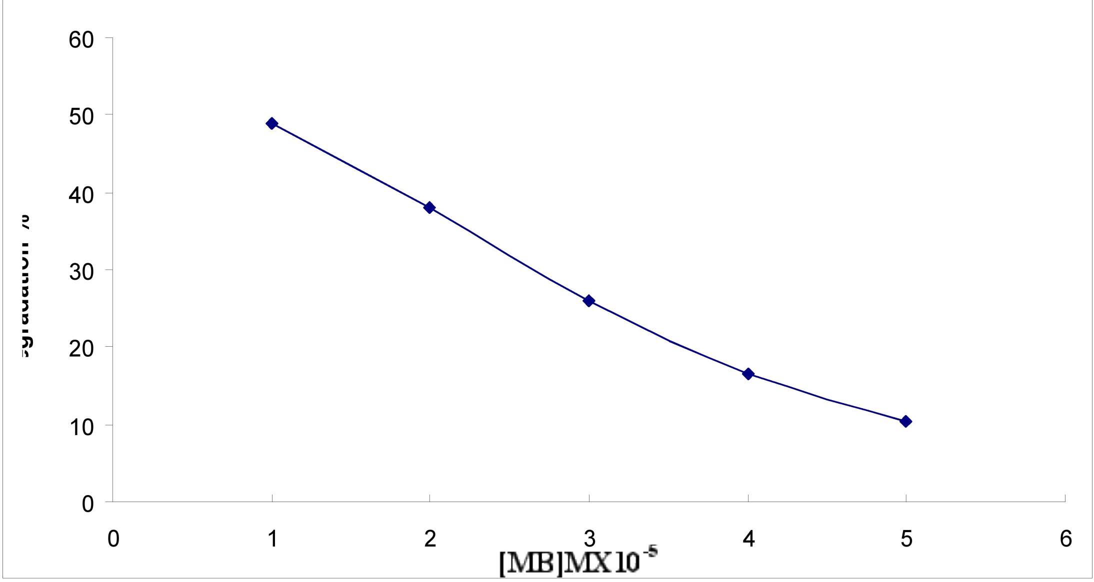
3. RESULTS AND DISCUSSION.

3.1. Effect of initial dye concentration .

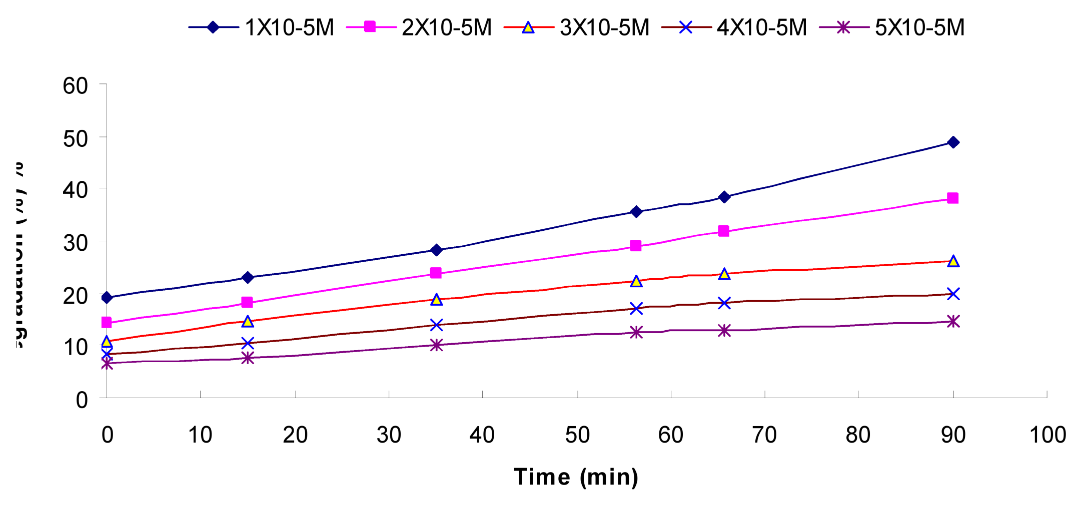
In this study, the effect of various initial dye concentration in the range 1x10^{-5}M- 5x10^{-5}M on the degradation from Methylene Blue dye was investigated by using UV irradiation for 90 minute. The percent of color removal from MB decreases from 49% to 14% with increasing the concentration of dye from 1x10^{-5}M to 5x10^{-5}M in presence of UV irradiation. Higher dye concentrations increased the absorption of UV radiation, therefore decreasing the availability of UV light for reactions , so lowering the formation of hydroxyl free radicals in the (27). Fig (4) refers the result . The effect of UV irradiation on various initial dye concentration for decolorization is shown in Fig(5). The degradation rate was first-order kinetic, The kinetic constant can also be calculated by Eq. (1):

$$\mathrm{Ln}\,\frac{A}{A_o} = -kt \qquad \ldots\ldots\ldots\ldots(1)$$

Where : A_o and A are the initial and final absorbance before and after irradiation. k : reaction rate constant.



Fig(4): Effect of dye concentration on color removal of MB dye at pH=6,T=298K

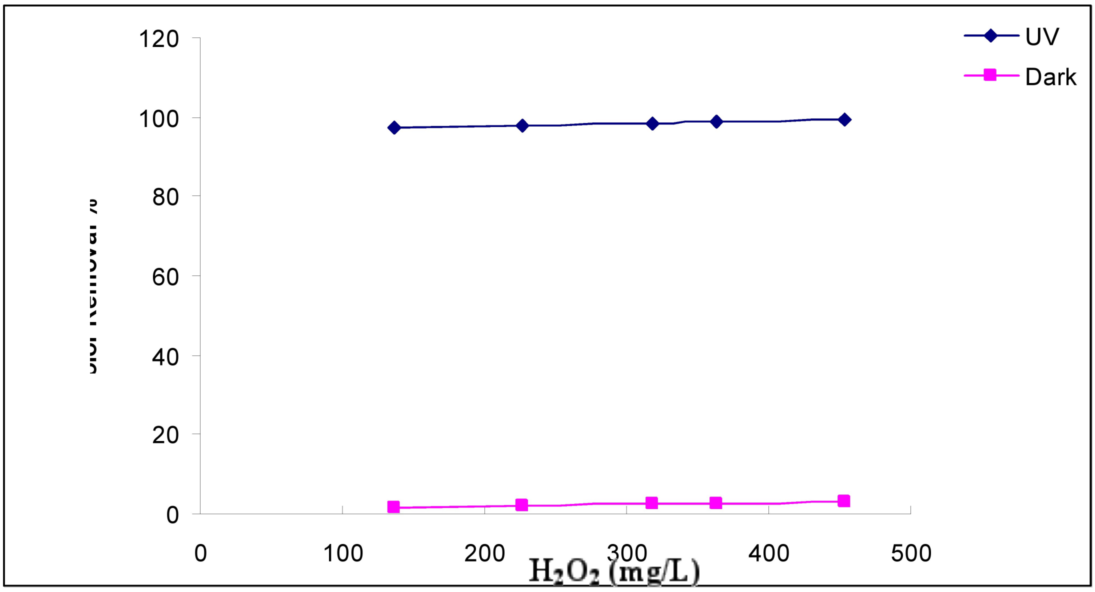


Fig(5): The percentage of photo degradation of MB dye with time at different initial concentrations.

3.2. Effect of initial Hydrogen peroxide concentration.

These experiments are carried out on Methylene Blue dye with ($1x10^{-5}$M) concentration by using varying the initial H_2O_2 concentration in the range (100-500) mg/L . At low hydrogen peroxide concentrations, formation of •OH is the kinetic determining step. Hydrogen peroxide cannot generate enough hydroxyl radicals and the oxidation rate is logically slow. At higher hydrogen peroxide concentration more $^{\bullet}OH$ was produced leading to a faster oxidation rate. Also, these free radicals preferred to react with the excess of H_2O_2 dosages(28). The results show that the higher color removal in presence light was 96.1% for 500mg/L of H_2O_2 . The dark experiments without irradiation showed no degradation was detected because that H_2O_2 generate very high active $^{\bullet}OH$ only under UV or visible light. Ultraviolet radiation is used to cleave the (O-O) bond in hydrogen peroxide and generate the hydroxyl radical . The results are shown in Fig (6). Photolysis of H_2O_2 by (H_2O_2/UV) generates hydroxyl free radical according to following (29) :

$$H_2O_2 + h\upsilon \rightarrow 2HO^{\bullet} \qquad (1\text{-}7)$$
$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad (1\text{-}8)$$
$$HO^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + O_2 \qquad (1\text{-}9)$$



Fig(6):Effect of different H_2O_2 concentration on colorremoval, [MB]=$1x10^{-5}$ M, pH=6 at T=298K.

3.3. Effect of initial pH.

The effect of pH on photodegradation is very important , experiments are conducted at 1 x 10^{-5}M dye concentration in presence of 500mg/L H_2O_2 dose at different initial pH values ranges from 1 to 10, for 90 minutes at T=298K, the result is shown in Fig(7) .The results show that, high color removal from MB 99.4% is observed at pH equal 4 and decrease slightly in alkaline media in presence UV and (45%) from the dye in pH=1 in dark at the same conditions. The degradation rate under UV/ H_2O_2 should decrease with increasing pH because the concentration of $^{\bullet}OH$ will decreased . Hydrogen peroxide undergoes decomposition in alkaline medium produced oxygen and water rather than producing hydroxyl free radicals under UV light (30).

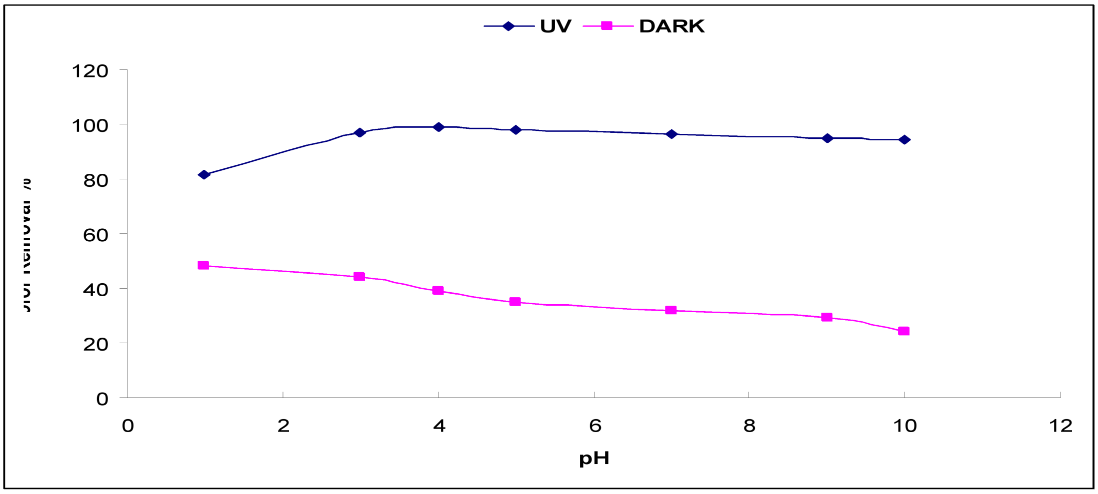


Fig (7):Effect of different pH media on the degradation of dye.
[MB]=1x10^{-5} M, [H_2O_2]=500mg/L,T=298K.

3.2. Photolysis of ZnO.

In our previous studies (31,32,5) , we reported that titanium dioxide and zinc oxide have good photocatalytic properties nominated both catalysts to be promising substrates for photodegradation of water pollutants and show the appropriate activity in the range of visible irradiation .

The color removal rate was increased significantly by increasing the amount of ZnO .The increasing in the amount of catalyst increases the number of active sites of the ZnO surface that in turn increases the number of $^{\cdot}OH$ and O_2 radicals(33) . To optimize the concentration of ZnO needed for the highest degradation rate the following quantities were used starting from 0.1 to $1.0 gl^{-1}$ depending on the nature of the dyes(34) . Complete photobleaching requires 120 min in solar irradiation of dye. The amount of semiconductor is also likely to affect the process of dye degradation and hence, different amounts of photocatalyst were used. This increase in the rate of bleaching may be attributed to increase in the exposed surface area of the semiconductor. But after certain limit (0.80 g), if the amount of zinc oxide is increased further, there will be no increase in the exposed surface area of the photocatalyst . Several authors (35-36) related this observation to the light scattering and consequent reduction in light penetration through the solution induced by lightproof suspended catalyst . The results are reported in Fig (8), this results is similar to the study was carried out by (37-38). Efficiency of photocatalytic degradation processes was determined from the equation (1) (39).

$$\text{Degradation } (\%) = (C_o - C_t) / C_o \times 100 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where C_o is the initial value of dye solution at t=0 min and C_t is the final value of dye solution during different periods of time of photocatalysis processes in presence of ZnO .

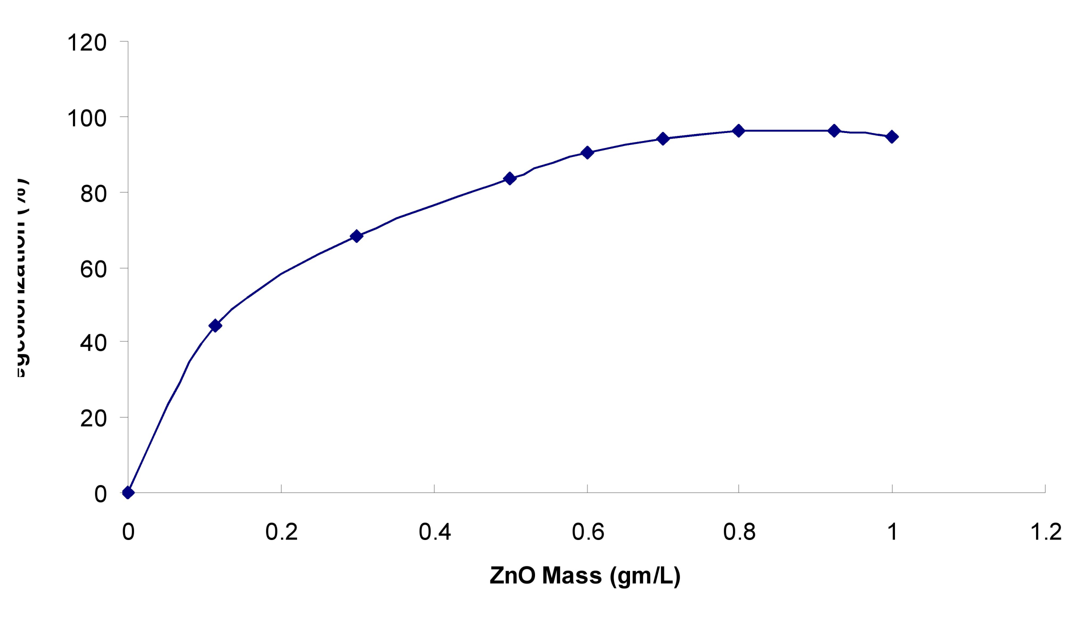


Fig (8): Mass effect of ZnO on decolorization% of [MB] dye= 1.0 X10^{-5} M under direct solar light.

3.2.1. Effect of pH .

The pH of the solution is likely to affect the degradation of (MB) and hence, experiments are conducted at 1 x 10^{-5}M dye concentration in presence of 0.80 g of ZnO at different initial pH values (3, 5, 9 and 12) for 120 minutes at T=298K, the Fig(9) shows the gradient of relative dye concentration Ct/Co under increasing of irradiation time. Degradation removal efficiency is evidenced to be affected by pH photocatalytic degradation under direct solar light all this experiment could be achieved at the range of temperature (35-41) ˚C and the time of irradiation was between 1.00 am - 3.00 pm . Photocatalyzed intermediates seem to have slightly different functional groups, also can due the bleaching degradation to generations of •OH radicals, which are produced from the interaction of •OH and hole (h+) of the semiconductor these •OH oxidize the dyes molecules in their forms (40). The increase in the rate of photocatalytic degradation may be due to greater availability of OH^{-} at higher pH values. The OH^- will generate more •OH radicals by combining with the photogenerated holes in the semiconductor and these hydroxyl radicals are considered responsible for this photocatalytic degradation. pH plays an important influence the adsorption of dye molecules on the ZnO surfaces an important step for the photodegradation have already reviewed that acid-base properties of the metal oxide surfaces can have important considerable (41).

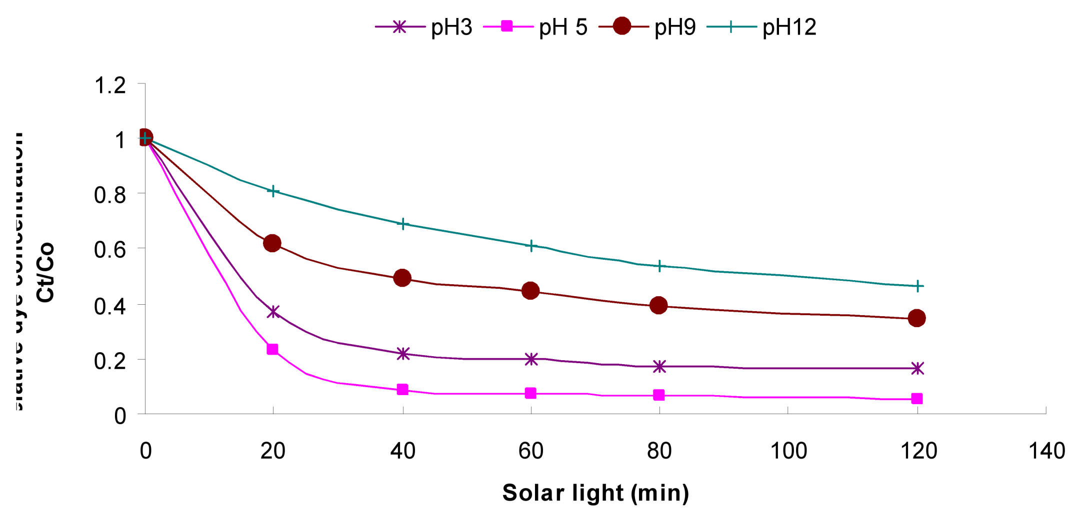


Fig (9): Effect of different pH value on color removal of MB dye as function of solar light, [MB]=$1X10^{-5}$M, ZnO =0.80g/L of under direct solar light .

4. Conclusions .

1- The photooxidation of Methylene Blue dye by using the UV/H_2O_2 is more effective in an acidic medium with the initial dosage of H_2O_2 ranging between 100-500 mg /L.

2- The degradation was strongly influenced by various parameters, particularly the initial H_2O_2 dosage, dye concentration, pH and amount of semiconductor .

3- The uses of amount semiconductor oxides as photocatalyst in sun light has been established in case of bleaching of Methylene Blue dye. Solar energy has been proved more efficiency for removal the dyes .

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التحطم الضوئي لصبغة المثلين الازرق في محاليلها المائية باستخدام طرق الأكسدة المتقدمة وأشعة الشمس .

أزل شاكر وهيب
قسم الكيمياء, كلية العلوم - جامعة المثنى

الخلاصة

يشتمل البحث علي جزئيين , الأول يتضمن دراسة التحطم الضوئي للصبغة باستخدام عمليات الأكسدة المتقدمة (AOP 'S) وبدرجة حرارة المختبر بوجود وغياب الاشعة فوق البنفسجية . تضمن الجزء الثاني من البحث دراسة التفاعل الضوئي المحفز الذي اجري للصبغة بوجود ضوء الشمس على سطح ZnO. اثبتت عمليات الاكسدة المتقدمة كفاءة عالية في تحطيم مدى واسع من الملوثات في مياه الصرف. ان الهدف من هذه الدراسة تضمن دراسة تأثير تركيز الصبغة الابتدائي ، pH المحلول , جرعة بيرو كسيد الهيدروجين المستخدمة والتحفيز الضوئي باستخدام ZnO . وجد وبصورة عامة أن سرعة الأكسدة الضوئية للصبغة عالية بوجود الاشعة فوق البنفسجية . . أشارت حركية التجزئة ان سرعة التجزئة الضوئية للصبغة هي حركيات من الدرجة الاولى. لقد تمت جميع التجارب خارج المختبر على السطح والوقت كان محصور مابين 1.00 صباحا إلى 3.00 ظهرا وكان تاريخ إجراء التجارب هو شهر تموز .