

Photocatalytic Removal of Methyl Orange in aqueous solution by TiO₂ using solar irradiation process

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Abstract

An aqueous solutions of methyl orange were investigated in an open vessel equipped with sun light using three weights of TiO₂ as catalyst to select the best.

The effect of initial concentration for Methyl orange dye was studied for three concentrations 9.17×10^{-5} M , 9.17×10^{-7} M and 9.17×10^{-8} M and the results showed that the photodegradation percentages and the rate constants of low concentration was more than high concentration of same dye and the solution becomes colorless , and the mechanism of this process was proposed. The kinetic were studied at different intervals for four hours also the percentages of degradation were studied also.

The determination of maximum wave length was done.

The work was done on the roof of the laboratory building and the time of irradiation was between 10.00 am - 3.00 pm .The date of experiments was in November and the mean of temperature was 20C⁰

الخلاصة

تم دراسة تأثير التركيز الابتدائي للصبغة وكذلك ميكانيكية التفاعل وقد بينت النتائج انه في التراكيز الواطئة تكون النسبة المئوية للتكسر الضوئي وكذلك ثابت سرعة التفاعل اكبر مما لو كان في التراكيز العالية لنفس الصبغة مما يؤدي إلى اضمحلال اللون.

تمت عملية التكسر الضوئي لصبغة الميثيل البرتقالي في وعاء مفتوح معرض لضوء الشمس كمصدر للأشعة فوق بنفسجية واستخدام ثلاث اوزان من ثنائي اوكسيد التيتانيوم كعامل مساعد وتم اختيار الافضل. كذلك تم دراسة حركية التفاعل في أوقات مختلفة لتراكيز مختلفة من الصبغة وكذلك تم دراسة حركات التفاعل لها وكذلك تم تحديد الطول الموجي الأعظم للصبغة وذلك من خلال قياس الامتصاصية في أطوال موجية مختلفة. لقد تمت جميع التجارب خارج المختبر على السطح والوقت كان محصور ما بين ١٠,٠٠ صباحا إلى ٣,٠٠ ظهرا وكان تاريخ إجراء التجارب هو شهر تشرين الثاني وكانت معدل درجة الحرارة 20C⁰.

Introduction

There are three different types of titanium dioxide, anatase, rutile, and brookite. Most of the studies have been performed on the anatase and rutile types. The adsorptive affinity of anatase for decomposition of organic compounds is larger than that of rutile. Due to irradiation of anatase titanium dioxide particles by UV light ($\lambda < 300\text{nm}$), it has a large band gap around 3.2 eV; rutile has a 3.0 eV band gap under wavelengths less than 410 nm⁽¹⁾. Titanium dioxide has a good capacity to degraded organic compounds⁽²⁾ by oxidation and also remove heavy metals by reduction of them⁽³⁾. It is relatively inexpensive, insoluble in water and nonpoisonous⁽⁴⁾. The process of photo catalysis is relatively simple. Light energy from ultraviolet radiation in the form of photons, below 390 nm, excites the electrons on the surface of titanium atoms suspended in the contaminated water⁽⁵⁾. On the other hand, when TiO₂ is illuminated with the light of $\lambda < 390\text{ nm}$, electrons are promoted from the valence band to the conduction band of the semi-conducting oxide to give electron-hole pairs. The valence band (h^+_{VB}) potential is positive enough to generate hydroxyl radicals at the surface and the conduction band (e^-_{CB}) potential is negative enough to reduce molecular oxygen⁽⁶⁾. The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of TiO₂. It causes photo oxidation of pollutants⁽⁷⁾. By contrast, photo catalytic reduction takes place when hole scavenger is adapted, and the photo generated electrons are allowed to undergo cathode reaction. Carla and coworkers have been studies photo oxidation of cork manufacturing wastewater by different homogeneous (H₂O₂/UV-Vis and H₂O₂/Fe²⁺/UV-Vis) and heterogeneous (TiO₂/UV-Vis and

TiO₂/H₂O₂/UV-Vis) systems, with degradation performances being evaluated in terms of total organic carbon (TOC) removal⁽⁸⁾. Yinhua Jiang and coworkers have studied the solar photocatalytic decolorization of C.I. Basic Blue 41 in an aqueous suspension of TiO₂-ZnO. They showed the nano-sized TiO₂-ZnO powder displayed high photocatalytic activity towards the decolorization of C.I. Basic Blue 41 in water under solar irradiation and Ti/Zn molar ratio of 1:1 showed highest photocatalytic activity. Hasnat and coworkers have been studied the adsorption and photocatalytic decolorization of a synthetic dye erythrosine over anatase TiO₂ and ZnO. He showed the influence of H₂O₂ on decolorization efficiency was found noticeable since it is a hydroxyl radical provider, the decolorization efficiency was also investigated over the pH range of 5.0 – 10.0 indicating that increasing pH enhances decolorization efficiency⁽⁹⁾.

Experimental

Methyl orange was obtained from sigma chemia GMBH (Germany) and used without further purification. The photocatalyst used in this work was the non ionized TiO₂ which was supplied Degussa P25, surface area 50 m² / g. This photocatalyst was used without further treatment.

Methyl orange (MeO) (C₁₄H₁₄N₃SO₃Na) structure is indicated in Fig.1, it is characterized by sulphonic group which is responsible for the high solubility of this dye in water.

The reaction mixture was carried out using 100ml Pyrex glass reservoir placed outside the laboratory building. Pyrex glass beaker containing methyl orange dye sample (50ml) and 50 mg of the TiO₂ catalyst was placed in the reaction vessel. The concentrations of MeO were

9.17×10^{-5} M, 9.17×10^{-7} M and 9.17×10^{-9} M. Sun light was collected by using concave lens with a focal length of 250mm. The solution was kept homogeneous by using a magnetic stirrer in the suspended colored solution dye.

The time of irradiation was closed between 10.00 am– 3.00 pm. The UV-visible spectrum of methyl orange (MeO) dye was measured using UV-visible spectrophotometer (PD-303 Spectrophotometer, APEL Japan), where $\lambda_{\max} = 490\text{nm}$.

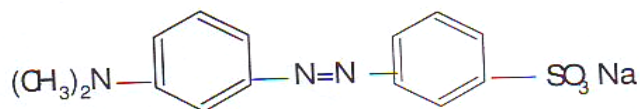


Figure 1: structure of Methyl Orange

Results and Discussion :

The photodegradation of MeO was followed by measuring the absorbance of treatment samples, this absorbance

of MeO was decreased with increasing of time in the presence of TiO₂ and sun light as shown in Figures (2, 3, and 4)

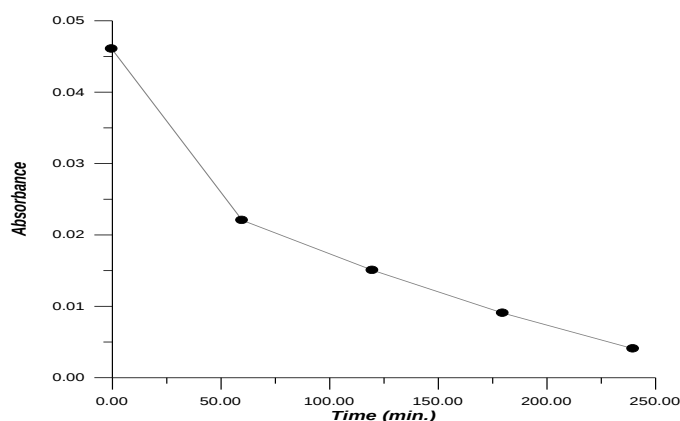


Figure 2: effluence of photocatalytic degradation on the 9.17×10^{-7} M of MeO at different times.

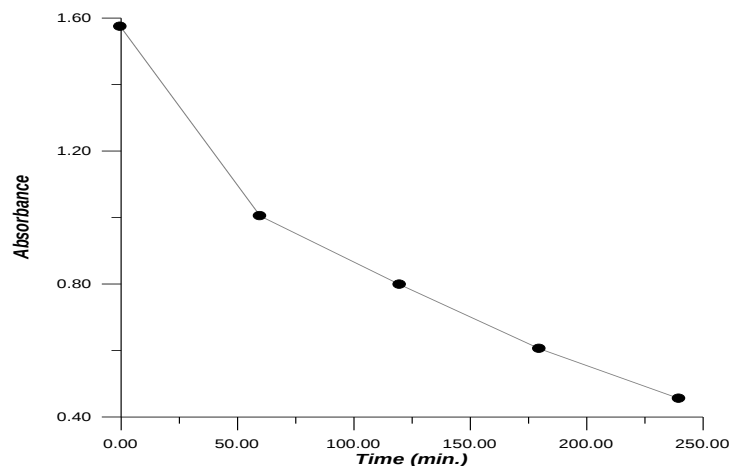


Figure 3: effluence of photocatalytic degradation on the 9.17×10^{-5} M of MeO at different times.

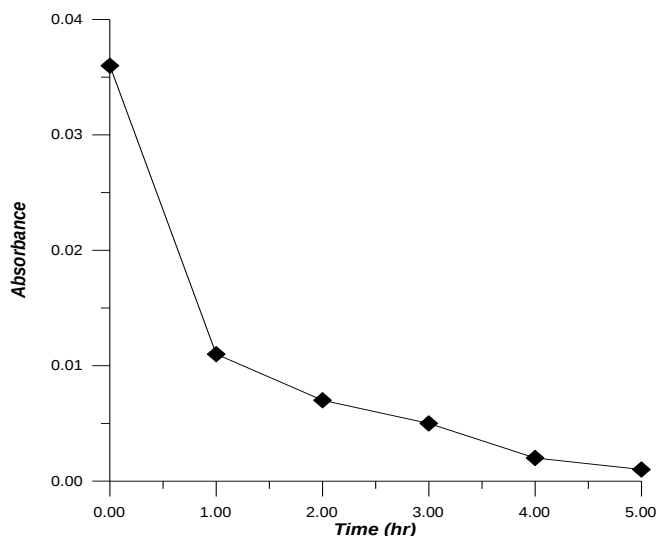


Figure (4) Effluence of photocatalytic degradation on the 9.17×10^{-8} M of MeO at different times

Effect of Initial Concentration

The degradation percentage for 9.17×10^{-5} M and 9.17×10^{-7} M of MeO was increased with time of illumination Fig. 5 according to the following equation

Deg% = $\{(A_0 - A_t)/(A_0 - A_\infty)\} \times 100\%$. Where A_t is the absorbance after time t and A_0 is the absorbance of dye at $t = 0$, and A_∞ is absorbance at $t = 5$ hr. It is generally noted that the degradation rate increases with the increase of dye concentration to a certain concentration and a further increase leads to decrease in the dye

degradation rate¹⁰. The decrease of dye degradation as the dye concentration increase is as a result that the generation of $\text{OH}^\cdot$ Radicals on the catalyst surface is reduced since the active sites are covered by dye ions¹¹. Also Kansal¹² concluded that the photocatalytic degradation of methyl orange, using TiO_2 as a catalyst and UV source, decrease as the dye concentration increase. They explained this decrease as the result of increasing the number of photon absorption by the catalyst in lower concentration⁽¹³⁾.

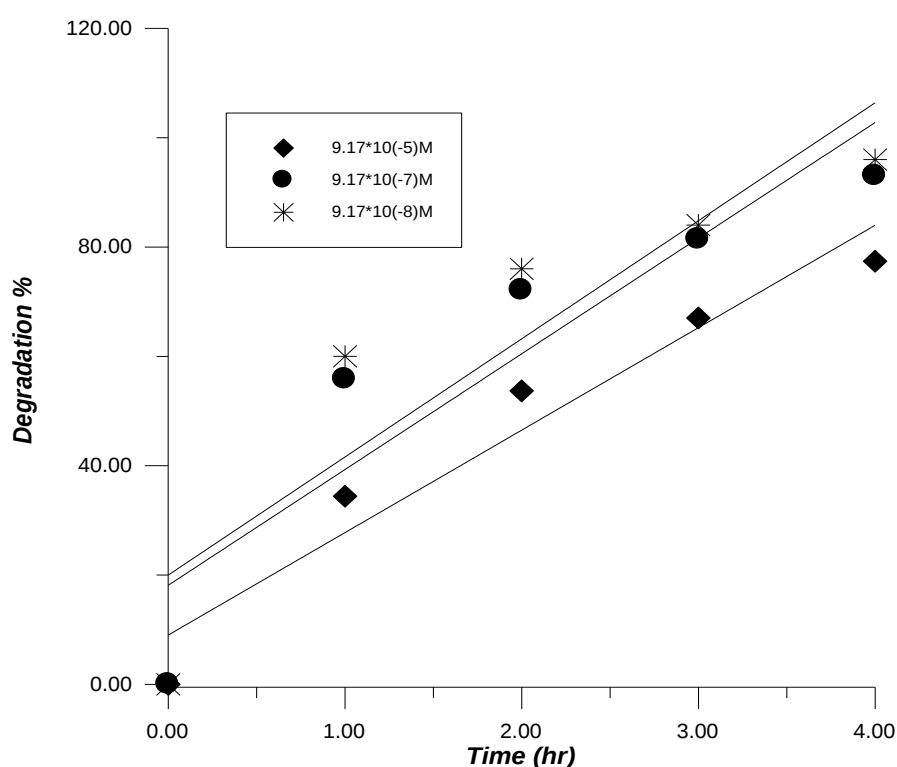


Figure (5) The percentage of photocatalytic degradation of MeO with time at different initial concentrations.

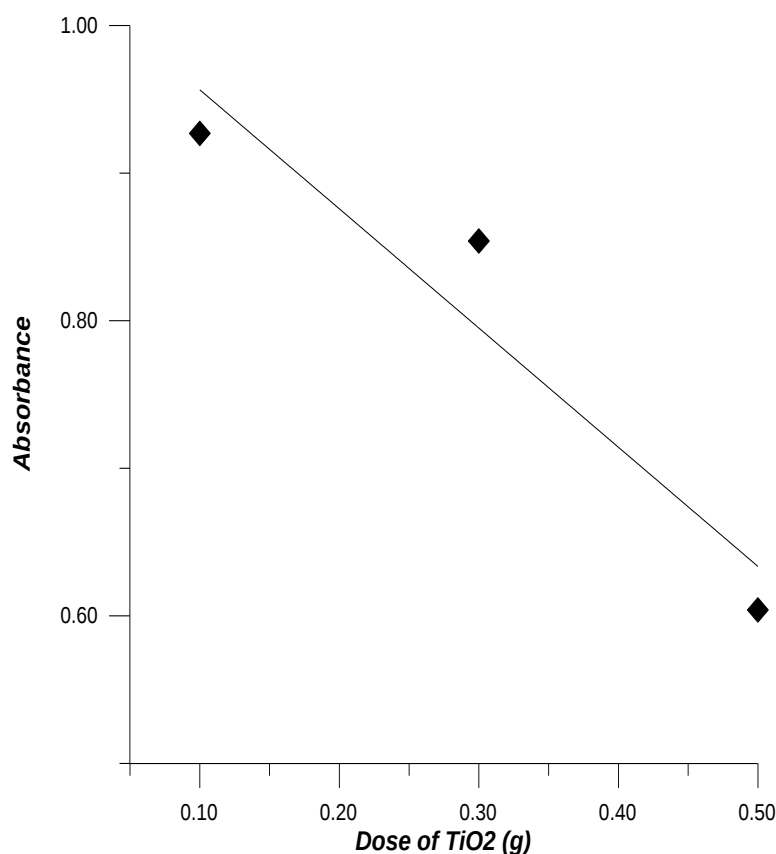
Table (1) Relation ship between initial concentration of dye and Deg % .

Concentration of dye	Degradation Percentage (Deg %) of irradiated dye			
	1 hr	2 hr	3 hr	4 hr
9.17×10^{-5} M	39.42	53.67	67.01	77.39
9.17×10^{-7} M	55.81	72.09	81.4	93.02
9.17×10^{-8} M	60	76	84	96

Effect of the Amount of Catalyst on the Color Removal

The effect of TiO_2 concentration on decolourization was investigated on the methyl orange dye .Accordingly the color removal rate was increased significantly by increasing the amount

of TiO_2 .The increasing in the amount of catalyst increases the number of active sites of the TiO_2 surface that in turn increases the number of OH and O_2 radicals¹⁴ .Figure (6) explain that the degradation of dye increases with increasing catalyst



Figure(6) :Variation of the absorbance with different amount of TiO_2

The Kinetic Study

The kinetics of disappearance of MeO with time at different initial concentrations is illustrated in Fig. 7 and (Table2) . The data showed that the photocatalytic decolorization of MeO dye can be described by first order kinetic^(15,16) model $-\ln (C/C_0) = kt$.

Where C_0 is the initial concentration , and C is the concentration at time t .

$C_0 = A_0 - A_\infty$, $C = A_t - A_\infty$,
Therefore $-\ln [(A_t - A_\infty)/(A_0 - A_\infty)] = kt$

Plot - $\ln [(A_t - A_\infty)/(A_0 - A_\infty)]$ against t , to obtain the **slope = k**

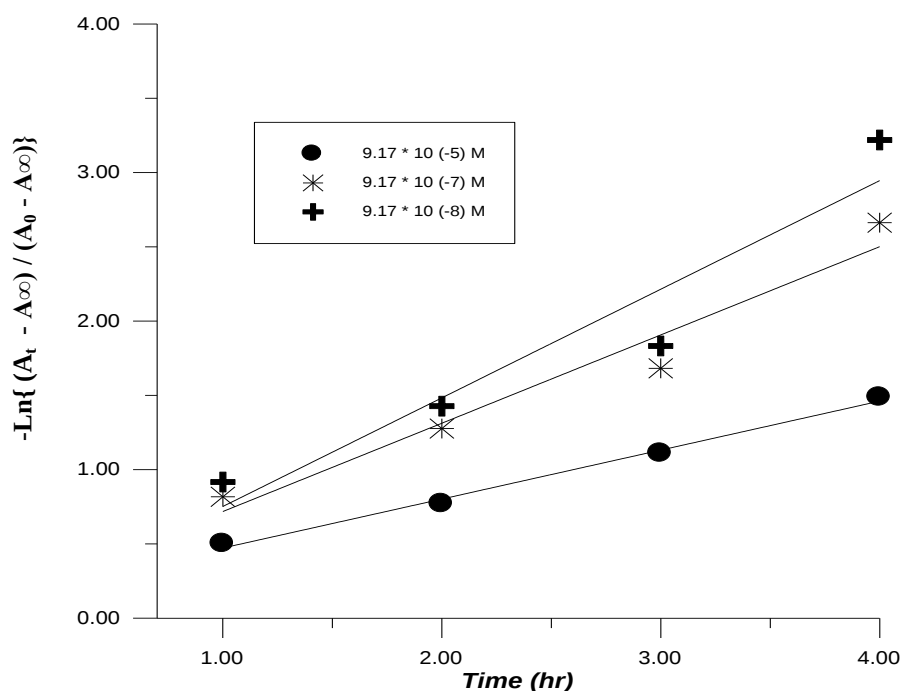


Figure (7) : Pseudo – first order kinetics for methyl orange photocatalyzed degradation

The plots of the concentration data gave a straight line .The correlation constant for the fitted line was calculated to be $R^2 = 0.9942$, 0.952 and 0.914 for methyl orange concentrations $9.17 \times 10^{-5} \text{ M}$, $9.17 \times 10^{-7} \text{ M}$ and $9.17 \times 10^{-8} \text{ M}$ respectively . The rate constants were calculated to be 0.3296 , 0.594 and $0.7313 \text{ (hr}^{-1}\text{)}$ for the

previous concentrations for methyl orange respectively.

Table2: Rate constant and correlation constant for catalytic photodegradation of MeO.

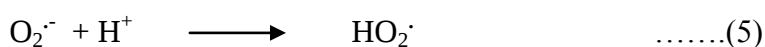
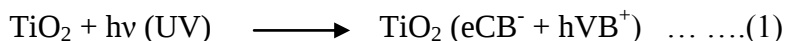
Concentration of MeO	Correlation constant R^2	Rate constant k (hr^{-1})
9.17×10^{-5} M	0.9942	0.3296
9.17×10^{-7} M	0.952	0.594
9.17×10^{-8} M	0.914	0.7313

Photocatalytic degradation mechanisms

Photocatalytic oxidation

The detailed mechanism of MeO dye catalyzed degradation states that conduction band electrons (e^-) and valence band holes (h^+) are generated when aqueous TiO_2 suspension irradiated with light energy greater than its band gap energy ($E_g = 3.2$ eV). The photo generated electrons could reduce the dye or react with electron acceptors such as O_2 adsorbed on the $Ti(II)$ – surface or dissolved in water reducing it to super oxide radical anion

$O_2^{\cdot-}$. The photogenerated holes can oxidize the organic molecule to form $R^{\cdot}$, or react with OH^- or H_2O oxidizing them into $OH^{\cdot}$ Radicals. Together with other highly oxidant species (peroxide radicals) they are reported to be responsible for the heterogeneous TiO_2 photodecomposition of organic substrates as dyes. According to this, the relevant reactions at the semiconductor surface causing the degradation of dyes can be expressed as follows:



The resulting $OH^{\cdot}$ Radical, being a very strong oxidizing agent (standard redox potential +2.8 V) can oxidize most of methyl orange dye the mineral end –products. Substrates not reactive toward hydroxyl radicals are degraded employing TiO_2 photo catalysis with rates of decay highly influenced by the semiconductor valence band edge position¹⁷.

Conclusion

The photocatalyzed degradation of methyl orange in TiO_2 suspension was carried out in two different concentrations of MeO using solar irradiation. The photocatalytic degradation processes were influenced by the initial concentration of MeO. Color change from orange to colorless is irreversible and the degradation rate

of the MeO followed the pseudo-first order kinetics. The rate constant and photodegradation percentage of dilute solution is more than that of concentrated solution .

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