

Photocatalytic Reduction of Iron (III) by Using Pure, Coupled and Sensitized TiO₂ in Aqueous Solution

Asmaa H.AL-Alwani
College of Pharma
Babylon University

Fatima AL-Zahra'a G.
College of Pharmacy
Babylon University

Fouad F.AL-Qaim
College of Science for Women
Babylon University

Alzahraafatema6@gmail.com Fouadalkaim@yahoo.com.

Abstract

Photocatalytic reduction reaction of iron (Fe⁺³) in aqueous suspension containing TiO₂ under near UV –visible light in presence of atmospheric oxygen has been studied .This reaction is effective to convert harmful ions to nontoxic product in water .

Primary experiment have been done to determined optimum condition of photocatalytic reaction .Firstly experiments variable amount TiO₂ concentration were used at constant Fe⁺³ concentration . It was found that the ideal TiO₂ concentration was equal to 0.2 gm/L . The effect of Fe⁺³ concentration was studied .The highest photoreduction reaction rate was obtained at 40 ppm of Fe⁺³ concentration in aqueous suspension containing 0.2 gm /L TiO₂ concentration . The Langmuir – Hinshelwood kinetic model has been applied to calculate apparent rate reaction constant and adsorption constant.

The results shows the rat of photocatalytic reduction reaction was increased when TiO₂ was sensitized with riboflavin photosensitizer, but the best photoreduction was obtained by using coupled CdS/TiO₂ photocatalytic semiconductors. Also half life time was calculated and the general photocatalytic reaction mechanism for this reduction process was suggested.

Keywords: TiO₂ Semiconductor, photo catalytic reaction, purification of waste water by using semiconductors.

الخلاصة

تضمن البحث الحالي دراسة التفاعل الضوئي المحفز لايونات الحديدك باستخدام المحلول المائي العالق لل TiO₂ في باستخدام الأشعة فوق البنفسجية القريبة ومنطقة الطيف المرئي بوجود الاوكسجين الجوي. يهدف البحث الى تحويل الايونات السامة في المحلول المائي إلى مركبات غير سامة في الماء ,

إجريت سلسلة من التجارب الابتدائية لتحديد الظروف المثلى لتفاعل التحفيز الضوئي 0 تضمنت التجارب الأولى استخدام كميات مختلفة من TiO₂ وتثبيت تركيز ايونات Fe⁺³ حيث وجد أن استخدام 0.2 gm/L من TiO₂ يعد تركيز مثالي لحدوث التفاعل الضوئي. كما تم دراسة تأثير تركيز ايونات Fe⁺³ وباستخدام 0.2 gm/L من عالق 2 TiO حيث وجد أن أعلى سرعة اختزال ضوئي عند تركيز 40 ppm من Fe⁺³ في الحلول المائي. تم تطبيق معادلة Langmuir –Hinshelwood لحساب ثابت سرعة التفاعل الظاهري وثابت الامتزاز.

أوضحت النتائج أن سرعة تفاعل الاختزال الضوئي تزداد باستخدام TiO₂ مع صبغة الريبوفلافين كمتحسس ضوئي إلا إن أفضل سرعة اختزال ضوئي تم الحصول عليها باستخدام شبه الموصل المزدوج CdS/TiO₂ كعامل مساعد . كما تم حساب عمر النصف الضوئي وعلى ضوء النتائج اقترحت ميكانيكية التفاعل الضوئي المحفز العام لعملية الاختزال الضوئي .
الكلمات المفتاحية: TiO₂ شبه الموصل، التفاعل الضوئي، تطهير الايونات السامة في الماء باستخدام شبه الموصل.

Introduction

TiO₂ was found to be an excellent catalyst to treatment of water pollution with petroleum in aqueous environment under weathering condition photosensitization of TiO₂ showed an increase in the activity of catalyst for photocatalytic oxidation reduction of pollutant and decolonization of industrial water (Mirero, 1997).

There are three different kinds of TiO₂ anatase , rutile and brookite (Rajeev and Shalinis, 2008) .Most of photocatalytic reaction have been performed on the anatase and rutile types . The adsorptive affinity of anatase for remove heavy metals by reduction of them is larger than that of rutile , due to irradiation of anatase particles by

near UV light The band gap energy of anatase is 3.2 eV (Maness *et. al.*, 1999) and therefore absorbs in near UV light while to generate pair electron and hole . These pairs reacted with atmospheric oxygen and water to yield reactive oxygen species (Aliwi and Abdul Kadir,2001)as shown in figure (1):-

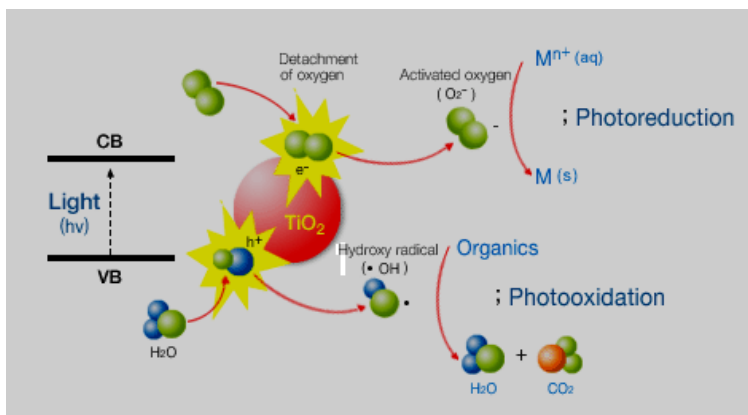
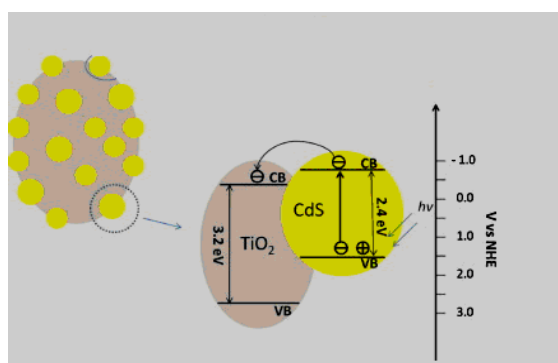


Figure (1) :- photocatalytic oxidation reduction process on TiO₂ semiconductor .

CdS particle has band gap energy about 2.5 eV and absorbs visible light (Calza, 1997).CdS semiconductor undergo rapid photocorrosion so that coupled TiO₂/CdS semiconductors are more stable than CdS and absorbs larger wave length than naked TiO₂ particle (Turchi and Ollis,1990).coupled semiconductors can be shown as the following scheme:



Figure(2). Schematic formation of TiO₂/CdS composites and the transferring routes of photo generated electrons.

Iron (III) has a very low solubility in seawater(Weus and Mayer ,1995)and rapidly becomes hydrolyzed into various iron (III) hydroxides. 99% of the iron in the ocean is organically complexes (Borer *et. al.*, 2005)increasing the solubility of iron. Iron (III) is the dominant redox species in the natural oxygenated waters, while iron (II) ,although better soluble at seawater pH ,becomes rapidly oxidized by O₂ and H₂O (Bullen *et al.* 2005).

The redox cycle of iron initiated by photochemical processes is mentioned as an important mechanism by which (colloidal) iron is converted in more reactive iron species (defined by the method applied) resulting in a higher bioavailability to phytoplankton Furthermore, Fe(II) is expected to be a bioavailable species (Fialho *et al.*, 2006).

The aim of the present work is to explore the possibility of solar radiation for detoxification of Fe^{+3} in water by using naked ,coupled CdS/TiO₂ and sensitized TiO₂ photocatalyst.

Chemicals

Titanium dioxide was purchased form Degussa p25 (mostly anatase BET 55 m²g⁻¹) FeCl₃ and riboflavin were supplied from fluka .CdS , KSCN and ethanol were supplied from BDH.

Instrumental

High pressure mercury lamp radium (HPML) (125 w) was used as a source of irradiation .Cintra -5 UV visible spectrophotometry was used to determined Fe^{+3} concentration.

Magnatic stirrer (LMS-1007) was used to keep the solution in homogenous suspension through the photolysis process .The incident light intensity was measured

Preparation of coupled TiO₂/CdS semiconductor system.

The coupled TiO₂/CdS semiconductors was prepared by precipitating CdS salt in a solution containing the same amount of dispersed TiO₂ and the product was washed with acetone ,water and finally with absolute ethanol and dried at 110 C⁰. The sample containing CdS was dried at 400 C⁰for one hour .

Photocatalytic reduction experiment :-

Aqueous Fe^{+3} solution was prepared by dissolved certain quantities of FeCl₃ in distilled water and addition 0.2gm/ml of TiO₂ or CdS/TiO₂ and sensitized TiO₂.The reaction mixture was carried out by using 200 ml Pyrex glass reservoir placed in the laboratory temperature (25 C⁰) and kept homogenously by stirring on the magmatic stirrer. pyrex glass beaker was surrounded by cellophane cover to keep light inside vessel and this cover provided with hole to pass atmospheric air .light source was focused directly on the solution vertically without use of lens.

Measurement :- Fe^{+3} concentration solutions were measured by using potassium thio cyanate and analyzed by UV visible spectrophotometry at $\lambda_{\text{Max}}=510 \text{ nm}$

Results and Discussion

Effect of TiO₂ Concentration

Figure (3) shows the effect of TiO₂ concentrations on the photocatalytic reduction process The lower amount of TiO₂ gave direct proportionality between the weight of catalyst and the rate of photoreduction reaction .This is because the amount of Fe^{+3} absorbed on the semiconductor surface generally increases when increasing the TiO₂ loading (Masznat *et al.*, 2005). However further increase of catalyst decreased the photoreduction process efficiency of the Fe^{+3} .This can explained that the adsorption rat on the TiO₂ and photo decomposition rats (upon UV/TiO₂)of pollutants are influenced by the active site and the photo absorption of the catalyst used .A adequate loading of the electron /hole pair for promoting the degradation of pollutants(AL-Qaim ,2009).However addition of high amount of catalyst decreases the light penetration by the photo catalyst suspension (Litter and Navio,1994). Figure (4) shows 0.2 gm/L was ideal TiO₂ concentration which produce the best efficiency for photocatalytic degradation of Fe^{+3} in aqueous solution, so that this ideal concentration was used in all the following photocatalytic experiments .

Effect of initial concentration

Fig (5) illustrate the effect of the variation of the concentration of Fe^{+3} on the activity of the photoreduction reaction in presence of 0.2 gm/L TiO₂ concentrations . the results show that the rate of photoreduction was increased with increasing the concentration of Fe^{+3} because when Fe^{+3} concentration was increased some of the photons were absorbed by the substantial amount of Fe^{+3} . The quantity of effective

photons which was absorbed by the surface of semiconductor was reduced (Davis et. al.1994) .The quantity of excited TiO₂ electrons produced by effective photons decreased the generation holes lessened while a large amount of Fe⁺³ and other impurities were probably adsorbed on the surface of TiO₂ , making it more difficult for holes to enter the solution ,So fewer ions to produce hydroxyl radicals the main oxidizing species responsible for the photo oxidation reduction of impurities (Malik and Saha, 2003).It was noted that the reduction of Fe⁺³ solution was decreased with the increasing concentration. Fig (6) shows the highest photocatalytic reduction rate was obtained at 40 ppm of Fe⁺³ concentration ,so that this ideal concentration was used for all the other experiments.

The Kinetic Study

The kinetic study of photocatalytic reduction of Fe⁺³ with different times in presence of 0.2 gm/L TiO₂ concentration are illustrated in figure (7).The plot gave straight line which confirmed that the photodegradation process follows first order reaction (Rijkenbery et. al.,2005). Apparent rate constant were calculated from the slope of the straight line which is equal(8x10⁻⁵ mmole.L⁻¹.Sec⁻¹) and half life time from the reaction can be calculated from the following equation .

$$t_{1/2} = 0.693/k_d \quad \text{----- (1)}$$

where $t_{1/2}$ is half life time which is equal (8.662 Sec)

So that rate of reaction can be calculated by application of equation (2)and equal (3.5 X 10⁻⁵)

$$\text{Rate} = k_d C_0 \quad \text{----- (2)}$$

Where C₀ is initial concentration (0.447 mMole) and k_d is apparent rate constant

The photocatalytic reduction kinetic of Fe⁺³ follows a Langmaer-Hinshel Wood mechanism with a reaction rate (R) varying proportionally to the fraction of surface converted by the substrate as follows :-

$$\text{Rate} = -\frac{dc}{dt} = \frac{kKC_o}{1 + kC_o} \quad \text{----- (3)}$$

Where k is the reaction rate constant, K is the equilibrium adsorption constant and C_o is the initial concentration (Malik and Saha, 2003)

The above equation could be modified to linear type equation (4)

$$\frac{1}{r} = \frac{1}{k} + \frac{1}{kKC_o} \quad \text{----- (4)}$$

Figure (8) shows The relation ship between (1/r) and (1/C) for Fe⁺³ to calculate apparent rate constant and adsorption constant.

Photocatalytic reduction of Fe⁺³ by using sensitized TiO₂:-

Figure () shows the effect of sensitizer on the activity of TiO₂ .This activity was increased compared with the same amount of naked TiO₂ . Riboflavin photosensitizer has good over lapping of its spectrum with low absorption of TiO₂ ,it has max in 545 nm (Fabbri et.al., 2004).

Riboflavin absorbs radiation lowest energy of the absorption spectrum for TiO₂ catalyst and inject their excited electrons into the conduction band of the TiO₂ ,where as the photo-holes are generated through the direct photooxidation of the reducing dye by the diffusion through the double layer of the inter – surface to generate the electrons and the photo-holes by an indirect by using sun light due to the existence of riboflavin as sensitizer (Nasr et al., 1995).

Photocatalytic reduction of Fe^{+3} by using coupled CdS/TiO₂ semiconductors :-

Figure (9) illustrate the efficiency of photocatalytic reduction of Fe^{+3} was increased by using 0.2 gm/L coupled CdS /TiO₂ semiconductor instead of naked TiO₂. This observation can be explained that the band gab of CdS equal (2.5 ev) ,it mean CdS absorbs visible light to generate excited negative electrons and positive holes .These excited electrons are injected in to the conduction band of TiO₂ to produce oxidizing radical species (Diener and Ausubel,2005).These oxidizing agents were reduced Fe^{+3} ions in aqueous solution .

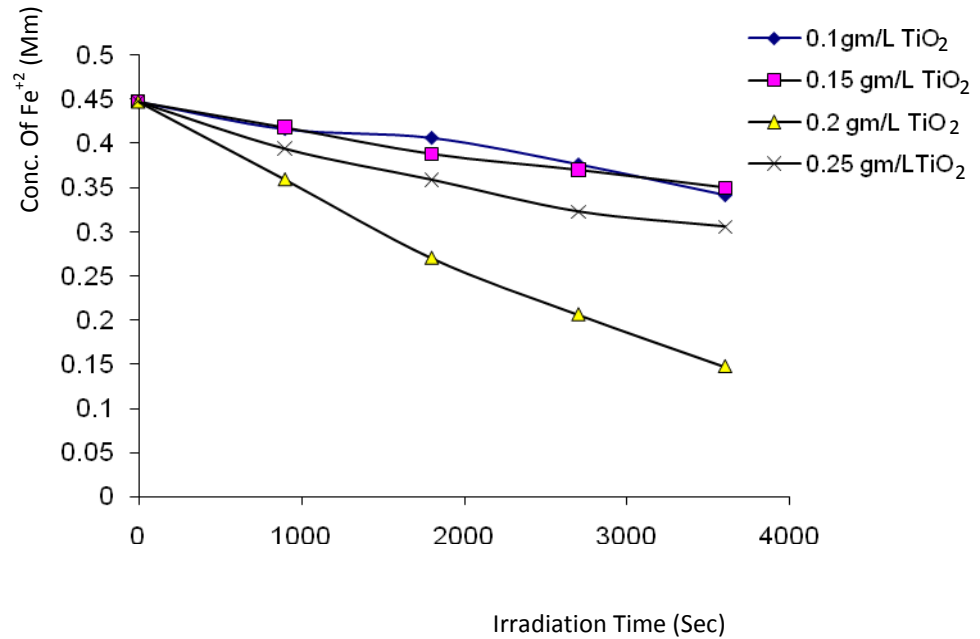


Figure (3):-photocatalytic reduction of Fe^{+3} with different weight of TiO_2 at 25 C^0 .

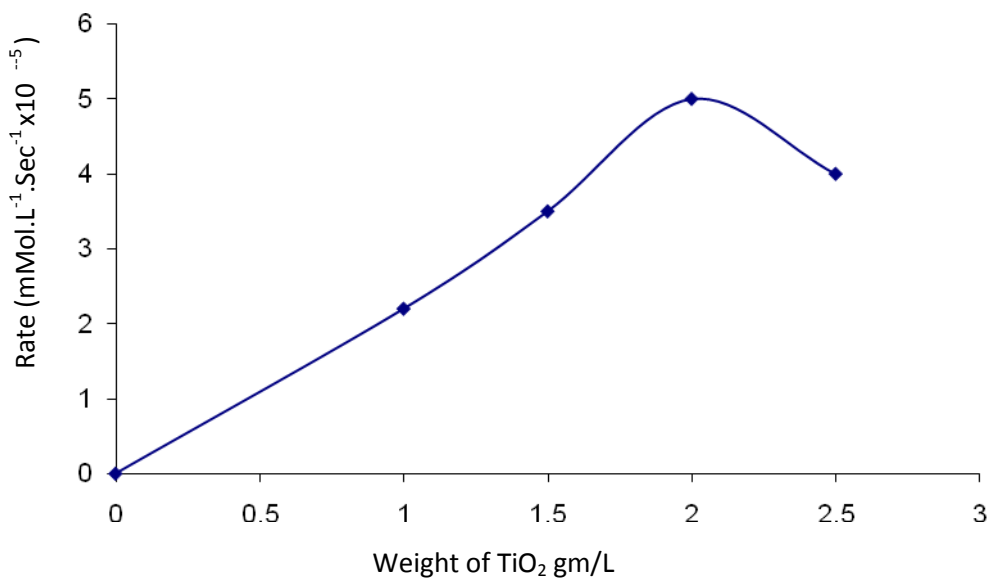


Figure (4) : the relation ship between rate of photoreduction of Fe^{+3} and weight of TiO_2 .

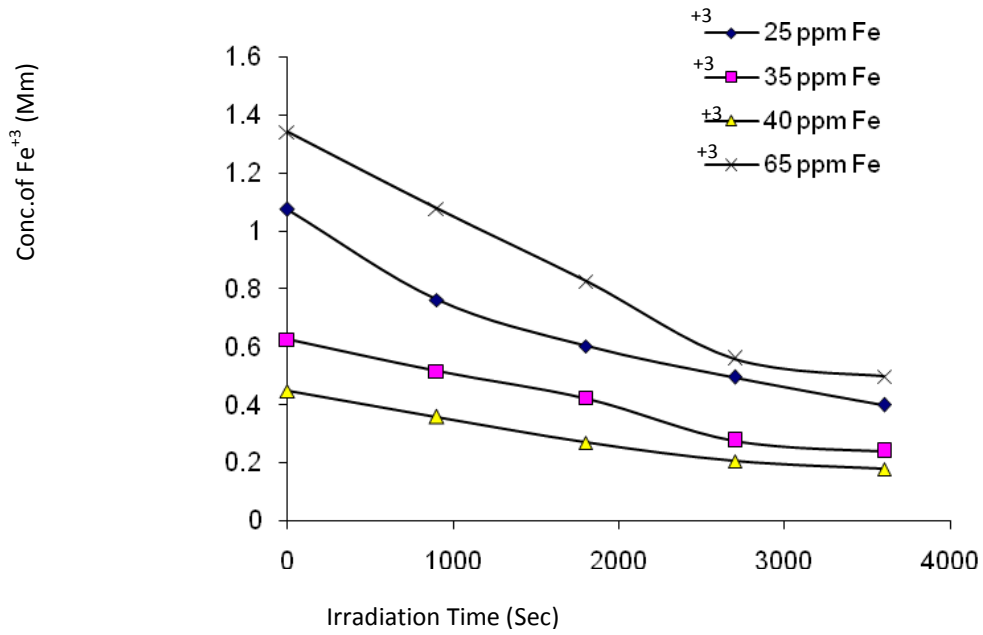


Figure (5):-photocatalytic reduction of Fe⁺³ in aqueous solution with different Fe⁺³ concentrations at 25 C⁰.

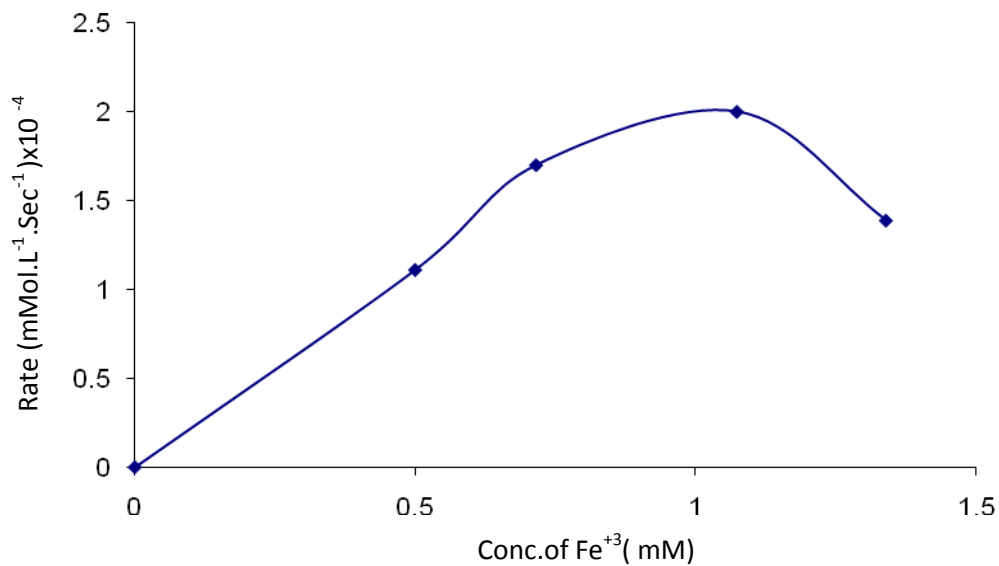


Figure (6) : the relation ship between rate of photoreduction of Fe⁺³ and weight of TiO₂.

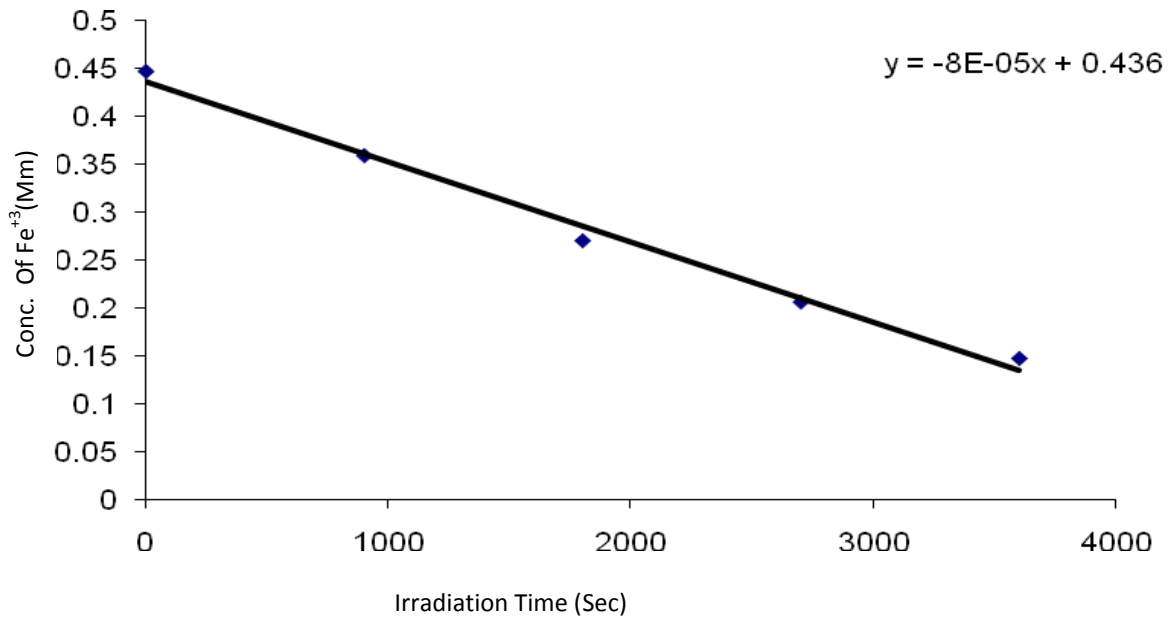


Figure (7) :-The relation ship between Fe⁺³ concentration in aqueous solution and irradiation time at 25 C⁰.

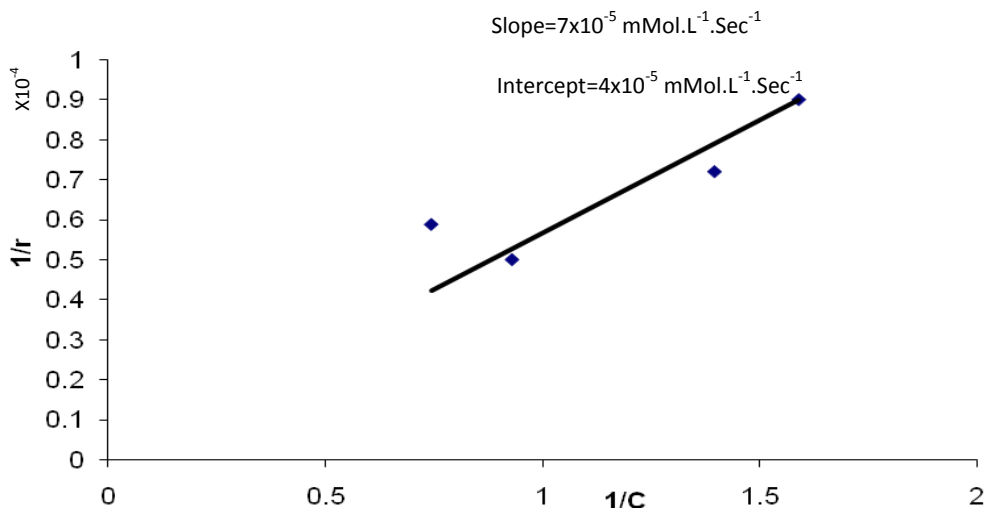


Figure (8) :-The relation ship between (1/r) and (1/C) for Fe⁺³ to calculate apparent rate constant and adsorption constant.

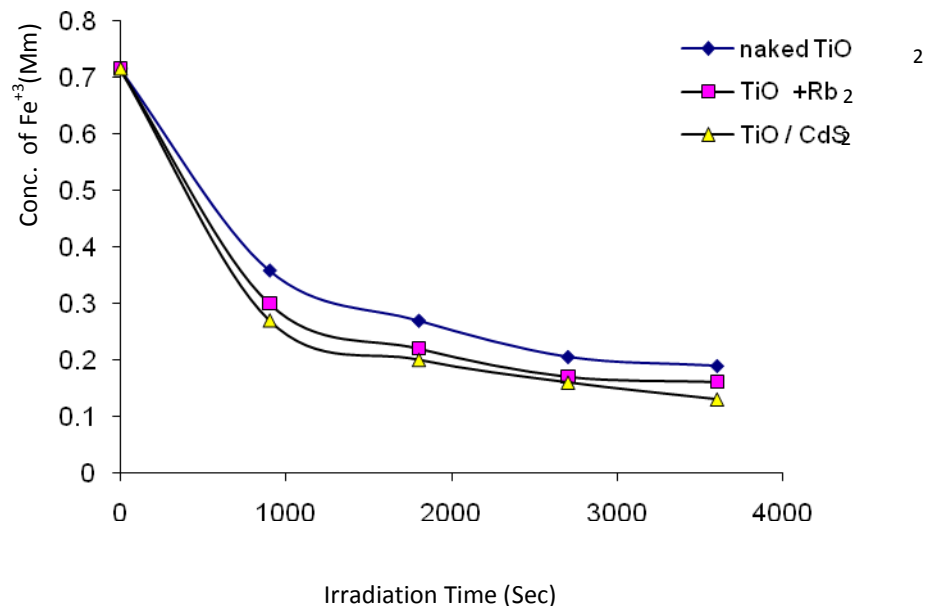
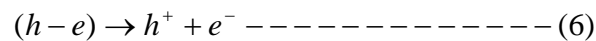
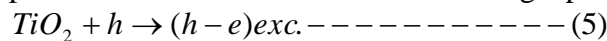


Figure (9):-photocatalytic reduction of Fe⁺³ in aqueous solution under various conditions at 25 C⁰.

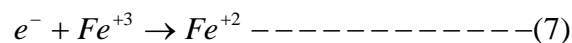
The Suggested Mechanism of Photocatalytic reduction reaction :-

1-Naked TiO₂

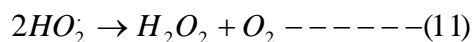
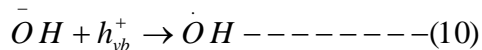
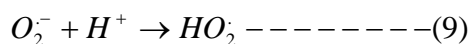
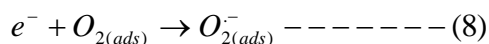
When TiO₂ particle irradiated with light of energy(3.2 ev) an electron will promoted from valance bond and leaving a positive hole in the conduction band .



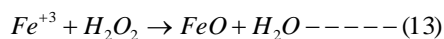
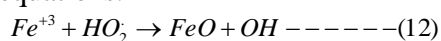
Electrons conduction band react with Fe⁺³ according to the following equation :-



Also these existed electrons was reacted with atmospheric oxygen and water to yield reactive oxygen species such as supper oxide O₂ .hydroxyl radical OH and hydrogen dioxide (H₂O₂) according to the following equations :-

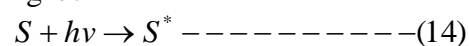


HO₂ and H₂O₂ can be reacted with Fe⁺³ to produce Fe⁺² according to the following equations:-

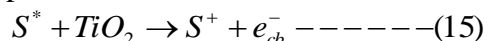


2-Sensitized TiO₂ :-

The first step of photoreduction is excised riboflavin sensitizer molecule after absorption light :-



Riboflavin has an oxidation potential equal to (-1.05 eV) which is higher than the oxidation potential for the TiO₂ conduction band .so that the electron can be injected from the excited photosensitizer molecule into TiO₂ conduction band (Miaofan,2008) .



These electrons conduction band were used to reduced Fe⁺³ and oxygen molecules adsorbed on TiO₂ surface to yield super oxide as in the previous step (eqs 8-13)

3- Coupled TiO₂/CdS :-

Naked TiO₂ photocatalyst is effective only up on irradiation of UV-light (387nm) (Calza ,1997),but when coupled TiO₂/CdS was used as photocatalyst the potential application have been identified to be active upon visible light it is also behaved that coupled TiO₂/CdS partials have large surface area adsorption for Fe⁺³ in aqueous solution (Augugliaro *et al.*, 1997).

When CdS particle absorb visible light to generate negative electron in the conduction band and positive holes in the valance band. These excited electrons are injected to TiO₂ conduction band (Chica *et. al.*,2006)

Reactive oxygen species were generated according to equations(8-11) and these species reacted with Fe⁺³ according to equations (12-13)

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