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Effect of Operating Parameters on Colour and COD Removal Treatment of Textile Wastewater

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ABSTRACT
In the present study, the effect of process parameters on photocatalytic degradation Bismarck brown Y dye has been examined in a batch reactor under UV light in heterogeneous slurry utilizing various concentrations of different semiconductors commercial catalysts (TiO_2 , ZnO , CdS and ZnS). Parameters has been studied (catalyst type, catalyst concentration , pH of dye solution and dye concentration at the beginning). The results show that the best values of TiO_2 , ZnO , CdS and ZnS are 1 , 0.5 , 1.25 , 1 g/l respectively and the optimum pH are (10 , 6 , 8 and 10) using TiO_2 , ZnO , CdS and ZnS respectively. Moreover the comparative assessment of the photocatalytic efficiency was made for different photocatalytic powder. It was noticed that the best photocatalytic efficiency as ZnO > TiO_2 > ZnS > CdS respectively. The percentage removal of chemical oxygen demand (COD) of the dye solutions was higher than that of the degradation of dye for the same conditions of catalyst.

تأثير عوامل التشغيل على معالجة الالوان والمتطلب الاوكسيجيني للمياه الناتجة من معامل الانسجة

الخلاصة
في هذا البحث تم دراسة تأثير بعض العوامل على ازالة الصبغة البنية في مفاعل الوجبات تحت تأثير ضوء الأشعة فوق البنفسجية في المحلول الغير متجانس باستخدام انواع مختلفة من أشباه الموصلات كعوامل مساعدة وهي (ثنائي اوكسيد التيتانيوم وأوكسيد الزنك و كبريتيد الكادميوم وكبريتيد الزنك). ان العوامل المؤثرة على عملية الازالة التي تم دراستها هي (نوع العامل المساعد المستخدم وتركيزه والدالة الحامضية للمحلول وتركيز الصبغة الابتدائي في المحلول). ثنائي اوكسيد التيتانيوم ,لقد اوضحت النتائج ان افضل العوامل المساعد كانت (اوكسيد الزنك وكبريتيد الزنك ثم كبريتيد الكادميوم) والتي حققت اعلى نسبة ازالة للصبغة بالإضافة الى تحديد افضل التراكيز للعوامل المساعدة المستخدمة . كذلك ان النتائج اثبتت ان نسبة ازالة المتطلب الاوكسيجيني كانت اكبر من نسبة ازالة الصبغة لنفس العمل المساعد وتحت نفس الظروف.

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Introduction

Different dyes containing wastewaters reached to nearly 35% of the industrial effluents and this can be observed obviously in China[1]. So the environmental problems as results of wide manufacturing and employment of dyes have been brought large interests [2]. The treatment processes of this wastewater stay presents a roughly technical challenge to reach the emission standard in spite of various wastewater treatment processes such as physical–chemical and biological ways have been constituted in most of the textile manufacturing plants in China, [1,2]. Azo dyes representing about 70% of all textile dyestuffs produced so it can be considered one of the important reasons that are disobedient to biodegradation and their textures are complicated and extremely varied in the effluents [3].

A considerable problems in treatment plants caused by dyes presents in textile industry wastewaters since those compounds are complex to degrade by biological methods. Some of the effective chemical and physical methods state a high activity of color removals such as coagulation-flocculation, advanced oxidation and electrochemical methods [4–6]. All these methods have operational problems such as high sludge formation in chemical ways in addition to that more expensive. Adsorption can be considered an unattractive method for degradation objective because of the cost of adsorbent and regeneration requirement. However, recent studies specified the possibility of using some natural or low-cost adsorbents for color removal such as wood, ash and soil [7–9].

The aim of this work, is to remove the Bismarck brown Y under UV light with various commercial semiconductors catalysts (CdS , ZnS ,TiO_2 and ZnO) by varying process parameters such as (semiconductor photocatalyst , concentration , pH , and feed concentration) to choice the optimum condition for all catalysts.

Experimental Part

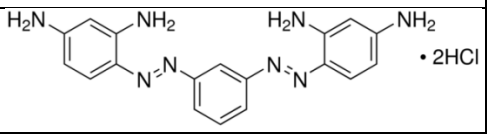
1. Materials

Material was exported from the original company the details of these materials as shown in table 1. It was used the bismarck brown Y dye as contaminated material this dye used in textile. Table 2 shows the chemical and physical properties of bismarck brown Y dye.

Table (1) The properties of materials that were used in this paper.

Material	Chemical Formula	Company\ Country	Purity
Titanium Dioxide Commercial	TiO_2 79.9 (g/mol)	Merck \ Germany	99 %
Zinc Oxide Commercial	ZnO	Merck \ Germany	99 %
Cadmium Sulfate	CdS 144.47 (g/mol)	Merck \ Germany	99 %
Zinc Sulfate	ZnS 161.47 (g/mol)	Merck \ Germany	99 %
Hydraulic Acid	HCl 36.46 (g/mol)	Merck \ Germany	99 %
Sodium Hydroxide	NaOH 40 (g/mol)	Merck \ Germany	99 %
Distilled Water	H_2O 18 (g/mol)	Local Production	100 %

Table (2) The chemical and physical properties of Bismarck brown Y dye.

Chemical Formula	**$C_{18}H_{18}N_8 \cdot 2HCl$**
Chemical Structure	
Molecular Weight	419,33 g/mol
Absorption Maximum in Water	468 nm
Appearance	Dark brown powder
Company	Merck (Germany)

2. Preparation of Feed Solutions

The different amount (10 , 20 , 40 and 60) mg of Bismarck brown Y dye to be dissolved in one liter of distilled water at room temperature. In order to prepare feed dye solutions with different pHs (2 , 4 , 6, 8, 10 and 12), the several drops of prepared

solutions of (0.1 M) of HCl and NaOH to be added for varying pH of dye solution.

3. Reaction Vessel

Photochemical degradation reaction of the solution compound occurred in the insulation walled reaction vessel to keep the temperature constant this reaction vessel has (800 ml) volume and it was instilled in the UV box contained (8) UV tubes light (eighteen watt Philips of each) with 365 nm wavelength. The value of UV light intensity was estimated by special light meter "UVA light meter Model UVA-365 Lutron" and it was observed to be 0.5 mW/cm^2. The mixing of the solution at all period time of each experiment using a magnetic stirrer (a type of BOECO MSH-330N Germany). When the water circulating in the jacketed wall reactor, the temperature was kept steady during the reaction time.

4. Dark Experiments

At the dark and for twenty-five minutes a heterogeneous solution was stirred magnetically to complete adsorption–desorption equilibrium between the catalyst and dye. Irradiation was executed in an open air condition. 100 ml of a dye solution with catalyst were constantly aerated atmosphere, furthermore for the perfect mixing of a reaction solution. 6ml samples of solution taken at the constant period time by a syringe and then separation catalyst from solution by special Millipore syringe filter of 0.45 μm.

5. Photocatalytic Experiments

All photocatalytic degradation experiments were carried out under similar conditions UV light. For the reaction vessel, an open small cylinder glass of 800 ml and height of 15 cm and diameter of 10 cm was used. The suspension consisting of a mixture of 100 ml of the feed dye solution and photo catalyst was exposed to UV light. At various time periods, the 6 ml of sample was drawn with help of syringe and then filtered over a miliporose syringe filter. At that point, the decolonization rate was noticed in expressions of change in consistency at λ_{max} of the dye and the absorption spectra of the dye solutions were recorded.

6. Absorbance Measurements

The absorption spectrum was recorded using double beam UV-1800 Shmadzo spectrophotometer compared with distilled water as a reference liquid and the percentage rate of degradation was noticed in terms of change in intensity at λ_{max} of the dyes during irradiation time.

The percentage of photocatalytic degradation estimated according to the following formula :

$$\text{Photodegradation \%} = \frac{\text{Initial Absorption} - \text{Absorption at time t}}{\text{Initial Absorption}} \times 100$$

Results and Discussion

1. Adsorption Experiments

The experimental results are shown in Figures (1, 2 , 3 , and 4) for the different catalyst (ZnO , TiO_2 , ZnS, and CdS) respectively . At various catalyst concentrations for all type of catalyst, it was clearly from results that the adsorption equilibrium of the dye was reached nearly to 20 min from the time of equilibration [10].

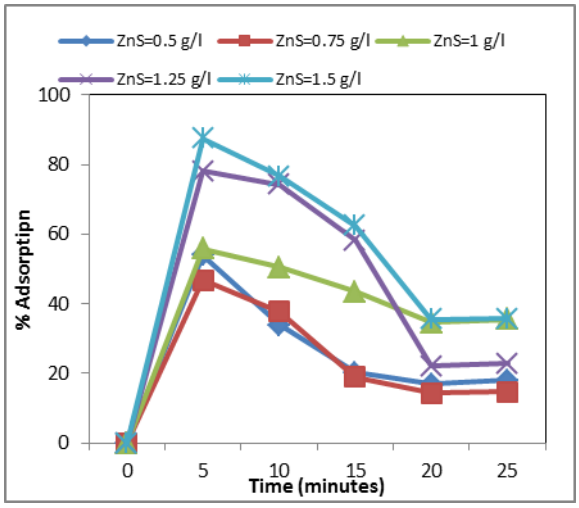


Figure. 1 Adsorption – Desorption behavior of Bismarck brown Y dye at different ZnO concentration

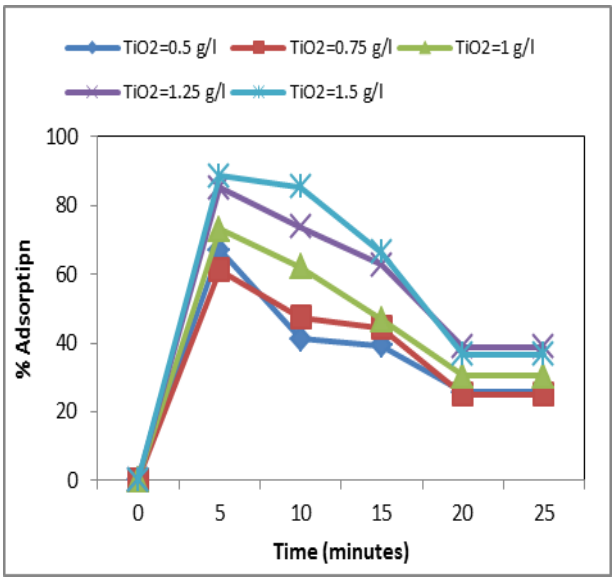


Figure. 2 Adsorption – Desorption behavior of Bismarck brown Y dye at different TiO_2 concentration

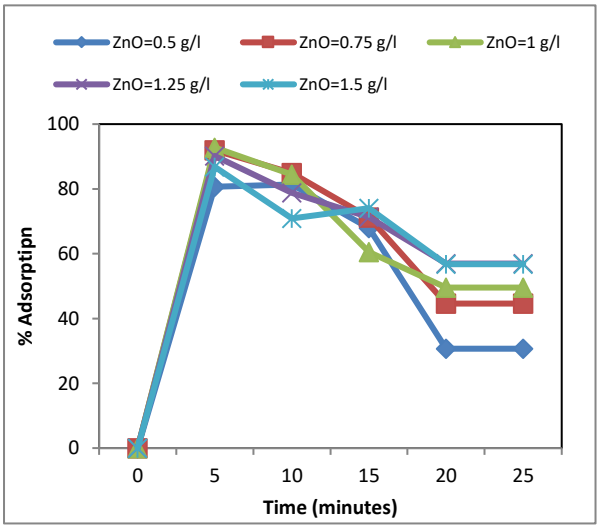


Figure3 Adsorption – Desorption behavior of bismarck brown Y dye at different ZnS concentration

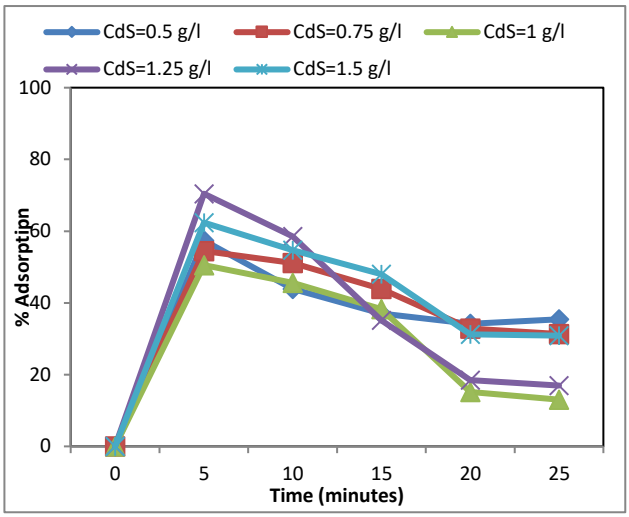


Figure. 4 Adsorption – Desorption behavior of Bismarck brown Y dye at different CdS

2. Optimum Photo catalyst Concentration

Experiments have been done with different concentration for each photo catalyst of CdS , ZnS, TiO_2 and ZnO, so as to choice the best concentration of each catalyst for the treatment of Bismarck brown Y dye. The photoreaction runs were achieved using various catalysts at a concentration of dye equal to 25 ppm, and catalyst capacity ranges of (0.25 , 0.50 , 0.75 , 1 , 1.25 and 1.5) g/l for each catalyst through 20 minutes of irradiation. The results in Figures (5 , 6 , 7 and 8) shows the photo degradation of solution was increased up to (0.5 , 1 , 1 , and 1.25) g/l for the catalyst of (ZnO , TiO_2 , ZnS, and CdS) respectively and then the photo degradation is decreased. This case can be clarified in terms of the UV light permeation through the solution and active sites availability on the catalyst surface. When increasing the concentration of catalyst, the total effective surface area will increases. At the same time, there is a decrease in solar light permeation because of an increase in the turbidity of the suspension as a result of increased scattering impact and for that reason the photo activated volume of suspension will decreases. Furthermore, it is hard to keep up the suspension homogenous at high catalyst capacity because of particles agglomeration, that decreases the number of active sites [11-13].

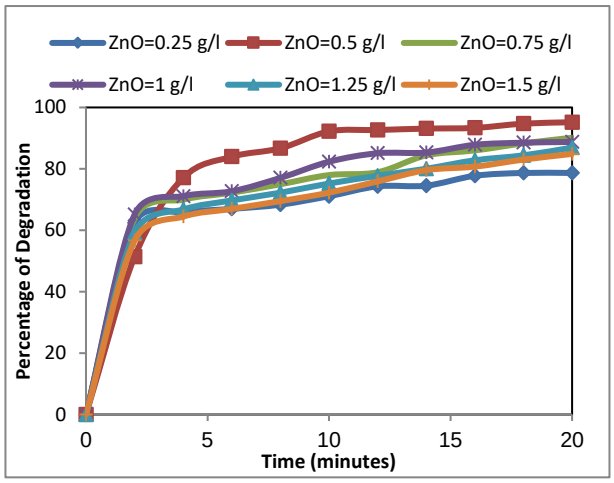


Figure. 5 Photocatalytic degradation behavior of Bismarck brown Y dye at different ZnO concentration

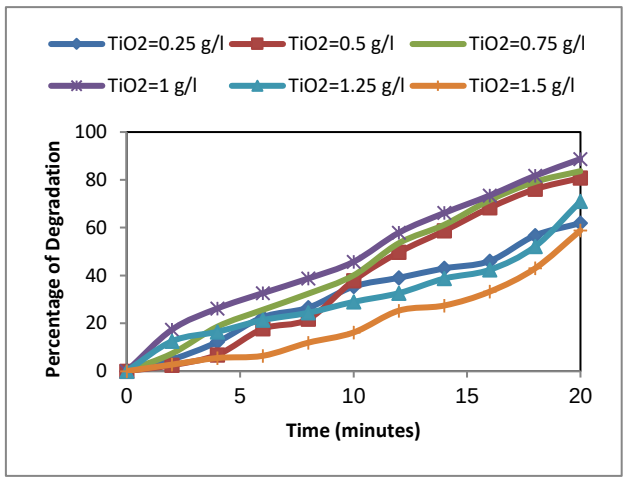


Figure. 6 Photocatalytic degradation behavior of Bismarck brown Y dye at different TiO_2

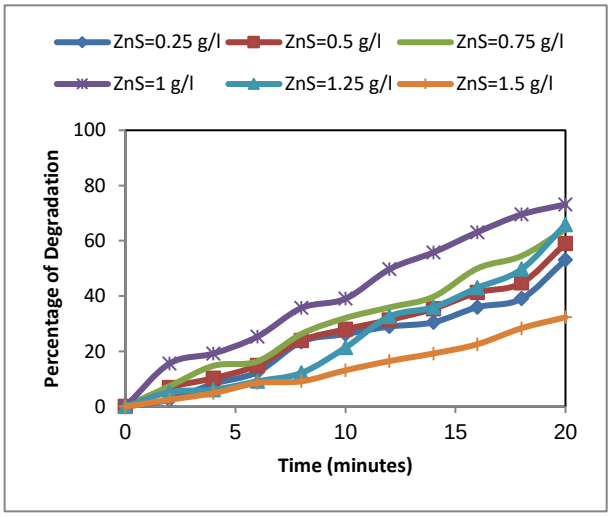


Figure. 7 Photocatalytic degradation behavior of Bismarck brown Y dye at different ZnS concentration

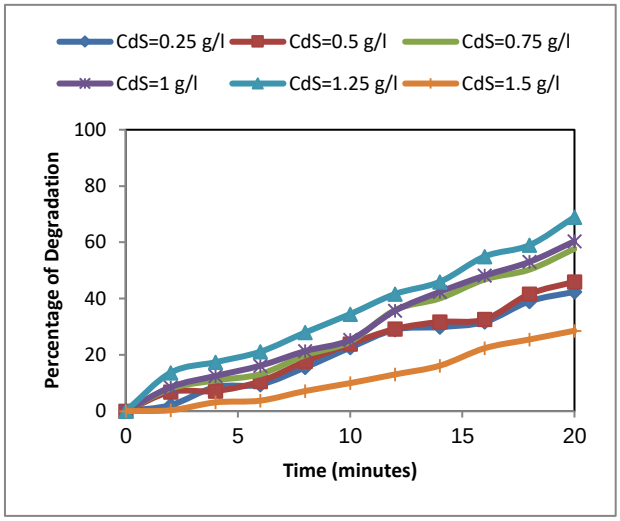


Figure. 8 Photocatalytic degradation behavior of Bismarck brown Y dye at different CdS concentration

that zinc oxide (ZnO) give best photocatalytic efficiency than the others. The quantum effectiveness of its powder is larger than titanium dioxide because zinc oxide bandgap equal to 3.17 eV, so from here higher effectiveness was showed for zinc oxide [14]. Zinc sulfide has bandgap energy equal to 3.6 eV, the energy light is not sufficient to promote the catalyst activity. Otherwise cadmium sulfide bandgap energy equal to 2.4 eV. A lesser photocatalytic effectiveness for degradation was noticed and the smaller bandgap award fast recombination of hole and electron. Furthermore, the metal sulfide semiconductors are not suitable based on the constancy demands in that they easily undergo photoanodic corrosion. The order of degradation efficiency of various photocatalysts is Zn > TiO_2 > ZnS > CdS for degradation for Bismarck Brown Y. In addition to higher activity, the other feature of zinc oxide and titanium dioxide is lower cost. Consequently, next runs were achieved with zinc oxide and titanium dioxide to improvement the various operational parameters viz. catalyst concentration, pH value ,.

concentration at the beginning of experiment and COD removal of the substrate affecting photo degradation of feed mixtures[15,16]. Finally, the comparison of photocatalytic activity efficiency was observed that the better photocatalytic efficiency as ZnO > TiO_2 > ZnS > Cd S respectively

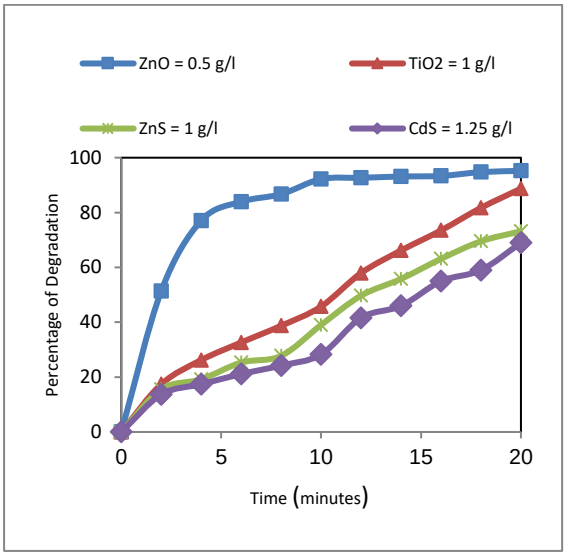


Figure. 9 . Comparison of photocatalytic degradation behavior of Bismarck brown Y dye at different kind of catalyst

3. Effect of pH on Solution Treatment

The wastewater is produced at different pHs, therefore, study of pH is very important on photodegradation of dye. Experiments have been done at different values of pH varying from 2 to 12 for 25 mg/L dye solution concentration and for the best of two catalyst concentration (0.5 and 0.1) g/l of ZnO and TiO_2 respectively. Figures 10 and 11 shows the percentage photodegradation of Bismarck brown Y against values of pH. It is clearly increasing in pH up to 6 and 10 for ZnO and TiO_2 respectively cause increasing in photodegradation activity [17]. The utilizing of ZnO as the catalyst is more appropriate at high pH values with the textile effluent. The interpretation of pH effects on the efficiency of the decolonization is a complex subject because many reactions can be occur to dye degradation such as "hydroxyl radical reaction, direct oxidation by the positive hole and direct reduction by the electron in the conducting band". The importance of each one depends upon the substrate nature and pH

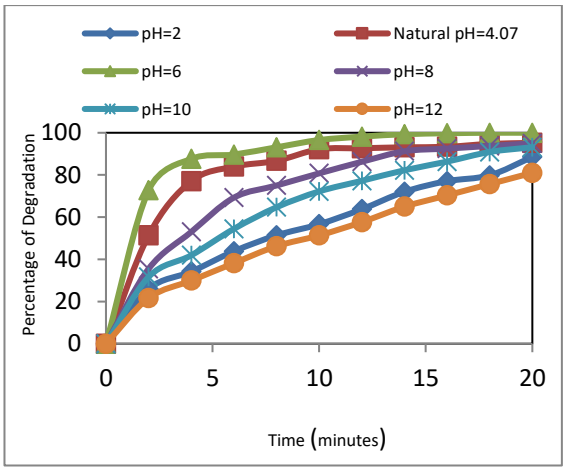


Figure. 10 . Effect of pH on photocatalytic degradation behavior of Bismarck brown Y dye solution using best concentration of ZnO

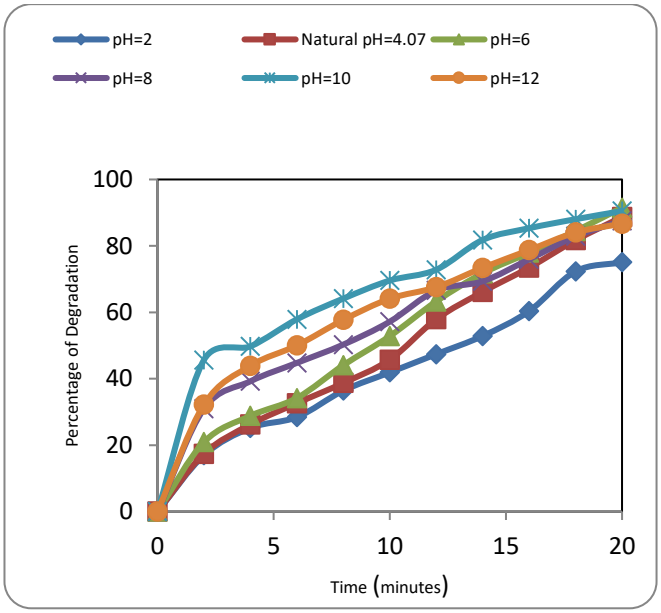


Figure. 11 . Effect of pH on photocatalytic degradation behavior of Bismarck brown Y dye solution using best concentration of TiO_2

4. Effect of Feed Dye Concentration on Treatment

The results in Figure 12 shows for the 20 minutes irradiation time using the ZnO as a photocatalyst the photodegradation efficiency of Bismarck brown Y dye for the initial dye concentration (10 , 20 , 40 and 60) g/l is (100 , 95 , 82 and 75) % respectively. But the results in Figure 13 shows for the 20 minutes irradiation time using the TiO_2 as a photocatalyst the photodegradation efficiency of Bismarck brown Y dye for the initial dye concentration (10 , 20 , 40 and 60) g/l is (98 , 89 , 76 and 63) % respectively.

It was noticed that the wavelength of the UV light entering the solution decreases when the initial dye concentration of Bismarck brown Y increases, otherwise for the low concentration of initial Bismarck brown Y dye the efficiency of photodegradation increase, thereby increasing the amount of UV light pass through the solution in lower concentration [18,19].

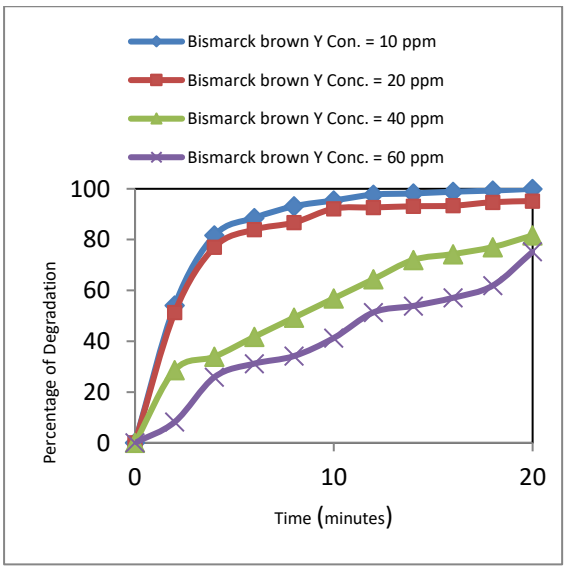


Figure. 12 . Effect of dye concentration on photocatalytic degradation behavior of Bismarck brown Y dye solution using best concentration of ZnO

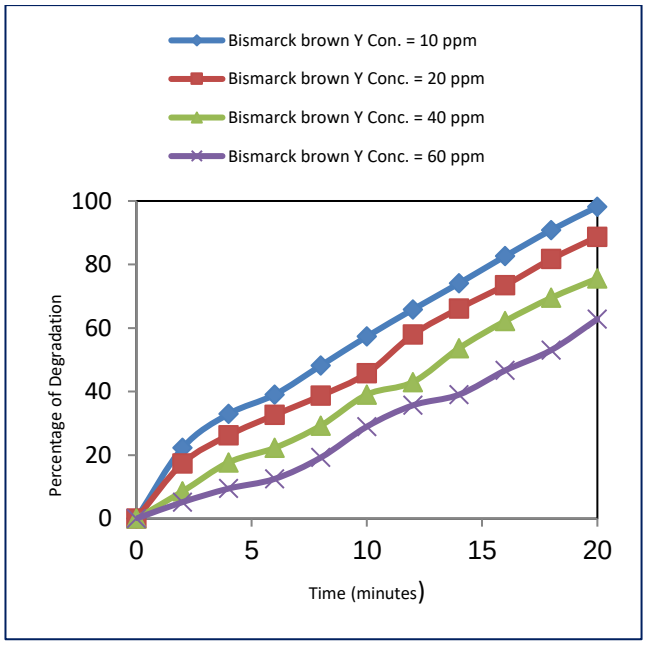


Figure. 13 . Effect of dye concentration on photocatalytic degradation behavior of Bismarck brown Y dye solution using best concentration of TiO_2

5. Chemical Oxygen Demand

The experiments also show the mineralization behavior of Bismarck brown Y dye, the efficiency of chemical oxygen demand (COD) removal was studied under best conditions at 30 minutes of irradiation for both catalysts (TiO_2 and ZnO). Figures (14 and 15) shows the efficiency of COD removal as a function of irradiation time. The results also showed the COD removal is lesser than percentage photodegradation. It indicates that it took longer irradiation time to obtain high removal mineralization of dyes. More reactive hydroxyl radical species will be photogenerated because of the higher concentration of hydroxide ions in the solution of dye [20,21].

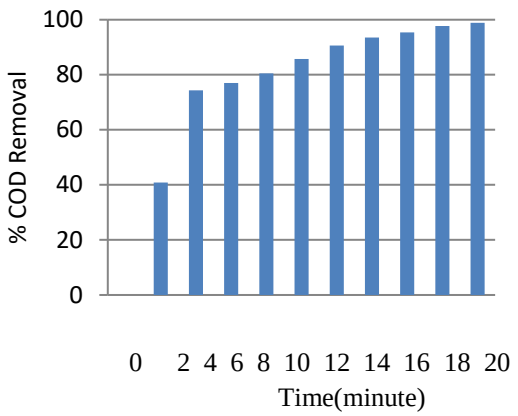


Figure. 14 . Efficiency of COD Removal of Bismarck brown Y dye solution using best concentration of ZnO

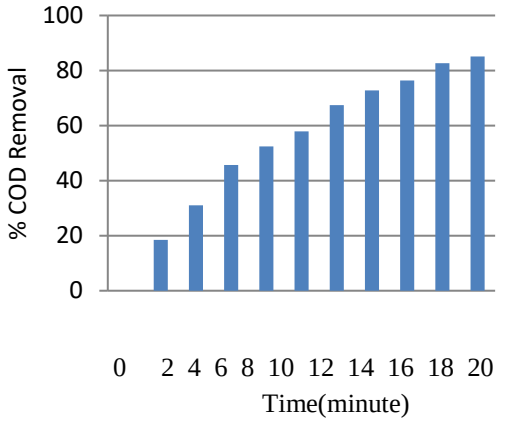


Figure. 15 . Efficiency of COD Removal of Bismarck brown Y dye solution using best concentration of TiO_2

Conclusions

The comparison of photocatalytic degradation efficiency and COD removal of different type of catalyst and parameters affecting on photocatalytic degradation process of Bismarck brown Y dye has been examined in a batch reactor under UV light in heterogeneous slurry the catalysts like (TiO_2 , ZnO , CdS, and ZnS). Parameters have been studied like (catalyst type , catalyst concentration , pH of dye solution , and initial dye concentration).

The difference was obviously when ZnO catalyst compared with TiO_2 catalyst as well as, that the ZnO presented better photocatalytic degradation efficiency and removal COD for Bismarck brown Y dye because the bandgap value for zinc oxide is equal to 3.17 eV, the powder quantum activity is larger than titanium dioxide and here higher activity appeared for zinc oxide.

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