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Decolorization of Bromophenolblue Dye Under UV- Radiation with ZnO as Catalyst

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Abstract

In this research, the efficiency of ZnO by photocatalytic degradation of bromophenolblue dye was studied. Effects of some parameters such as, catalyst concentration ,dye concentration , irradiation time ,and pH on the degradation rate of dye solution were also examined. In addition, the feature of bromophenolblue dye was studied by using UV-Vis spectroscopy techniques. Adsorption is a prerequisite for the metal oxide-mediated photodegradation/photodecolorization and the extent of decolorization has been discussed in terms of the Langmuir-Hinshelwood model.

الخلاصة

درس في هذا البحث كفاءة أوكسيد الزنك في الأكسدة الضوئية المحفزة لصبغة برومو فينول الأزرق ,حيث تضمن دراسة تأثير بعض المتغيرات مثل تركيز العامل المحفز وتركيز الصبغة و زمن التشعيع و الدالة الحامضيه على سرعة تكسير (تحطيم) محلول الصبغة. بالإضافة إلى ذلك فأن مظهر (طيف) صبغة برومو فينول الأزرق درست باستخدام تقنية مطيافية الأشعة فوق البنفسجية– المرئية . ان الامتزاز يتطلب وجود أوكسيد الفلز كوسيط لتكسير الضوئي / إزالة اللون الضوئية , كما أن شمولية إزالة اللون نوقشت وفقا لنموذج لانكمير–هينشلوود.

Introduction

From long time , problem of wastewater became very important both for the sake of increasing amount and its variety , In recent years, environmental contamination has been considering as one of the greatest problems of modern society variety [1,2].

Removing color from waters is often more important than other colorless organic substances, because the presence of small amounts of dyes is clearly visible and influence the water environment considerably. [3]

Azo dyes are a versatile class of colored organic compounds, characterized by the presence of unsaturated groups (chromophores) such as –C=C-, -N=N- and -C≡N , which are responsible for the dye colors, and of functional groups responsible for their fixation to fibers as for examples, $-NH_2$, -OH, -COOH and $-SO_3H$ dyes have extensively been used in industry for applications such as textiles, paper, leathers, additives and analytical chemistry. [4]

The dying and textile industries are pointed out as it produce a large amount of effluents which can cause serious environmental problems as they contain colored compounds resulting from dyes unfixed to fibers during the dying process. [5]

Wastewater from the dyeing/textile industries has thrown into nearby water bodies like river, canals, ponds etc without any treatment in developing countries [4] that causes severe environmental problems.

Most of the organic dyes are not easily degradable by standard biological methods.

Methods such as adsorption on activated carbon, ultra filtration, reverse osmosis, coagulation, ion exchange and oxidation with peroxide are usually applied efficiently. Nevertheless, they do not destruct the pollutant molecule [6-8]. Recently, the efficiency of advanced oxidation processes (AOP) for the degradation of recalcitrant compounds has been extensively used. These processes generally involve UV/H_2O_2, UV/O_3 or UV/Fenton's reagent for the oxidative degradation of contaminants [9-11].

Among the various AOPs, semiconductor-mediated photocatalysis has been given great credit over the past few years due to its potential to destroy awide range of organic and inorganic pollutants at ambient temperatures and pressures, with no harmful by-products [12].

semiconductor is that it absorbs only a small portion of solar spectrum in the UV region. Hence, in order to tap maximum solar energy, it is essential to shift the absorption threshold towards the visible region.

With this cause in mind we have undertaken the ZnO assisted photocatalytic degradation in the visible light. Although the detailed mechanism differs from one pollutant to another, it has been widely recognized that hydroxyl radical •OH acts as active reagent for the mineralization of organic compounds.

The radicals are formed by the scavenging of their electron-hole pair by molecular oxygen and water (Eqs. 1-4).

$ZnO + h\upsilon \rightarrow ZnO\ (e_{CB-} + h_{VB+})$ formation of electron-hole pair-------------- (1)

$h_{VB}+ + Dye \rightarrow$ direct oxidated dye------ (2)

$h_{VB}+ + H_2O \rightarrow H+ + {}^{\bullet}OH$ formation of hydroxyl radical------------------ (3)

$h_{VB} + + -OH \rightarrow {}^{\bullet}OH$ formation of hydroxyl radical------------------------ (4)

Electrons in the conduction band (e_{CB-}) on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. 5).

This radical, in the presence of organic scavengers, may form organic peroxides (Eq. 6) or hydrogen peroxide (Eq. 7).

$e_{CB-} + O_2 \rightarrow {}^{\bullet}O_2^{-}$------------------------- (5)

${}^{\bullet}O_2^{-} + Dye \rightarrow Dye\text{–}OO^{\bullet -}$ -----------------(6)

${}^{\bullet}O_2^{-} + HO_2^{\bullet} + H+ \rightarrow H_2O_2 + O_2$------- (7)

Electrons in the conduction band are also responsible for the production of hydroxyl radicals which have been shown to be the primary cause of organic matter mineralization (Eq. 8).

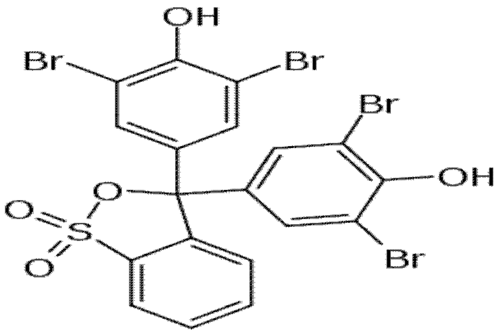
${}^{\bullet}OH + Dye \rightarrow$ degradation of the dye--- (8)

The photo corrosion of ZnO is complete at pH lower than 4 [13,14] and ZnO can be photo-oxidized to Zn(II) and oxygen (Eqs. 9 and 10). Therefore, comparative experiments were performed at pH values higher than 4.

$ZnO + 2h_{VB+} \rightarrow Zn(II) + \frac{1}{2}O_2$---------- (9)

$ZnO + 2H^{+} \rightarrow Zn(II) + H_2O$ --------- (10)

In this work, the effects of some parameters such as spectra feature of bromophenolblue, dye concentration, pH, irradiation time and concentration of catalysts on the degradation rate of dye solution were examined.



Fig(1) -The structure formula of bromophenolblue dye (BPB).

Experimental

Bromophenolblue dye (4,4'-(1,1-dioxido-3*H*-2,1-benzoxathiole-3,3-diyl)bis(2,6-dibromophenol, M.W. =669.96 g mol^{-1}$C_{19}H_{10}Br_4O_5$) was supplied from BDH , and used without further purification, sodium hydroxide, hydrochloric acid, ZnO powder with 99.5% purity (particle size: 200 nm) were obtained from Merck. Solutions were prepared by dissolving appropriate amount of the dye in double distilled water before each experiment. The dye chemical structure is shown in Fig (1).

Photocatalytic experiments were performed in open Pyrex vessel of 500 cm^3 capacity and a magnetic stirring setup. The radiation source ,a UV lamp (125W, medium pressure mercury lamp, Philips, Holland) as a source for near-UV radiation, was irradiated perpendicularly to the surface of solution, and the distance between the UV source and vessel containing reaction mixture was fixed at 12 cm.

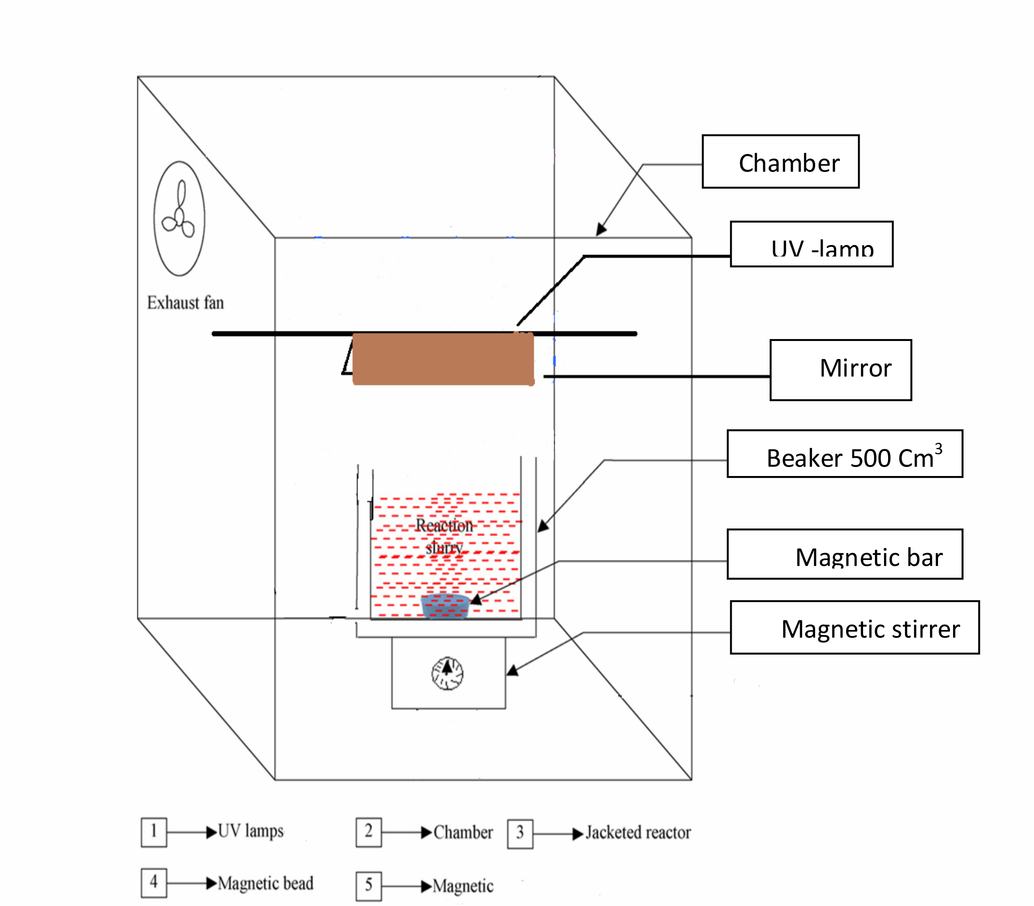
The whole photocatalytic reactor was insulated in a wooden box to prevent the escape of harmful radiation and used fan to minimized temperature fluctuations caused by draughts. Before irradiation, dye solution was stirred in the dark for 30 min after the addition of the catalyst. Next, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained by a magnetic stirrer to keep the suspension homogeneous.

The required amount of the catalyst was suspended in 200 cm^3 of aqueous solutions of bromophenolblue dye, using a magnetic stirrer. At predetermined times; 5 cm^3 of reaction mixture was collected and centrifuged (3500 rpm, 15 minutes) in an 800B centrifuge.

The supernatant was carefully removed by a syringe with a long pliable needle and centrifuged again at same speed and for the same period of time. This second centrifugation was found necessary to remove fine particles of ZnO. [15-17]

After the second centrifugation the absorbance at 590 nm of the supernatants was determined using ultraviolet-visible spectrophotometer, type UV-1650pc, Shimadzu and UV- visible spectrophotometer (Apel-303 England).

The effects of concentrations of zinc oxide were investigated. The concentration of the catalyst was found significant only up to 0.6 g L^{-1}. Beyond this value was stable and then there is a smaller alteration towards decreasing .The suspension pH values were adjusted at desired level using 0.01 N NaOH or 0.01 N HCl solutions and, then, the pH values were measured *via* pH meter (Metrohm744). The homemade reactor was use as shown in Fig(2).



Fig(2) The homemade reactor .

Results and Discussion

The Effect of UV Irradiation and ZnO Catalyst

Control experiments were carried out since some dyes are degraded by direct UV irradiation. [18] One set was performed with bromophenolblue dye solution exposed to ZnO without the presence of UV light .

The second set was done by exposing bromophenolblue dye solution to UV without the presence of ZnO . The third set was performed through exposing bromophenolblue dye solution to UV irradiation in the presence of ZnO (the photocatalysis condition). The results are presented in Fig.(3).

These experiments demonstrated that both UV light and photocatalyst are needed for the effective destruction of bromophenolblue dye solution.

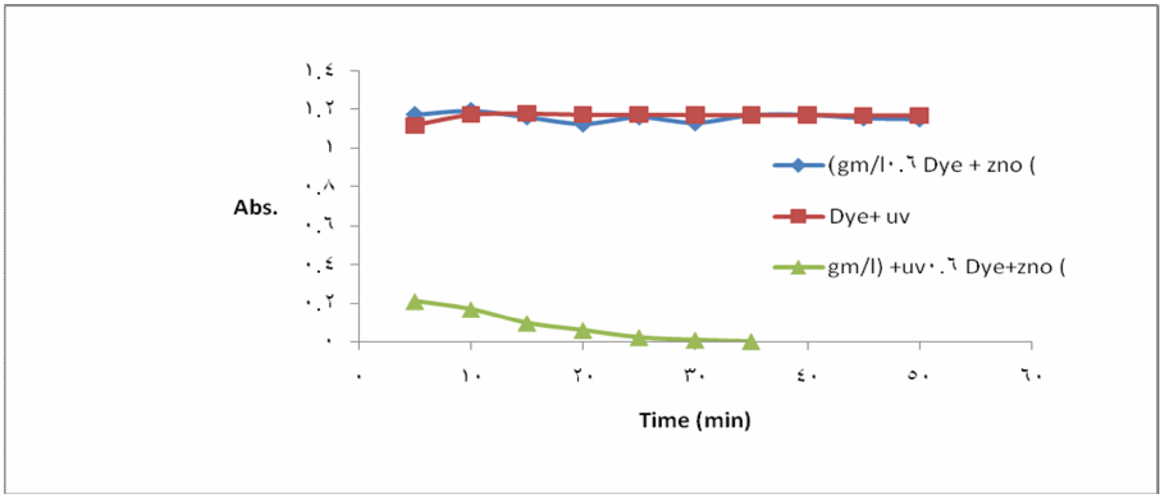


Fig. (3) Effect of UV light and ZnO on photocatalytic degradation of BPB dye (15 ppm),ZnO ,0.6 gm/l .

UV-Visible spectra of BPB dye

Fig. 4 shows uv-visible absorption spectra of three different concentration of bromophenol blue dye solution such as (5,10,15) ppm .

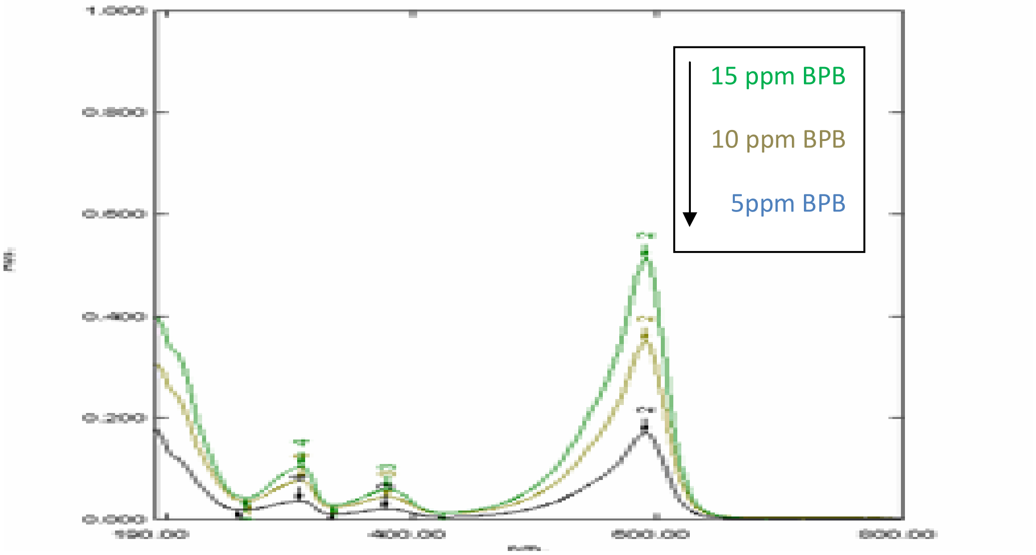


Fig. (4) uv-visible absorption spectra of three different concentration of bromophenol blue dye

The Effect of the Initial Dye Concentration

The influence of initial concentration of the dye solution on the photocatalytic degradation is a significant aspect of the study. The initial concentrations of bromophenoleblue dye solution were selected in the range of 5-15 ppm and it was revealed that the percentage of photodegradation decreased as initial concentration of the dye solution increased, as shown in Fig. 5. One possible explanation of such circumatances is that as initial concentration increases, more and more organic wood model . [19,20]

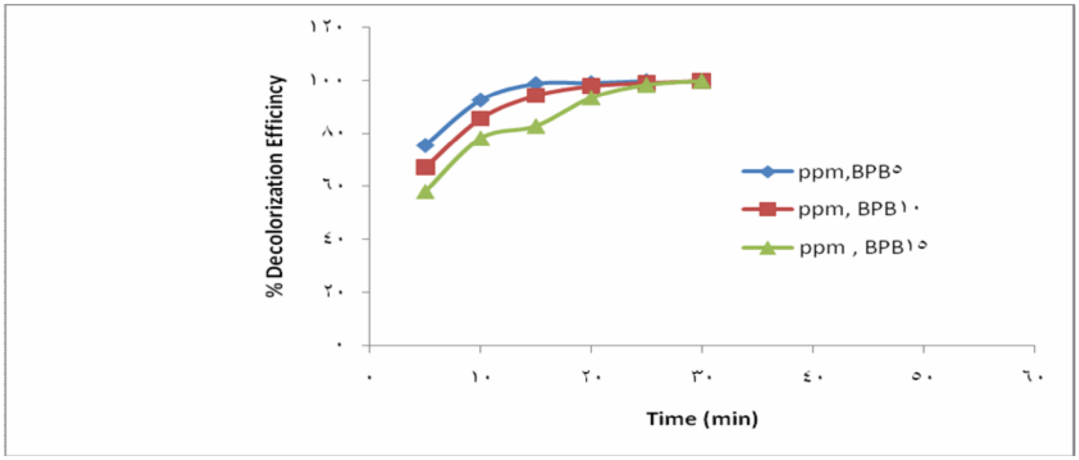


Fig.5. Effect of the initial dye concentration on photocatalytic degradation of BPB dye .

Effect of pH

Wastewater containing dyes is discharged at different pH; therefore it is important to study the role of pH on decolorization of dye.

To study the effect of pH on the decolorization efficiency, experiments were carried out at various pH values, ranging from 2 to 10 for constant dye concentration (15 mg/l) and catalyst loading (0.6 g/l). Fig. 6 shows the color removal efficiency of bromophenolblue dye solution as a function of pH. It has been observed that the decolorization efficiency increases with increase in pH exhibiting maximum rate of degradation at pH 8 .

Similar behavior has also been reported for the photocatalytic efficiency of ZnO for decolorization of azo dyes [21-23].

The interpretation of pH effects on the efficiency of the photocatalytic degradation process is a very difficult task because of its multiple roles. First, it is related to the acid base property of the metal oxide surface and can be explained on the basis of zero point charge. The adsorption of water molecules at surficial metal sites is followed by the dissociation of OH^- charge groups leading to coverage with chemically equivalent metal hydroxyl groups (M OH) [24].

Due to amphoteric behavior of most metal hydroxides, the following two equilibrium reactions are considered (Eqs. (6) and (7)):

$\mathrm{M\ OH} + \mathrm{H}^{+} \rightarrow \mathrm{M\ OH}^{2+}$ ------------------(6)

$\mathrm{M\ OH} \rightarrow \mathrm{M\ O}^{-} + \mathrm{H}^{+}$--------------------- (7)

The zero point charge (zpc) for ZnO is 9.0±0.3. ZnO surface is positively charged below pH 9 and above this pH, surface is negatively charged by adsorbed OH^- ions. The presence of large quantities of OH^- ions on the particle surface as well as in the reaction medium favors the formation of OH• radical, which is widely accepted as principal oxidizing species responsible for decolorization process at neutral or high pH levels and results in enhancement of the efficiency of the process [25].

the dyes occurred in basic region than in case of acidic solution.

For bromophenolblue dye solution , rate of photodecolorization increased with increase in pH, exhibiting maximum efficiency (100%) at pH 8, beyond which the rate of degradation remained constant. This may be attributed to the electrostatic interactions between the positive catalyst surface and dye anions leading to strong adsorption of the latter on the metal oxide support.

Although the adsorption of dye molecules are low at alkaline pH, the possible reason for this behavior may be the formation of more •OH radicals. observed similar behavior in their studies on Acid Brown 14 dye. [26]

The interpretation for the same could be amphoteric behaviors of the ZnO catalyst.

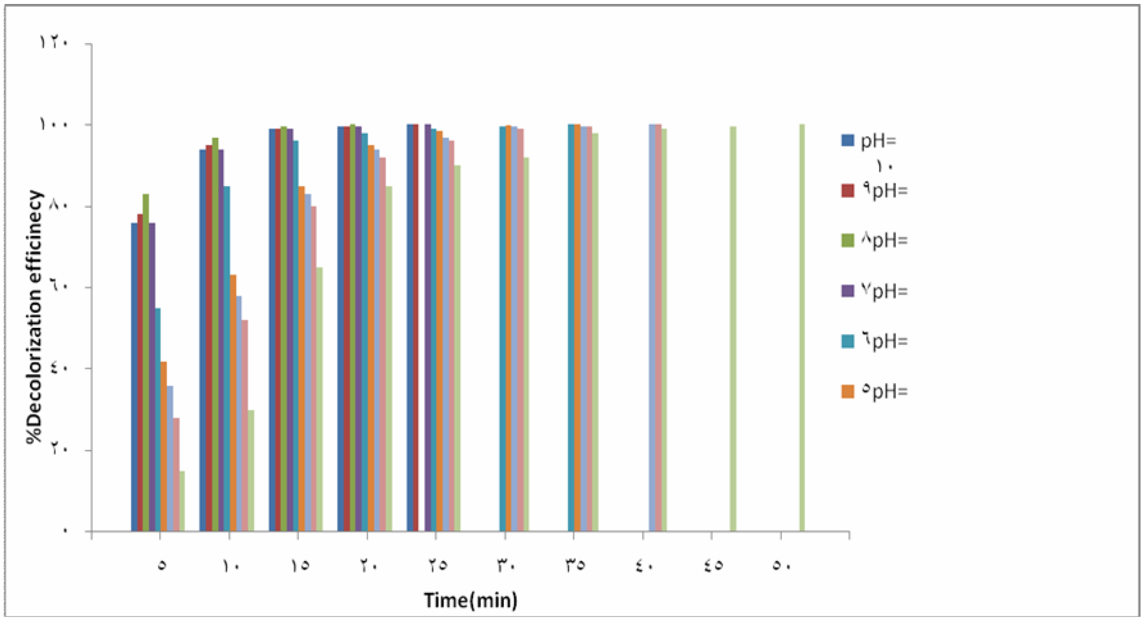


Fig.6. Effect of pH on photocatalytic degradation of BPB dye .

Effect of catalyst concentration

Fig. 7 shows the effect of catalyst concentration ranging from 0.1 – 1.0 g/L on the decolorization of bromophenoleblue dye solution in the presence of ZnO. The results indicated that the percent of decolorization increases with increasing the amount of catalyst and are effective to decolorize the bromophenoleblue dye solution . For economic removal of dye effluent from wastewater, it is necessary to find the optimum amount of catalyst for efficient degradation.

Several authors have investigated the reaction rate as a function of catalyst dosage in photocatalytic oxidation process [27,28]. As the concentration of the catalyst increased from 0.1 to 1.0 g/L the initial rate of removal of dye increases sharply from 100 % decolonization at 30 min irradiation time in the presence of ZnO. This is due to increase in the number of photocatalysts particles, which increases the number of photons absorbed and also the number of the dye molecules adsorbed. Increase of the catalyst dosage from 0.1-1.0 g/L the initial rate is almost constant. Increase of the catalyst dosage beyond 1.0 g/L may cause light scattering and screening effects. These reduce the specific activity of the catalyst [29].

At high concentrations of catalysts, particle aggregation may also reduce the catalytic activity. The optimum amount of catalyst dosage is found to be 0.6 g/L for the decolorization of bromophenoleblue dye solution.

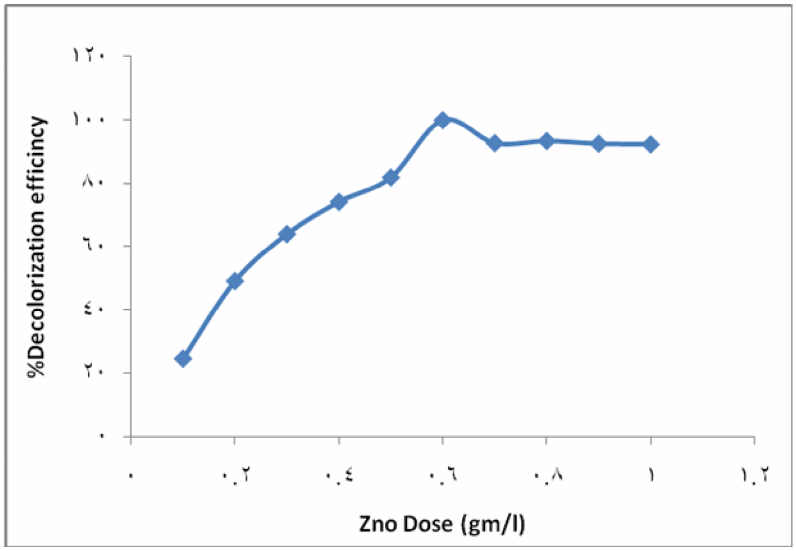


Fig.7. Effect of Dose of catalyst (ZnO) on decolonization of BPB dye .

Kinetic study

Fig.8 show the kinetics of disappearance of bromophenolblue dye solution for an initial concentration of 15 mg/l under optimized conditions. The results show that the photocatalytic decolorization of the dye in aqueous ZnO can be described by the first order kinetic model, $\ln(C0/C) = kt$, where $C0$ is the initial concentration and $C$is the concentration at any time, t. The semi logarithmic plots of the concentration data gave a straight line. The correlation constant for the fitted line was calculated to be $R^2 = 0.983$. The rate constants were calculated to $174*10^{-3}$ s^{-1}.

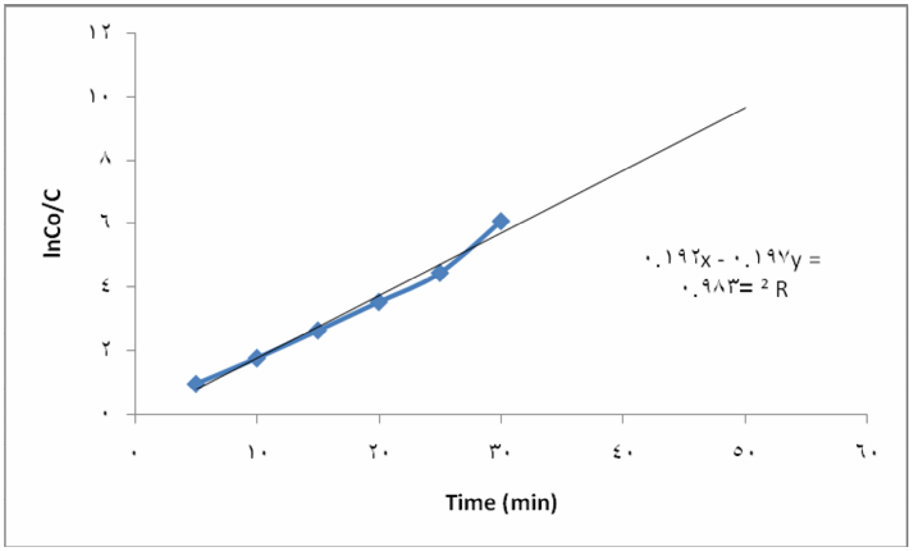


Fig.8. Kinetic analysis of BPB dye under optimized conditions .

Conclusion

The dye, bromophenoleblue is easily decolorized by the ZnO assisted photocatalysis in aqueous dispersion under irradiation by UV light (320 nm). The dye is resistant to direct photolysis. The adsorption of bromophenoleblue dye solution on the metal oxide semiconductors was found favorable by the Langmuir approach. The adsorption was maximum at pH 8 for ZnO.

The optimum physico-chemical conditions for the decolorization of 15 mg/L dye solution at room temperature were determined to be: ZnO concentration 0.6 g/L; initial pH range for ZnO: 2.0 – 10.0. The photocatalytic decolorization follows pseudo-first order kinetics at low initial dye concentration. The initial decolorization rates could be fitted to empirical Langmiur-Hinshelwood equation up to 15 mg/L. decolorization rate of the bromophenoleblue dye solution. According to the Langmiur-Hinshelwood kinetic model, it is concluded that ZnO acts as a better photocatalyst to degrade the bromophenoleblue dye solution under the present experimental conditions.

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