Photocatalytic Degradation of Bismarck Brown G Using Irradiated ZnO in Aqueous Solutions

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Abstract: In this study, a homemade photoreactor equipped with 125w/542 high pressure mercury lamp as a source for near-UV radiation, was used for photocatalytic degradation of aqueous solutions of Bismarck brown G, (C₁₈H₂₀N₈Cl₂), 4-[5-(2,4-Diamino-5-methylphenyl)diazenyl-2-methylphenyl] diazenyl-6-methylbenzol-1,3-diamin using zinc oxide. The disappearance of the original colored reactant concentrations with irradiation time was monitored spectrophotometrically by comparison with unexposed controls. It is noticed that the photocatalytic degradation process was high at the beginning and then decreased with time following pseudo first-order kinetics according to the Langmuir–Hinshelwood model. The effects of zinc oxide mass, dye concentration and temperature on photocatalytic decolorization efficiency (P.D.E.) were studied. P.D.E. reached 95.76% for Bismarck brown G after 50 minutes of irradiation at 293.15 K P.D.E. was found to increase with increasing temperature and the activation energy of photocatalytic degradation was calculated and found to be equal to 32±1 kJ mol⁻¹.

Keywords: Photocatalytic decolorization efficiency (P.E.E.), Photocatalytic degradation, Zinc oxide, Bismarck brown G, Activation energy.

Introduction

In recent years, interest has been focused on the use of semiconductor in photocatalytic decolorization of different types of wastewater. The band gap for zinc oxide is (~ 3.2 e.V), indicating that their photocatalytic activities are shown only under UV irradiations¹⁻³. However, the existence of colored compounds on the surface of the semiconductor could absorb a radiation in the visible range⁴⁻⁷ and then excited by a process called photosensitization process. The hydroxyl group radical (·OH), which is formed by the photocatalytic process, from the photosensitization processes; will oxidize all the organic compounds to CO₂ and H₂O (mineralization). This is attributed to very strong oxidizing

power of $\cdot\text{OH}$ which has the standard redox potential of + 2.8 V. The oxidative degradation of adsorbed colored organic or inorganic molecules is attributed to indirect reaction at the positive holes, which is formed in the valence band of semiconductor and then migrates to the surface of catalyst and participates in interfacial oxidation-reduction reactions. In this process, the adsorbed water or hydroxyl groups are oxidized to hydroxyl radicals⁸⁻⁹. In our previous studies^{7,10-14}, 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 present work, aims to study the photocatalytic decolorization of Bismarck brown G using ZnO in aqueous solutions. Bismarck brown G whose structure is shown in Figure 1, is a certified biological stain, for microscopy, histology and cytology and also used in textile industries.

Figure1. The structural formula of Bismarck brown G.

Experimental

A homemade photoreactor equipped with a Philips 125w/542, high pressure mercury lamp (Holland) as a source for near-UV radiation, was used to determine P.D.E.. The reactor was consisted of graduated 400 cm³ Pyrex glass beaker and a magnetic stirring setup. The lamp was positioned perpendicularly above the beaker. The distance between the lamp and the graduated Pyrex glass was 12 cm. The whole photocatalytic reactor was insulated in a wooden box to prevent the escape of harmful radiation and minimized temperature fluctuations caused by draughts.

Zinc oxide with 99.5% purity was supplied by Carlo ERBA. Bismarck brown G (analytical grade) was purchased from Fluka (packed in Switzerland) and used without further purification. Solutions were prepared using distilled water.

In all experiments, the required amount of the catalyst was suspended in 100 cm³ of aqueous solutions of Bismarck brown G, using a magnetic stirrer. At predetermined times; 2 cm³ of reaction mixture was collected and centrifuged (4,000 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. After the second centrifugation the absorbance at 448 nm of the supernatants was determined using ultraviolet-visible spectrophotometer, type UV-1650pc, Shimadzu and visible spectrophotometer type V-1000, T-ChromoTech. P.D.E. of Bismarck brown G was followed spectrophotometrically by a comparison of the absorbance, at specified interval times, with a calibration curve accomplished by measuring the absorbance, at 448 nm, with different concentrations of the dye solution as shown in Figure 2.

The effects of concentrations of zinc oxide were investigated. The concentration of the catalyst was found significant only up to 3.5 g L⁻¹. Beyond this value P.D.E. was stable and then there is a smaller alteration towards decreasing of P.D.E..

Figure 2. UV-Visible spectra of different concentrations of Bismarck brown G.

Results and Discussion

Experimental results indicated that no dark reaction in the existence of ZnO and no irradiated reaction were observed in the absence of ZnO. These results demonstrate that decolorization of the dye was dependent on the presence of light and catalyst. It is noticed that the P.D.E. of Bismarck brown G follows pseudo first-order kinetics according to the Langmuir–Hinshelwood model¹⁵⁻¹⁷, so the rate of photodegradation of Bismarck could be expressed by the following equation:

$$C_t = C_0 e^{-kt} \quad (1)$$

where C_t represents Bismarck brown G concentration at time t , C_0 its initial concentration, k the apparent reaction rate constant, and t irradiation exposure time.

$$C_t / C_0 = e^{-kt} \quad (2)$$

$$\ln C_t / C_0 = -kt \quad (3)$$

$$k = \ln C_t / C_0 / t \quad (4)$$

Figure 3 represents the first order plots of photocatalytic decolorization of Bismarck brown G at different temperatures (278.15-293.15). R^2 values are 0.998-0.999.

Figure 3. First order plots of photocatalytic decolorization of Bismarck brown G at different temperatures.

Arrhenius plot shows that the activation energy for photocatalytic degradation of Bismarck brown G is equal to $32 \pm 1 \text{ kJ mol}^{-1}$. The experimental activation energy was associated with the energy required to promote photoelectrons from trapping centers into zinc oxide conduction band¹⁸⁻²⁰. The difference between the previous activation energy for photocatalytic decolorization of textile industrial wastewater on ZnO ¹⁴ and the present value probably arises from the differences in the surface area and the purity of two catalysts.

Figure 4. Arrhenius plot for photocatalytic degradation of Bismarck brown G on ZnO

Figure 5 shows the effect of initial Bismarck brown G concentrations ($0.25 \times 10^{-4} \text{ M}$ – $3 \times 10^{-4} \text{ M}$) on P.D.E. after 10 minutes of irradiation at 293.15 K. The results indicated that the rate of decolorization increases with the decreasing of initial concentration of Bismarck brown G. P.D.E. was only 30% when $3 \times 10^{-4} \text{ M}$ of dye was irradiated for 10 minutes at 293.15 K. However, this percentage doubled when the initial concentration of dye reduced to $0.25 \times 10^{-4} \text{ M}$. The inverse proportionality between dye concentrations and photocatalytic degradation efficiency is related to the maximum amount of dye adsorbed on the surface of zinc oxide.

Figure 5. Effect of initial Bismarck brown G concentrations on P.D.E.

Conclusions

Photocatalytic decolorization of Bismarck brown G using zinc oxide and visible light was found to be efficient technique and photocatalytic decolorization efficiency could be reached 100% after less than one hour of irradiation. Dye concentration, catalyst concentration and temperature were found to have a considerable effect on P.D.E. The photocatalytic degradation processes were influenced by the initial concentrations of Bismarck brown G. Color change from original color to colorless is irreversible and the photocatalytic degradation of Bismarck brown G followed the pseudo first-order kinetics according to the Langmuir–Hinshelwood model.

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