Abstract

Photocatalytic removal of methylene blue dye by using of ZnS and

CdS

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Key words

Photocatalytic degradation of methylene blue was studied using CdS and ZnS as catalyst. The photocatalytic activity of the specimen was studied by exposing to UV-radiation. The result shows that the degradation efficiency of the dye for CdS micro-particles was 92% after 7 hours and for ZnS micro-particles was 88.29% for the same time interval.

Photocatalytic, methylene blue, ZnS, CdS.

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إزالة صبغه أزرق المثيلين بالتحفيز الضوئي بأستخدام كبريتيد الزنك وكبريتيد الكادميوم زينب رحيم مسلم و رقيه فؤاد كاظم قسم الفيزياء، كلية العلوم، جامعة بغداد

الخلاصة

تم في هذا البحث دراسة الانحلال الضوئي المحفز لصبغة أزرق المثيلين باستخدام (CdS) و (ZnS) كمحفزات. حيث درست فعاليه التحفيز الضوئي للعينة بواسطة تعرضها للأشعة فوق البنفسجية. أظهرت النتائج أن كفاءة انحلال الصبغة لجسيمات CdS كانت 92% بعد 7 ساعات ولجزيئات ZnS كانت %88.29 لنفس الفترة الزمنية.

Introduction

Many industries such as textile and printing are using dyes and pigments and thus producing colored waste effluents. Disposal of these wastes into water causes environmental problems. The removal of these compounds from waste waters is of a great importance, because many dyes and their degradation products are toxic and carcinogenic, posing a serious hazard to the environment [1, 2].

Degradation of organic pollutants and dyes such as methylene blue, bromo phenol blue, and Chicago sky blue from industrial waste water remains as a challenge because of low visible light photo catalytic activity of metal oxides and sulphides [3].

Photocatalysis can be defined as a change in the rate of chemical reactions or their initiation under light in the presence of a photocatalyst. Photocatalysts are a class of compound that produces electron-hole pairs upon the absorption of light quanta and they induce chemical transformations in reaction substrates that come into contact with them. Then they undergo regeneration to their original electronic composition. Many semiconductors have been synthesized and studied as photocatalysts including cadmium sulfide (CdS with energy gap 2.5eV),

and Zinc sulfide (ZnS with energy gap 3.6eV) [4].

In the presence of air or oxygen, UV irradiated semiconductor (ZnS and CdS) are capable of destroying many organic contaminants. The activation of ZnS and CdS by light (*hv*) produces electron-hole pairs which are powerful oxidizing and reducing agents, respectively:

 $\operatorname{ZnS} + hv \rightarrow h^+ + e^-$

$$CdS + hv \rightarrow h^+ + e^-$$

The oxidative and reductive reactions are expressed as: $OH^- + h^+ \rightarrow OH$

 $O_{2ads} + e^- \rightarrow O_{2ads}^-$

In the degradation of organic compounds (MB), the hydroxyl radical which comes from the oxidation of adsorbed water or adsorbed OH⁻, is the primary oxidant; and the presence of oxygen can prevent the re-combination of hole-electron pairs. For a complete reaction, the final products of the reaction among others are CO₂ and H₂O [5, 6]:

 $\begin{array}{l} MB + \cdot OH \rightarrow products \; (CO_2 + H_2O + \\ NH_4^{\; +} + NO_3^{\; -} + SO_4^{\; 2^-} + Cl^-) \end{array}$

Fig.1 shows schematic presentation of the mechanism of the generation of oxidative species from a photocatalytic study [4].



Fig. 1: The mechanism of photocatalysis [6].

Experimental work 1. Material used

Commercially available Methylene blue (MB) organic dye purchased from CDH –India and specified to be of 99% purity using to show the photocatalytic degradation.

Zinc sulfide (ZnS) and Cadmium Sulfide (CdS), manufactured by BDH were used as catalysis.

2. Devices

- UV-Lamp 400W Mercury lamp, *asrom VMI40/22-sc* (Spain), was selected as UV light source.
- Centrifuge *PLC- 03*(Taiwan), was used to separate the suspended particles from aqueous solutions.

- Magnetic Stirrer (England) for mixing the powders with the aqueous solutions.
- Sensitive Balance, *Mettlar H35AR* (United States) of accuracy (0.1mg).
- UV-Vis spectrophotometer, *Shimadzu SP-8001*(Taiwan), was used to determine the absorption spectra for the solutions.

3. Analytical methods

Photocatalytic degradation of methylene blue by ZnS was studied under UV light irradiation at room temperature. In this experiment each of ZnS and CdS microparticles of weight (10mg) were dispersed well in 100 ml aqueous methylene blue solution under stirring for 15 min. in dark conditions in order to make certain adsorption equilibrium on the surface of the catalysts. The suspension was irradiated to UV light by a 400 W mercury lamp.

After every 1 hour of irradiation, part of the suspension was collected and sealed in separate containers. They were centrifuged to separate the catalysts from the MB solution and then their UV-Vis spectra were recorded.

Results and discussion

1. Photocatalytic activity of ZnS and CdS

The absorbance of MB dye as a function of wavelength was studied and shown in Fig. 2, the main peak of MB dyes at 663.36nm.

Fig. 3 and 4 show the effect of CdS and ZnS on the absorbance of MB dye aqueous solution under UV-light radiation. The absorbance was decreased with the increasing the time of radiation due to degradation of dyes in the presence of photocatalyst upon irradiation with UV-light because of their absorption in the visible region [7].

The absorbance peak of CdS was lower than ZnS; this means that CdS was more active than ZnS due to the difference in band gap; As a result of its large band gap, ZnS (3.7ev) gives a poor response to visible light. In contrast, the small band gap of CdS (2.4ev) makes it a good absorber of visible light [8].

These results effect on the decoloration of samples, Fig. 5 and 6 show that higher decoloration of CdS was higher than ZnS in which removal of color was reaches (7hrs). The photodegradation of MB dye using CdS was 92.2% which is higher than ZnS 88.29%, this is because in the degradation of organic compound (MB), the hydroxyl radical which comes from the oxidation of adsorbed water or adsorbed OH, is the primary oxidant, and the presence of oxygen can prevent the re-combination of hole-electron pairs. For a complete reaction, the final products of the reaction among others are CO₂ and H₂O [9].



Fig.2: Absorption spectra of MB.



Fig.3: Absorption spectra of CdS in various times.



Fig. 4: Absorption spectra of ZnS in various time.

Fig. 5 and 6 shows the absorption spectra of reactive MB dye solution. The intensity of absorption spectra decreases with time of irradiation increases. The intensity of the main absorption peaks decreased due to the degradation of MB dye, CdS and ZnS which have been taken at different intervals after exposing the solution with UV–Visible light.



Fig.5: Decoloration of 5 ppm MB by CdS.



Fig.6: Decoloration of 5 ppm MB by ZnS.

2. Degradation percentages

A UV-Vis. Spectrophotometer was used to study the absorption spectra of the prepared samples at wave length range 200-800 nm. Periodically, 2ml of MB solution was taken out from the own solution every 1h and analyzed using UV-Vis. Spectrophotometer. The absorption spectrum was used to determine the degradation percentage (D %) of MB, which can be calculated via:

 $D\% = \frac{A - A}{A} \times 100$

where A the initial dye absorbance (gm. L^{-1}) and A is the dye absorbance after the treatment. It can be noted that A - A is referred to the losing in the absorbance of solution by degradation process.

Fig. 7 and 8 show the degradation of the methylene blue (MB) versus UV illumination time. From these figures, the prepared catalysts show that the high photo-catalytic activity and degradation of methylene blue (MB) was achieved using CdS.



Fig.7: Degradation percentage versus time of CdS.



Fig.8: Degradation percentage versus time of ZnS.

Conclusions

Decoloration was higher for CdS than ZnS, and it is achieved in 7hrs with degraded effect 92% as compared to ZnS, where the decoloration efficiency was observed in 7hrs with degraded effect 88.29%.

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