Textile dye Reactive Black 5 (RB5) removal by visible light photocatalyst and its characterization

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Abstract. Visible light photocatalysis is now a subject of interest for researchers to explore further in the treatment of wastewater as it can save costs and be environmentally friendly. Cadmium sulphide (CdS) is one of the photocatalysts of visible light that has excellent properties and a low band gap. The toxicity and carcinogenicity of textile industry effluent containing predominantly textile dyes disturbs the environment. In this study, the removal of reactive black 5 (RB5), the most used dyes with CdS as visible light photocatalyst, was tested. Using X-ray diffraction (XRD), scanning electron microscope (SEM), ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometers and photocatalytic tests under visible light, the physical and chemical properties of CdS were characterised. CdS has an irregular shape and this can be demonstrated through SEM. The band gap obtained was 2.12 eV and this was associated with the degradation efficiency of CdS under visible light as it can degrade RB5 after 360 minutes of exposure by up to 80 percent. This study proves that CdS is a strong photocatalyst of visible light that has a small band gap and crystalline particles.

1. Introduction

In March 2019, a case reported in Sungai Kim Kim, Pasir Gudang, Johor, Malaysia about industrial factories that eliminate their chemical wastes into the river [1]. The river affected the community in large radius from the river. After the air contaminated with the poisonous gases, more than 5000 people get affected with difficulties to breath, nausea and vomit symptoms [2]. This case shows that our environment is sick and the awareness among us about the important to keep our earth healthy is low.
For textile industry specifically, it consume huge quantity of water as it hold as second in the world’s largest water consumer and more than 90% disposed [3]. It also discharged their effluents into environment. Their effluents are made up of metals, dyes and other pollutants [4]. 15-20% of wastewater and 17-20% of industrial effluent composed of textile dyes. While during the colouring process, 90% of the dyes used are released as effluents [5]. Dyes could affects the ecosystem as it quite high in pH, colour, chemical oxygen demand, suspended solids, metals, temperature, salts and biochemical oxygen demand [4]. It also a toxic substance, has carcinogenic and mutagenic properties and not only affecting water bodies, but also cause diseases towards humans and animals [6].

There is a law under Malaysia Environmental Quality Act 1974, Quality of Environment (Scheduled Wastes) Regulations 2005 that specify chemicals waste from industrial are scheduled waste. There are five types of waste under this law, SW1-SW5 which consist of metal wastes, inorganic substances, organic substances, waste with organic or inorganic substances and other wastes. Thus, any type of industries needs to obey and dispose their waste through this scheduled waste channel. However, our environment still affected by the irresponsible party.

There are several conventional method to remove textile dyes such biological methods, physical methods and chemical methods [7]. Ozonation, photochemical and oxidative process grouped under chemical methods, decolorization by white-rot fungi and adsorption by microbes are under biological methods while ion exchange, irradiation, membrane filtration and adsorption by activated carbon are some of physical methods. However, these methods gives out common drawbacks to the process such formation of secondary compound, not effective for all dyes, intense sludge formation and not cost effective [8].

Photocatalysis is an alternative to save the environment as currently our environment needs our help due to excessive exposure especially from industry effluents. Photocatalysis is a process that require catalyst and light to accelerate a chemical reaction. This process has been used in organic pollutant degradation especially in wastewater, hydrogen production, air purification and as disinfectant. Photocatalysis made up of two distinct process which are homogenous process and heterogeneous process [9].

Homogenous process needs metal compound and under certain condition, hydroxyl radicals generated by the high metal ions oxidation state react with the organic matter and degrade the organic matters. Heterogenous process require semiconductor materials as the catalyst. Titanium dioxide (TiO₂) and zinc oxide (ZnO) are the most common used semiconductor materials. The process needs just a light pressure and temperature and low in maintenance cost. To be a great catalyst, the material needs to fulfil few criteria which can utilize UV or visible light, inert in terms of biologically and chemically, photocorrosion stable, low cost and safe [9]. However, TiO₂ and ZnO can only activated under UV light and a low band gap photocatalyst is preferable as it can activated under visible light.

Cadmium sulfide (CdS) is an amazing substance. It has multifunction and has been applied in various area. The combination of cadmium and sulfur forming cadmium sulfide exist in vivid yellow to brown colour. It has molecular weight of 144.46 g/mol and specific gravity of 4.82 g/cm³. It exists in solid but in two polymorphs, cubic hawleyite and hexagonal greenockite and has a sublimation point of 980 °C. The speciality of this substance is it does not soluble in water either its hot or cold [10]. CdS is grouped into II–VI semiconductor and has a 2.42 eV bandgap at 515 nm wavelength [11]. It has been applied in photocatalysis, gas sensor, infrared and laser detector, solar cells which act as buffer layer in Copper-Indium-Gallium-Selenide solar cells, catalyst in photochemical, nonlinear optical materials and devices of luminescence and optoelectronic [10].
Textile industry effluent which mainly contains the textile dyes are disturbing the ecosystem with its toxicity and carcinogenic properties. It also may threaten aquatic life habitat and endangered species may facing extinction. Thus, this study was conducted to remove of Reactive Black 5 (RB5) which is the most frequent used dyes in textile industry using visible light photocatalyst CdS. The physical and chemical properties of CdS was characterized using Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), Ultraviolet-Visible-Near Infra-Red (UV-Vis-NIR) spectrophotometer and the photocatalytic test under visible light.

2. Methodology

2.1 Materials
Cadmium sulfide (CdS, Sigma Aldrich, USA) was used as main component. Textile dye Reactive Black 5 (RB5, Sigma Aldrich, USA) used as contaminant to be degraded by photocatalyst.

2.2 Characterization

2.2.1 Scanning Electron Microscopy (SEM). The morphological and structural characteristic of the CdS surface were examined using scanning electron microscopy (SEM; TM3000, Hitachi) analysis. Each sample was placed on a stub and coated with gold for 3 minutes under vacuum condition. The SEM image for the sample was taken for different magnifications 2000x and 5000x.

2.2.2 X-ray Diffraction (XRD). CdS crystallinity and phase identification was analysed by X-ray Diffraction (XRD). The analysis was carried out at 40 kV and 30 mA. The sample also employed CUK-β radiation at wavelength of 0.15418 nm at an angular incidence of 2θ = 20-80° with a scan step speed of 1°/min.

2.2.3 Ultraviolet-Visible-Near Infra-Red (UV-Vis-NIR) spectrophotometer. UV-Vis-NIR spectrophotometer was used to determine CdS band gap value and the optical property on light absorption capability under UV and visible light irradiation was examined through this method. The sample was clamped to the sample holder and scanned between 200-1000 nm using the spectrophotometer. A graph projected from the analysis and the band gap can be determined from the graph.

2.3 Photocatalytic test under visible light
Photocatalytic activity of CdS to degrade RB5 as textile dye measured under visible light irradiation. 0.1 g CdS powder added in several concentration of RB5 which are 10 ppm, 15 ppm and 20 ppm. The suspension then stirred in dark place for 30 min to reach adsorption-desorption equilibrium. 10 ml of suspension taken and filtered, and the absorbance measured using Perkin Elmer UV-Visible Spectrophotometer at 597 nm for every 30 minutes interval in 360 minutes. The results then calculated using equation below to obtain the degradation of RB5 percentage [12].

\[
\text{Degradation of organic contaminants} = \frac{C_0 - C_t}{C_t} \times 100
\]  

(1)
Equation of photocatalytic activity percentage where \( C_0 \) is the initial concentration at \( t=0 \) and \( C_t \) is concentration at time 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330 and 360 minutes.

3. Results and discussion

3.1 Physical properties

Figure 1 (a) and (b) are the image of CdS powder under magnification of 2000x and 5000x. The shape showing that CdS has crystalline shape although the image quite not clear. It has a range of 17-22 nm size of particles. As compared with [10] Sahare (2018) research, CdS have a crystalline structure and irregular particle which in more detail, it has hexagonal wurtzite and sphalerite structure and with more larger particle size range 30-50 nm. The crystalline, irregular structure and smaller particle size helps the CdS having large total surface area and higher photocatalytic performance as larger surface area exposed towards the source of light.

![Figure 1](image-url). Image from SEM of CdS under (a) 2000x and (b) 5000x magnification

The result showed that the substance is 100% contained CdS particle and proved the CdS exist in crystalline shape as XRD only can detect crystalline solid. Besides, it was found the diffraction peak at 25.03°, 43.58° and 51.78° as in Figure 2. The DB Card Number is 01-089-0440. Compared to [13] Aggarwal (2016) research, the peaks quite similar to this study which are \( 2\Theta = 26^\circ, 44^\circ \) and \( 52^\circ \) confirming the powder contained fully crystalline CdS particle.
Band gap determination from UV-Vis-NIR spectrophotometer proving CdS is photocatalyst with a band gap value 2.12 eV (Figure 3). Band gap value 2.12 eV portrayed that the CdS can works as photocatalyst the best under visible light and can work under ultraviolet but not at its best performance. CdS can excites its electron from the valence band to conduction band without the aid of ultraviolet lamp thus it saves the cost. The visible light region which in the range of 400 nm to 765 nm wavelength are the spectrum that can be seen by human eyes. Thus, as the CdS can be activated with the spectrum up to 585 nm, it only needs normal visible light and by using visible lamp during night. Compared with a study by [14] Pan and Zhu (2015), CdS has a band gap of 2.42 eV which a little bit higher than found in this study. This happened may due to the CdS used in this study was the commercialized CdS and the CdS used by [14] Pan and Zhu (2015) was synthesized CdS. Thus, the band gap may change a little bit due to distance between conduction band and valence band may differ.

**Figure 2.** Graph from XRD of CdS
Photocatalytic activity of CdS to degrade Reactive Black 5 (RB5) as textile dye under visible light irradiation was analysed. The absorbance of the RB5 for every 30 minutes interval in 360 minutes was measured using Perkin Elmer UV-Visible Spectrophotometer at spectrum of 597 nm. Figure 4 showed the effectiveness of CdS powder which able to degrade textile dye RB5 up to 93.72% at 10 ppm, 92.57% at 15 ppm and 90.66% at 20 ppm in 360 minutes under visible light irradiation.

In comparison with a study by [12] Ismail et al. (2019), raw bauxite without any modification able to degrade 67% of RB5 under visible light in 360 minutes. CdS showed better performance as have higher degradation percentage in same degradation time. Other than that, a study by [15] Lucas et al. (2013) also focused on degradation of textile dye RB5 by using other substance, the hybrid nanoparticle of Fe3O4@SiO2@TiO2. The nanoparticle successfully degraded 91% of RB5 after 60 minutes of exposure but the drawback of this study is the duration of time needed to prepare the nanoparticle as it is not commercially available compared to CdS that is buyable. Besides, RB5 also been degraded by n-doped TiO2 with degradation percentage of 88.4% after six hours of exposure [16]. Thus, making CdS is better than n-doped TiO2, bauxite and Fe3O4@SiO2@TiO2 with better degradation of textile dye RB5.
4. Conclusions

Cadmium sulfide has very low band gap and crystalline structure. It also a good visible light photocatalyst in removing 93.72% 10 ppm textile dye Reactive Black 5 (RB5) in 360 minutes under visible light exposure. Thus, CdS can be use as a photocatalyst to remove dyes in textile industry wastewater as the photocatalysis process itself is safe, degrading the pollutants into carbon dioxide and water.

5. Conflict of interest

The authors declare that they have no conflict of interest

6. Acknowledgement

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