Mini Review

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Recent Advances in the Photocatalytic Degradation of Direct Blue Dyes: A Critical Minireview and Analysis Study

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ABSTRACT

Different dyes are used in numerous industries, including food, paper, ink, and the textile industry. Among various dye types, Direct Dyes have great significance because of their properties and applications. Such applications are paper, cotton, leather, and cellulose. The textile industry is considered a main contributor to the water pollution problem because it releases large quantities of coloured liquid waste. The majority of dyes and their products are considered carcinogenic, toxic, and resistant compounds. Therefore, the application of common wastewater treatments is not sufficient for dye removal such as adsorption, biological and chemical degradation. The advanced oxidation process using photocatalytic oxidation is an effective technique that can mineralize complicated aromatics and different organic dyes among various treatment methods. In this review, the photocatalytic degradation of Direct Blue dyes is discussed. The review is mainly focused on the recent advances in the photocatalysts and their activity improvement using different dopants.

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In different things, including foods and various materials, gaining certain colours is generally obtained by adding substances widely known as dyes and pigments [1,2]. In the applied medium, water or oil, dyes are soluble materials primarily used for textile materials, whereas pigments are typically insoluble substances utilized via a dispersion method to obtain different products: inks and paints [1-4]. Different dyes are utilized for various product colorations in the textile industry, with an estimated amount between 7×10^5 and 7×10^7 tons worldwide annually [5,6]. The dye structure generally consists of two main constituents, namely, chromophore and auxochromes. The function of chromophores is light absorption to produce a certain colour. Hence, they are fundamentally responsible for the dye colour. Examples of chromophore groups are azo (-N=N-), carbonyl (C=O) and methine (-CH=). Meanwhile, auxochromes have two different functions: playing a role in colour enhancement, more precisely, increase the colour intensity and a role in dye attachment to the surface of the applied medium, in the textile industry, attached dye to the fiber surface. In dyes, the auxochromes are classified into two main groups: acidic and basic groups.

While acidic auxochromes can include -OH, -COOH, and -SO3H, the basic groups of auxochromes involve $-NH_2$, NHR, and $-NR_2$ [1-3,7-8]. Dyes are categorized into various classes depending on different aspects. However, the classification based on their usage and chemical structure are the most popular ways. Depending on the type of applied method to the used substrate, dyes are categorized into different groups. Such groups include Acid Dyes, Basic Dyes, Direct Dyes, Reactive Dyes, Disperse Dyes, Solvent Dyes, Sulfur Dyes, Vat Dyes and Mordant Dyes [3,8]. Among different dye types, Direct Dyes have great importance due to both their characteristics and applications. In terms of their applications, Direct Dyes are applied with no requirements for the fixing process, precisely without the step of affixing agent. This leads to a simplified dyeing process and lowered process operating costs. Their applications include paper,

cotton, leather, cellulose, and nylon. These dyes are typically water-soluble with a strong affinity to cellulose fibers. Their solubility is enhanced due to the presence of sulfonate groups in some types.

Though such substances are anionic dyes, their categorization is not under the acid dyes class. This is because the attachment to the fiber surface does not usually occur by acid groups [8-11]. The textile industry waste is a major contributor to aquatic life pollution among different waste types due to releasing a huge amount of coloured wastewater to the environment. The reason behind such significant wastewater amounts is the features of the dyeing process itself. The dye bath tank's draining and cleaning after each dyeing process are the two main factors responsible for releasing coloured wastewater [12]. As the dye's usage is dramatically increased due to their numerous applications, the effluent of their usage, especially textile industries, is considered a big challenge in the wastewater treatment area. This is because of various factors: high levels of Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) [13,14]; most dyes and their by-products are carcinogenic and highly toxic compounds [15-19] and difficult to be completely degraded because they are more resistant substances for the typical water treatment methods such as adsorption, photolysis, biological and chemical degradation [20-22].

Among different alternative treatments, applying the Advanced Oxidation Process (AOP) using the photocatalytic oxidation approach is a promising method for resistant materials such as complicated aromatics and organic dyes. The use of the photodegradation technique leads to degrading highly toxic compounds to environmentally friendly minerals [3,20,23-26]. Therefore, this way has been attracted many researchers. This minireview paper addresses the application of AOP using the photocatalytic degradation approach for Direct Blue dyes. This paper's main focus is discussing the recent advances in photocatalytic degradation in terms of using different photocatalysts and their modifications using various dopants.

Literature Review

In terms of Direct Blue dyes, El-Bahy, et al. [27] examined the photocatalytic degradation of Direct Blue dye (DB53) using various lanthanide ions doped with TiO_2. Under UV irradiation, the study demonstrated that the type of dopant has a high degree of impact on the catalyst surface properties such as texture structure, particle size and bandgap. Gd-TiO_2 appeared to be the most effective catalyst, resulting in the highest dye removal due to its excellent surface properties. Using a Cu_2O catalyst, it was observed that the hydrothermal temperature has a key role in determining the main properties of the synthesized catalyst, including the bandgap, shape, and surface area. In terms of DB53 degradation, the catalyst with a nanorod shape was highly effective compared to other catalyst shapes [28]. In contrast, Mohamed, et al. [29] changed the hydrothermal time for preparing YVO_4 nanoparticles from 4 h to 24 h. Their study found that the YVO_4 nanoparticles with a size of 11 nm exhibit the optimum behaviour of catalyst activity. Sobana, et al. [30] applied 2% Ag-doped TiO_2 for the degradation of DB53 using both UV and solar light irradiation.

The application of solar irradiation for the Ag-doped TiO_2 registered a higher DB53 degradation than UV light utilization. Sobana, et al. [31] concluded that the catalyst activated carbon AC-ZnO has a good activity for DB53 removal under solar light irradiation. While alkaline pH appeared to be more preferable than acidic pH, catalyst grinding showed a negative impact on DB53 degradation efficiency. Mohamed, et al. [32] observed that the energy band gap of Pt/Ti-Na-mordenite catalyst proportionally decreases when the amount of Pt is increased. The doping of Pt at high concentration (0.4 wt.%) had no significant impact on energy bandgap reduction. Under visible light irradiation, 100% DB53 dye removal was registered at a Pt concentration of 0.3 wt.% after 60 min irradiation, resulting in the highest degradation. Sobana, et al. [33] used Ag-doped TiO_2 for the degradation of DB53 aqueous solution. Under UVA irradiation, the study outcomes proved that the photocatalyst activity increases as the dopant concentration is increased. Ag particles on the catalyst surface work as electron traps, resulting in a significant enhancement of electron-hole separation and resulting in the reduction of recombination rate.

In terms of reaction rate, the obtained results showed that DB53 dye degradation is described by pseudo-first order kinetics using different catalyst types [29-32]. DB71 was degraded under UVC irradiation. The findings suggested that high dye removal is achieved for two different cases: UV irradiation and UV/TiO_2. In terms of pH solution and temperature, there was little effect on DB71 degradation Saien, et al. [34,35] found that the prepared catalyst CuO-ZnO has a significantly higher photoactivity compared to reagent-grade ZnO under visible light irradiation. The nanocomposite with (1:3) CuO-ZnO was the most successful application due to obtaining the highest DB71 removal. Habibi, et al. [36] demonstrated that the efficiency of DB71 removal reached 82% using a bi-component nanocomposite that consists of cobalt metatitanate and cobalt oxide. In the presence of $K_7[PMo_2W_9O_{39}].19H_2O$ and H_2O_2, the DB71 removal rate registered 65% for 60 min. The optimal conditions of DB71 removal were 0.6 g/L, 0.08 mol/L, and 90 min for catalyst loading, H_2O_2, and reaction time, respectively. Under such conditions, the percentage of DB71 degradation was approximately 87% Tabatabaee, et al. [37,38] tested the ability of $CuFeO_2$/ZnO as a photocatalyst for degradation of DB71.

The study demonstrated that the dye mineralization is confirmed by TOC measurements at natural pH under visible light. Pugazhenthiran, et al. [39] discussed the possibility of Au-Nx-TiO_2 and Au-TiO_2 nanospheres application in the degradation of DB71. Under solar irradiation, the obtained results showed that the synthesized catalysts exhibit a superior photoactivity performance. In terms of catalyst stability, the prepared catalysts

had no photoactivity reduction even after eight consecutive tests. Sathishkumar, et al. [40] aimed to increase ZnO photoactivity by doping $CoFe_2O_4$ on its surface. Under visible light irradiation, the activity synthesized catalyst was examined for DB71 degradation using a 150 W lamp with a wavelength ($\lambda \geq 400$ nm). The study findings manifested a reduction of optical bandgap energy. In the presence of both used catalyst and PMS, the highest value of DB71 degradation rate was achieved. Interestingly, a power-law model is registered for the DB71 degradation kinetics. Though the degradation rate was expressed as a sum of two terms: photolysis and photocatalysis, the individual terms had a power order with a value of 1.83 and 2.16, respectively Saien, et al. [34].

In contrast, the obtained data of DB71 degradation was accurately fitted by pseudo-first order reaction kinetics Boumaza, et al. [38] As a part of their study, Habibi, et al. [41] investigated the degradation of DB160 solution using commercial TiO2 catalyst. With a UV source of 400 W, the obtained results found that complete decolorization is successfully achieved. With respect to the reaction kinetics, pseudo-first order kinetics clearly described the DB160 degradation. It was also observed that inorganic ions have an inhibitory effect on the DB160 degradation rate Saroj, et al. [42] tested different concentrations of Fe-doped TiO2 ($Ti_{1-x}Fe_xO_2$). Two different irradiation methods, namely, UV light and direct sunlight, were applied for DB199 degradation within real industry wastewater. The results revealed that the catalyst $Ti_{0.96}Fe_{0.04}O_2$ has the highest photoactivity in both reactor types, indicating that the reactor type has no influence on the catalyst activity. The DB129 degradation was examined by applying the ZnO catalyst. By applying the sol-gel method, ZnO nanoparticles were prepared using Arabic gum (AG) as a template. Under visible light, it was observed that using ZnO nanoparticles leads to a high dye removal up to 95% Fardood, et al [43].

With respect to DB15 dye, Lamba, et al. [44] synthesized CeO_2-ZnO nanodisks using a precipitation method. In a double-walled reactor, an aqueous solution of 50 mg/L DB15 was irradiated using natural solar light for 4 h during the time between 10 am to 2 pm. Their study found that the CeO_2-ZnO catalyst shows excellent activity that could possibly be due to an enhanced recombination rate Ebrahimi, et al. [45] discussed the impact of transition metal doped ZnO nanoparticles on the photodegradation of DB 15 using both UV and visible light irradiation. The synthesized ZnO was doped with three different transition metals: Ag, Cu, and Mn. The findings demonstrated that the transition metal-doped catalyst has higher activity in comparison with undoped ZnO. For UV irradiation, the optimum dye removal was 74%, registered for Ag-doped ZnO. In contrast, the Cu-doped ZnO had the highest degradation rate with a value of 70% under visible light irradiation. The influence of catalyst morphology on its photocatalytic activity was investigated by Jo, et al. [46] Among different morphologies, the catalyst with nanoflower morphology registered the highest photoactivity.

Depending on the surface morphology, the DB15 degradation had the following order: nanoflowers > nanotubes > nanospheres Deng, et al. [47] increased the surface area of Fe-based metallic glass ribbons using etched porous ribbons and evaluated for DB15 degradation. The outcomes revealed that the application of etching treatment in 20% HF solution for 40 min leads to a big improvement in the catalytic activity due to obtaining higher rates of DB15 degradation. Zhan, et al. [48] synthesized Copper hydroxide nitrate ($Cu_2(OH)_3NO_3$) by a solvothermal method using anhydrous ethanol. The synthesized catalyst appeared to have a complex structure with spherical morphology evaluated for DB15 degradation. The catalyst registered a high activity in the DB15 removal compared with the catalyst prepared by the typical reaction of NaOH and Cu $(NO_3)_2$ in an aqueous solution.

Conclusion

While scanning the relevant literature of Direct Blue dyes, the main conclusions are as follows:

1. The majority of previous studies have been mainly focused on two dyes, namely: DB53 and DB71. Meanwhile, few studies have been registered for the evaluation of DB15 photodegradation.

2. Different dopants have been applied for TiO2 or ZnO photocatalyst modification. It is observed that the dopant concentration has an impact on the photocatalyst performance. However, the higher dopant concentrations have no effect on the catalyst photoactivity.

3. The dopant type influences the photocatalyst surface characteristics such as surface texture, particle size and energy bandgap.

4. With different photocatalysts, the photodegradation of Direct Blue dyes is well described by pseudo-first order kinetics.

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