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Review

Recent developments in photocatalytic dye degradation upon irradiation with energy-efficient light emitting diodes

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ABSTRACT

Light emitting diodes (LEDs) are gaining recognition as a convenient and energy-efficient light source for photocatalytic application. This review focuses on recent progress in the research and development of the degradation of dyes in water under LED light irradiation and provides a brief overview of photocatalysis, details of the LEDs commonly employed, a discussion of the advantages of LEDs over traditional ultraviolet sources and their application to photocatalytic dye degradation. We also discuss the experimental conditions used, the reported mechanisms of dye degradation and the various photocatalytic reactor designs and pay attention to the different types of LEDs used, and their power consumption. Based on a literature survey, the feasibility, benefits, limitations, and future prospects of LEDs for use in photocatalytic dye degradation are discussed in detail.

1. Introduction

An urgent need exists for solutions to current water pollution problems. The recent rapid growth of the industrial sector has led to environmental problems and to high levels of pollution worldwide. Additionally, there is an increase in demand for water in the industrial, agricultural, and domestic sectors, which generate large amounts of polluted wastewater. The general classes of compounds that occur in contaminated water are solvents, dyes, dioxins, dibenzofurans, pesticides, polychlorinated biphenyls (PCBs), chlorophenols, asbestos, arsenic, and heavy metals [1,2]. Among these, dyes are a serious contributor to pollution. Dyes are often difficult to decompose in water as they have composite molecular structures that cause them to be more stable toward light and resistant to biodegradation [3,4]. A considerable amount of dye-containing wastewater is generated in industries such as fabrics, leather, paper, food, cosmetics, agricultural research, pharmaceuticals, electroplating, and distillation. This causes damage to the environment as dyes are toxic to aquatic life [5,6]. Additionally, wastewater from the dye industry generally contains residual dyestuff, intermediary dyes, and non-reacted raw materials such as odorous amines, inorganic and organometallic salts, and waste solvents. These are found in different quantities and concentrations and are from different stages of the dye production process. Dye wastewater is generally considered to have an elevated chemical oxygen demand (COD) because of the presence of organic compounds, a high inorganic and organic dissolved substance content, inconsistent pH, and low degradability by biological reagents. During the reduction of dyes and their intermediates the creation of strong carcinogenic or mutagenic compounds can occur, which has a detrimental impact on microorganisms and aquatic life [6]. Human consumption of water contaminated with these compounds can cause a variety of

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adverse health effects such as wide-ranging immune suppression, breathing problems, central nervous system (CNS) disorders, behavioral problems, allergic reactions, tissue necrosis, and infections of the skin and eyes [7].

Dye molecules usually consist of two main components: chromophores and auxochromes. The chromophore absorbs a certain wavelength of light to produce the color. The auxochrome supplements the chromophore and helps the molecule dissolve in water, thus enhancing its color. Dyes show considerable structural variety and are classified by their chemical composition and the fabric type they are applied to. Dyes may also be classified on the basis of their solubility in various solvents. These include acidic, basic, direct, mordant, reactive and metal complex based dyes. Insoluble dyes include various types of azoic, sulfur, vat and disperse dyes. Furthermore, dyes may also be characterized based on the presence and type of azo and/or anthraquinone unit. More than 100000 commercial dyes are currently available on the market and throughout the world more than 7×10^5 tons of dyestuff are produced annually [8]. It is estimated that 10%–15% is lost in wastewater during manufacturing and application processes. This constitutes a huge environmental problem as these dyes are resistant to removal by irradiation with light or washing with water (or other chemicals) because of their robust chemical composition [9].

The primary methods of water treatment such as coagulation, flocculation, filtration, electro-flocculation, reverse osmosis, and adsorption do not degrade pollutants but instead decrease their levels by converting the pollutants from one form to another, thereby creating secondary pollution [10]. Because of the non-biodegradability and high solubility of dyes in water, activated sludge processes have been found to be ineffective for dye removal, and dyes are resistant to aerobic treatment. It has also been reported that the production of carcinogenic compounds such as aromatic amines can occur during the anaerobic treatment of dyes [11]. An alternative method used to degrade dyes in wastewater is oxidation [12]. The oxidation process uses oxidants such as molecular oxygen, ozone, or H_2O_2. However, a limitation of this process is the poor oxidation potentials of the oxidants and thus long treatment time is required. Therefore, there is a need to discover new materials with higher oxidation potentials to treat dye wastewater [13]. The "advanced oxidation" process can also be used in which hydroxyl radical species are generated to degrade the dyes in wastewater [14]. This technique requires a high energy light irradiation source (usually an ultraviolet (UV) light source) and an oxidant to generate hydroxyl radicals. Typical systems employed to date are UV/hydrogen peroxide, UV/ozone, UV/Fenton reagent and UV/TiO_2 [15]. These photocatalytic degradations have been carried out in the presence of natural sunlight or a mercury vapor lamp [16,17]. However, energy-efficient light emitting diodes (LEDs) have recently been used as an alternative light source for the photocatalytic degradation of various pollutants present in water [18,19] and in air [20,21].

LEDs are emerging as a new irradiation source and many researchers are studying the photocatalytic activity of synthesized photocatalysts under LED irradiation and exploring photocatalytic reactor designs. To date, only two review articles have been published that focus on the use of LEDs in photocatalysis and in plant tissue culture [22,23]. This review mainly focuses on recent developments in photocatalytic dye degradation and the mechanisms by which it occurs. We also briefly discuss the basic principles of photocatalysis, the details of some of the LEDs used, the advantages of LEDs over conventional UV light sources, the development of photocatalytic degradation reactors using LEDs, and the future prospects of LEDs in this field.

2. Basic principles of photocatalysis

Heterogeneous semiconductor photocatalysis has been widely explored over the last few decades for various environmental application. These studies typically investigated the use of different sources of light irradiation and the nature of the solid semiconductor on the degradation of liquid and gas-phase pollutants [24]. 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 produce electron-hole pairs upon the absorption of light quanta and they induce chemical transformations in reaction substrates that come into contact with them. They then undergo regeneration to their original electronic composition. Many semiconductors have been synthesized and studied as photocatalysts including zinc oxide (ZnO, 3.2 eV), titanium dioxide (TiO_2, 3.2 eV), strontium titanate ($SrTiO_3$, 3.4 eV), iron oxide (Fe_2O_3, 2.2 eV), cadmium sulfide (CdS, 2.5 eV), tungsten trioxide (WO_3, 2.8 eV), zinc sulfide (ZnS, 3.6 eV), ilmenite ($FeTiO_3$, 2.8 eV), zirconium dioxide (ZrO_2, 5.0 eV), vanadium oxide (V_2O_5, 2.8 eV), niobium pentoxide (Nb_2O_5, 3.4 eV), and tin oxide (SnO_2, 3.5 eV). Of these, TiO_2 has been found most suitable for general environmental remediation [25–27].

TiO_2 is widely used as a photocatalyst because it is inexpensive, stable in biological and chemical environments, and is stable to photocorrosion. TiO_2 has a unique property in that natural (solar) UV light generates electron-hole pairs for redox reactions. This is because TiO_2 has a suitably sized bandgap between its valence band (VB, +3.0 eV) and conduction band (CB, –0.2 eV) resulting in a bandgap of 3.2 eV allowing energy of near-UV light with a wavelength greater than 387 nm to generate electron-hole pairs. Although ZnO has characteristics similar to TiO_2 and appears to present a suitable alternative, it dissolves in solutions at low pH and cannot be used for the photocatalytic degradation of pollutants [28].

When sufficiently energetic photons strike a semiconductor, an electron may be excited out of its energy level from the valance band and thus leave a hole. This phenomenon is termed electron-hole pair generation. These electron-hole pairs are continuously generated in the presence of a constant energy source. Unselective degradation occurs at the surface of the photocatalyst via similar and successive redox reactions in which the oxidized organic compounds are the end products. A schematic presentation of the mechanism of the generation of oxidative species from a photocatalytic study is shown in Fig. 1.