



Visible light-driven photoactivity of zinc oxide impregnated chitosan beads for the detoxification of textile dyes



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ABSTRACT

The photocatalytic decolorization of model textile dyes, namely, Methylene Blue (MB) and Rhodamine B (RB) dyes using zinc oxide (ZnO) and zinc oxide impregnated chitosan beads (ZCB) under UV and visible light irradiations were investigated. ZCB was synthesized in order to enhance the photoresponse of ZnO toward visible light using chitosan, a well-known biopolymer. The ZnO and ZCB photocatalysts were characterized by Fourier transform-infrared spectra (FT-IR), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), diffuse reflectance spectra (DRS) and X-ray diffraction studies (XRD). In order to optimize various experimental parameters viz., irradiation time, the amount of catalyst, pH, co-ions, initial concentration of dye, experiments were conducted under UV and visible light irradiations. The percentage of decolorization of MB and RB dyes using ZnO and ZCB is in the order of $ZnO/UV > ZCB/vis > ZnO/vis$. The mineralization of dyes was assessed by measuring chemical oxygen demand (COD) at optimized conditions. The rate of photodecolorization of MB and RB dyes follows the pseudo-first-order kinetics. The reuse of ZCB in the photocatalytic decolorization of textile dyes has also been studied.

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1. Introduction

The prevalent usage of polluted water turns into a serious concern all over the world. It is a must to control the detrimental effects of pollutants and recover the environment [1]. Water polluted with dyes is a foremost risk to the environment. At present, the treatment of highly colored wastewater containing hazardous industrial chemicals is found to be important for consideration of environmental protection. The dyes have various applications in paper, leather, plastics, printing, cosmetics and drug industries and approximately 80% of the synthetic dyes are consumed by the textile industry [2]. Some statistical data reports that about 12% of the synthetic textile dyes used during a year is lost during the manufacturing and operational procedures; also, from this 12% release of synthetic textile dyes, 20% will be ultimately released into the ecosystem through the industrial stream discharges [3]. This kind of discharge of dyes into the water bodies is highly undesirable, as they pose direct toxicity to the microbial populations, obstructing light penetration, decelerate photosynthetic activity and cause oxygen deficiency in water bodies [4]. From the synthetic nature and

the aromatic structure of dyes with delocated electrons and various functional groups present in them causes adverse effects in aquatic environments which make them considerably resistant to degradation [5,6]. The possibility of human exposure to wastewater containing dyes is found to be a major concern owing to its carcinogenic effect or cause allergies, dermatitis or skin irritation, showing high resistance against biological, physical and chemical reactions [5–7]. Removal of dyes using the common techniques viz., chemical, physical and biological processes [8] are inefficient, due to their high molecular weight and biochemical stability [9]. The traditional techniques developed to remove organic dyes from the wastewater are coagulation [10], filtration [11], adsorption [12], reverse osmosis [13] and treatment with ozone [14]. Each method has its own advantages and disadvantages. For instance, low cost methods such as adsorption by activated charcoal, which have been proven to be effective, but incompletely as they produce large amounts of solid wastages for further disposal thus adding to further pollution and environmental hazards. Thus, these methods either fail to achieve the complete degradation, or produce large amount of toxic sludge facing trouble in disposal.

Hence, advanced oxidation processes (AOPs) have been found to resolve the above said problem of dye removal. Among AOPs, heterogeneous photocatalysis has been shown to be probably advantageous, as it may lead to complete mineralization of the pollutants into CO_2 , H_2O and mineral acids [15].

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Even though TiO_2 has been extensively investigated as one of the most active photocatalysts [16], ZnO is renowned to be one of the important photocatalysts owing to its unique advantages viz., low cost, high photocatalytic activity, high stability and non-toxicity. Accordingly, ZnO has attracted a great deal of attention for use as a catalyst in the photooxidation of organic pollutants [17]. It has been suggested that ZnO is a suitable alternative to TiO_2 for the removal of organics in aqueous solutions, as it has similar band gap energy of 3.2 eV and its photocatalytic mechanism is similar to that of TiO_2 [18–20]. Indeed, in comparison to TiO_2 , ZnO has been reported to have higher photocatalytic efficiency [21].

The semiconductor ZnO shows a photocatalytic activity only under UV light irradiation as it accounts for only a small fraction of the solar energy, i.e., ~5%, since it has a wide band gap. Hence, in order to make them active in the visible region, the band gap of semiconductor need to be reduced. Since, the sun is an abundant source of photons, where visible light accounts for a large fraction of spectrum of ~45% [22], its energy can be easily exploited for the irradiation of semiconductor materials. The main objective of the present article is to consider the most essential attempts that have been made in past decades to shift the semiconductor absorption from the UV region to the visible-light region. To facilitate the visible light source by semiconductors, many methods such as metal/non-metal doping, dye sensitization, the addition of another metal oxide and surface modifications have been used [23–26].

In recent times, chitosan, a biopolymer, has outstanding properties for the adsorption of heavy metals [27], organic [28,29] and inorganic pollutants [30,31], which are primarily due to the presence of high content of amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) groups present in the polymeric matrix which can serve as co-ordination and reaction sites for adsorption [32]. Consequently, in the present work, ZnO was incorporated into the chitosan to synthesize ZCB, in an attempt to develop its dual task as adsorbent and photocatalyst. There are copious reports have recently been dedicated to the practice of photocatalyst–chitosan microporous materials and suggest that such materials are hopeful for advanced technologies to be applied to water purification [33].

Therefore, this research article is focused on the synthesis of zinc oxide impregnated chitosan beads (ZCB) and its photocatalytic activity against color induced by two cationic dyes, Methylene Blue (MB) and Rhodamine B (RB) dyes of different classes, under visible light irradiation at various experimental conditions such as irradiation time, catalyst dosage, pH, initial dye concentrations, and co-ions. Articles devoted to decolorization and mineralization of the MB and RB dyes by ZCB using visible light irradiations have seldom been reported. Besides, a comparative study on dye decolorization has been carried out by ZnO/UV and ZnO/vis at similar experimental conditions. The mineralization of both MB and RB dyes has been confirmed by COD measurements. Langmuir–Hinshelwood kinetics well explains the rate of photocatalytic decolorization of textile dyes selected for the present study. The reusability of as-synthesized ZCB was assessed.

2. Materials and methods

2.1. Materials

Chitosan (85% deacetylated) was procured from Pelican Biotech and Chemicals Labs, Kerala, India. Zinc oxide from CDH, Mumbai and the commercially available textile dyes Methylene Blue (MB) and Rhodamine B (RB) were obtained from M/s Sree Chemidyes, Bangalore and used as such without further purification for color removal study. The structure and properties of MB and RB dyes are given in Fig. S1 and Table S1, respectively. NaOH, HCl, glacial acetic acid, glutaraldehyde was purchased from Merck chemicals and all other chemicals and reagents were of analytical grade.

2.2. Synthesis of zinc oxide impregnated chitosan beads (ZCB)

About 10 g of zinc oxide was dissolved in 2% acetic acid solution. To this solution, 5 g of chitosan dissolved in 250 mL of 2% acetic acid solution was added and stirred until a homogeneous solution was achieved. Beads were formulated by dispensing the solution into 0.5 M NaOH solution and kept overnight. The beads were washed in distilled water to reach neutral pH. The wet beads were cross-linked with 2.5 wt.% glutaraldehyde solution. Cross-linking reaction occurred for 48 h to attain stability and the cross-linked beads were washed with distilled water to remove any free glutaraldehyde and dried at room temperature as reported by Jeon and Holl [34].

2.3. Photoreactor and light source

The photocatalytic decolorization of both MB and RB dyes were studied using ZnO impregnated chitosan beads (ZCB) under UV and visible light irradiations. Heber multilamp photoreactor model HML-LP44 was used for photocatalytic reaction. The model consists of eight medium pressure Mercury Lamps (8W) set in parallel emitting 365 nm wavelength. It has a reaction chamber with specially designed reflectors made of highly polished aluminum and built by a cooling fan at the bottom. It was provided with the magnetic stirrer at the center. Open boro-silicate glass tube of 100 mL capacity, 40 cm height and 20 mm diameter was used as the reaction vessel. The irradiation was carried out using four parallel medium pressure mercury lamps. The UV power of the four lamps was 32 W. The solution with the photocatalyst and the respective dye molecules was continuously aerated by a pump to provide oxygen and for complete mixing of reaction solution.

Visible light irradiation was carried out using 150 W halogen lamp which is placed perpendicular to the reaction vessel of 200 mL capacity. The photoreactor setup was also provided with a cooling fan at the backside of the chamber. The distance between the reaction vessel and light source is 16 cm. The reaction vessel containing the respective dye solution with the photocatalyst was continuously stirred for the complete mixing by the magnetic stirrer provided.

2.4. Photocatalytic decolorization experiments

The experiments were carried out by employing the photocatalysts viz., ZnO and zinc oxide impregnated chitosan beads (ZCB) under different experimental conditions. The MB and RB dyes were treated with ZnO and ZCB in the dark as well as in the presence of UV and visible light irradiations separately. To study the effect of important parameters like irradiation time, catalyst dosage, pH, co-ions, and initial concentration of respective dyes, a batch experiment was conducted under UV as well as visible light irradiations. After irradiation with UV for a fixed time, the solution was filtered and the concentration of respective dyes was measured by UV-vis spectrophotometer (Pharo 300 Merck) at the wavelength of 664 nm for MB dye and 554 nm for RB dye which is given in Table 1. In case of experiments using visible light irradiations, after a specified interval of irradiation time, a 5 mL aliquot of the reaction mixture was centrifuged, filtered and measured using UV-vis spectrophotometer as mentioned earlier.

The kinetics for the removal of dyes from aqueous solution was carried out at different time intervals. In the photocatalytic experiments, the extent of decolorization of dye in terms of the percentage has been calculated using the following relationship.

$$\text{Decolorization (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of dye (mg/L) and C_t is the final concentration of dye (mg/L).

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