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Titanium/chitosan composites as photocatalysts in textile dyes removal

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Abstract
Recently, TiO_2/CS composites have attracted the attention of many scientific researchers because of their interesting technological properties and applications. This review describes some typically reported composites of TiO_2/CS and modified TiO_2/CS which exhibited high photo catalytic activity for removal of textile dyes in the wastewater treatment.

Keywords: TiO_2/CS, photo catalyst, removal, efficiency, environment

Introduction

Textile wastewater contains dyes and pigments that are the main cause of pollution water contamination in many previous kinds of research. Most dyes and pigments are organic toxic compounds with rather poor biodegradability [1]. Some of them partially decompose after entering the environment. These toxic substances may cause health effects in humans who are exposed over long periods [2, 4]. Dangerous disease must be mentioned as cancer [5]. Therefore, the removal of dyes and pigments from textile wastewater is a critical issue and pays much more attention to researchers on the remediation of these pollutants. Several methods have been used to remove dyes and pigments out of the water environment such as the physico chemical method, bio-method, and chemical method [6, 8]. Among them, the photo catalyst method is widely used and becomes potential; especially the semiconductor Titanium dioxide (TiO_2) [9, 12]. Titanium dioxide (TiO_2) has been widely applied as a photo catalyst in many environmental and energy applications because of its efficient photo activity, high chemical stability, low cost, and non-toxic to the environment and humans. The semiconductor TiO_2 decomposes effectively organic contaminants, purifying water, cleaning the air, water splitting for hydrogen production, surface self-cleaning, antibacterial, and strong oxidation ability. After irradiation by UV light, the electron is excited from the valence band (VB) to the conduction band (CB). Electronic transition causes the formation of a pair in particles, consisting of the hole (h_{vb}^+) and electron (e_{cb}^-). The reaction of these photo generated holes species with water at the particle's surface leads to produce activated hydroxyl radicals ($HO^\bullet$) and directly oxidate dyes into their oxidation products [13]. Currently, the small size of TiO_2 in the mixture of rutile, anatase, or mixture of anatase, rutile, brookite was studied and applied in many scientific fields such as solar cells, fabrication photochemical agent to synthesize organic compounds, self-cleaning paint, production of electronic devices and sensor in sterilization field. A new application of nano TiO_2 is mainly based on its redox stability. Because of high catalyst activity and non-toxic properties, TiO_2 material is one of the best materials to tackle many serious problems as well as challenges from environmental pollution. However, TiO_2 semiconductor remains some limitations. Due to its small size, TiO_2 is difficult to hold back in the material. Thus, it needs a substrate to retain TiO_2 in the material for long use. Additionally, rapid recombination of electrons and holes leads to a decrease in the efficiency of the photo catalytic [14].

On the other hand, chitosan (CS) is a natural biopolymer (linear polysaccharide composed of β-(1–4)- linked d-glucosamine (deacetylated unit) and N-acetyl-d-glucosamine (acetylated unit), that has biodegradable and biocompatible properties [15]. Commercially, chitosan is produced by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (such as crabs, and shrimp). Chitosan possesses interesting properties including the ability to form film for food and pharmaceutical applications such as packaging material, or drug-eluting carrier [15, 17]. Additionally, chitosan can also be used as an absorption material due to its absorptive capacity to remove heavy metal and polluted organic compounds as dyes and pigments [18]. It is compatible with several organic and inorganic compounds because of the presence of amino and hydroxyl functional groups in its molecular structure. In the combination with TiO_2, CS acts as a solid substrate to keep TiO_2 inside the material; therefore, it can enhance the mechanical, physical, and biological properties of this polymer [16, 19], giving them a great potential for food, pharmaceutical or biomedical, and environmental applications.

This paper summarizes some recent works of chitosan/TiO_2 composites and modified chitosan/TiO_2 composites as photo catalysts for textile waste-water treatment.

TiO_2/Chitosan composite, modified TiO_2/chitosan composites and their photo catalytic activity

TiO_2/Chitosan composites

TiO_2 is a semiconductor and normally exists in 3 basic forms: Rutile, anatase, and brookite. The most common forms are anatase and rutile. The bandgap energy of rutile is 3.02 eV while that of anatase is 3.23 eV. The density of rutile is 4.2 g/cm^3 while the density of anatase is 3.9 g/cm [3]. Anatase can be converted to rutile by heating up to 700 °C. [20]

TiO_2/chitosan has an excellent photo catalytic degradation Efficiency against methyl orange (MO) dye due to its good crystallinity and lowering band gap [21]. In this work, the different weight ratios of TiO_2 and CS (72:25, 50:50, 25:75) nano composites were prepared and checked for these photo catalytic activities. The results indicated that nano composites TiO_2/CS (75:25) material showing greater degradability efficiency against MO dye. Moreover, the recycling outcome of TiO_2/CS (75:25) displayed a strong and stable performance (Figure 1). +

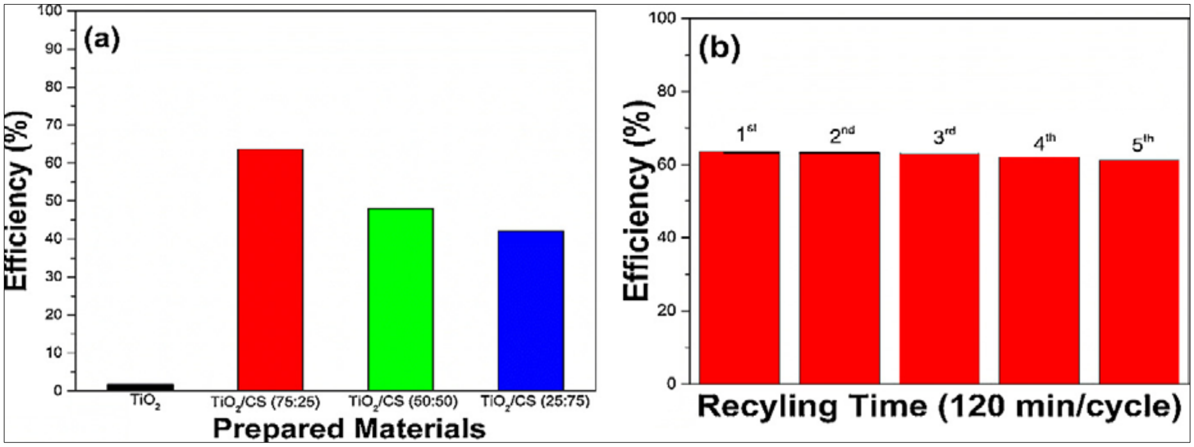

Fig 1: (a) Photocatalytic degradation efficiency of all prepared materials against MO dye and (b) Recycling ability of TiO_2/CS (75:25) against MO dye. Reproduced from R. Saravanan *et al.*[21]

Carolina E. Zubieta *et al*. evaluated photo degradation of two reactive dyes, Methylene Blue (MB) and Benzopurpurin (BP) in an aqueous solution by TiO_2/CS [22]. Two different weight ratios of TiO_2/CS composite materials were synthesized and the material photo degradation properties were evaluated. MB photo degradation on both TiO_2/CS was relatively high (91% and 41% for 2 types of TiO_2/CS), and increased with chitosan content. For BP, it is highlighted that the process in the darkness resulted in high photo degradability capacity than in the UV-light presence. In the research of Saba Afzal *et al.*[23] TiO_2/CS exhibited a complete degradation of MO within 90 min of UV exposure. The effect of calcination on the physicochemical and adsorption-photo decolorization properties of TiO_2/CS was investigated. The photo catalytic activity decreased when the calcination temperature increased, because of the thermal degradation of CS (Figure 2).

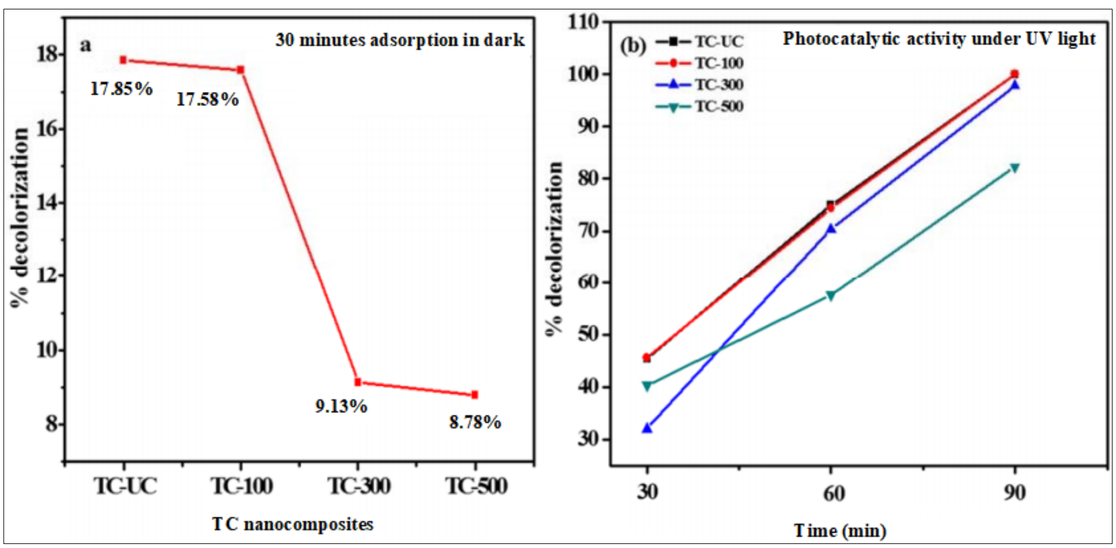

Fig 2: Adsorption-photo decolorization studies of prepared TiO_2/CS. Reproduced from Saba Afzal *et al* [23].

In the study of Qiang Li *et al.* [24] the degradation of MO can be achieved to 90% by TiO_2/CS composite. This result is a consequence of the effects of both CS and TiO_2.

Modified TiO_2/Chitosan composites

Zhu *et al.* mentioned that CdS nanocrystals deposited on TiO_2/CS composite could decolorize MO solution up to 99.1% after real solar light irradiated for 300 min. The composite could be used repeatedly and the decolorization rate still maintains at 89% of the initial decolorization rate after 5 batch reactions (Figure 3) [25].

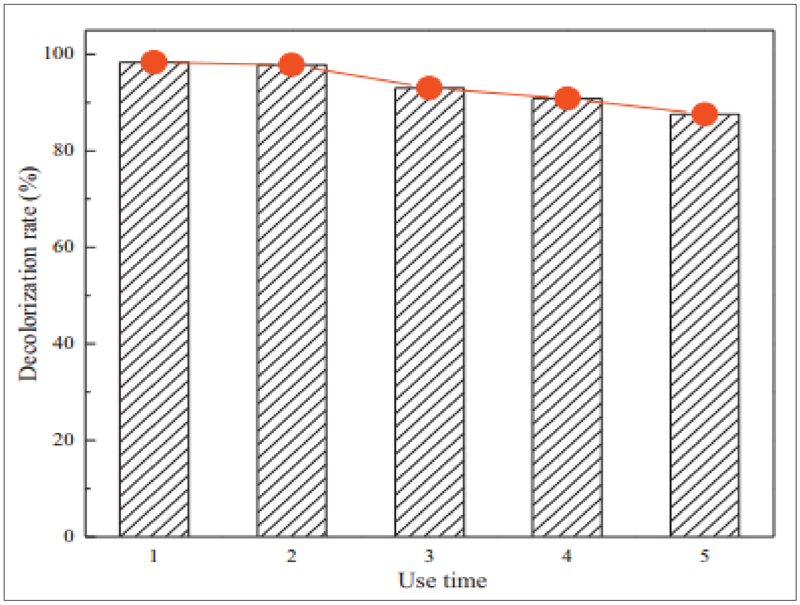

Fig 3: Cycling runs of MO decolorization in the presence of CdS/TiO_2/CS. Reproduced from Huayue Zhu *et al* [25].

Huayue *et al.* [26] also reported the TiO_2/ZnO/CS nanocomposite thin films with high photo catalytic activity under simulated solar irradiation. Over 97% of MO solution was decolorized with 0.5 g L^{-1} of the photo catalyst. The authors illustrated that the introduction of ZnO and TiO_2 in nanocomposite photo catalyst is beneficial in improving the charge separation and the response to visible light. Recycling experiments were carried out to check photo catalytic stability. The decolorization (%) of MO in the presence of TiO_2/ZnO/CS is much higher than those in the presence of TiO_2/CS, ZnO/CS (Figure 4).

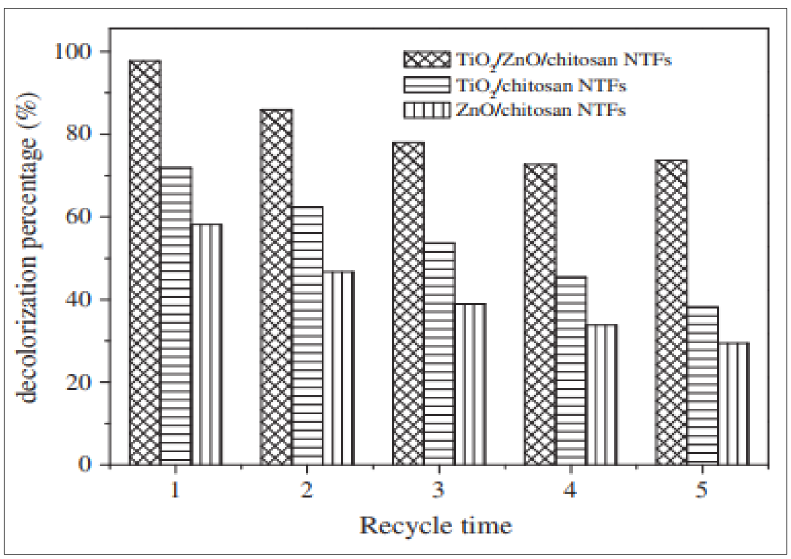

Fig 4: Decolorization of MO using different composites. Reproduced from Huayue Zhu *et al*.[26]

Meanwhile, it is reported that a novel composite TiO_2/CS/reduced graphene oxide (rGO) with 1.0 wt% of rGO exhibited an excellent photo catalytic degradation of MO (97%) [27]. The results in this research also showed that if the rGO contents above 1.0 wt% lead to the decrease of the photo catalytic activity due to reduction of surface area. A novel thiourea-modified ion-imprinted TiO_2/CS composite was fabricated for the removal of cadmium and 2, 4-dichlorophenol [28]. The degradation efficiency for 2, 4-DCP was reached 98%. The author proposed that the major decomposition route of 2, 4-DCP is related to the reductive dechlorination and reaction with hydroxyl radicals. Recently, Wei Zhang *et al* [29]. Reported novel chitosan (CS) -vanadium-titanium-magnetite (VTM) composite as a superior adsorbent for Congo red dyes treatment. The optimal adsorption performance was achieved for CS-VTM-0.5 composite (a mass ratio of 0.5 between CS and VTM). The adsorption process was described by the Langmuir isotherm model, and the maximum adsorption capacity was 90.9 mg/g. The removal efficiency was 99.1% when the dose of CS-VTM-0.5 was greater than 2.0 g/L. Novel CS-VTM could be a promising and environmentally friendly adsorbent for the highly efficient and effective removal of organic dyes.

Previous scientific researches demonstrated that composites of TiO_2/CS and modified composite of TiO_2/CS become attractive materials with high photo catalytic performance, low-cost, reusable, and environmentally friendly for removal of inorganic dyes.

Conclusion

Evidence shows that the combination of TiO_2 and Chitosan matrix is an efficient method to enhance the mechanical, physical, photo catalytic, and biological properties of both compounds. TiO_2/CS and modified TiO_2/CS have become an active research area for biomedical environment remediation applications and; therefore, they are potential for wastewater treatment in the textile industry as well as for industrial applications. However, the researcher needs to pay more attention to the preparation method to standardize, further develop and modify TiO_2/CS composite to achieve high photo catalytic ability, long reuse time, and economic efficiency.

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