

RESEARCH ARTICLE

Impact of TiO₂ content on Titanium oxide supported chitosan photocatalytic system to treat organic dyes from wastewater

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Abstract

Titanium dioxide (TiO₂) nanoparticles are used enormously for treating wastewater pollutants due to their unique optoelectronic and physiochemical properties. Though, wide bandgap, fast recombination of e⁻ - h⁺ pair, and low adsorption toward organic pollutants limit their applications. However, immobilization of TiO₂ on Chitosan (Cs) is believed to overcome these limitations. Cs with plenty of NH₂ and OH groups in their structure are expected to enhance their adsorption and consequently photocatalytic performance. A series of TiO₂/Cs photocatalysts have been prepared using a chemical co-precipitation method. Amount of TiO₂ is varied from 0.25, 0.50, and 0.75 to 1.0 g. The photocatalysts are characterized by using FESEM-EDS, CHNS Elemental Analyser TGA, FTIR, and UV-Vis spectroscopy. These characterization results revealed the formation of a good interface between TiO₂ and Cs matrix. Increasing TiO₂ content significantly increased the thermal stability of the photocatalyst up to 600°C. The photocatalytic activity of Cs/TiO₂ is observed under UV light which is found to be more significant with 1:1(TiO₂: Cs) composition for the degradation of methylene blue dye at 85 % and be maintained up to 4 numbers of cycles. This demonstrated open new insight into the application of Cs as a support materials and adsorption agent in TiO₂ based photocatalyst system

Keywords: Chitosan; Titanium dioxide; adsorption; Photodegradation; Methylene blue

1. Introduction

Wastewater pollution arises significantly during the past few decades due to increasing industrialization such as textile, packaging, dyeing, and plastic industries. Heavy metal ions, hormones, pathogen, aromatic compounds (including phenolic derivatives and polycyclic aromatic compounds), and dyes are added into the water stream as a pollutant [1-5]. Although waste discharge from industries has to be limited to 5 % of polluted water this percentage is still alarming for human and aquatic life [6]. Due to the shortage of freshwater supplies, wastewater needs to be treated to ensure the availability of clean and safe water to use.

Many techniques introduced to treat polluted water, however, conventional methods like coagulation, flocculation, sedimentation, ultrafiltration and reverse osmosis [7-8] are not very effective due to non-biodegradability and chemical stability of pollutants [3;6]. Furthermore, some of these techniques generate huge amounts of sludge, increasing the cost of separation [2;4]. Alternatively, advanced oxidation procedures like photocatalysis utilizing semiconductor molecules gain special interests as it has a strong tendency towards pollutant degradation. This is due to the generation of electron-hole pairs by the illumination of light (UV or Vis) equal or greater than their bandgap energy of semiconductors, producing reactive species like H_2O_2 , OH, and O_2^{\cdot} [6;9] (Figure 1). These reactive species degrade pollutant molecules into less harmful CO_2 , H_2O , and H_2 (1,3).

Among semiconductors, TiO_2 is widely utilized for the treatment of wastewater due to its photostability, chemically/biologically inertness [5-8] and availability, and low cost [10-12]. However, electron-hole recombination, difficult separation, and agglomeration at higher loading are some properties that limit the applications of TiO_2 [11;13]. These series of limitations can be overcome by introducing some support such as natural or synthetic fabrics, polymer membranes, activated carbon, quartz, glass, optical fibers, zeolites, aluminum, stainless steel, and titanium metal [14-16]. Support material must have strong surface bonding characteristics with catalyst, high specific surface area, good adsorption capability, high separation ability, and chemically inert [15].

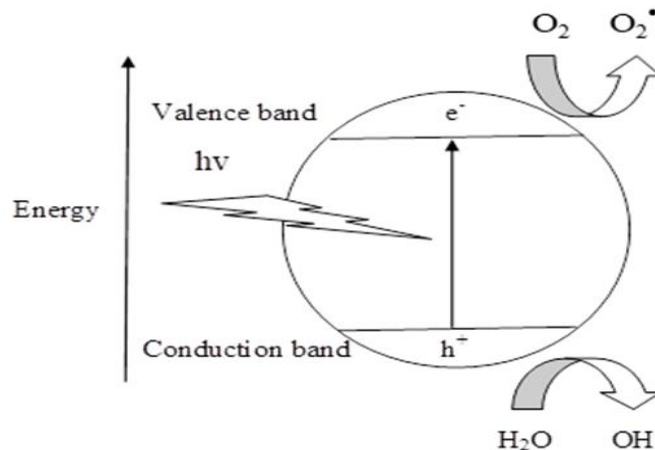


Figure 1. Photocatalytic mechanism of semiconductors for photodegradation of synthetic compounds

Chitosan (Cs) is a type of natural polymer found abundantly and has the potential to use as a support material [17-19]. It contains plenty of NH_2 and OH groups in its structure (Figure 2), which gives special properties to the Chitosan [18;20]. It can be used extensively as a support for the preparation of heterogeneous catalysts in the form of colloids, flakes, gel, and beads [21-22]. The promising hydrophilic character of Cs is due to the large number of OH groups gave advantages in absorption properties. Besides that, Cs will prevent TiO_2 from agglomeration and make the separation process more efficient.

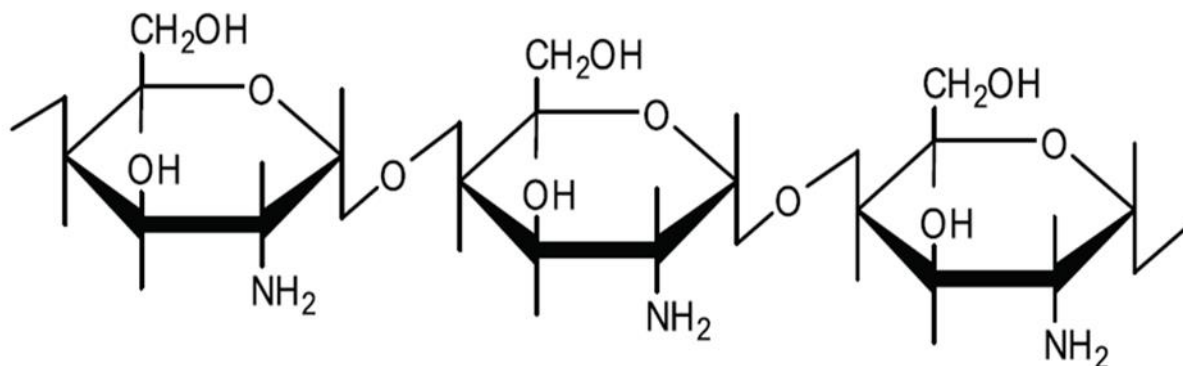


Figure 2. Chemical configuration of Cs biopolymer

The present work aims to synthesis Cs-TiO₂ photocatalyst by varying concentrations of TiO₂ to achieve the best ratio of Cs-TiO₂ photocatalyst. It is expected that the optimized photocatalyst is thermally more stable and gives better interactions between TiO₂-Cs matrix and performs efficiently in the photodegradation process.

2. Methodology

2.1. Preparation of TiO₂/Cs photocatalyst

TiO₂/Cs photocatalyst beads were prepared by using the chemical co-precipitation method. Cs solution is prepared by dissolving 1g CS in acetic acid followed by the addition of TiO₂ powder (0.25, 0.5, 0.75, and 1.0 g) with continuous stirring of 24 hours. The as-prepared TiO₂/CS solution is sprayed into a precipitation bath containing NaOH (500 ml; 1.5 M). The NaOH solution neutralizes the acetic acid within the Cs gel and is transformed into spherical uniform gel beads. The wet TiO₂/Cs gel beads were rinsed with distilled water to remove NaOH residues. The beads are filtered and air-dried for about 30 min/h.

2.2. Characterization

The photocatalyst TiO₂/CS is characterized using various characterization techniques such as FTIR analysis is carried out using Perkin-Elmer Instrument (model FTIR spectrum 400) to determine the functional groups present on TiO₂/Cs photocatalyst. The samples (2mg) are mixed with Potassium Bromide (KBr) powder (98 mg) ground and compressed at 400 psi to produce thin films. Thermogravimetric analysis is performed on a Perkin-Elmer Pyris 1 TGA Analyzer (25°C to 650°C at 10°Cmin⁻¹) in a nitrogen atmosphere to determine the weight loss percentage over temperature. Elemental analysis is conducted using CHNS Elemental Analyzer 2 (Perkin-Elmer) to provide information on the carbon, nitrogen, and hydrogen element content of the sample.

2.3. Adsorption–photodegradation Activity

Photocatalytic tests were conducted under a UV lamp (96 Watt) provided with an air pump to ensure the continuous supply of oxygen. 10 ppm of MB solution is filled in a quartz tube and catalyst loading (TiO₂/Cs photocatalyst) set at 0.01 g. Before the UV light exposure, the solution is placed under the dark for 30 min to set adsorption-desorption equilibrium. The aliquots of 3 mL are taken at the 15 min interval for analyzing adsorption photodegradation by UV-Vis

spectroscopy. After the photodegradation process, an MB solution is centrifuged for 15 min at 3000 rpm to separate the beads and solution. The recycling activities of the photocatalyst have been done according to the optimum composition of TiO₂: Cs with optimum experimental conditions.

3. Results and discussion

3.1. FESEM-EDS analysis

The morphology and homogeneity of TiO₂ nanoparticles within the Cs matrix are analyzed using FESEM. SEM micrographs of the photocatalysts at varying TiO₂ weight ratios are shown in Figure 3. Furthermore, the elemental composition of all the synthesized photocatalysts at varying TiO₂ ratios is determined using EDS. SEM micrographs of all photocatalysts demonstrated that spherical TiO₂ nanoparticles disperse uniformly; however, the uniformity and homogeneity increase as the weight ratio of TiO₂ increases as obvious from Figure 3d. It indicated that TiO₂ and CS with identical wt. ratios give good homogeneity of the photocatalyst. Furthermore, EDS analysis indicated the presence of Ti, O, N and C elements which suggest the presence of TiO₂ and its incorporation with the Cs matrix [5-9]. The presence of N suggests that the possible interactions between metal oxides (TiO₂) are with the NH₂ group of Cs [17].

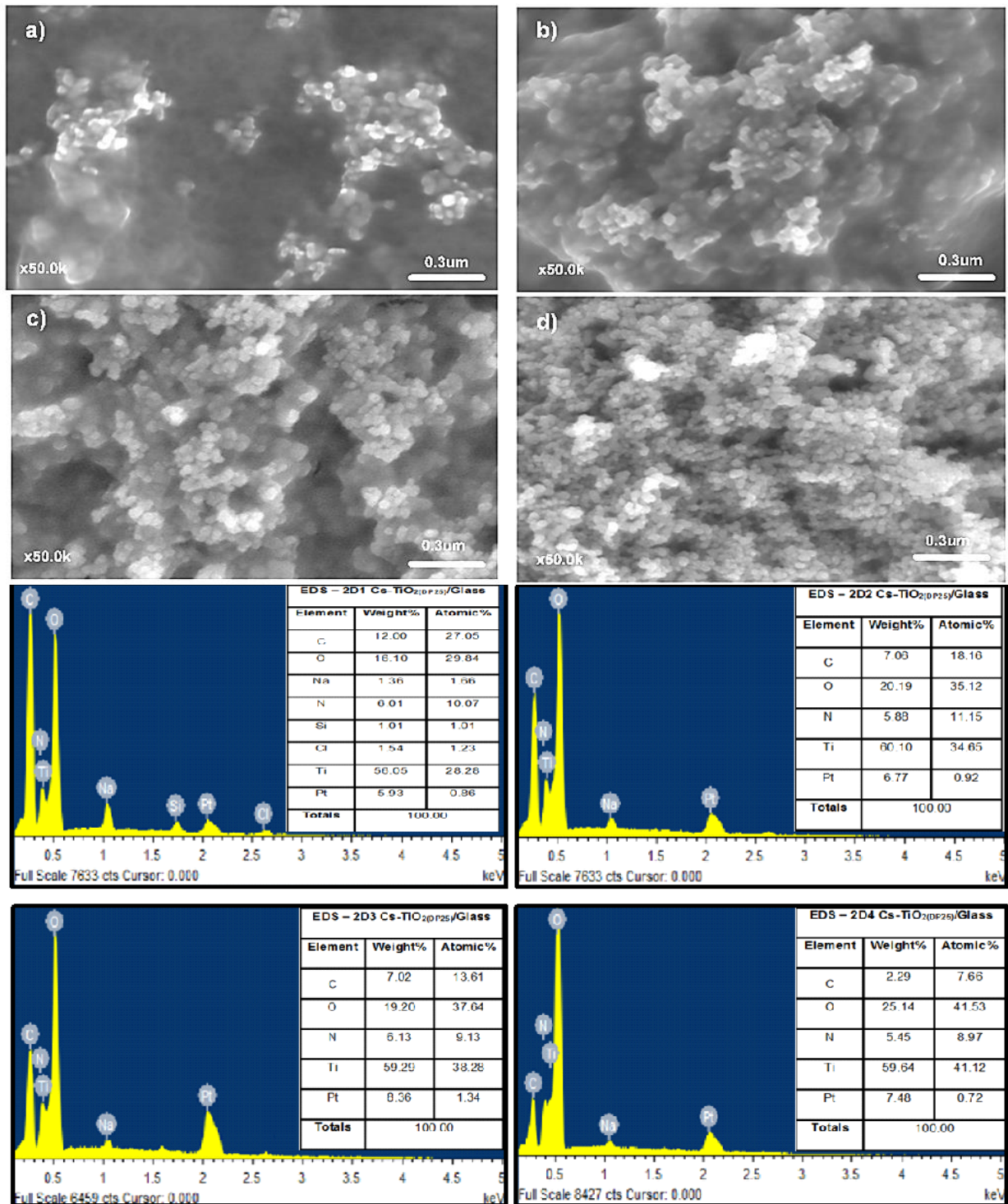


Figure 3. FESEM-EDS micrographs of TiO₂/Cs with weight ratio of (a) 1.0:0.25 (b) 1.0:0.5 (c) 1.0:0.75 and (d) 1.0:1.0

3.2. Elemental analysis

Figure 4 demonstrated the EA results of the TiO₂/Cs photocatalyst system on varying TiO₂ content. It is evident from the bar diagrams that as the concentration of TiO₂ increases the percentage of C, H, and N elements gradually decreased as CS is an organic polymer and these elements play a vital role in the bonding interactions with metal oxides [18-19]. Therefore, the gradual decrease of these elements indicates the successful synthesis of TiO₂/Cs photocatalyst at varying TiO₂ content; however, the overall bonding interaction is confirmed further by using other characterization techniques, including FTIR.

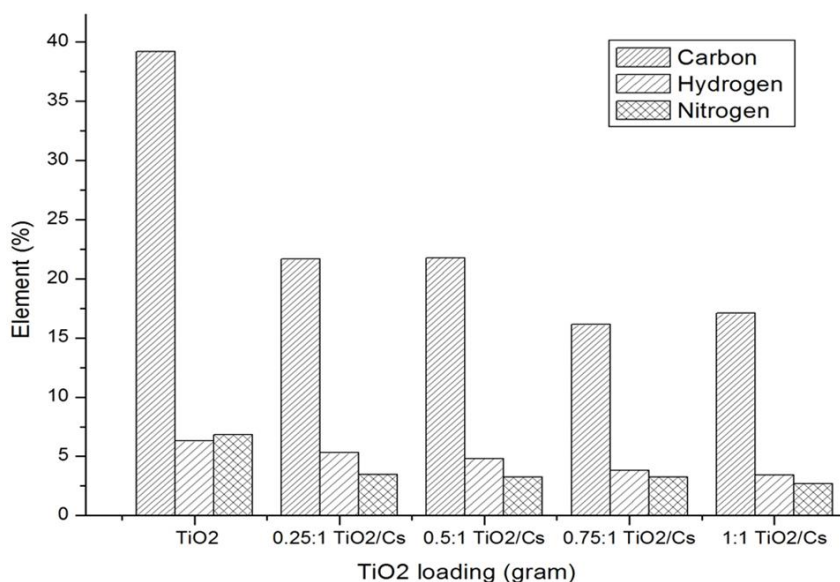


Figure 4. The elemental composition of TiO₂/Cs photocatalyst

3.3. Thermogravimetry Analysis

Thermogravimetry analysis (TGA) of TiO₂/Cs photocatalyst at different TiO₂ is shown in Figure 5. As observed from the thermograms, all samples showed an almost similar pattern with three stages of decomposition except pure TiO₂ which shows single-step degradation. The first degradation occurred between 50 °C to 100 °C which was attributed to the removal of moisture. This might be due to the hydrophilic characteristic of Cs [12]. The second degradation was observed between 135 °C to 200 °C due to the decomposition of organic content Cs [19]. The third

degradation step occurred around 600 °C due to metal oxide and after that, no prominent degradation is observed. The sample with lower TiO₂ content degrades earlier as organic compounds (Cs) thermally less stable. The addition of TiO₂ into Cs increases its thermal stability [16-19]. Therefore, the thermal stability of TiO₂/Cs is linearly increased with the content of TiO₂. The weight loss percent went up to 56 % for pure Cs, 53.9 % (0.25 g), 37.4 % (0.5 g), 33.1 % (0.75 g) and 26.2 % (1.0 g). The amounts of TiO₂ in the samples can estimate from the residual mass percentages that are 24, 28, 40, and 45 % as increased TiO₂ loading from 0.25 until 1.0 g.

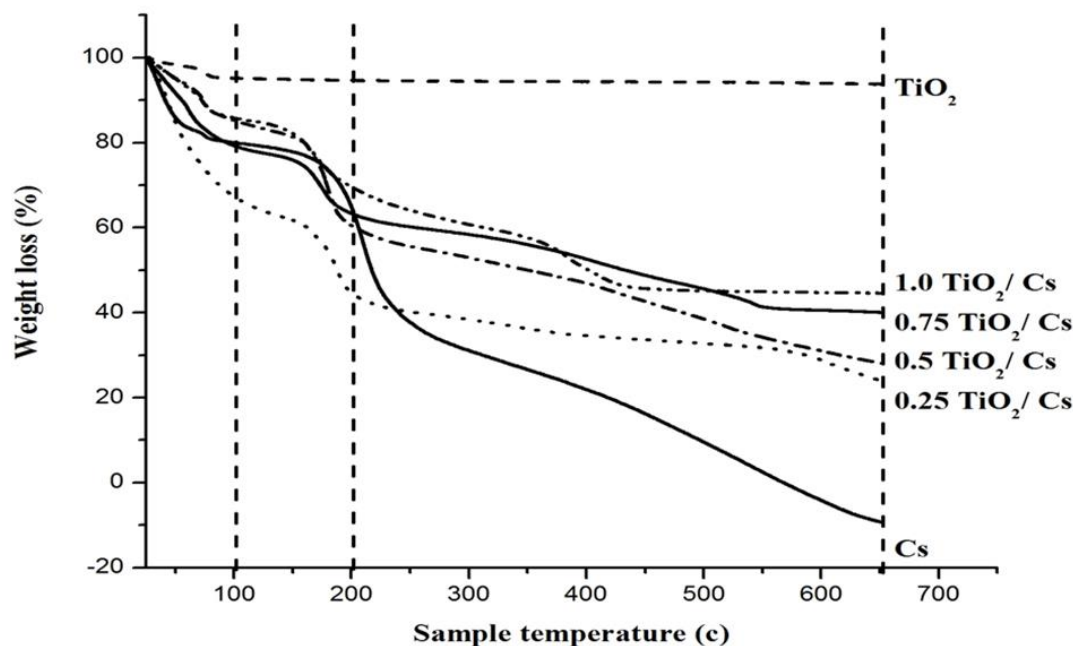


Figure 5. The thermal degradation of TiO₂/Cs photocatalysis (35 to 600°C)

3.4. Fourier Transform Infra-Red (FTIR) analysis

The composition of photocatalysts and bonding interactions between a metal oxide and Cs is further confirmed through FTIR (Figure 6). The FTIR spectra of all the photocatalysts showed almost similar patterns with a prominent variation in peak intensity. The peak in the range of 3450 cm⁻¹ is attributed to NH₂ and OH groups of the Cs network. Literature shows the presence of Inter and intra-molecular hydrogen bonding co-existed at this range [19, 20]. The peak in the range of 1661cm⁻¹ corresponds to the bending vibration of the N-H group. Stretching vibration from C-O groups is observed at 1393cm⁻¹. The characteristic peak of the C-N group of Cs is observed at 1156

cm^{-1} . For raw TiO_2 , a prominent signal was observed at 580 cm^{-1} that corresponds to the O-Ti-O bond [3;5]. The FTIR spectra show a gradual decline in peak intensities ($1661, 1393, 1156 \text{ cm}^{-1}$) as the TiO_2 content increases. This might be due to the less availability of free NH and OH groups of CS and their involvement in bonding with metal oxide (TiO_2) [10-13]. Hence the sample with a 1:1 ratio of Cs- TiO_2 shows better interactions and expected to perform well in the photocatalytic process.

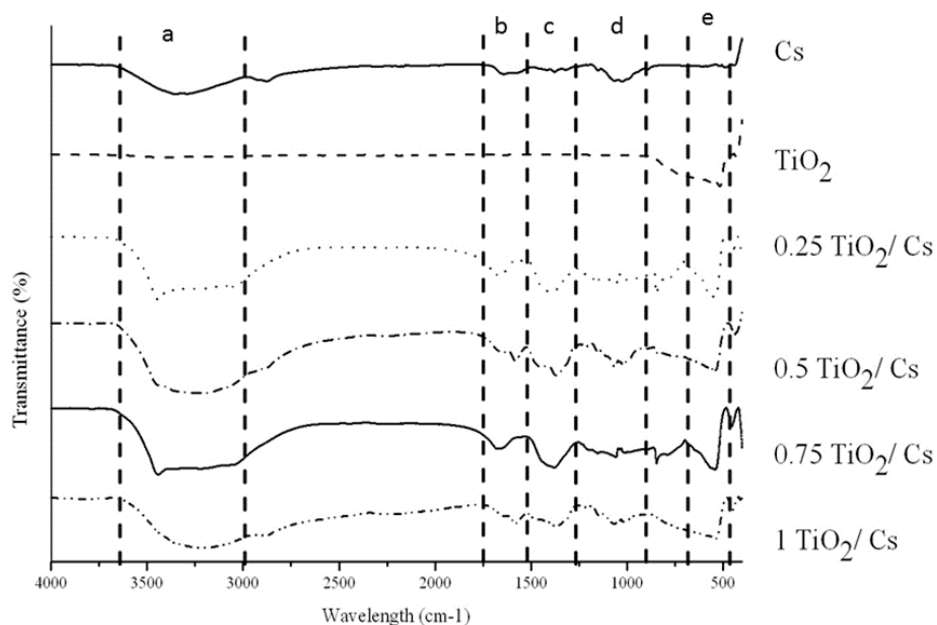


Figure 6. The FTIR spectrum of TiO_2/Cs at different compositions of TiO_2 nanoparticles

3.5. Photocatalytic Activity

The photocatalytic performance of all the composite samples is assessed by degradation of the MB as a model pollutant under UV light. Figure 7 shows that comparing other photocatalyst TiO_2/Cs with a 1:1 ratio shows the complete decolorization of dye solution within 2h of UV light exposure. This was due to the high amount of TiO_2 which is responsible for the contribution of more free electrons and holes to undergo a faster degradation process. It can also be attributed that the equal ratio of TiO_2 and Cs gives better interactions which consequently minimize the recombination of electrons and holes, and photocatalyst performs well in the degradation process [12-14].

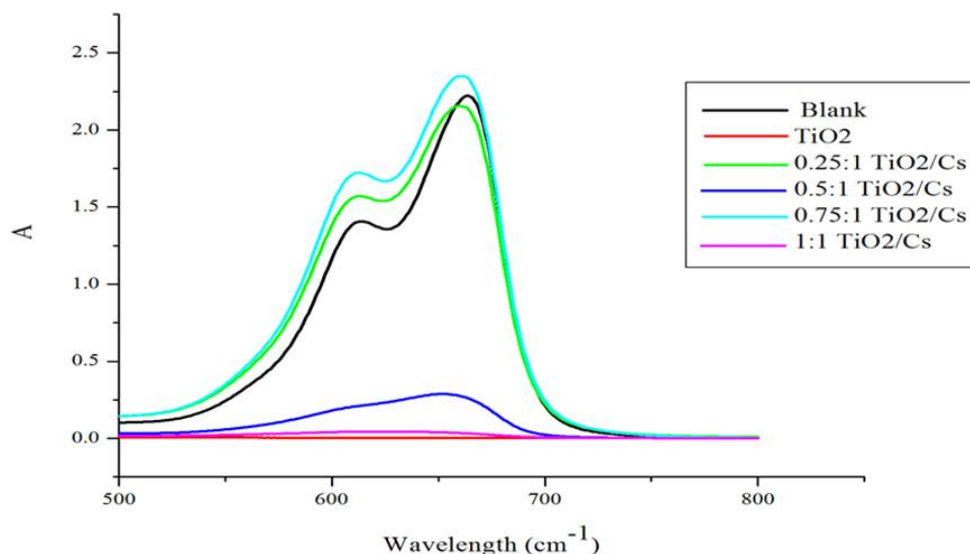


Figure 7. The decolorization of MB by TiO₂/Cs under UV Vis spectroscopy analysis

Furthermore, an illustration of the mechanism of MB photodegradation over TiO₂/Cs photocatalyst is represented in Figure 8 *viz* the whole photodegradation process, from the adsorption of MB dye molecules on the surface of the photocatalyst to the decomposition of MB molecules by reactive radicals by TiO₂. The degradation of MB does not necessarily correspond to the oxidation and mineralization of the molecule, and the reduced form of MB which is colorless has been produced in the presence of light [9-12]. The lack of coincidence among the best performing samples concerning either decolorization or mineralization has been the result of different routes followed by MB during irradiation.

The MB molecule can be transformed into Leuco MB through reduction by electrons in the conduction band or oxidized by interactions with the valence band holes or native OH species, starting with a de-methylation step to be finally mineralized. For long reaction times also Leuco MB can be further degraded and mineralized [11].

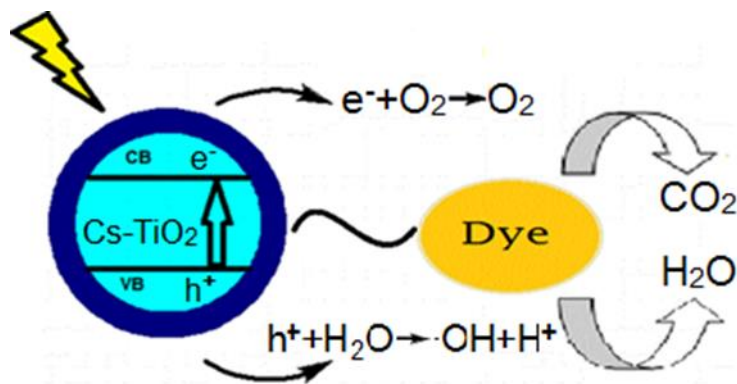


Figure 8. Photodegradation mechanism of MB dye over TiO₂/Cs photocatalyst

3.6. Photocatalyst recovery and reusability

To evaluate the performance of TiO₂/Cs for environmental applications, the reusability test was performed for four catalytic cycles and the results are presented in Figure 9. After completing MB degradation, the TiO₂/CS sample was collected and utilized for the next cycle under optimal conditions. The reusability results indicated that after four consecutive runs, the removal of MB by the TiO₂/CS sample still reached 87-89 % within two hours of light exposure, indicating that there is a slight reduction in the catalytic activity of the TiO₂/CS. The interactions between the constituent elements of TiO₂/CS are sufficient to maintain its morphological and optical properties during the degradation process. As a result, the composite sample can be used effectively for wastewater treatment.

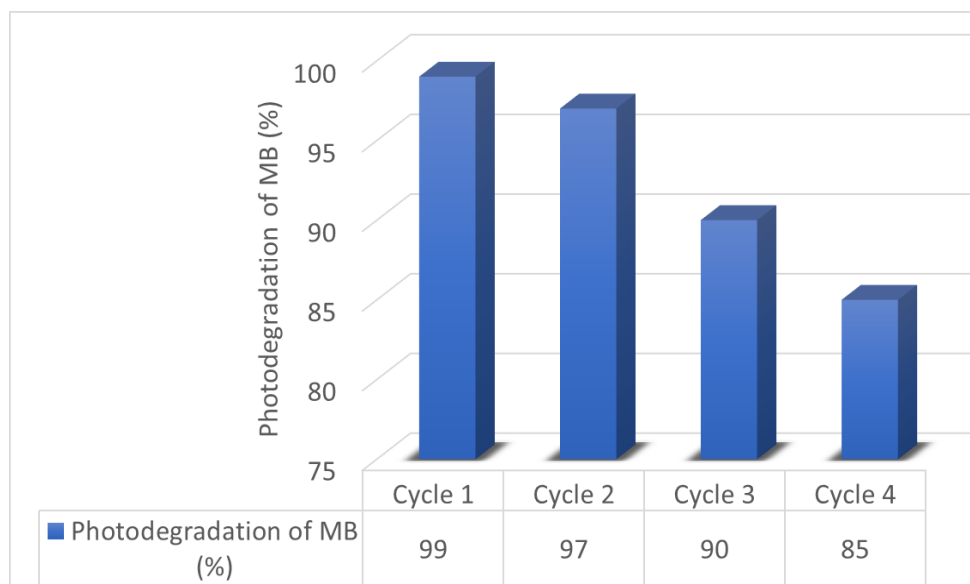


Figure 9. Reusability data over TiO₂/CS in degradation of MB UV light

Conclusion

The present work reports the synthesis of TiO₂/Cs photocatalyst on varying TiO₂ concentrations. Characterization results indicate that the photolysis with the identical ratio of Cs and TiO₂ is thermally more stable than samples with lower TiO₂ content. Similarly, TiO₂/Cs (1:1) shows the better interactions between TiO₂ and polymer Cs as expressed from FTIR results which further corresponds to its higher degradation rates towards MB dye. Thus, the work provides a base for understanding the significance of metal oxide concentration in synthesizing photocatalyst systems and its application towards the photodegradation of various wastewater pollutants.

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