Enhanced decolourization of methyl orange by immobilized TiO$_2$/chitosan-montmorillonite

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**ABSTRACT**

Many attempts have been made to improve the photocatalytic performance of immobilized photocatalysts for large-scale applications by modification of the photocatalyst properties. In this work, immobilized bilayer photocatalyst composed of titanium dioxide (TiO$_2$) and chitosan–montmorillonite (CS–MT) were prepared in a layer-by-layer arrangement supported on glass substrate. This arrangement allows a simultaneous occurrence of adsorption and photocatalysis processes of pollutants, whereby each layer could be independently modified and controlled to acquire the desired degree of occurring processes. It was found that the addition of MT clay within the CS composite sub-layer improved the mechanical strength of CS, reduced its swelling and shifted its absorption threshold to higher wavelengths. In addition, the band gap energy of the photocatalyst was also reduced to 2.93 eV. The immobilized TiO$_2$/CS–MT exhibited methyl orange (MO) decolourization rate of 0.071 min$^{-1}$/C$_0$ under light irradiation, which is better than the single TiO$_2$ due to the synergistic processes of adsorption by CS–MT and photocatalysis by TiO$_2$ layer. The MO dye took 6 h to achieve complete mineralization and produced sulfate and nitrate ions as the by-products. Furthermore, the immobilized TiO$_2$/CS–MT could be reused for at least ten cycles of application without significant loss of its activity.

**Key words** | bilayer, chitosan, immobilization, methyl orange, montmorillonite, titanium dioxide

**HIGHLIGHTS**

- TiO$_2$/chitosan–montmorillonite (TiO$_2$/CS–MT) bilayer photocatalyst was fabricated.
- The MT clay improved the physical, chemical and optical properties of CS.
- The band gap energy of the TiO$_2$/CS–MT was reduced to 2.93 eV.
- Decolourization of MO was enhanced via synergy adsorption–photocatalysis processes.
- The TiO$_2$/CS–MT was reusable under UV–Vis and total visible light irradiations.

doi: 10.2166/wst.2020.349
INTRODUCTION

Synthetic dyes originating from textile and coloured-based industries have become the main contributors to water contamination around the globe for decades. The lifetime of such dyes is longer than natural dyes because they contain poorly soluble or hardly decomposable ingredients, which make them more persistent once they enter the environment (Setyawati et al. 2017). Various techniques and methods have been extensively investigated in the search for an effective dye removal that can be classified either as physical, chemical or biological treatments. These methods, namely flocculation, coagulation, microbial degradation, filtration and catalysis, are frequently combined to eliminate their incoherence and limitation. In this case, combined adsorption and photocatalysis processes have attracted much attention due to their simplicity, efficiency and economic feasibility.

Titanium dioxide (TiO2)-mediated photocatalysis is preferably used in the environmental clean-up due to the stability and low toxicity of TiO2. However, TiO2 suffers from some significant drawbacks, such as fast recombination of electron-hole pairs, limitation to UV light irradiation, poor degradation and low adsorption capability especially for non-polar organic pollutants (Saracino et al. 2018). Meanwhile, the adsorption process simply requires an adsorbent to concentrate the contaminants on its solid surface from the bulk solution. The utilization of low-cost adsorbents from natural materials, agricultural and industrial wastes has regained their economic value because most wastes frequently end up being neglected and disposed. Among the low-cost adsorbents is chitosan (CS), a naturally derived polysaccharide from the deacetylation process of chitin that can be obtained from outer shellfish waste.

The combination of TiO2 with polymers has been very popular among researchers because some polymers can shift the photoactivity of TiO2 towards the visible light region, such as polyethylene glycol (Nawawi et al. 2017) and microcrystalline cellulose (Habibi & Jamshidi 2019). Other polymers like polystyrene (Ata et al. 2018) and polypyrrole (Krehula et al. 2019) can act as synthetic adsorbents when combined with TiO2 for trapping the target pollutants and thus enhance the photocatalytic oxidation. Recently, biopolymers received remarkable interest due to their biodegradability, low/non-toxicity, low immunogenicity and good biocompatibility. Some other examples of polymeric adsorbent used in the TiO2-wastewater treatment is chitin (Dassanayake et al. 2018), cellulose (Li et al. 2018), alginate (Lam et al. 2017) and CS (Saravanan et al. 2018). These combined materials demonstrated the synergy of adsorption–photocatalysis processes during pollutants’ removal.
Despite having good adsorption capacity and high photocatalytic activity, one of the drawbacks of the TiO₂-polymer-based photocatalysts in wastewater treatment is the suspension-type applications. The powdered photocatalysts will require to be separated and recovered from the treated water, which is costly due to energy, materials and tool consumption. Recently, our group reported a bilayer arrangement of TiO₂-polymer-based photocatalysts immobilized on glass supports for the improved degradation of phenol (Sabar et al. 2019) and methyl orange (MO) (Bahrudin et al. 2018). The bilayer consists of TiO₂ as the top layer and polymer as the sub-layer. This arrangement avoids the direct exposure of the polymer to light and allows the photocatalyst to be used for repeated applications. In addition, this arrangement improves the performance of the immobilized photocatalyst due to the synergistic effect of adsorption and photocatalysis. A separate modification or alteration can also be done to improve the properties of each layer for desired degree of occurring processes. The synergy between these two processes that occur simultaneously improves the overall photocatalytic activity.

To the best of our knowledge, only Vijayalekshmi (Vijayalekshmi 2015) reported on the TiO₂/CS–MT combination, but the author used the composite in the powdered form and only focused on its antibacterial properties. Therefore, this study came up with a prime objective to investigate the photocatalytic activity of the TiO₂/CS–MT in the form of layer-by-layer assembly. The TiO₂ on the top layer and the CS–MT adsorbent as the sub-layer were deposited on a glass support, which was then referred to as an immobilized TiO₂/CS–MT bilayer photocatalyst. The physical, chemical and optical properties of the photocatalyst were investigated using several analyses. The photocatalytic activity of the TiO₂/CS–MT photocatalyst and its reusability were evaluated under UV–visible (UV–Vis) and visible irradiation using an anionic azo dye MO.

**Methods**

**Materials**

TiO₂ Aeroxide® nanopowders (TiO₂; 80% anatase, 20% rutile) was purchased from Jebsen & Jessen Degussa Chemicals (M) Sdn Bhd. CS flakes (68.2% degree of deacetylation with a molecular weight of 322 g mol⁻¹) and MT powder (K-10) were purchased from Sigma-Aldrich. Glacial acetic acid (99.8%) was bought from System®. MO dye (Color Index Number: 15025, chemical formula: C₁₄H₁₄N₃NaO₃S, MW: 327.35 g mol⁻¹, λmax: 464 nm) was supplied by BDH Chemicals Ltd. Epoxidized natural rubber with 50% epoxidation (ENR) and polyvinyl chloride (PVC) powder were obtained from Guthrie Group Sdn. Bhd. and Petrochemical (M) Sdn. Bhd., respectively. Toluene and dichloromethane were bought from R & M Chemicals. Acetonitrile (high-performance liquid chromatography grade) used for eluent preparation was purchased from Merck. Ultra-pure water (18 mΩ·cm) was used for dilution and solution preparation.

**Preparation of immobilized TiO₂/CS–MT bilayer photocatalyst**

Approximately 0.75 g of CS flakes and 0.09 g of MT powder was ground in 50 mL of 5% (v/v) acetic acid solution using a ball mill grinder for 6 h at 40 rpm in a Schott bottle. Glass plates, with dimensions of 4.7 cm × 7.0 cm × 0.2 cm, were first cleaned and rinsed with water and technical acetone, before drying at room temperature. The produced CS–MT solution was cast evenly on the surface of the glass plates before being dried at room temperature for 24 h and oven dried at 100 °C for 48 h. The preparation of the TiO₂ formulation has previously been described in detail (Nawi & Zain 2012) and this formulation was coated onto the prepared CS–MT layer by dip-coating technique. Different loadings of TiO₂ on the CS–MT layer was achieved by varying the number of dip-coating in TiO₂ formulation.

**Analyses and characterization**

The strength test, swelling test and the solid addition method for point-of-zero charge determination for CS and CS–MT plates was carried out based on the procedure reported by Ngoh & Nawi (2016) and Nawi & Zain (2012). A razor blade was used to peel off the film from the CS and CS–MT plates for the latter analysis. Scanning electron microscope (LEO Supra 50 VP Field Emission SEM model) was used to observe the surface morphology and measure the thickness of the CS–MT and TiO₂ layers. The UV–Vis diffuse reflectance analysis was performed on a UV–Vis diffuse reflectance spectrophotometer (Lambda 35, Perkin Elmer) within 250–600 nm scan range using a magnesium oxide (MgO) disc as the reflectance standard.

**Photocatalytic experiments**

The photocatalytic reactor was equipped with a 45 W fluorescent lamp (Philips) with emitted UV and visible intensity of 2.78 and 300 W m⁻², respectively, as measured by a
radiometer (Solar Light Co., model PMA 2100). The experiments were conducted in a glass cell (length 5.0 cm, width 1.0 cm and height 8.0 cm) using 20 mL of MO dye solution with a concentration of 20 mg L\(^{-1}\) unless stated otherwise, 40 mL min\(^{-1}\) of aeration rate and at room temperature (30 °C). The fabrication of TiO\(_2\)/CS–MT was optimized at different CS–MT (0.3 to 1.9 mg cm\(^{-2}\)) loadings. For the reusability study, the TiO\(_2\)/CS–MT photocatalyst was subjected to UV–Vis and total visible light irradiations for the adsorption–photocatalysis of MO dye where each cycle took 60 min until ten cycles of application. A total visible light irradiation was performed by placing a UV filter between the lamp and the glass cell containing the coated plate. Between each cycle, the plates were washed with distilled water and irradiated under the same lamp for 2 h. After washing, the distilled water was replaced by a fresh MO dye solution and the adsorption–photocatalysis process was continued. The concentrations of MO dye were measured every 15 min for a total contact time of 60 min using a direct reading spectrophotometer (HACH DR/2000) at 464 nm. The photocatalytic performance of the TiO\(_2\)/CS–MT was evaluated using the linearized Langmuir–Hinshelwood kinetic model and the equation is expressed as:

\[
\ln\left(\frac{C_0}{C_t}\right) = kt
\]

where \(C_0\) and \(C_t\) is the concentration of MO dye (mg L\(^{-1}\)) at initial and time, \(t\), respectively, and \(k\) is the apparent pseudo-first-order rate constant or the decolourization rate (min\(^{-1}\)).

Mineralization study

A total organic carbon (TOC) analyzer (Shimadzu, H561048) was used to detect dissolved organic carbon content in the treated solution, while the evolution of anionic ions during the mineralization was detected using ion chromatography (IC) (Methrom, model 792). The conditions of the IC instrument were as follows: conductivity 15–16 μS cm\(^{-1}\); flow rate 0.7 mL min\(^{-1}\); and pressure 6.8 MPa. The mass spectrum (MS) analysis of the treated water samples was done on a liquid chromatography–mass spectrometry (LC–MS) instrument from Agilent Technologies under the flow rate of 0.3 mL min\(^{-1}\), ultra-pure water/acetonitrile (50:50) eluent and a 25 cm × 4.6 cm × 5 μm reversed phase column (LC-18 Supelcosil) from SUPELCO\textsuperscript{TM}. The mass values were obtained using Mass Hunter Qualitative Analysis B.04.00 software. The immobilized plates were first photo-etched in ultra-pure water for 10 h under light irradiation to eliminate any possible organic interferences from the degradation of polymer adhesive. Next, the photo-etched samples were irradiated in 20 mg L\(^{-1}\) of MO dye solution for 6 h and the aliquot was withdrawn from the solution every 2 h interval for further analysis.

RESULTS AND DISCUSSION

Characterization

Physicochemical properties

The bilayer photocatalysts consist of TiO\(_2\) as the top layer and the adsorbent as the sub-layer. Therefore, each layer was analyzed separately so that the individual properties were known beforehand as shown in Table 1. For the TiO\(_2\) layer, Nawi & Zain (2012) reported that the addition of ENR/PVC adhesive for the immobilization of TiO\(_2\) powder decreased the Brunauer–Emmett–Teller (BET) surface area \(S_{BET}\) and the pore volume from 56 to 29 m\(^2\) g\(^{-1}\) and 0.18 to 0.16 cm\(^3\) g\(^{-1}\), respectively, but increased the composite pore diameter from 0.97 to 1.06 nm. Apparently, the \(S_{BET}\) decrement was also observed for polyaniline (Bahrudin et al. 2018) adsorbent when mixed with ENR/PVC adhesive. Nevertheless, the immobilized TiO\(_2\) showed good mechanical strength where more than 80% of the photocatalyst still adhered to the glass plate after the strength test due to the addition of PVC into the TiO\(_2\) formulation (Nawi & Zain 2012). The pH at the point-of-zero charge (pH\(_{pzc}\)) for TiO\(_2\) powder and its composite are within 4.0–4.4, which indicates that below pH 4.5, the surface of TiO\(_2\) is positively charged and thus will be adsorb anionic dye molecules.

<table>
<thead>
<tr>
<th>Properties</th>
<th>TiO(_2) (p(a))</th>
<th>TiO(_2) (i)</th>
<th>CS (p(a))</th>
<th>CS (i)</th>
<th>MT (p(a))</th>
<th>MT (i)</th>
<th>CS–MT (p(a))</th>
<th>CS–MT (i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area, (S_{BET}) (m(^2) g(^{-1}))</td>
<td>56</td>
<td>29</td>
<td>3.8</td>
<td>205</td>
<td>4.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore volume, (V_t) (cm(^3) g(^{-1}))</td>
<td>0.18</td>
<td>0.16</td>
<td>0.08</td>
<td>0.31</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore diameter (nm)</td>
<td>0.97</td>
<td>1.06</td>
<td>8.39</td>
<td>7.09</td>
<td>6.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanical strength (%)</td>
<td>–</td>
<td>&gt; 80</td>
<td>83.1</td>
<td>–</td>
<td>92.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Swelling index (%)</td>
<td>–</td>
<td>–</td>
<td>93.6</td>
<td>–</td>
<td>56.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH at the point-of-zero charge (pH(_{pzc}))</td>
<td>4.0</td>
<td>4.4</td>
<td>6.5</td>
<td>2.8</td>
<td>6.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

p, powder; i, immobilized.
\(aNawi & Zain (2012).\)
\(bNgoh & Nawi (2016).\)
\(cBahrudin et al. (2019).\)
As for the CS–MT adsorbent layer, the presence of MT clay in the CS matrix can avoid the drawbacks of the polymer, which has high solubility in acidic media and exhibits poor mechanical strength in aqueous environment (Jamróz et al. 2019). A few selected tests have been conducted on the CS and CS–MT to determine the influence of MT clay on CS (Bahrudin et al. 2019). It was observed that the addition of the clay into the CS matrix improved the $S_{BET}$ value from 3.82 to 4.38 m$^2$ g$^{-1}$. This observation could be related to the large surface area (203 m$^2$ g$^{-1}$) of MT that increased the surface area of the composite. An increment in the mechanical strength from 83.1 to 92.6% was also obtained, while the swelling properties of CS reduced to 56.5 from 93.6%. The MT clay hardens when it is in contact with water, which results in a stronger adhesion of the composite on the solid support. In addition, the volume expanded and the distance of water molecules was lengthened, thus inducing the hydrophobicity of the composite layer (Wang & Jing 2017). The improvement in the physicochemical properties of CS–MT suggests that the immobilized composite adsorbent would work better in aqueous media compared to CS only.

**Surface morphology**

The SEM images of the immobilized TiO$_2$ and CS–MT are shown in Figure 1(a) and 1(b), respectively. It can be observed that the TiO$_2$ nanopowders are well distributed and closely packed together on the fixed glass surface. The pores/cavities on top of the surface can be seen clearly and most of them are covered with the TiO$_2$ particles. This made the photocatalyst layer denser and more compact. On the other hand, the immobilized CS–MT exhibits a rough and heterogeneous surface layer due to the

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**Figure 1** | The surface morphology of immobilized (a) TiO$_2$, (b) CS–MT at ×500 magnification and (c) cross-section of immobilized TiO$_2$/CS–MT bilayer photocatalyst at ×750 magnification.
distribution of MT clay particles, as well as some undissolved CS flakes throughout the composite matrix. It could be seen that the TiO₂ formulation was smoothly coated on the CS–MT layer's surface when the two layers were combined as a bilayer photocatalyst, as shown in Figure 1(c). The visual image of both layers became more transparent and the layers can be easily distinguished. From the image, the top layer is a dense layer packed of TiO₂ particles, while the CS–MT sub-layer is a hardened film layer.

**Optical properties**

The absorption of TiO₂/CS–MT in the UV and visible region was compared with TiO₂ and TiO₂/CS photocatalysts within the range of 250 to 600 nm, as shown in Figure 2(a). The TiO₂/CS–MT photocatalyst shows the highest absorbance in the visible region, followed by TiO₂/CS and TiO₂. Following the TiO₂ absorption pattern, the photon absorption wavelength was enhanced at the edge of 416 and 423 nm for the TiO₂/CS and TiO₂/CS–MT photocatalysts, respectively. The subsequent addition of CS and MT within the adsorbent sub-layer increased the absorption in the UV and visible regions compared to the TiO₂ single layer. Similarly, high UV light absorption was also observed using potato starch/MT/TiO₂ nanocomposites due to the presence of an empty orbital of Fe³⁺ in the MT structure that absorbs photons (Oleyaei et al. 2016). The enhanced visible absorption of both bilayer photocatalysts is attributed to the interaction at the interface of the adsorbent and the TiO₂ surface. In this case, CS–MT adsorbent absorbs photon at the longer wavelength better than CS.

The band gap energy of the photocatalysts can be determined using the Tauc plot, which is a plot of the Kubelka Munk equation, \( (F(R)h\nu)^{1/2} \) versus energy (eV), as shown in Figure 2(b). The reflectance \( (R) \) is obtained from the conversion of absorbance value from the UV reflectance spectrum. It could be seen that the presence of CS under the TiO₂ layer reduced the band gap energy of TiO₂/CS from 3.03 to 2.98 eV, whereas the subsequent addition of MT to the CS composite within TiO₂/CS–MT further reduced the band gap energy to 2.93 eV. The red shift in the absorption wavelength and a reduction in the band gap energy corresponds to the less photon energy required to excite the electrons of TiO₂ from its valence (VB) to the conduction band (CB). It also means that TiO₂/CS–MT required less photons for the successful production of hydroxyl radicals than the TiO₂/CS and single TiO₂ photocatalysts. Eventually, the photocatalytic activity of the TiO₂/CS–MT system would be better than the TiO₂/CS and TiO₂ single layer systems. Moreover, this system could possibly operate in the visible light region due to the red shift. The reduced band gap energy in the presence of sublayer adsorbent was also reported for TiO₂/MT (Ngoh & Nawi 2016) and TiO₂/CS using similar assemblage system as in the present study. This was further strengthened by the work of Vijayalekshmi (2015) who observed the reduction in the band gap energy of the synthesized TiO₂/CS–MT nanocomposite powder.

**Comparison of the process performances**

The bilayer arrangement of the adsorbent and the photocatalyst allows dual processes, involving adsorption and photocatalysis, to run simultaneously under light irradiation. In this case, the CS–MT layer concentrates the dye molecules closer to the surface of TiO₂ top layer. At the same time, the electrons from the VB of TiO₂ were excited to its
CB, leaving behind the photoholes. On the other hand, some of the adsorbed MO dye on the TiO₂/CS–MT will act as a photosensitizer and will donate its electrons to the CB of TiO₂ under visible light irradiation (Bahrudin & Nawi 2019). The accumulation of electrons at the CB of TiO₂ will reduce O₂ to superoxide ions and later to ‘OH radicals, which is a strong oxidizing species responsible for the degradation of MO dye. On the other hand, adsorption is the sole process if the experiment was conducted in the dark.

Figure 3 shows the decolourization rate (k) of MO dye for the single TiO₂ and the bilayer TiO₂/CS–MT photocatalyst after 60 min of treatment under UV–Vis and total visible light irradiations. By referring to Figure 3(a), the removal of MO dye by the TiO₂/CS–MT via the adsorption–photocatalysis processes shows the highest decolourization rate among the photocatalysts studied with a rate of 0.071 min⁻¹. On the other hand, the decolourization rate of TiO₂/CS via the same process is 0.067 min⁻¹. This could be related to the high adsorption rate of both photocatalysts, which are 0.051 and 0.040 min⁻¹, respectively. The single TiO₂ photocatalyst gives a lower decolourization rate of 0.028 min⁻¹ as a result of its lower adsorption rate of 0.004 min⁻¹.

Under visible light irradiation, the TiO₂/CS–MT exhibited decolourization rate of 0.055 min⁻¹ compared to the TiO₂/CS and TiO₂ photocatalysts with rates of 0.041 and 0.008 min⁻¹, respectively. It could be seen that the
photocatalytic activity was highly dependent on the amount of MO dye adsorbed on both the photocatalyst and the adsorbent. Furthermore, the optical characterization agrees well with the observed photocatalytic activity as the TiO$_2$/CS–MT system showed the highest decolourisation rate among the other photocatalysts. This is due to its reduced band gap energy and better light absorption spectrum, which decreases the energy barrier required for electron excitation and promotes its optical response in the visible light region. A comparison of the decolourisation efficiency of MO dye in Table 2 revealed that the TiO$_2$/CS–MT photocatalyst as prepared in this study is equal to or better than other photocatalysts reported in the literatures for decolourisation of MO dye. This is due to the positive combination of CS and MT as adsorption and adsorption–photocatalysis increased linearly from 0.049 to 0.074 min$^{-1}$.

**Fabrication of immobilized TiO$_2$/CS–MT**

**Effect of CS–MT loading**

The loading of the CS–MT sub-layer within the TiO$_2$/CS–MT can influence the efficiency of both adsorption and photocatalytic decolourisation of MO dye because it provides the main adsorption sites for the photocatalyst. For this investigation, the loading of CS–MT sub-layer was varied from 0.3 to 1.9 mg cm$^{-2}$, while maintaining the TiO$_2$ top layer loading at 1.6 mg cm$^{-2}$. Zero CS–MT loading corresponds to the single TiO$_2$ layer acting as a control. Figure 4 shows the effect of CS–MT loading on the decolourisation rate of MO dye by the TiO$_2$/CS–MT during adsorption and adsorption–photocatalysis processes.

As the CS–MT loading increased from 0.3 to 1.3 mg cm$^{-2}$, the decolourisation rate of adsorption and adsorption–photocatalysis increased linearly from 0.049 to 0.073 min$^{-1}$ and 0.072 to 0.090 min$^{-1}$, respectively. It could be seen that the overall photocatalytic decolourisation of MO dye was predominantly dependent on the adsorption by the CS–MT sub-layer, with a small contribution from the adsorption by the TiO$_2$ layer with a rate of 0.007 min$^{-1}$. Upon light irradiation, the decolourisation became faster due to the two concurrent processes running simultaneously, namely adsorption by CS–MT and TiO$_2$ layers, and photocatalysis by the TiO$_2$ top layer.

However, further increment in the CS–MT loading up to 1.9 mg cm$^{-2}$ decreased the decolourisation rate of both adsorption and adsorption–photocatalysis to 0.049 min$^{-1}$ and 0.074 min$^{-1}$, respectively. This is probably because higher loading in the CS–MT produced a thicker and more compact film layer due to the fixed area of the glass plate, as shown in the SEM cross-sectional image (Figure 5(a)–5(c)). The results indicate that the loading of CS–MT is proportionally related to the thickness of the layer in which the thickness increased from 3.57 ± 0.87 to 12.84 ± 0.56 μm as the loading of CS–MT increased from 0.63 to 1.9 mg cm$^{-2}$. Hence, fewer MO dye molecules would be able to penetrate

### Table 2 | Comparison of the TiO$_2$/MT and TiO$_2$/CS combination on the decolourisation of MO dye

<table>
<thead>
<tr>
<th>Combination</th>
<th>Experimental conditions</th>
<th>Decolourisation (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/MT</td>
<td>Light = 250 W mercury lamp; [MO] = 40 mg L$^{-1}$; V = 0.5 L; t = 135 min</td>
<td>100</td>
<td>Butman et al. (2018)</td>
</tr>
<tr>
<td>TiO$_2$/MT</td>
<td>Light = 30 W UV lamp; [MO] = 20 mg L$^{-1}$; V = 0.01 L; t = 50 min</td>
<td>100</td>
<td>Huo et al. (2018)</td>
</tr>
<tr>
<td>TiO$_2$/CS</td>
<td>Light = 6 W UV lamp; [MO] = 10 mg L$^{-1}$; V = 0.15 L; t = 75 min</td>
<td>70</td>
<td>Amir et al. (2016)</td>
</tr>
<tr>
<td>TiO$_2$/CS</td>
<td>Light = Solar simulator; [MO] = 16.4 mg L$^{-1}$; V = 1 L; t = 120 min</td>
<td>63.6</td>
<td>Saravanan et al. (2018)</td>
</tr>
<tr>
<td>TiO$_2$/CS</td>
<td>Light = 45 W UV–Vis lamp; [MO] = 20 mg L$^{-1}$; V = 0.02 L; t = 60 min</td>
<td>96.7</td>
<td>This study</td>
</tr>
<tr>
<td>TiO$_2$/CS–MT</td>
<td>Light = 45 W UV–Vis lamp; [MO] = 20 mg L$^{-1}$; V = 0.02 L; t = 60 min</td>
<td>98.2</td>
<td>This study</td>
</tr>
</tbody>
</table>
and adsorb onto the interior surface of CS–MT sub-layer due to intra-particle mass transfer resistance that led to poor decolourization rate. Moreover, the adsorption sites made available by the thicker CS–MT would be in excess as the concentration of MO dye used in this study was fixed. Based on the results presented, the optimum loading of the CS–MT sub-layer was found to be at 1.3 mg cm\(^{-2}\) and was applied for the following experiment.

**Effect of TiO\(_2\) loading**

The amount of TiO\(_2\) on top of the CS–MT sub-layer is also an important parameter because it can affect the adsorption properties of both TiO\(_2\) and CS–MT layers. Different amounts of TiO\(_2\) ranging from 0 to 3.8 mg cm\(^{-2}\) were coated on the optimized CS–MT sub-layer. Figure 6 shows the decolourization rate of the MO dye by the single TiO\(_2\) and the bilayer TiO\(_2\)/CS–MT at different TiO\(_2\) loadings via adsorption and adsorption–photocatalysis processes. A high decolourization rate was observed without TiO\(_2\) loading due to the strong adsorption of MO dye by the CS–MT sub-layer. The adsorption rate of the single TiO\(_2\) also slightly increased from 0.006 to 0.011 min\(^{-1}\) as the loadings increased from 0.6 to 3.8 mg cm\(^{-2}\). However, when the TiO\(_2\) layer was coated on the CS–MT sub-layer, the adsorption of MO dye ceased with increasing loading until 1.9 mg cm\(^{-2}\) before it became constant. This was probably because the increasing of TiO\(_2\) loading from 1.3 to 3.8 mg cm\(^{-2}\) would increase the thickness of TiO\(_2\) layer from 19.21 ± 0.38 to 47.03 ± 0.39 μm, as shown in Figure 5(b), 5(d) and 5(e). The increased thickness of the TiO\(_2\) layer exhibited inhibitory effects related to an increase in mass transfer resistance, which suppressed the intra-particle diffusion of MO dye to reach the interior surface of the CS–MT sub-layer and subsequently remained constant afterward.

Increasing the TiO\(_2\) loading would essentially increase the adsorption and adsorption–photocatalysis rate of the single TiO\(_2\). In contrast to its adsorption counterpart, the decolourization of MO dye at increasing TiO\(_2\) loadings by the TiO\(_2\)/CS–MT followed the same pattern shown by the single TiO\(_2\) under light irradiation. The decolourization rate increased from 0.059 to 0.082 min\(^{-1}\) with the TiO\(_2\)
loading from 0.6 to 2.5 mg cm\(^{-2}\). In this case, the decolourization rate was highly dependent on the oxidative radicals produced on the TiO\(_2\) surface, which substantially increased with loading. At the same time, the contribution from the adsorption by CS–MT sub-layer remained constant. Beyond 2.5 mg cm\(^{-2}\), the decolourization rate became constant as the thickness of the TiO\(_2\) top layer was 5.9 times thicker than the CS–MT sub-layer, creating a multilayer and inhibiting the diffusion of MO dye molecules into the interior surface of CS–MT sub-layer. The thick TiO\(_2\) top layer in the bilayer arrangement would isolate the CS–MT from the dye molecules and cause it to behave predominantly like the TiO\(_2\) single layer. Therefore, the adsorption by the CS–MT sub-layer became less significant. This discussion supported our earlier observation on the relation of oxidative species production and mass transfer resistance with loading upon light irradiation. A similar finding was also observed for TiO\(_2\)/MT in the removal of methylene blue dye (Ngoh & Nawi 2016). Consequently, 2.5 mg cm\(^{-2}\) was selected as the optimum TiO\(_2\) loading because it exhibited the highest decolourization rate for the synergy adsorption–photocatalysis, with two and four times better than the decolourization of MO dye during adsorption and the single TiO\(_2\) photocatalysis process, respectively.

### Mineralization of MO dye

The mineralization of MO dye by TiO\(_2\)/CS–MT and TiO\(_2\) photocatalysts were compared based on the TOC and IC analyses and the results are displayed in Figure 7(a) and 7(b), respectively. In addition, the MS spectrum in Figure 7(c) was used to confirm the mineralization of MO dye (m/z = 304).

As observed, the TiO\(_2\)/CS–MT photocatalyst mineralized the MO dye better than the single TiO\(_2\) photocatalyst, whereby 80% of mineralization degree was achieved within 4 h of irradiation. The single TiO\(_2\) mineralized the MO dye much slower throughout the reaction period and reached a mineralization degree of only 22% after 6 h of irradiation. As discussed earlier, the enhanced mineralization of MO dye by the TiO\(_2\)/CS–MT photocatalyst was due to the synergistic adsorption–photocatalysis processes and enhanced optical properties of the photocatalyst.

The evolution of nitrate (NO\(_3^-\)) and sulphate (SO\(_4^{2-}\)) ions also corresponds to the degree of mineralization of MO dye solution because the molecular structure of MO dye consists of an azo bond (\(^{-\text{N=N-}\} bonding), a dimethylamino group and sulfonate (R-SO\(_3^-\)) functional groups. For both photocatalysts, the concentration of NO\(_3^-\) ions increased with increasing irradiation time. The concentration of NO\(_3^-\) ions
detected after 6 h of irradiation were 0.234 and 0.166 mg L\(^{-1}\) for TiO\(_2\)/CS–MT and TiO\(_2\), respectively. The conversion of the nitrogen atom from the azo and dimethylamino groups to NO\(_3^-\) ions by the TiO\(_2\)/CS–MT was higher than that of TiO\(_2\).

On the other hand, 0.532 and 0.087 mg L\(^{-1}\) of SO\(_4^{2-}\) ions were produced after 6 h of irradiation by TiO\(_2\)/CS–MT and TiO\(_2\), respectively. Most of the CS-based sorbent favoured the adsorption of SO\(_4^{2-}\) ions and, therefore, the ions tended to bind with the active sites on CS–MT sub-layer rather than diffuse into the bulk solution during the irradiation (Hu \textit{et al.} 2015). Nonetheless, the increasing concentration of NO\(_3^-\) and SO\(_4^{2-}\) ions with increasing reaction time was in line with the decreasing TOC values. This indicates that the MO dye molecules were oxidized to CO\(_2\) and H\(_2\)O while producing NO\(_3^-\) and SO\(_4^{2-}\) ions as the by-products.

The MS spectrum in Figure 7(c) and the corresponding structure in Table 3 can be used to describe the degradation pathway of MO dye (m/z = 304) by the TiO\(_2\)/CS–MT. Upon irradiation, one of the –CH\(_3\) from the dimethylamino group was detached from the MO dye molecules because the cleavage of the –C=N– bond (305 kJ mol\(^{-1}\)) occurred faster due to its lower bond energy as compared to –N = N– bonding (418 kJ mol\(^{-1}\)) (Gupta & Pal 2014). This reaction produced the m/z = 290 and subsequently m/z = 276 species. The reaction of NH\(_3\) from one end of the aromatic ring with hydrogen species forms the ammonium ion (NH\(_4^+\)), which then slowly oxidizes into the stable NO\(_3^-\) ion (m/z = 62). The cleavage of the azo (–N = N–) bond of the MO dye produced m/z = 173 species, and further oxidation led to the formation of N\(_2\) as one of the mineralization products. The SO\(_3^-\) functional group, which is attached to another aromatic ring of m/z = 157 species, was detached upon oxidation by the hydroxyl radicals and further oxidized to SO\(_4^{2-}\) ions. The findings proved that NO\(_3^-\) and SO\(_4^{2-}\) ions were the by-products formed during the degradation of MO dye intermediates.

**Reusability study**

The advantage of using an immobilized photocatalyst is its convenience for recycling the same catalyst for extended
usage. In the present study, the reusability of the single TiO$_2$ and the bilayer TiO$_2$/CS–MT for MO dye decolourization were compared for up to ten cycles of applications under UV–Vis and total visible light irradiation (Figure 8). The reusability of the bilayer photocatalyst by adsorption (dark experiment) was also performed as a control.

Under a UV–Vis light irradiation, the adsorption–photocatalysis by the TiO$_2$/CS–MT shows a fluctuated, but with a sustainable, decolourization rate until the seventh cycle, which gave an average value of 0.090 min$^{-1}$. At the eighth cycle, the decolourization rate started to decrease until the tenth cycle from 0.082 to 0.074 min$^{-1}$. A similar trend was also observed for the decolourization of the MO dye by the TiO$_2$/CS–MT under visible light irradiation with an average rate of 0.019 min$^{-1}$. However, the observed rates were still lower than those obtained for TiO$_2$/CS–MT under UV–Vis and visible light irradiation due to low adsorption of MO dye on the TiO$_2$ surface.

**CONCLUSIONS**

An immobilized TiO$_2$/CS–MT bilayer photocatalyst has been successfully fabricated and optimized using MO dye as the probe pollutant. The physicochemical properties of the CS–MT revealed that the composite was more stable in aqueous environment compared to their individual components. The optical properties of the TiO$_2$/CS–MT were enhanced and the band gap energy reduced to 2.93 eV. Under UV–Vis irradiation, the adsorption of MO dye on the surface of the CS–MT sub-layer facilitated the
photocatalytic oxidation at the TiO₂ surface, which eventually improved the decolourization rate of the MO dye compared to the single TiO₂. The loadings of CS–MT and TiO₂ layers influenced the adsorption and photocatalytic performance of the TiO₂/CS–MT. The TOC, IC and MS analyses confirmed that the intermediates were mineralized to CO₂, H₂O and produced sulfate and nitrate ions as the by-products. It was apparent that the presence of CS–MT as the adsorbent sub-layer of TiO₂ in the bilayer photocatalyst aided in faster decolourization and mineralization of the MO dye than the single TiO₂ layer due to synergy of adsorption and photocatalysis processes. In addition, the decolourisation of the MO dye by the TiO₂/CS–MT was sustained for at least ten cycles of application, with an average decolourisation rate of 0.08 ± 0.01 min⁻¹. The enhanced photoactivity under visible light irradiation indicates that the TiO₂/CS–MT material is of high potential for solar and indoor light applications.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Universiti Sains Malaysia for the research facilities and financial support through the Research University (Individual) Grant (1001/ PJP/10UH/8011028). The authors would also like to thank the Malaysian Ministry of Education for funding this work through the research grant (FRGS, 203/PKIMIA/6711228) and scholarship granted to N.N. Bahrudin under My Brain 15 program.

DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

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First received 16 April 2020; accepted in revised form 15 July 2020. Available online 30 July 2020