Materials Research Express

PAPER

Photocatalytic degradation of methylene blue under visible light by dye sensitized titania

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Keywords: TiO$_2$ nanotubes, photocatalytic degradation, natural dyes

Abstract
The use of textile dyes remain relevant in the issue of water pollution. With the potential harm it may possess on the local flora and fauna, various methods of dye removal have been researched and employed, including photocatalytic degradation. TiO$_2$, being a suitable semiconductor for this purpose needs to be sensitized prior to use, either by doping or chemical adsorption in order to activate in visible light. In this study, various natural dyes were employed to sensitize TiO$_2$. It was found that chlorophyll was superior in dye degradation, with about a 60% reduction in dye concentration over a target 2 h, greater than that of the synthetic sensitizer N-719. This places chlorophyll based photocatalytic reactors as a potential tool for organic pollutant degradation which are also easy to manufacture and abundant in nature.

Introduction
The use of dyes in the textile industry is not a new occurrence, dating back to more than 4000 years ago [1]. Dyes were used to improve the overall color of a piece of clothing, or to even add to it in fashionable wear. At the same time, the clothing of royalty was dyed deep purple or yellow as a symbol of nobility while uniformed clothing such as those in the military blue or red to intimidate their foes. Even to this day, textiles are dyed in various colors, mostly for fashion but nevertheless it is a growing industry.

Most of the dyes used in the past were organic dyes which were sourced from local flora [2], but after the discovery of mauve as the first synthetic dye, synthetic dyes were also researched and produced. The dye known as Methylene Blue were one of these dyes. Although predominantly used in the scientific community as a staining agent [3], it was also used in the textile industry owing to its deep blue coloration [4].

The process of dyeing textiles is not a perfect one, and as such, at least 10 percent of the dye is washed away into the sewage [5]. Toxic runoff other than the dyes include sulphur, chromium compounds, acids, heavy metals, formaldehyde based compounds and hydrocarbon compounds [6]. Flora and fauna in the local ecosystem are the first to be affected by the runoff through consumption of solid wastes or by absorption through the water. If the local waterways are then sourced for human consumption or usage, they would be thus affected by the toxic runoff as well.

In order to find a solution for this predicament, a method of eliminating the runoff should be found. Fortunately, there are many solutions for water waste management, such as mechanical filtration can be used. Mechanical filtration include ultrafiltration and reverse osmosis, which involve forcing the water through a porous filter membrane as to allow only certain particles through [7]. Mechanical filtration does not discern between molecules which may end up filtering wanted micronutrients in the water alongside the toxic runoff, and may leak with an increase in pressure during filtration [8].

Biological filtration is another possible treatment facility used for wastewater management [9]. Biological filtration is divided into two types, aerobic and anaerobic treatment. The distinction is the involvement of oxygen in the treatment, where aerobic treatment requires oxygen while anaerobic treatment does not. While biological treatment has some success in textile dye treatment, it is still not completely effective in the removal process [8].
Photocatalytic degradation of textile runoff is another wastewater treatment process. Instead of filtering out the runoff, photocatalytic degradation involves breaking down the matter into non-toxic constituents, commonly water and carbon dioxide [10]. It is for this that photocatalytic degradation works best with organic substances, which includes most dye runoffs. Photocatalytic degradation is commonly done using TiO2 or titania as an active material, with an ultraviolet light source. As the bandgap of TiO2 is between 3.0–3.2 eV, a UV-light source is essential as visible light simply does not have the required energy to induce photocatalysis. While there are other material with visible light reactivity such as Fe2O3, with a bandgap of 2.3 eV [10], most of these other materials simply are not strong enough to withstand corrosion and long term usage, along effective photocatalytic reaction, unlike TiO2 [11].

Thus it is necessary to lower the bandgap of TiO2 into the visible range. One method is by doping the TiO2, either with metallic elements such as Cu [12], Fe [13], Ni [14] or non-metallic elements such as N [15], C [16] and H [17]. Other than doping, sensitization is another possible method to increase visible light reactivity. While most sensitized TiO2 research was done towards photocatalytic water splitting [18], very little research was done towards photocatalytic degradation where sensitization is done prior to degradation. Commonly, the pollutant dye acts as sensitizer and self-degradation occurs [19] Visible light-induced degradation of carbon tetrachloride on dye-sensitized TiO2. Sensitization is done by the adsorption of dye molecules, whether natural or synthetic onto the surface of the TiO2 [20]. This offers more economical approach to preparing the TiO2 as sensitization generally costs lower than doping [21, 22].

Another factor in the photocatalytic degradation of water-based pollutants that should be addressed is the morphology of the TiO2 substrate. As reactivity correlates with surface area, a high specific surface area should be obtained. Taking 3.84 g cm\(^{-3}\) as the density of TiO2 [23], a 1 cm\(^3\) cube of TiO2 that is completely flat would have a surface area of 6 cm\(^2\), or 1.56 cm\(^2\) g\(^{-1}\), whereas nanostructures such as nanotubes, nanoparticles and nanorods can have specific surface areas between 50 m2 g\(^{-1}\) to 345 m2 g\(^{-1}\) [20, 24, 25]. Nanotubes were chosen in this study as the preferred morphology due to the fine morphological control achievable by the anodization of TiO2 to form the nanotubes [26].

Finally, the photocatalyst system should be considered. Most photocatalytic reactor systems involve the dispersion of the photocatalyst into the pollutant solution [27–29]. While this method offers superior photocatalytic performance, additional steps must be taken to properly separate the TiO2 particles from the solution post-treatment. Thus, a free-standing approach would mitigate this issue.

In this study, TiO2 nanotubes are sensitized by four different dyes, three natural dyes that is chlorophyll old and new, anad β-carotene, and one synthetic dye, N-719. The sensitized TiO2 nanotubes on a Ti substrate will act as a photocatalyst to degrade methylene blue as the sample pollutant under visible light.

**Methods**

**Anodization of TiO2 nanotubes**

TiO2 nanotubes were prepared by anodization of a Titanium foil. The foil was first cut into 2 cm by 4 cm strips, which were then cleaned ultrasonically in decon-90, ethanol, and acetone for 10 min each, with a final rinse and cleaning done with DI water for 10 min as well. The electrolyte medium for the anodization process consists of 0.3 wt% NH4F, 3 vol% H2O and Ethylene Glycol. The counter electrode used was a platinum wire, placed parallel to the foil with a 1 cm gap between them. The anodization was performed at 60 Volts for 4 h.

After anodization the foil was cleaned by ultrasonication in a 1:5 solution of Ethanol and DI water. This was to remove any excess impurities on the surface of the anodized Ti foil. To crystallize the TiO2 nanotubes, the strips were sintered at 500 °C for 3 h to ensure uniform crystallinity.

**Preparation of natural dyes**

To prepare the dyes, samples of some local fauna were obtained, that is the leaves of spinach for fresh chlorophyll, browned leaves of the Millettia Pinnata tree for old chlorophyll, and the freshly dropped flowers of the Peltophorum Pterocarpum tree for a β-carotene source. 200 g of each of the obtained samples were sonicated in 300 ml of acetone (Fine Chemicals, Tech. Grade) for 10 min at 60 W power. This was done in a dimmed lighting condition to avoid premature photo-degradation of the light sensitive compounds.

A second extraction step was then done by adding 200 ml of Heptane (QReC, AR Grade) to the acetone. This was left to extract for 24 h in a darkened cabinet. The heptane layer was then separated and kept in a darkened bottle.
Preparation of N-719 dye
N-719 was prepared by adding N-719 powder to butanol to create a 20 mg ml$^{-1}$ solution of N-719. This mixture was stirred magnetically for 2 min, in the same light absent conditions as was the preparation of the natural dye extract. The mixture was stored similarly as well. All the dyes were analysed by UV–vis spectroscopy.

Preparation of dyed TiO$_2$ nanotubes
The TiO$_2$ was dyed by the immersion of the TiO$_2$ foil into the dye solutions. To ensure complete adsorption the TiO$_2$ foil was left in the dye for 24 h before being removed. The foil was then cleaned by a short ultrasonication in ethanol and then promptly dried. UV–vis Spectroscopy was performed on the dyed TiO$_2$ to confirm the adsorption of the dye on the surface of the nanotubes. To perform the photocatalytic experiments, 200 ml beakers of methylene blue solution were prepared, one for each of the dyed TiO$_2$ foils and one more as a control sample. The samples hence are labelled as S–C for control, S-NChl for new Chlorophyll, S-OChl for old Chlorophyll, and S–B for $\beta$-carotene dye, and S–N for the synthetic N-719 dye. Solution samples were taken at 15-minute intervals and tested by UV–vis spectroscopy to determine the rate of dye degradation. The light source for the experiment was a 150 W halogen lamp, situated 15 cm above the samples with a spot size of 30 cm. The surrounding area was kept unlit to ensure no external sources of light affected the photocatalysis reactions.

Results and discussions

UV–vis spectroscopy of the extracted dyes
The UV–vis Spectroscopy of the dye extracts are shown in Fig. 1. From the data certain peaks can be seen attributed to the main chemical compounds found in the dye (see figure 1). Chlorophyll, for example has two visible light peaks, one located between 660 nm–665 nm and another between 428 nm–432 nm [30]. This corresponds to the red and blue peaks respectively, hence giving chlorophyll its distinctive green coloration. In the case of S-NChl, the peaks are seen at 660 nm and 475 nm, the change in the peak position likely attributed to the solvent used as that may cause shifting in UV–vis peaks [31]. S-OChl on the other hand shows a much different visible light response, owing to the minute amount of chlorophyll present in fallen leaves, but nevertheless the UV-response of both samples between 200 nm–300 nm were similar. The blue peak of the S-OChl were noted but greatly attenuated, suggesting that the old chlorophyll extract may not be purely chlorophyll, but a mixture of chlorophyll and other components that were broken down during senescence [32].

Sample S-B shows a low absorption between 450 nm to 800 nm, but peaks between 350 nm–400 nm. For $\beta$-carotene, the absorption peak is expected to occur at around 449 nm and 478 nm but was blue shifted due to the solvent, heptane, that was used [33]. There is very little absorption noted for S-B in the UV-light region of the spectra in contrast to the other dyes, but this is consistent with reported data [34].

The UV–vis absorption spectra for S-N is consistent as well with reported data, showing the two characteristic peaks at 383 nm and 527 nm, with a larger peak at 304 nm. Again, there would be minute shifts in the UV–vis spectra from reported values of up to 15 nm due to the different solvents used, in this case, butanol was used, causing shifts in the peaks due to the optical properties associated with the polarity of the solvent [35].
Spectroscopy of the adsorbed dyes on the TiO$_2$ nanotube substrate

The adsorption process was assessed by a UV–vis reflectance test performed on the TiO$_2$ substrate before the adsorption process and then after. To ensure uniform and consistent readings the TiO$_2$ substrates were dried thoroughly after dyeing and promptly tested. Figure 2 shows the reflectance spectra obtained from the samples.

From the data the effect of dye absorption can be immediately seen as a drop of approximately half the reflectance of S-C at 400 nm. This is confirmed visually with a darker coloration on the dyed titania with a hue similar to the dyes used. All the samples have a similar spectral shape with that of S-C, with the exception of S-B. The color peaks of the dyes can be faintly seen as dips in the spectra, as seen in the two dips seen at 421 nm and 672 nm in S-NChl, close to the peaks of Chlorophyll seen in the extracted dyes. S-OChl has more vague dips, a broad dip located at 691 nm and a very shallow dip at 574 nm. This is caused by the presence of by-products of chlorophyll senescence.

S-N also has the two dips at 400 nm and 547 nm. S-B has the most unusual spectra out of the samples, with the highest reflectance readings among the dyed titania at about 40% reflectance between 400 nm to 700 nm. How this affects the performance of the substrates would be determined in the methylene blue degradation section of this study.

Methylene blue degradation by visible light

The results for the methylene blue dye degradation can be seen in f. From the data, it is interesting to note the drastic effectiveness of Chlorophyll as shown in S-NChl, which shows a reduction of methylene blue concentration by more than a half, where as the other dyed titania only managed to remove approximately 40% of the methylene blue in solution. The control sample is closely behind at 65%.

Chlorophyll in plants have two roles, that is to for both light harvesting and transference of energy [36]. This allows effective electron transfer between the chlorophyll dye and the TiO$_2$ substrate. S-B is also noted to have a near similar degradation response as β-carotene also plays an important role in photoreactive reactions of green plants [37].

The role of Chlorophyll as a photocatalyst was also investigated by other scientific groups as well [38, 39]. Chlorophyll by nature can easily absorb photonic energy due to its polyene structure. The mechanism proposed for the degradation of methylene blue in this study is as Equations (1)–(5) below. The Chlorophyll molecule (Chl) can reach an excited state (Chl$^+$) when presented with a photon of suitable energy [40]. The energy of Chl$^+$ is transferred to the TiO$_2$, causing an excited state within the TiO$_2$ (TiO$_2$$^+$), similar to the sensitization of ZnO by natural pigments [39]. Two routes are possible now for the formation of the radicals, that is via oxidation or reduction of the excited electron at the conduction band (CB) or the filling of the valence band (VB) of the TiO$_2$.

The excited electron at the CB forms a superoxide with the dissolved Oxygen in the solution (O$_2$$^-$), which then protonates into H$_2$O$_2$. On the other hand, the filling of the VB is mediated by H$_2$O, which forms OH$^-$ and H$^+$. With this there are at least three possible radicals that can oxidize Methylene Blue leading to degradation, that is O$_2$ (equation (2)), H$_2$O$_2$ (equation (4)), and OH$^-$ (equation (5)), and other studies have shown that the
hydroxyl radical is the main component in the photocatalytic degradation of methylene blue [41].

\[
Chl \rightarrow Chl^* \tag{1}
\]

\[
Chl^* + TiO_2 \rightarrow TiO_2(e_{CB}^- + h_{VB}^+) + Chl \tag{2}
\]

\[
TiO_2(e_{CB}^-) + O_2 \rightarrow O_2^- + TiO_2 \tag{3}
\]

\[
2O_2^- + 2H^+ \rightarrow H_2O_2 + O_2 \tag{4}
\]

\[
TiO_2(h_{VB}^+) + H_2O \rightarrow OH^- + H^+ + TiO_2 \tag{5}
\]

The generation of free radicals by natural dyes on an immobile surface is limited in the absence of stirring, which is in this case, as noted with the mini plateaus in f. This is also noted in literature [42], and a possible method of avoiding such occurrences would be with stirring, which is beneficial to dye removal [43], but would also increase operational costs for construction and maintenance on a large scale device.

S-N, having been sensitized with N-719, displays superior performance to the S-NChl between 30–45 min. After 45 min the performance of the S-N is quite similar to the other samples. This discrepancy can arise from the light sources’ close proximity to the samples, which generated heat which led to the increase in solvent temperature. N-719, while being chemically superior to most natural dyes when used as a photosensitizer for dye sensitized systems [44], suffer from thermal instability, with even a constant 25 °C having a long term effect on the stability of the molecule [45]. In a large scale operation thermal stability is an important factor as the temperature may fluctuate daily or with the season, and maintaining a constant temperature will be costly, especially for a system that relies on visible light photocatalytic degradation, which inevitably would have temperature fluctuations due to exposure to sunlight or a high intensity light source. The temperature rises even more for polluted water, which is the focus of this degradation study [46].

Thermal energy is also useful in aiding the degradation of the pollutants. As seen in f the control experiment also experienced degradation over time. This is a common occurrence noted in various studies [47]. While temperature may assist in the degradation process, it is noted that temperatures above 47 °C may inhibit the degradation rate [48], but that is assumed to be a low concern in photocatalytic degradation as elaborated further in the paper.

Table 1 shows the change in temperature over time for the samples. As the distant of the light was constant over the samples, there was minimal fluctuations between the individual sample temperatures of up to 0.2 °C, which was averaged to obtain the results shown. The temperature of the solution increased steadily over the 120 min period the study was conducted, from 22.6 °C to 31.8 °C.

The change in temperature is an important aspect of application studies as most devices function in non-homeostatic conditions. Photodegradation devices such as the ones in this study need to operate in tropical regions where temperatures may reach 36 °C daily, as these are places where water pollution has a greater effect on the local ecosystems. In such conditions, attempting to regulate the internal temperatures of the photodegradation chamber would be costly and thus not a financially viable solution. The samples of S-OChl, S-B, and S-N respectively can be seen to have minimal thermal stability, as the performance of these samples
become almost similar to each other after 30 min into the study. At this point, the temperature was raised by 4 °C. Water agitation such as stirring or flowing may reduce this effect by thermal convection and will be used for further studies to optimize the device.

For the chlorophyll sample on the other hand, that is, S-NChl, dye degradation by the sensitizer continues to occur after 45 min to 120 min. Chlorophyll is known to be at the very least stable up to 40 °C, after which certain lipids start to break down \[49\]. While S-B should have higher thermal stability \[50\], it features a lower degradation rate, attributed to a low degradation rate when using \(\beta\)-carotene sensitizers.

For the two samples S-OChl and S-NChl, a very contrasting outcome is observed. This would be due to the general concentration of chlorophyll in the two samples. Using the calculation method of Jeffrey and Humphrey \[51\], it is estimated the concentration of chlorophyll in S-NChl to be 30 times larger than that in S-OChl, at 896.9 \(\mu\)g l\(^{-1}\) for S-NChl and 29.0 \(\mu\)g l\(^{-1}\) for S-OChl. Although this is an estimate based on calculation, it can be seen that the concentration of chlorophyll is 30 times greater in S-NChl than in S-OChl. As such the findings for S-OChl appears to be quite similar to that of the other samples at 120 min, but before 120 min it is noted that the degradation of methylene blue with S-OChl was greater than the other samples. It was in fact equal to that of S-N between 45 min to 75 min and was greater until 120 min where it plateaued.

From this it is inferred that perhaps the potential of chlorophyll based organic pollutant photocatalytic degraders was greater that what was initially thought. Further experiments would be beneficial in determining how effective chlorophyll units will be for the degradation of methylene blue or other organic dyes. There would be a possibly other mechanisms involved that allow chlorophyll to work effectively. As green plants are abundant, and fallen leaves even more so, this will be an effective method to recycle fallen vegetative matter. The two-step method outlined in this study can be easily scaled to process larger quantities of vegetative matter, and when kept in a dark environment can easily keep for many months.

The adsorption of chlorophyll onto the TiO\(_2\) substrate should also be considered. Higher concentrations of chlorophyll may increase the degradation rate of the methylene blue to a certain point \[42\], which would require further study for optimization. The use of a higher concentration of chlorophyll would also prevent the adsorption of methylene blue onto the TiO\(_2\) surface \[52\], which would inhibit the photocatalytic rate of the pollutant.

One factor to consider in the degradation is the possible use of agitation within the photoreactor. In it is noted that the degradation route appears as steps and is not quite a linear degradation throughout the study. This is attributed to localized pockets of varying concentrations of methylene blue. As the dye is degraded over the reactor, the concentration of dye decreases, but without agitation or stirring the concentration in the beaker is not homogenous, which may affect degradation. Thus for future studies stirring, or a flow-through reactor will result in better performance of the photocatalyst.

Another factor that can cause this to happen would be the adsorption of the methylene blue on the TiO\(_2\) nanotubes prior to degradation. This is a lesser reason the performance of the photocatalysts drop after the first 30 min, where over 20% of the methylene blue was degraded from the solution. Self-degradation is a possible outcome in the event that there are no sacrificial electron donor, such as alcohols \[19\]. Due to inefficient electron flow or close proximity with the generated radicals, this results in photocatalytic degradation of the dye itself, which then provided local sites for the adsorption of methylene blue, subsequently it will sensitize TiO\(_2\) \[53\], albeit not as efficient as actual photosensitizers. S-NChl appears to have the most resistance to this and would potentially be an area of interest to be investigated further.

| Time (minute) | Temperature (°C) |
|---------------|------------------|
| 0             | 22.6             |
| 15            | 24               |
| 30            | 26               |
| 45            | 28               |
| 60            | 28.9             |
| 75            | 30               |
| 90            | 31               |
| 105           | 31.4             |
| 120           | 31.8             |
Conclusion

The use of dye sensitizers on TiO$_2$ was investigated for potential use as in a photocatalytic dye degradation system, here tested with methylene blue. The study showed that the concentration of methylene blue decreased to 40% of its initial concentration when degraded with extracted chlorophyll. The potential use of dye sensitization as a cost-effective photocatalysis is the key to effective recycling of waste vegetation and would be beneficial to an ecofriendly method of reduction in organic pollution when fully optimized.

Acknowledgments

The authors would like to gratefully thank Nippon Sheet Glass Foundation for Materials Science and Engineering, Japan for sponsoring this work under Account No.: 304/ PFIZIK/ 6501011/ N120. All support from Universiti Sains Malaysia (USM) is gratefully acknowledged.

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