Decolorization of Aqueous Solution Containing Organic Synthetic-Dye via Dark-Catalysis Process Using Hydrothermally Synthesized Semiconductor-Oxides Nanotubes

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The removal of an organic synthetic-dye from an aqueous solution via the adsorption and decolorization processes, typically occurring in the dark-condition on the surface of semiconductor-oxides nanotubes-based adsorbents, has been demonstrated for the first time without the use of any external power-source such as the radiation, potential-difference, microwave-generator, and ultrasonicator. “Two-step” and “one-step” dye-removal methods have been developed by utilizing the hydrothermally processed hydrogen titanate (H$_2$Ti$_3$O$_7$) and anatase-titania (TiO$_2$) nanotubes in combination with the strong oxidizer such as the hydrogen peroxide (H$_2$O$_2$). In the “two-step” dye-removal method, conducted in the dark-condition, the organic synthetic-dye is adsorbed from an aqueous solution on the surface of nanotubes and decolorized in another aqueous solution containing H$_2$O$_2$. In contrast to this, in the “one-step” dye-removal method, the simultaneous dye-adsorption and dye-decomposition (decolorization) take place in the dark-condition on the surface of nanotubes only in one aqueous solution containing H$_2$O$_2$. The comparison shows that the dye-removal rate-capacity in the “one-step” dye-removal method is ∼ 2–3 times higher relative to that in the “two-step” dye-removal method. In both the methods, the nanotubes recovered after the end of the first dye-removal cycle can be reused as catalyst for the multiple dye-removal cycles operating under the dark-condition. The underlying dye-removal mechanism is termed as “dark-catalysis” in which the presence of both the nanotubes and H$_2$O$_2$ has been shown to be an essential condition for the complete decolorization in the dark-condition. Due to its several benefits, the dark-catalysis mechanism appears to be a commercially viable process compared with the conventional photocatalysis mechanism.


1. INTRODUCTION

The organic synthetic-dyes are extensively used in various industries such as the textile, leather tanning, paper production, food technology, agricultural research, light-harvesting arrays, photo-electrochemical cells, and hair-coloring. Due to their large-scale production, extensive use, and subsequent discharge of colored waste-waters, the toxic and non-biodegradable organic synthetic-dyes cause considerable environmental pollution and health-risk factors. Moreover, they also affect the sunlight penetration and oxygen solubility in the water-bodies, which in turn affect the under-water photosynthesis activity and life-sustainability. In addition to this, due to their strong color even at lower concentrations, the organic synthetic-dyes generate serious aesthetic issues in the waste-water disposal. Therefore, the removal of highly stable organic synthetic-dyes from the industry effluents and aqueous solutions is of prime importance.

Photocatalysis has been the most promising technique for the removal of toxic organic synthetic-dyes from the industrial waste-water.$^1$ The nanocrystalline semiconductor titania (TiO$_2$) has been the most commonly applied photocatalyst since it is inexpensive, chemically stable, and its photo-generated holes and electrons are highly oxidizing and reducing for degrading the dye molecules present in an aqueous solution. In photocatalysis, the
semiconductor-oxide particles are dispersed in an aqueous dye solution which is then exposed to an external-radiation (ultraviolet (UV), visible, or solar) having energy comparable with the band-gap energy of the photocatalyst. The electron–hole pairs created within the particle volume, as a result of the radiation-exposure, travel to the particle surface and take part in the redox reactions generating the hydroxyl radicals (OH\(^{•−}\)) which attack and degrade the surface-adsorbed dye molecules. The traditional methods used for the separation of photocatalyst particles from the treated effluent such as the coagulation, flocculation, and sedimentation are tedious, expensive, and need critical process control.\(^2\) In order to ease the separation of TiO\(_2\)-based photocatalysts, the photocatalyst particles are coated on the surface of magnetic ceramic particles, known as the “magnetic photocatalyst,” which makes their separation from an aqueous solution possible using an external magnetic field.\(^3\) The major advantage of the conventional nanocrystalline TiO\(_2\)-based dye-removal technology is the recyclability of photocatalyst particles as their surfaces remain clean after the photocatalysis process. However, the radiation-exposure is required for the removal of organic synthetic-dye via the photocatalysis mechanism using the nanocrystalline TiO\(_2\)-based photocatalysts. Moreover, in order to make the photocatalyst suitable for the solar and visible-radiations, its band-gap energy is required to be tuned via dopants.\(^4\) These factors make the photocatalysis process relatively more hazardous and expensive.

Recently, the use of high surface-area nanotubes of hydrogen titanate (H\(_2\)Ti\(_3\)O\(_7\)) and anatase-TiO\(_2\) have been reported for the removal of organic synthetic-dyes from an aqueous solution via the surface-adsorption process involving the electrostatic attraction mechanism.\(^5\) The dye-removal is further aided by the ability of these nanotubes to exchange cations in the solution with the protons (H\(^{+}\)) present in their structure.\(^6\) Since these mechanisms operate effectively in the dark-condition (that is, without an exposure to the external-radiation (UV, visible, or solar)) and without any band-gap tuning requirement, these nanotubes provide a cost-effective approach for the removal of organic synthetic-dyes from an aqueous solution. To ease the separation of nanotubes with the surface-adsorbed dye using an external magnetic field, a “magnetic dye-adsorbent catalyst” has been recently developed.\(^7\) However, these nanotubes-based dye-adsorbents pose major problems in their recycling for the next cycle of dye-adsorption due to the difficulty in removing the previously adsorbed-dye from their surfaces which results in the major handling and disposal issues, and subsequently the secondary pollution. This has been a major hurdle in the commercialization of nanotubes-based adsorbents in the dye-removal application. Recently, in order to overcome these issues, the decomposition of organic synthetic-dyes via the voltage,\(^8,^9\) ultrasonicator,\(^8,^9\) and microwave\(^d\) induced dark/photo-catalysis has been reported. However, even these methods require an external energy-source for the decolorization/decomposition of an organic synthetic-dye in the dark-condition. From this point of view, in this article we demonstrate for the first time a new process conducted in the dark-condition involving the use of semiconductor-oxides nanotubes-based dye-adsorbents and a strong oxidizer which eliminates the need for an external power-source for the complete decolorization of an organic synthetic-dye in an aqueous solution. Moreover, a new technique for the recycling of semiconductor-oxides nanotubes-based dye-adsorbents is also demonstrated here for the first time.

2. EXPERIMENTAL DETAILS

2.1. Processing of H\(_2\)Ti\(_3\)O\(_7\) and Anatase-TiO\(_2\)

Nanotubes via Hydrothermal Method

The H\(_2\)Ti\(_3\)O\(_7\) and anatase-TiO\(_2\) nanotubes were processed via the hydrothermal method as demonstrated first by Kasuga et al.\(^5d\) and later modified by us.\(^5c,^d\) 3 g of as-received nanocrystalline anatase-TiO\(_2\) powder (Central Drug House (CDH) Laboratory (P) Ltd., New Delhi, India) was suspended in a highly alkaline aqueous solution containing 10 M sodium hydroxide (NaOH, Assay 97%, S.D. Fine-Chem Ltd., Mumbai, India) filled up to 84 vol.% of Teflon-beaker placed in a stainless-steel (SS 316) vessel of 200 ml capacity. The process was carried out with continuous stirring in an autoclave (Amarp Equipment Pvt. Ltd., Mumbai, India) at 120 °C for 30 h under an autogenous pressure. The autoclave was allowed to cool naturally to room temperature and the hydrothermal product was separated by decanting the top solution. The product was then washed using 100 ml of 1 M HCl solution (35 wt.% Ranbaxy Fine Chemicals Limited, India) for 1 h followed by washing using 100 ml of pure water for 1 h. The product obtained after the first washing-cycle was then subjected to the second washing-cycle. In this cycle, the product was washed once using 100 ml of 1 M HCl and then multiple times (8–9) using 100 ml of distilled water till the pH of filtrate became almost constant or neutral. The product was separated from the solution using a centrifuge (R23, Remi Instruments India Ltd.), dried in an oven at 80 °C overnight to obtain H\(_2\)Ti\(_3\)O\(_7\) nanotubes which were calcined at 400 °C for 2 h to obtain the anatase-TiO\(_2\) nanotubes.

2.2. Dye-Adsorption/Dye-Decomposition Measurements in the Dark

The dye-adsorption/dye-decomposition measurements were conducted via the “two-step” and “one-step” dye-removal methods by using the methylene blue (MB, > 96%, S.D. Fine-Chem Ltd., Mumbai, India) as a model catalytic dye-agent. In the “two-step” dye-removal method, Figure 1, 75 ml of aqueous solution containing 7.5 μM of MB dye was prepared. 0.4 g·l\(^{-1}\) of either H\(_2\)Ti\(_3\)O\(_7\) or anatase-TiO\(_2\) nanotubes were suspended in this solution and stirred in the dark-condition for total 3 h. 8 ml aliquots...
Fig. 1. The “two-step” dye-removal method, conducted in the dark-condition, using the hydrothermally processed nanotubes of H$_2$Ti$_3$O$_7$ or anatase-TiO$_2$. The step-1 (dye-adsorption) involves the hydrothermally processed nanotubes of H$_2$Ti$_3$O$_7$ or anatase-TiO$_2$ (a), the MB dye solution (b), the addition of nanotubes to the MB dye solution (c) (which is followed by stirring in the dark-condition for specific amount of time), the centrifuged and dried nanotubes with the surface-adsorbed MB dye (d). (c) and (d) are repeated to adsorb sufficient amount of MB dye on the surface of nanotubes. The step-2 (surface-cleaning treatment) involves $\sim$ 1 M H$_2$O$_2$ solution (e), the addition of nanotubes with the surface-adsorbed MB dye to the solution in (e) (f) (which is followed by stirring in the dark-condition for specific amount of time), and the centrifuged and dried (recovered) catalyst-powder (g) which is recycled (h) for the next-cycles of dye-adsorption conducted in the dark-condition.

were taken out after each successive 30 min time interval, centrifuged to separate the nanotubes, and the filtrates were used for obtaining the absorption spectra using the UV-visible absorption spectrophotometer (UV-2401 PC, Shimadzu, Japan) to determine the MB dye concentration remaining in the solution. The data was further used to calculate the amount of MB dye adsorbed on the surface of nanotubes using the following equations.

$$\% \text{MB adsorbed} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

which is equivalent of the form,

$$\% \text{MB adsorbed} = \left( \frac{A_0 - A_t}{A_0} \right) \times 100 \quad (2)$$

where, $A_0$, $A_t$ are the intensities of the main absorbance peak of MB dye solution located at 656 nm, and $C_0$, $C_t$ the corresponding MB dye concentrations in the solution at the start and after the contact time of $t$ respectively.

To prepare the nanotubes for the subsequent surface-cleaning treatment, the MB dye was adsorbed continuously for 3 h without the removal of aliquots. After the first-cycle of dye-adsorption in the dark-condition, the powder was separated from the solution using a centrifuge operated at 3000 rpm for 15 min and dried in an oven at 80 °C for 1 h. The dried-powder with the surface-adsorbed MB dye having blue-color was used for the next-cycle of dye-adsorption conducted for 3 h in the dark-condition. The entire sequence was repeated until sufficient amount of MB was adsorbed on the surface of nanotubes in the dark-condition. The dried-powder with the surface-adsorbed MB was then subjected to the surface-cleaning treatment to decompose the previously adsorbed-dye on the surface in the dark-condition. For this, the powder was suspended and stirred continuously for 1 h in 100 ml of 3 wt.% H$_2$O$_2$ (equivalent of $\sim$1 M H$_2$O$_2$) (Aldrich Chemicals, Bengaluru, India) solution in the dark-condition. The blue-colored catalyst-powder, which was obtained after the several cycles of MB dye-adsorption, was noted to become yellow in color which was then separated by using a centrifuge operated at 3000 rpm for 15 min, dried in an oven at 80 °C for 1 h, and then used for the next dye-adsorption cycle in the dark-condition.

In the “one-step” dye-removal method, Figure 2, 75 ml of $\sim$1 M H$_2$O$_2$ solution containing 7.5 µM of MB was first prepared. 0.4 g·l$^{-1}$ of either H$_2$Ti$_3$O$_7$ or anatase-TiO$_2$ nanotubes were suspended in this solution and stirred in the dark-condition for total 1 h. The aliquots were taken out after 10 min time interval, centrifuged to separate the nanotubes, and the filtrates were used for obtaining the absorption spectra to determine the MB dye concentration.
Decolorization of Aqueous Solution Containing Organic Synthetic-Dye via Dark-Catalysis Process

Babu et al.

ARTICLE

remaining in the solution, which further provided the amount of MB dye simultaneously adsorbed and decomposed on the surface of nanotubes. After the first-cycle of dye-decomposition in the dark-condition, the powder was separated from the solution using a centrifuge operated at 3000 rpm for 15 min and dried in an oven at 80 °C for 1 h. The dried yellow-color powder was then used for the next-cycle of simultaneous dye-adsorption and dye-decomposition in the dark-condition. (Note: The term “%MBadsorbed” in Eqs. (11) and (12) is to be replaced with “%MBdecomposed” for the “one-step” dye-removal method). In another set of experiments, the “one-step” dye-removal method was demonstrated and compared in pure H2O, ∼1 M H2O2 without and with the presence of hydrothermally processed anatase-TiO2 nanotubes.

3. RESULTS AND DISCUSSION

In the present work, the H2Ti3O7 and anatase-TiO2 nanotubes have been processed via the hydrothermal method. The mechanism of formation of nanotubes via this method has been already discussed in detail by us5c and others.6b Their use in the dye-removal application in the dark-condition via the surface-adsorption and ion-exchange mechanisms has also been reported.5 The maximum dye-adsorption capacity of 105 and 380 mg·g⁻¹ for the MB dye10 and basic green 5 (BG5)5c have been reported for the hydrothermally processed H2Ti3O7 nanotubes. The dye-adsorption on the surface of H2Ti3O7 nanotubes follows the pseudo-second-order kinetics model5f and the adsorption equilibrium follows either Langmuir or Dubinin–Kaganer–Radushkevich (DKR) isotherms depending on the initial solution-pH.10 Nevertheless, all these earlier reports lack in decomposing the previously adsorbed-dye on the surface of nanotubes especially in the dark-condition for recycling them as catalyst for the multiple dye-adsorption cycles conducted in the dark-condition. The “two-step” and “one-step” dye-removal processes are, hence, developed here in the dark-condition using the combination of nanotubes of H2Ti3O7 or anatase-TiO2 and the hydrogen peroxide (H2O2) which is a strong oxidizer.


3.1.1. H2Ti3O7 Nanotubes

The variation in the normalized surface-adsorbed MB dye concentration, obtained in the dark-condition using the H2Ti3O7 nanotubes, as a function of contact time is presented in Figure 3(a) for the different number of dye-adsorption cycles. It is observed that in the cycle-1, more than 98% MB adsorption is reached in just 30 min. Repeated dye-adsorption cycles are conducted, and after cycle-7, the MB dye adsorption is observed to be reduced to ∼80%. Total 1.211 mg of MB dye is adsorbed on the surface of H2Ti3O7 nanotubes in the dark-condition. In order to remove the previously adsorbed MB dye from the surface, the powder is subjected to the surface-cleaning treatment under the dark-condition in ∼1 M H2O2 solution. The surface-cleaned catalyst-powder is then used for the next cycle of dye-adsorption (cycle-8) as shown in Figure 3(b). It is seen that the surface-cleaned dye-adsorbent powder exhibits ∼95% of dye-adsorption under the dark-condition in just 30 min. Thus, the original dye-adsorption capacity is successfully restored in the “two-step” dye-removal method involving the dye-adsorption occurring under the dark-condition in one aqueous solution and dye-decomposition, also occurring under the dark-condition, in another aqueous solution. Since the total time required for conducting the “two-step” method is estimated to be 19.83 h (including the time required for the centrifuging and drying), the dye-removal rate-capacity (here defined as the amount of MB dye adsorbed and decomposed under the dark-condition in 1 h per unit mass of adsorbent) in the present case is calculated to be 2.14 mg·g⁻¹·h⁻¹.

The variation in the maximum normalized concentration of surface-adsorbed MB (at equilibrium), obtained in the dark-condition using the H2Ti3O7 nanotubes, as
Fig. 4. (a) Variation in the maximum normalized concentration of surface-adsorbed MB as a function of number of dye-adsorption cycles conducted in the dark-condition, obtained using the H₂Ti₃O₇ nanotubes. The arrow indicates the cycle-number after which the dye-adsorbent powder is subjected to the surface-cleaning treatment conducted in the dark-condition. (b) Variation in the color of H₂Ti₃O₇ nanotubes powder under the different conditions—as-synthesized (i); with the surface-adsorbed MB obtained after the cycle-number as marked by arrow in (a) (ii); and after subjecting the dye-adsorbent powder to the surface-cleaning treatment (iii) (“two-step” dye-removal method).

3.1.2. Anatase-TiO₂ Nanotubes

The variation in the normalized surface-adsorbed MB dye concentration, obtained in the dark-condition using the anatase-TiO₂ nanotubes, as a function of contact time is presented in Figure 5(a). The surface-cleaning treatment conducted in the dark-condition is applied after the cycle-7 as indicated by an arrow and its effect is clearly evident from the sudden increase in the amount of dye-adsorbed under the dark-condition in the following dye-adsorption cycle. The variation in the color of catalyst-powder, at the different stages, consisting of H₂Ti₃O₇ nanotubes is shown in Figure 5(b). The catalyst-powder is initially white and changes to dark-blue after the cycle-7 due to the surface-adsorption of sufficient amount of MB dye. After the surface-cleaning treatment, since the dye is decomposed on the surface of nanotubes, the powder-color is changed to yellow which exhibits very high dye-adsorption capacity comparable with the original white-color catalyst-powder.

Fig. 3. (a), (b) Variation in the normalized concentration of surface-adsorbed MB as a function of contact time obtained using the H₂Ti₃O₇ nanotubes for the different number of dye-adsorption cycles conducted in the dark-condition. In (b), the cycle-8 is obtained after subjecting the H₂Ti₃O₇ nanotubes, with the surface-adsorbed MB dye, to the surface-cleaning treatment conducted in the dark-condition (“two-step” dye-removal method).
Decolorization of Aqueous Solution Containing Organic Synthetic-Dye via Dark-Catalysis Process

Babu et al.

**ARTICLE**

![Graph](image)

**Fig. 5.** (a), (b) Variation in the normalized concentration of surface-adsorbed MB as a function of contact time obtained using the anatase-TiO$_2$ nanotubes for the different dye-adsorption cycles conducted in the dark-condition. In (b), the cycle-4 is obtained after subjecting the anatase-TiO$_2$ nanotubes with the surface-adsorbed MB to the surface-cleaning treatment conducted in the dark-condition (“two-step” dye-removal method).

![Graph](image)

**Fig. 6.** (a) Variation in the maximum normalized concentration of surface-adsorbed MB as a function of number of dye-adsorption cycles, conducted in the dark-condition, obtained using the anatase-TiO$_2$ nanotubes. The arrow indicates the cycle-number after which the dye-adsorbent powder is subjected to the surface-cleaning treatment conducted in the dark-condition. (b) Variation in the color of anatase-TiO$_2$ nanotubes powder under the different conditions— as-synthesized (i); with the surface-adsorbed MB obtained after the cycle-number as marked by arrow in (a) (ii); and after subjecting the dye-adsorbent powder to the surface-cleaning treatment (iii) (“two-step” dye-removal method).

3.2. “One-Step” Dye-Removal Method

3.2.1. H$_2$Ti$_3$O$_7$ Nanotubes

The variation in the normalized decomposed MB dye concentration, obtained in the dark-condition using the...
H$_2$Ti$_3$O$_7$ nanotubes, as a function of contact time for the different number of dye-decomposition cycles is presented in Figure 7. It is observed that in the cycle-1, $\sim100\%$ MB decomposition is reached in just 10 min which is retained for 8 successive cycles of simultaneous dye-adsorption and dye-decomposition in the dark-condition. After the cycles-9 and 10 (latter is not shown in Fig. 7 for clarity), the decomposition of MB dye is observed to be reduced to $\sim86$–$88\%$. At the end of cycle-10, total 1.744 mg of MB dye is simultaneously adsorbed and decomposed on the surface of H$_2$Ti$_3$O$_7$ nanotubes. Since the total time required for conducting the “one-step” method is estimated to be 15.83 h (including the time required for the centrifuging and drying), the dye-removal rate-capacity in the present case is estimated to be 3.67 mg·g$^{-1}$·h$^{-1}$. Thus, the comparison shows that, for the H$_2$Ti$_3$O$_7$ nanotubes, the dye-removal rate-capacity in the dark-condition obtained via the “one-step” dye-removal method is $\sim1.7$ times higher than that obtained via the “two-step” dye-removal method.

The variation in the maximum normalized decomposed MB dye concentration (at equilibrium) as a function of number of dye-decomposition cycles is presented in Figure 8(a). The amount of MB dye decomposed is clearly seen to decrease below 100% only after the cycle-8. The variation in the original white-color of H$_2$Ti$_3$O$_7$ nanotubes catalyst-powder after each successive dye-decomposition cycle in a “one-step” dye-removal method is presented in Figure 8(b). It is seen that the original white-color of catalyst-powder changes to pale-yellow after the cycles-1 and 2 which further changes to grayish-yellow for each successive cycle. The blue-color as observed in the “two-step” dye-removal method, Figure 4(b), is not observed in the “one-step” dye-removal method due to the simultaneous dye-adsorption and dye-decomposition on the surface of H$_2$Ti$_3$O$_7$ nanotubes occurring under the dark-condition in $\sim1$ M H$_2$O$_2$ solution.

### 3.2.2. Anatase-TiO$_2$ Nanotubes

The variation in the normalized decomposed MB dye concentration, obtained in the dark-condition using the anatase-TiO$_2$ nanotubes, as a function of contact time is presented in Figure 9 for the different number of dye-decomposition cycles. It is observed that in the cycle-1, $\sim100\%$ MB decomposition is reached in just 10 min which is retained for three successive cycles of simultaneous dye-adsorption and dye-decomposition in the dark-condition. After the cycles-4 and 5 (latter is not shown in Fig. 9 for clarity), the MB dye decomposition is observed to be reduced to $\sim78$–$79\%$. At the end of cycle-5, total 0.8226 mg of MB dye is simultaneously adsorbed and decomposed on the surface of anatase-TiO$_2$ nanotubes. Since the total time required for conducting the “one-step” method is estimated to be 7.92 h (including the time required for the centrifuging and drying), the dye-removal rate-capacity in the present case is calculated to be...
Decolorization of Aqueous Solution Containing Organic Synthetic-Dye via Dark-Catalysis Process

Babu et al.

3.46 mg·g⁻¹·h⁻¹. Hence, the comparison shows that for the anatase-TiO₂ nanotubes, the dye-removal rate-capacity obtained via the “one-step” method is almost ∼ 2.9 times higher than that obtained via the “two-step” method.

The variation in the maximum normalized decomposed MB dye concentration (at equilibrium) as a function of number of dye-decomposition cycles is presented in Figure 10(a). The amount of MB dye simultaneously adsorbed and decomposed is clearly seen to decrease below 100% after the cycle-3. The variation in the original white-color of anatase-TiO₂ nanotubes powder under the different conditions—as-synthesized (i); cycle-2 to cycle-5 involving the simultaneous dye-adsorption and dye-decomposition in the dark-condition (ii)-(v) (“one-step” dye-removal method).

when ∼ 1 M H₂O₂ solution is utilized to form the suspension instead of pure H₂O. Hence, the presence of H₂O₂ is seen to enhance the rate of MB degradation in the dark-condition. However, in the presence of both anatase-TiO₂ nanotubes and ∼ 1 M H₂O₂, the complete dye-decomposition is achieved in just 10 min of contact time. This strongly suggests that the presence of both anatase-TiO₂ nanotubes and H₂O₂ is essential for achieving very high kinetics of MB dye decomposition in the dark-condition.

3.3. Mechanism of Dye-Decomposition in “Two-Step” and “One-Step” Dye-Removal Methods in the Dark-Condition

As demonstrated above the MB dye, which is cationic in an aqueous solution,¹¹ can be easily adsorbed on the surface of hydrothermally processed H₂Ti₃O₇ and anatase-TiO₂ nanotubes and decolorized under the dark-condition in the presence of H₂O₂ which is a strong oxidizer. The dye-adsorption and dye-decomposition (or decolorization) processes can be conducted either in two different steps or combined in a single-step. It is known that with the use of an external power-source such as the radiation-exposure (UV, sunlight, or visible) and potential-difference, an organic synthetic-dye such as MB can be degraded in an aqueous solution under the attack of OH⁻ which are formed on the surface of TiO₂.⁸ᵃ,⁸ᵇ,¹¹

\[
\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+ + 102\text{OH}^- \rightarrow 16\text{CO}_2 + 3\text{NO}_3^- + \text{SO}_4^{2-} + 6\text{H}^+ + 57\text{H}_2\text{O} \quad (3)
\]

Under these conditions, the electron–hole pairs are effectively generated within the semiconductor-oxide particles.

\[
\text{TiO}_2 \xrightarrow{\text{UV/Sunlight/Voltage}} e^- + h^+ \quad (4)
\]
The OH\(^{-}\) required for the degradation of MB dye, Eq. (3), are produced by the reactions of photo- or voltage-induced holes and electrons with the hydroxyl-ions, dissolved O\(_2\), and H\(_2\)O\(_2\), Eqs. (5)–(10).\(^{12}\)

\[
\begin{align*}
\text{OH}^{-} + h^{+} & \xrightarrow{\text{H}_2\text{Ti}_3\text{O}_7/\text{TiO}_2} \text{OH}^{\cdot} \quad \text{(5)} \\
\text{O}_2 + e^{-} & \xrightarrow{\text{H}_2\text{Ti}_3\text{O}_7/\text{TiO}_2} \text{O}^{2-} \quad \text{(6)} \\
\text{O}^{2-} + 2\text{H}^{+} + e^{-} & \xrightarrow{\text{H}_2\text{Ti}_3\text{O}_7/\text{TiO}_2} \text{H}_2\text{O}_2 \quad \text{(7)} \\
\text{H}_2\text{O}_2 + e^{-} & \xrightarrow{\text{H}_2\text{Ti}_3\text{O}_7/\text{TiO}_2} \text{OH}^{\cdot} + \text{OH}^{\cdot} \quad \text{(8)} \\
\text{H}_2\text{O}_2 + \text{O}_2 & \xrightarrow{\text{H}_2\text{Ti}_3\text{O}_7/\text{TiO}_2} \text{OH}^{\cdot} + \text{OH}^{\cdot} + \text{O}_2 \quad \text{(9)}
\end{align*}
\]

The OH\(^{\cdot}\) can also be produced by directly breaking the H\(_2\)O\(_2\) (internally generated or externally added) bonds via the absorption of microwave-energy\(^{6d}\) and UV-radiation having the wavelength below 254–300 nm.\(^{12a, 12c}\)

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{microwave/UV} \leq 254 \text{ nm}} 2\text{OH}^{\cdot} \quad \text{(10)}
\]

In this work, however, the use of any external power-source is not involved in both the methods of dye-removal. As a result, these mechanisms are not sequentially applicable for the degradation of MB dye in the dark-condition by using the combination of hydrothermally processed H\(_2\)Ti\(_3\)O\(_7\) and anatase-TiO\(_2\) nanotubes with H\(_2\)O\(_2\).

Moreover, the generation of OH\(^{-}\) in the dark-condition via the self-decomposition of H\(_2\)O\(_2\), Eq. (10), using the sonocatalytic process, and hence, the subsequent degradation of MB dye under these test-conditions have been demonstrated.\(^{8c}\) It has been further shown that the addition of both the hydrothermally processed nanotubes and H\(_2\)O\(_2\) can enhance the sonocatalytic dye-degradation efficiency. These results strongly suggest the possibility that the organic synthetic-dye such as the MB can be decomposed in the dark-condition using the combination of hydrothermally processed nanotubes and H\(_2\)O\(_2\) without the involvement of sonocatalytic process (and any other external power-source). Although not evident from the available report,\(^{8c}\) this has been successfully demonstrated in this investigation. To justify this further, in the present investigation, the decomposition of MB dye is examined under the dark-condition in pure H\(_2\)O and ~1 M H\(_2\)O\(_2\) solution without and with the presence of hydrothermally processed anatase-TiO\(_2\) nanotubes, Figure 11, without the involvement of any external power-source. In pure H\(_2\)O, the degradation kinetics of MB dye in the dark-condition is observed to be the slowest due to very low kinetics of the generation of superoxide-ions, Eq. (11), involving the chloride-ions (originating from the MB dye molecules) as the reducing agent.\(^{13}\)

\[
2\text{O}_2 + 2\text{Cl}^{-} \rightarrow 2\text{O}_2^{\cdot} + \text{Cl}_2 \quad \text{(11)}
\]

The OH\(^{\cdot}\) are then generated in pure H\(_2\)O via Eqs. (7)–(9) in the absence of both the hydrothermally processed nanotubes and externally added H\(_2\)O\(_2\). Equation (9) suggests that the presence of H\(_2\)O\(_2\) and superoxide-ions (O\(_2^{\cdot}\)) in substantial amount is essential for the rapid generation of OH\(^{-}\), and hence, for the rapid decomposition of MB dye in the dark-condition. As a result, compared with pure H\(_2\)O solution, an increased MB degradation kinetics is observed in ~1 M H\(_2\)O\(_2\) solution under the dark-condition, Figure 11. The MB degradation kinetics in the dark-condition is noted to be improved significantly with the addition of anatase-TiO\(_2\) nanotubes in ~1 M H\(_2\)O\(_2\) solution which strongly suggests that the activation of H\(_2\)O\(_2\) in the presence of hydrothermally processed nanotubes is possibly a result of latter acting as the source of superoxide-ions. Since the nanotubes of anatase-TiO\(_2\) (and also H\(_2\)Ti\(_3\)O\(_7\)) exhibit higher specific surface-area, they possibly possess large concentration of superoxide-ions (O\(_2^{\cdot}\) or O\(^{-}\)) on their surfaces, Eq. (12), which also provide a negative surface-charge to adsorb large quantity of cationic MB dye from an aqueous solution in the dark-condition.\(^{14}\)

\[
\text{O}_2 + V_o + e^{-} \xrightarrow{\text{H}_2\text{Ti}_3\text{O}_7/\text{TiO}_2} \text{O}_2^{\cdot} \quad \text{(12)}
\]

where \(V_o\) is the oxygen-ion vacancy. The point of zero-charge of H\(_2\)Ti\(_3\)O\(_7\) nanotubes, anatase-TiO\(_2\) nanotubes, and anatase-TiO\(_2\) nanoparticles has been reported to be 3.1–3.9,\(^{15b}\) 5.3,\(^{15b}\) and 5.9–6.5,\(^{14c, 15c, 15d}\) which further supports relatively higher negative charge present on the surface of both the nanotubes relative to that present on the surface of nanoparticles. In the case of H\(_2\)Ti\(_3\)O\(_7\) nanotubes, the negative surface-charge has been attributed to the dissociation of H\(_2\)Ti\(_3\)O\(_7\) to H\(^{+}\) and HTi\(_3\)O\(_7^{\cdot}\). Since the formation of HTi\(_3\)O\(_7^{\cdot}\) is not possible in the case of anatase-TiO\(_2\) nanotubes, it appears that the formation of superoxide-ions is responsible in creating the negative surface-potential for the anatase-TiO\(_2\) nanotubes which also has its own contribution in the case of H\(_2\)Ti\(_3\)O\(_7\) nanotubes. This also explains lower point of zero-charge as reported for the H\(_2\)Ti\(_3\)O\(_7\) nanotubes compared with that reported for the anatase-TiO\(_2\) nanotubes. Secondly, according to Eq. (7), if an excess H\(_2\)O\(_2\) is externally added, then the reverse reaction would be favored than the forward reaction in the presence of hydrothermally processed nanotubes. This in turn would produce large concentration of O\(_2^{\cdot}\) ions within the solution as required for the effective production of OH\(^{-}\), Eq. (9). As a consequence, during the surface-cleaning treatment of “two-step” dye-removal method and the simultaneous dye-adsorption and dye-decomposition in the “one-step” dye-removal method, the concurrent presence of hydrothermally processed nanotubes and H\(_2\)O\(_2\) provides the most optimum condition for the rapid degradation of MB dye in the dark-condition through the generation and direct attack of O\(_2^{\cdot}\) ions (and also possibly the attack of OH\(^{-}\) radicals). Since after the dye-decomposition essentially in the dark-condition, the nanotubes can be recycled in both the “two-step” and “one-step” dye-removal methods, we term the underlying...
mechanism of dye-removal in these two methods as the “dark-catalysis.” The calculations suggest that the dye-removal rate-capacity in the “one-step” dye-removal method is ~2–3 times higher relative to that in the “two-step” dye-removal method. This is attributed here to the combined effect of simultaneous dye-adsorption and dye-decomposition occurring in one aqueous solution and relatively less centrifuging and drying time in the case of “one-step” dye-removal method. Secondly, the H₂Ti₃O₇ nanotubes show better performance relative to that of anatase-TiO₂ nanotubes in the dye-removal via both the methods of dark-catalysis process. This is attributed to the possible presence of relatively larger concentration of superoxide-ions on the surface of former due to their higher specific surface-area (264–330 m²·g⁻¹) tougher than that (184 m²·g⁻¹) of latter as the anatase-TiO₂ nanotubes have been derived via the calcination treatment of H₂Ti₃O₇ nanotubes. Although the aqueous solution containing an organic synthetic-dye has been decolorized by utilizing the dark-catalysis mechanism, it would be essential to confirm the complete dye-degradation into CO₂, water, and harmful ions via the measurements of the removal of chemical oxygen demand (COD) and total organic content (TOC). Nevertheless, considering the fact that both the dark-catalysis methods do not involve the use of any external power-source (such as the radiation, potential-difference, microwave-generator, or ultrasonicator) and the nanotubes can be reused for the next dye-adsorption and dye-decomposition cycles operating in the dark-condition, it appears that these are commercially more viable methods for the removal of organic synthetic-dyes from the industry effluents as well relative to the conventional photocatalysis mechanism when compared on the basis of simplicity, effectiveness, cost, energy-saving, and safety.

4. CONCLUSIONS

"Two-step" and “one-step” dye-removal methods have been successfully developed for the adsorption and decomposition of MB dye in the dark-condition using the combination of hydrothermally processed nanotubes of H₂Ti₃O₇ and anatase-TiO₂ with H₂O₂ which is a strong oxidizer. In the “two-step” dye-removal method, the dye is adsorbed on the surface of nanotubes in one aqueous solution under the dark-condition and the surface-adsorbed dye is decomposed, also under the dark-condition, in another aqueous solution containing H₂O₂. In the “one-step” dye-removal method, the MB dye is simultaneously adsorbed and decomposed in the dark-condition on the surface of nanotubes only in one aqueous solution containing H₂O₂. It is shown that the presence of both the hydrothermally produced nanotubes (as the source of superoxide-ions) and H₂O₂ is essential for the complete decomposition of MB dye in the dark-condition through the attack of OH radicals generated via the reaction between O₂ and H₂O₂. Due to its several benefits in terms of simplicity, effectiveness, cost, energy-saving, and safety, the dark-catalysis mechanism has a strong potential for the commercialization in the near-future compared with the conventional photocatalysis mechanism.

Acknowledgments: Authors thank CSIR, India for the financial support through the projects #P81113, OLP216339, and NWP0010.

References and Notes


