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Predicting dye-adsorption capacity of hydrogen titanate nanotubes via one-step dye-removal method of novel chemically-activated catalytic process conducted in dark

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The dye-adsorption capacity of various adsorbents has been traditionally determined via conducting the equilibrium dye-adsorption/desorption experiments. We demonstrate here a new method for precisely predicting the dye-adsorption capacity of hydrothermally processed semiconductor-oxide nanotubes, such as the hydrogen titanate, which involves the use of one-step dye-removal method of novel chemically-activated catalytic process conducted in the dark. The methylene blue (MB) dye-adsorption capacity of hydrogen titanate nanotubes has been determined to be 121 mg g⁻¹ via the conventional method which is comparable with that (114 mg g⁻¹) predicted via the one-step dye-removal method of novel chemically-activated catalytic process conducted in the dark. The equilibrium MB adsorption on the surface of hydrogen titanate nanotubes follows both the Langmuir and Freundlich isotherms and the pseudo-second-order kinetics at the initial solution-pH of ~10 although the amount of surface-coverage by the MB dye supports only the Langmuir model.

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Introduction

Photocatalysis is a well-known technique for the removal of highly stable organic synthetic-dyes from the aqueous solutions and industry waste-waters [1-5]. The major advantage of conventional nanocrystalline titania (TiO₂)-based photocatalysts in the dye-removal technology is the recyclability as their surfaces remain clean after the photocatalytic process. However, the photocatalytic process has been associated with the several drawbacks such as the need for the radiation-exposure, requirement of both longer radiation-exposure time typically for the highly concentrated dye-solutions and the tuning of band-gap energy for the utilization of visible-light, and the difficulties in the separation of photocatalyst particles from the treated solution due to their non-magnetic nature. These factors make the photocatalytic process relatively more expensive and hazardous which in turn produce further issues during the commercialization of this conventional technology.

To overcome the limitations of photocatalysis mechanism, a new dye-removal technology based on the chemically-activated catalytic process conducted in the dark (that is, without any radiation-exposure) has been recently developed which involves the two-step and one-step dye-removal methods [6]. In the two-step dye-removal method, the organic synthetic-dye is adsorbed on the surface of hydrothermally processed semiconductor-oxides nanotubes (such as the hydrogen titanate (H₂Ti₃O₇, HTN) and anatase-TiO₂ (ATN)) in the dark and decomposed in another aqueous solution, also in the dark, containing a strong oxidizer such as the hydrogen peroxide (H₂O₂). In contrast to this, in the one-step dye-removal method, Scheme 1, the organic synthetic-dye is simultaneously adsorbed and decomposed, under the dark, on the surface of hydrothermally processed semiconductor-oxides nanotubes in the presence of a strong oxidizer such as H₂O₂. In both the methods of chemically-activated catalytic process conducted in the dark, the dye-decomposition in an aqueous solution takes place in the dark which is in contrast to the photocatalytic dye-degradation which involves the radiation-exposure for the dye-degradation.

At present, for the one-step dye-removal method of novel chemically-activated catalytic process conducted in the dark, the effect of initial H₂O₂ concentration on the amount of dye-decomposed in the dark has not been investigated in the literature. Moreover, the dye-adsorption capacity of semiconductor-oxides nanotubes has never been predicted using the one-step...
dye-removal method of novel chemically-activated catalysis process conducted in the dark. In view of this, the major goals of this investigation have been set to study systematically the effect of initial \( \text{H}_2\text{O}_2 \) concentration on the amount of dye-decomposed in the dark and to predict the demonstration of dye-adsorption capacity of semiconductor-oxide nanotubes, such as the HTN, via the one-step dye-removal method of novel chemically-activated catalytic process conducted in the dark by comparing the obtained data with that obtained using the conventional equilibrium adsorption/decomposition method.

## Materials and methods

### Chemicals

Titanium(IV)-isopropoxide (\( \text{Ti(OC}_3\text{H}_7)\text{Cl} \), 97%) and hydrogen peroxide (\( \text{H}_2\text{O}_2 \), 3 wt.%) were purchased from Sigma-Aldrich Chemicals, Bengaluru, India; ammonium hydroxide (\( \text{NH}_4\text{OH} \), 25 wt.%) from Qualigens Fine Chemicals, India; hydrochloric acid (\( \text{HCl} \), 35 wt.%, Ranbaxy Fine Chemicals Ltd., India); \( \text{H}_2\text{O}_2 \) (30 and 50 wt. %), 2-propanol (99.5%, ACS reagent), sodium hydroxide (\( \text{NaOH} \), Assay 97%), and methylene blue (MB, 96%) from S.D. Fine-Chem Ltd., Mumbai, India. Unless otherwise stated, all chemicals were used as-received without any further purification and/or modification.

### Preparation of dye-adsorbent catalyst

The nanocrystalline anatase-\( \text{TiO}_2 \) powder was synthesized via the sol–gel process using the hydrolysis and condensation of \( \text{Ti(OC}_3\text{H}_7)\text{Cl} \) in an alcohol medium [7–9]. The R’ value (defined as the ratio of molar concentration of water to that of alkoxide-precursor in the final solution) of 90 was selected for the present experiment [8,9]. The nanocrystalline anatase-\( \text{TiO}_2 \) obtained via the sol–gel process is used as a precursor for the hydrothermal processing of HTN.

During the hydrothermal processing, 3 g of nanocrystalline anatase-\( \text{TiO}_2 \) powder (which contains small amount of rutile-\( \text{TiO}_2 \) as shown later) was suspended in a highly alkaline aqueous solution containing 10 M \( \text{NaOH} \) 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 (Amar 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 separated from the remaining solution using a centrifuge (R23, Remi Instruments India Ltd., Mumbai, India) and washed using 100 ml of 1 M HCl solution for 1 h followed by washing using 100 ml of distilled-water for 1 h. The product obtained after the first washing-cycle was then subjected to the second washing-cycle. In the latter, 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 (Hanna HI 2210 Bench pH Meter, Aldrich Labware, Bengaluru, India) of filtrate became almost constant or neutral. The product was separated from the solution using a centrifuge and dried in an oven at 80 °C overnight to obtain HTN as the final hydrothermal product.

### Characterization

The morphologies of sol–gel and final hydrothermal products were examined using the transmission electron microscope (TEM, Tecnai G2, FEI, The Netherlands) operated at 300 kV. The crystallinity of different samples was confirmed via the selected-area electron diffraction (SAED) technique. The crystalline phases of different samples were determined via the X-ray diffraction (XRD, PW1710 Phillips, The Netherlands) using the CuKα (\( \lambda_{\text{Cu}} = 1.542 \) Å) X-radiation. The obtained patterns were utilized to determine the weight-fraction of rutile-\( \text{TiO}_2 \) using the equation:

\[
\text{Rutile-}\text{TiO}_2 \text{ (wt.%) = } \frac{I_{110 R}}{I_{110 R} + 0.8 I_{101 A}} \times 100
\]

where, \( I_{110 R} \) and \( I_{101 A} \) represent the linear-intensities of main-peaks of anatase-\( \text{TiO}_2 \) \( (101)_A \) and rutile-\( \text{TiO}_2 \) \( (110)_R \). The specific surface-area of final product was measured using the Brunauer, Emmett, and Teller (BET) surface-area measurement technique (Microetrics Gemini 2375 Surface Area Analyzer, U.S.A.) via nitrogen (\( \text{N}_2 \)) adsorption using the multi-point method after degassing the nanocrystalline \( \text{TiO}_2 \) powders in flowing \( \text{N}_2 \) at 200 °C for 2 h.

**Determination of dye-adsorption capacity via both one-step method of novel chemically-activated catalytic process conducted in dark and conventional equilibrium dye-adsorption/decomposition experiments**

In the one-step dye-removal method, 125 ml of \( \text{H}_2\text{O}_2 \) solution (with the initial concentration varying in the range of 3–50 wt.%) containing MB dye (with the initial concentration varying in the range of 30–1000 \( \mu \)M) was first prepared. (Note: 15 wt. % \( \text{H}_2\text{O}_2 \) solution was prepared via the dilution method. Moreover, 3, 15, 30, and 50 wt.% \( \text{H}_2\text{O}_2 \) approximately correspond to 1, 5, 10, and 16.7 M of \( \text{H}_2\text{O}_2 \), respectively, and the ratio of molar concentrations of MB and \( \text{H}_2\text{O}_2 \) is within the range of \( 1.8 \times 10^{-6} \) to \( 1.0 \times 10^{-3} \).) 0.4 g L\(^{-1}\) of HTN was suspended in this solution and stirred in the dark for total 1 h. (Note: Although the solution-pH is slightly decreased within the first 10–20 min of contact time, it remains constant thereafter within the range of 3.7–0.96 for the initial \( \text{H}_2\text{O}_2 \) concentration within the range of 3–50 wt.% as typically observed for the initial MB concentration of 150 \( \mu \)M.) The aliquots were taken after 10 min time interval and centrifuged to separate the nanotubes. (Note: In order to overcome the problem of separation, a magnetic dye-adsorbent catalyst (analogous to magnetic photocatalyst), has been recently developed which consists of the “core–shell” particles with the core of a magnetic ceramic particle and the shell of nanotubes [10]. Such a magnetic dye-adsorbent catalyst can be separated from the treated aqueous solution using an external magnetic field after the dye-adsorption/decomposition process.)
calculate time concentrations solution decomposed where, The of UV-2401 1982 % equations: MBdecomposed MB ¼ A t 0, of PC, Shimadzu, Japan) show, the remaining images the corresponding SAED patterns. Typical TEM images of nanocrystalline anatase-TiO₂ (a) and HTN (b). The insets show the corresponding SAED patterns.

process.) The filtrates were used for obtaining the absorption spectra using the UV–vis absorption spectrophotometer e(UV–2401 PC, Shimadzu, Japan) to determine the concentration of MB dye remaining in the solution. The data was further used to calculate the amount of MB dye simultaneously adsorbed and decomposed on the surface of nanotubes using the following equations:

\[ \%MB_{\text{decomposed}} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \]  \hspace{1cm} (2)

which is equivalent of the form,

\[ \%MB_{\text{decomposed}} = \left( \frac{A_0 - A_t}{A_0} \right) \times 100 \]  \hspace{1cm} (3)

where, \( A_0 \) and \( A_t \) are the intensities of 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 beginning and after the contact time of \( t \), respectively. The obtained data was then analyzed to determine the dye-degradation rate-capacity (\( \frac{\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}}{} \)) for a given initial H₂O₂ concentration defined as the amount of dye simultaneously adsorbed and decomposed in the dark per unit gram of catalyst per unit hour of contact time. The data was further analyzed to predict the dye-adsorption capacity of HTN.

The blank experiments (that is, the dye-decomposition experiments conducted under the dark in the presence of H₂O₂ but without the addition of catalyst) were conducted typically for the initial MB concentration of 150 μM. All other experimental conditions were similar to those described above. Under these conditions, Eqs. (2) and (3) provide the amount of MB decomposed as a result of H₂O₂ only (that is, the bleaching effect of H₂O₂). The equilibrium dye-adsorption/desorption experiments were also conducted in the dark which were also similar to those described above except that the H₂O₂ solution was replaced with distilled-water having the initial solution-pH of ~10 adjusted using the NH₄OH solution. Under these conditions, Eqs. (2) and (3) provide the amount of MB adsorbed on the surface of catalyst.

Results and discussion

Morphological and structural analyses

The TEM images of sol–gel derived precursor and the final hydrothermal product are shown in Fig. 1a and b. Although the sol–gel derived precursor consists of nanoparticles of average size of ~25 nm, the morphology of final hydrothermal product is confirmed to be the nanotube. The corresponding SAED patterns, shown as insets in Fig. 1a and b, exhibit a concentric ring patterns which are identified to be those of anatase-TiO₂ and H₂TiO₄.[8,11] The XRD patterns of sol–gel and hydrothermal products are presented in Fig. 2a and b. The XRD pattern of sol–gel derived precursor, Fig. 2a, consists of the peaks of anatase-TiO₂ and small amount (15 wt.%) of rutile-TiO₂ which are identified after comparing the obtained patterns with the JCPDS card numbers 21-1272 and 21-1276. The XRD pattern of final hydrothermal product, Fig. 2b, consists of the peaks of H₂TiO₄[12] and small amount of untransformed rutile-TiO₂. The amount of rutile-TiO₂ in the final hydrothermal product is calculated to be 11 wt.%. (Note: Since the rutile-TiO₂ does not take part in the dye-adsorption and dye-decomposition processes conducted in the dark, for the purpose of calculations, its actual mass is subtracted from the total mass of catalyst used to obtain the mass of HTN. Hence, unless otherwise stated, hereafter the final hydrothermal product is assumed to be consisting of only the HTN.) The N₂ adsorption/desorption curves obtained using the final hydrothermal product

![Fig. 1](image1.png)

![Fig. 2](image2.png)
are shown in Fig. 3 which suggest its mesoporous nature further supporting its nanotube morphology. The specific surface area of final hydrothermal product is estimated to be 288 m² g⁻¹. Thus, the final hydrothermal product primarily consists of a high surface area mesoporous HTN mixed with the small amount of nanocrystalline particles of rutile-TiO₂.

Prediction and confirmation of dye-adsorption capacity

The proposed mechanism of dye-decomposition in the dark using the H₂Ti₃O₇ nanotubes as catalyst and H₂O₂ as a strong oxidizer involves the generation of superoxide-ions (O₂⁻) and hydroxyl radicals (OH*) in the dark which attack and decompose the dye adsorbed on the surface of nanotubes [6].

\[
H_2O_2 \xrightarrow{H_2Ti_3O_7} O_2^- + 2H^+ + e^- \tag{4}
\]

\[
H_2O_2 + O_2 \xrightarrow{H_2Ti_3O_7} OH^* + OH^- + O_2 \tag{5}
\]

(Note: Due to the generation of O₂⁻ and OH* in the presence of H₂O₂ and a catalyst without the radiation-exposure, the novel chemically-activated catalytic process conducted in the dark can be classified as either advanced oxidation process (AOP) (Fenton-like system) or catalytic wet peroxide oxidation (CWPO) process [13,14]. As a result, the surface of nanotubes remains clean after the dye-decomposition process conducted in the dark and can be recycled for the successive cycles of dye-decomposition. The catalytic nature of HTN has been demonstrated earlier via conducting the several successive cycles of dye-decomposition. The catalytic nature of HTN has been demonstrated earlier via conducting the several successive cycles of dye-decomposition in the dark [6]. Since the solution-pH remains constant in an acidic region during the dye-decomposition via the one-step method of novel chemically-activated catalytic process conducted in the dark, within the investigated range of initial H₂O₂ concentration, it presently appears that the dye-decomposition predominantly takes place via the generation and attack of O₂⁻ ions rather than that of OH*.

The variation in the normalized MB concentration, simultaneously adsorbed and decomposed in the dark, as a function of contact time is presented in Fig. 4a–d for the initial MB and H₂O₂ concentrations varying in the range of 30–1000 μM and 3–50 wt.% In general, for a given initial H₂O₂ concentration, higher degradation kinetics is observed at lower initial MB concentrations and the former is noted to decrease with increase in the latter. With the increasing initial H₂O₂ concentration, the MB degradation kinetics is noted to increase; that is, the curves simultaneously tend to shift.

![Graph showing nitrogen adsorption/desorption isotherms](image)

**Fig. 3.** Nitrogen adsorption/desorption isotherms obtained using the HTN.

![Graph showing MB decomposed](image)

**Fig. 4.** Variation in the normalized concentration of MB decomposed in the dark as a function of contact time for the different initial H₂O₂ concentrations – 3 (a), 15 (b), 30 (c), and 50 wt.% (d). The initial MB concentration is varied as 30 (i), 60 (ii), 90 (iii), 150 (iv), 200 (v), 250 (vi), 500 (vii), 750 (viii), and 1000 μM (ix).
upwards and to left-side for a given initial H2O2 concentration with the increasing initial H2O2 concentration. The blank experiments (that is, the dye-decomposition experiments typically conducted, under the dark in the presence of H2O2 but without the addition of catalyst, for the initial MB concentration of 150 μM with the initial H2O2 concentration varying in the range of 3–50 wt.%) suggest that, within its investigated range of initial concentration, H2O2 has no bleaching effect on the MB dye. Moreover, no other chemical reagents, such as catalase, sodium hypochlorite, sodium thiocyanate and sodium sulfite, have been added externally which can quench the H2O2 [15]. As a result, in the present case, the only quenching (consumption) of H2O2 is due to the presence of a catalyst which generates the O2•− and OH• in the dark which in turn attack and decompose the dye adsorbed on the surface of nanotubes. It is believed that the quenching of H2O2 by the catalyst via Eqs. (4) and (5) would reduce the bleaching effect of H2O2 if the latter is present in the system. However, since the bleaching effect of H2O2 is not observed in the absence of catalyst, the dye-decomposition data presented in Fig. 4 is directly used to obtain the variation in the normalized MB concentration simultaneously adsorbed and decomposed in the dark, typically after 1 h of contact time, as a function of initial MB concentration, Fig. 5. It is noted that the amount of MB decomposed in the dark after 1 h of contact time is 100% for lower range of initial MB concentration independent of initial H2O2 concentration. Although the former is noted to decrease below 100% typically in higher range of initial MB concentration for a given initial H2O2 concentration, the critical value of initial MB concentration at which the drop begins is noted to shift to higher values with the increasing initial H2O2 concentration. As a result, for the initial H2O2 concentration of 50 wt.%, the MB decomposition is almost 100% for the entire initial MB concentration range investigated here. Hence, 50 wt.% appears to be the most suitable initial H2O2 concentration for decomposing the MB, under the dark, in a highly concentrated aqueous dye-solution.

The data presented in Figs. 4 and 5 is further utilized to calculate the amount of MB simultaneously adsorbed and decomposed in the dark per unit mass of HTN per unit hour q’ (mg g−1 h−1) for a given initial H2O2 concentration, using the equation of form:

\[ q' = \frac{(C_0 - C_t) \times V}{m_{HTN} \times t} \]

where, C_t (mg L−1) is the MB concentration within the solution at the contact time of t=1 h. (Note: if the dye is decomposed completely in less than 1 h, then t corresponds to the contact time (in hours) at which 100% dye-decomposition is first observed) V(l) the initial volume of MB solution, and m_{HTN}(g) the amount of HTN used as a catalyst. The obtained variation in q’ as a function of initial H2O2 concentration is presented in Fig. 6. It is seen that, for a given initial H2O2 concentration, q’ increases with the initial MB concentration, reaches a peak-value, and then decreases with further increase in the initial H2O2 concentration. The maximum value of q’ (q’m) and the corresponding initial MB concentration both shift to higher values with the increasing initial H2O2 concentration. The obtained linear-variation in the q’m as a function of initial H2O2 concentration is presented in Fig. 7. It is noted that the best-fitted straight-line (regression correlation coefficient, \( <r^2> = 0.987 \)) does not pass through the origin. The extrapolation of this linear-variation gives the Y-intercept (corresponding to the initial H2O2 concentration of zero) equal to 114 mg g−1 h−1. It is to be further noted that in the presence of H2O2 with the initial concentration varying in the range of 3–50 wt.%, the dye-removal takes place via the simultaneous dye-adsorption and dye-decomposition processes on the surface of catalyst. This mechanism primarily involves the generation of O2•− and OH• on the surface of HTN and their subsequent attack on the adsorbed MB dye molecules degrading them into the non-harmful species [6]. However, in the absence of H2O2 but in the presence of catalyst, the dye-removal essentially occurs only via the surface-adsorption process [12,16]. As a result, the Y-intercept value of 114 mg g−1 h−1 must correspond to the dye-adsorption capacity (114 mg g−1) of HTN since the

![Fig. 5. Variation in the normalized concentration of MB decomposed after the contact time of 1 h as a function of initial MB concentration for the initial H2O2 concentration varying as – 3 (i), 15 (ii), 30 (iii), and 50 wt.% (iv).](image)

![Fig. 6. Variation in q’ as a function of initial MB concentration for the initial H2O2 concentration varying as – 3 (i), 15 (ii), 30 (iii), and 50 wt.% (iv).](image)

![Fig. 7. Variation in q’m as a function of initial H2O2 concentration.](image)
dye-decomposition data obtained after the contact time of 1 h is used for the calculation within the entire range of initial MB concentration investigated here. Thus, by utilizing the one-step dye-removal method of novel chemically-activated catalytic process conducted in the dark, the dye-adsorption capacity of HTN, processed via the hydrothermal treatment of sol–gel derived nanocrystalline anatase-TiO₂, is estimated to be 114 mg g⁻¹.

In order to confirm the predicted value of dye-adsorption capacity, the dye-adsorption measurements, typically for 1 h duration of contact time at the initial solution-pH of ~10, were conducted via the conventional approach involving the equilibrium adsorption/desorption of dye molecules on the surface of adsorbent [12,16,17]. (Note: The dye-adsorption capacity of HTN has been determined earlier by varying the initial solution-pH within the range of 2.5–11 [12]. The maximum amount of dye-adsorbed on the surface of HTN varies as 11, 32, 105, 68 corresponding to the initial solution-pH of ~2.5 (acidic), 7.5 (neutral), 10 (basic), and 11 (basic). Thus, the predicted value (114 mg g⁻¹) of dye-adsorption capacity is comparable with that reported earlier at the initial solution-pH of ~10. Hence, in the present investigation, the dye-adsorption capacity has been determined for the present sample at the initial solution-pH of ~10.) The obtained variation in the normalized concentration of MB adsorbed on the surface of HTN as a function of contact time, as obtained for the different initial MB concentrations, is presented in Fig. 8. It is observed that the normalized concentration of MB adsorbed on the surface of HTN increases rapidly within first 10 min of contact time and then tends to attain an equilibrium with further increase in the contact time. The normalized concentration of MB adsorbed at equilibrium on the surface of HTN reaches almost 100% at lower initial MB concentrations and decreases with increase in the latter. The adsorption data presented in Fig. 8 is utilized to calculate the equilibrium amount of MB adsorbed on the

![Figure 8](image1.png)

**Fig. 8.** Variation in the normalized concentration of surface-adsorbed MB as a function of contact time at the initial solution-pH of ~10. The initial MB concentration is varied as 7.5 (i), 60 (ii), 90 (iii), 150 (iv), 200 (v), 250 (vi), and 750 µM (vii).

![Figure 9](image2.png)

**Fig. 9.** Variation in qₑ as a function of initial MB concentration at the initial solution-pH of ~10.

![Figure 10](image3.png)

**Fig. 10.** Langmuir (a), Freundlich (b), and DKR (c) isotherm plots at the initial solution-pH of ~10.
surface per unit mass of HTN, \( q_e \) (mg g\(^{-1}\)), using the equation of form [12,18]:

\[
q_e = \frac{(C_0 - C_e) \times V}{m_{HTN}}
\]  

(7)

where, \( C_e \) (mg L\(^{-1}\)) is the MB concentration within the solution at equilibrium (that is, after the contact time of 1 h). The obtained variation in \( q_e \) as a function of initial MB concentration is presented in Fig. 9. It is noted that \( q_e \) increases gradually with the initial MB concentration, reaches a maximum value (\( q_{m} \) (mg g\(^{-1}\)), regarded here as the dye-adsorption capacity since the measurements are conducted at the initial solution-pH of \( \sim 10 \)), and then decreases drastically with further increase in the initial MB concentration which has been explained in our earlier investigation [12]. The adsorption of MB dye molecules, which are cationic in an aqueous solution, on the surface of HTN is via an electrostatic attraction mechanism due to the negatively-charged surface of HTN at the initial solution-pH of \( \sim 10 \). When the initial MB concentration within the solution is very high, their strong interaction with the OH\(^-\) ions already present within the solution restricts the amount of latter adsorbed on the surface of HTN. This in turn reduces the amount of negative surface-charge developed, and hence, the amount of surface-adsorbed MB. The dye-adsorption capacity of HTN is thus observed to be 121 mg g\(^{-1}\). As per the earlier investigation, the dye-adsorption capacity of 105 mg g\(^{-1}\) has been reported for the HTN processed using the commercially available nanocrystalline anatase-TiO\(_2\) as a precursor for the hydrothermal treatment [12]. As a result, the predicted value of dye-adsorption capacity (114 mg g\(^{-1}\)) appears to fall well within the range (105–121 mg g\(^{-1}\)) as observed for the conventional method considering the different nature of precursors used during the hydrothermal treatment. Thus, it is confirmed that the dye-adsorption capacity of HTN can be precisely predicted via the one-step dye-removal method of novel chemically-activated catalytic process conducted in the dark even though the dye-adsorption and dye-decomposition occur simultaneously under this test-condition.

**Table 1**

<table>
<thead>
<tr>
<th>pH</th>
<th>( q_m ) (Exp)</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>DKR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_m )</td>
<td>( K_L )</td>
<td>( r^2 )</td>
<td>( R_L )</td>
</tr>
<tr>
<td>10</td>
<td>121</td>
<td>125</td>
<td>8</td>
<td>0.984</td>
</tr>
</tbody>
</table>

**Determination of equilibrium adsorption isotherm and kinetics models**

The equilibrium adsorption data, derived using Fig. 8, is fitted using the Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich (DKR) isotherms [12,16–18]. In their linear forms, these isotherm models can be represented as:

\[
\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L}
\]

(8)

\[
\ln q_e = \left( \frac{1}{n} \right) \ln C_e + \ln K_F
\]

(9)

\[
\ln q_e = \ln q_m - \beta c^2
\]

(10)

where, \( K_L \) (L mg\(^{-1}\)) and \( K_F \) (mg\(^{1-1/n}\) g\(^{-1}\) L\(^{1/n}\)) are the Langmuir and Freundlich constants related to the Gibb’s free-energy of adsorption and \( q_m \) the Freundlich constant which is related to the adsorption intensity, \( \beta \) (mol\(^2\) J\(^{-1}\)) a constant related to the adsorption energy, and \( \varepsilon \) the Polanyi potential which is given by the equation of form [12,16]:

\[
\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)
\]

(11)

where, \( R \) (J mol\(^{-1}\) K\(^{-1}\)) is a gas constant and \( T \) (K) the absolute temperature. The adsorption energy (\( E \), kJ mol\(^{-1}\)) can be calculated using the relationship of form [12,16,17]:

\[
E = \frac{1}{\sqrt{-2\beta}} \times 10^{-3}
\]

(12)

Further, change in the standard Gibb’s free energy, \( \Delta G^0 \) (kJ mol\(^{-1}\)), is estimated using the relationship of form [12,18]:

\[
\Delta G^0 = -RT \ln K_L
\]

(13)

Moreover, a dimensionless separation parameter, \( R_L \), indicative of the Langmuir isotherm shape that predicts whether an adsorption system is ‘favorable’ (0 < \( R_L < 1 \)) or ‘unfavorable’ (\( R_L > 1 \)), can be obtained using the expression of form [12,19,20]:

\[
R_L = \frac{1}{1 + (K_L \times C_0)}
\]

(14)

The values of different parameters of three isotherm models obtained from the slopes and intercepts of the best-fitted straight-lines, Fig. 10a–c, as well as the calculated values of \( E \), \( \Delta G^0 \), and \( R_L \) are tabulated in Table 1. It is noted that the \( <r^2> \) values are the highest and closest to 1 for the Langmuir and Freundlich isotherms. The \( <r^2> \) values as observed for these two models are also comparable. The value of \( q_m \) (125 mg g\(^{-1}\)) estimated using the former model is equivalent with the experimentally determined value of \( q_m \) (121 mg g\(^{-1}\)). Moreover, the value of \( R_L \) which is in between 0 and 1 and the negative \( \Delta G^0 \) value further support the Langmuir model which in turn suggests the maximum coverage.

![Fig. 11. Typical pseudo-second-order kinetics plots at the initial solution-pH of \( \sim 10 \). The initial MB concentration is varied as 7.5 (i), 30 (ii), 60 (iii), and 150 \( \mu \)M (iv).](image)
via the monolayer adsorption of MB on the surface of HTN [12]. Also, the value of $1/n$ (0.276) which is in between 0 and 1 strongly favors the Freundlich model which in turn suggests the presence of heterogeneity on the surface of catalyst during the dye-adsorption process [20,21]. Hence, the equilibrium adsorption of MB on the surface of HTN follows both the Langmuir and Freundlich isotherms which is in accordance with the earlier report considering the initial solution-pH of ~10 at which the dye-adsorption capacity is determined [12]. The rate at which the MB is adsorbed from an aqueous solution on the surface of HTN is analyzed using the three different kinetics models: Lagergren pseudo-first-order, pseudo-second-order, and intra-particle diffusion [20,22]. The linear forms of these kinetics models can be respectively expressed as,

$$
\log(q_e - q_t) = \log(q_e) - \left( \frac{k_t}{2.303} \right) t
$$

$$
\frac{t}{q_t} = \left( \frac{1}{k_2 \times q_e^2} \right) + \left( \frac{1}{q_e} \right)
$$

$$
q_t = (k_d)t^{0.5} + C
$$

where, $k_1$ (min$^{-1}$), $k_2$ (g mg$^{-1}$ min$^{-1}$), and $k_d$ (mg g$^{-1}$ min$^{-0.5}$) are the Lagergren pseudo-first-order, pseudo-second-order, and intra-particle diffusion rate-constants respectively, $q_t$ the amount of MB adsorbed on the surface per unit mass of HTN (mg g$^{-1}$) at time t, and C (mg g$^{-1}$) a constant. The equilibrium adsorption data presented in Fig. 8 is further utilized to fit the above kinetics models and the values of different parameters derived from the slopes and intercepts of the best-fitted straight-lines, Fig. 11, are tabulated in Table 2. It is noted that the $<r^2>$ values are the highest and closest to 1 only for the pseudo-second-order kinetics model. Moreover, the values of $q_e$ estimated using this model are comparable with the experimentally determined values of $q_e$ (specifically for lower range (7.5–150 μM) of initial MB concentration). The model predicts the dye-adsorption capacity of HTN to be 125 mg g$^{-1}$ which is also comparable with the experimentally determined value. Hence, it appears that the equilibrium adsorption of MB on the surface of HTN follows the pseudo-second-order kinetics in agreement with the earlier report [12]. The maximum fraction of the surface-area of HTN covered by the MB dye, at equilibrium, is calculated using the following equation [12],

$$
\text{Coverage}(\%) = \frac{q_m \times N_{AV} \times S_{AMB} \times S_{HTN}}{MW_{MB} \times S_{HTN} \times 10} \times 100
$$

where, $N_{AV}$ is the Avogadro’s number ($6.023 \times 10^{23}$ molecules mole$^{-1}$), $MW_{MB}$ the molecular weight of MB dye (319.85 g mole$^{-1}$), $S_{AMB}$ and $S_{HTN}$ the surface-area (m$^2$) of a single MB dye molecule ($8.723 \times 10^{-19}$ m$^2$); dimensions: 1.43 nm $\times$ 0.61 nm $\times$ 0.4 nm) [12,23] and the specific surface-area (288 m$^2$ g$^{-1}$) of HTN. (Note: In Eq. (18), $q_m$ has the value of 121 mg g$^{-1}$. It is noted that the MB dye covers 70% of the surface-area of HTN at the initial solution-pH of ~10. Hence, the possibility of excess MB adsorption is ruled out in the present case which also supports the monolayer adsorption of dye-molecules in accordance with the Langmuir model. Hence, it appears that the amount of surface-coverage by the MB dye favors the Langmuir isotherm over the Freundlich isotherm.

Lastly, it is essential to mention that only one catalyst and one organic dye molecule have been utilized in the present investigation to predict the dye-adsorption capacity via one-step method of novel chemically-activated catalytic process conducted in the dark. It would be appropriate to confirm the same using a new system by changing the catalyst and organic dye-molecule used. Such study would be undertaken and reported in the near-future.

Conclusions

The HTN are successfully synthesized via the hydrothermal technique using the sol–gel derived nanocrystalline anatase-TiO$_2$ as a precursor. The MB adsorption capacity of HTN measured via the conventional approach (121 mg g$^{-1}$) is precisely predicted (114 mg g$^{-1}$) for the first time using the one-step dye-removal method of novel chemically-activated catalytic process conducted in the dark. The equilibrium MB adsorption on the surface of HTN follows both the Langmuir and Freundlich isotherms and the pseudo-second-order kinetics at the initial solution-pH of ~10 although the amount of surface-coverage by the MB dye supports only the Langmuir model.

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References


