



## Photo-adsorption/degradation of methylene blue from wastewater on synthesized TNTs surfaces

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Methylene blue (MB), a well known carcinogenic organic dye was tried to remove from wastewater at room temperature on titanate nanotubes (TNTs) surfaces synthesizing by alkaline hydrothermal heat treatment in batch mode. XRD, SEM/EDX techniques were used to characterize the synthetic precursor. Dye removal technique from water medium followed both the mechanisms of adsorption (in dark) and photodegradation along with the photo-adsorption. Experimental results revealed 3 g/L dose of TNTs can efficiently remove ~98% organic with an initial concentration of 10 mg/L. Adsorptive behavior of TNTs was evaluated from Langmuir isotherm (151.51 mg/g). Adsorption process was found to be favorable but non-spontaneous and was understood by the  $R_L$  ( $0.008 < 1$ ) and Gibbs free energy changes values ( $\Delta G^\circ = 10.752$  kJ/mol). Photo-illumination study conducted in presence of some common ions in the aquatic system to understand their effect on dye degradation. Two cycle's turnover studies were carried out to make the exhaust material economic. Synthetic precursor was applied finally to remove MB from spiked pond water with water quality measures.

Keywords: Titanate nanotubes, hydrothermal treatment, MB dye, photo-adsorption/photodegradation, isotherm.

### Introduction

Sweet water is one of the primary requirements for the Earth to survive but is polluted in a number of ways. Directly or indirectly inorganic and organic pollutants/contaminants from the manufacturing industries or generated as by-products from the different industries/factories are discharged and are drained away<sup>1</sup>. These anthropogenic by products are causing the water pollution for both surface water and groundwater showing the adverse effects to the human health. Among the organic pollutants, the water soluble organic dyes are in concern in the present context. They may be natural or synthetic<sup>2</sup>. Due to the lack of rules and regulations several thousand mg/L dyes are used in different purposes and discharged, not only that but also are directly discharged to the environment from the commercial synthetic industries too. Till now more than 10,000 dyes have been known and used widely in different industries like textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries<sup>3</sup> and discharged of the same, changes the odor and

properties of surface water which may leach into the ground water<sup>4</sup>. Dye wastewater generated from the industries or synthetic laboratories are of highly contaminated with different types organicals or inorganicals and are not suitable for the domestic purposes<sup>5</sup>. There are several issues where the organic dye MB is used in different ways like, urinary tract infections,  $S^{2-}$  analysis in water testing, biological stain, as an indicator for the treatment of cyanide poisoning, also as a medication in Methemoglobinemia, not only that but also consumption of MB contaminated water causes headache, nausea, confusion, breathing problem with high blood pressure<sup>5</sup>. Much more efforts have been employed with different natural and synthetic material with different technologies to remove these toxic organic contaminants from aquatic environment and were reviewed<sup>6</sup>. Different technologies along with adsorption<sup>6</sup>, photodegradation<sup>7</sup>, coagulation flocculation<sup>8</sup>, chemical oxidation<sup>9</sup>, biological process<sup>10</sup> and many more have been implemented to remove/decolour the dyes from the aqueous media. The developed technologies were

found good towards dyes, however having a numbers of limitations specially the produced sludge. Photocatalysts are found to eco-friendly cost-effective hence, are attracted to the scientists to use for the remediation organics from the aquatic environments<sup>11</sup>. Numerous semiconductor photocatalyst have been used to degrade the solute dye(s) from water medium using UV-rays. The common semiconductors photocatalyst used are of  $\text{TiO}_2$  (Anatase, P-25),  $\text{SnO}_2$ ,  $\text{ZnO}$  and doped or composite photocatalyst were also used because of their low band gaps (for  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{ZnO}$  are 3.2 eV, 3.6 eV and 3.37 eV, respectively). Among these catalysts titanium dioxide ( $\text{TiO}_2$ ) is found to be used more frequently due to its low band gap with high conductivity.  $\text{TiO}_2$  is eco-friendly and shows highly photocatalytic activity due to its larger surface area<sup>11</sup>. It has been found that the  $\text{TiO}_2$  derived materials like  $\text{TiO}_2$  nanotubes have also the tendency to degrade dyes and thus can be used as a photocatalyst. Many studies have been done by taking titanium nanotubes but the extensive study has not been done yet. In the present study, using the lower band gap of synthesized precursor of 3.2 eV, methylene blue is tried to remove (adsorption/photodegradation or photo-adsorption) from the aqueous media. It is true that biosorbents are very efficient not only towards dye(s) but also is true for the heavy metals. Contaminants having more affinity towards activated carbon, one of the expensive adsorbent, but having no band gap between the VB to CB to transit the electron(s) to degrade the organics.

## Materials and methods

The chemicals used in this study were of analytical reagent grade and used as received. Concentrated hydrochloric acid, sodium hydroxide, sodium nitrate, di-sodium hydrogen phosphate, sodium silicate, di-sodium ethylene diamine tetracetate, calcium chloride, sodium chloride, ferric chloride, and sodium sulphate were procured from Merck (India). Solutions of all salts were prepared in double distilled water. Stock 500 mg/L MB ( $\text{C}_{16}\text{N}_3\text{H}_{18}\text{ClS}$ ,  $\lambda_{\text{max}} = 663 \text{ nm}$ , Himedia) solution was prepared and diluted when required. Titanium dioxide was purchased from Loba chemicals.

In a home designed fabricated Teflon lined sealed stainless steel hydrothermal unit 25 g of commercially available titanium dioxide powder was mixed homogenously with 400%

aqueous sodium hydroxide and stirred. The device was then put in a hot air oven for 14 h at  $150^\circ\text{C}$ . The required temperature was raised within one hour of switching on the oven. The alkaline hydrothermal heat treatment for a long time caused the formation titanate nanotubes<sup>12</sup>. The obtained white cooled slurry was repeatedly washed with double distilled water (pH  $\sim 7$ ) and dried at  $90^\circ\text{C}$  for 6 h, kept in a dry black container for the further use in experimental studies, characterized by XRD, SEM/EDX (FEI-SEM, Apreo LoVac). Precursor treated with  $10^{-2} \text{ M HCl}$  (3 g in 10 mL, 1 h interval with 6 times), which may help to replace the sodium ions by proton, washed ( $\sim 7$  pH) and dried, called HTNT and characterised<sup>12,13</sup>. Heat or any other chemical treatments may help to phase transformation of the precursor as TNTs are very less stable. Adsorption/photodegradation as well as photo-adsorption studies were conducted to understand the sorption, photodegradation and simultaneous photo-adsorption efficiency (%) of titanate nanotubes. Titanate nanotubes are used for the entire studies as the close MB removal efficiency (%) was observed in both cases of TNTs and HTNTs.

Both the prepared precursors with a dose of 3 g/L were mixed with 50 mL of organic dye (10 mg/L) solution separately at pH of  $6.8 \pm 0.3$ , taken in a 500 mL beaker ( $55.44 \text{ cm}^2$ , light source to solution surface distance is 13.2 cm), and then stirred on a magnetic stirrer, at  $520 \pm 20 \text{ rpm}$  with a magnetic needle/bar ensuring the system had enough oxygen at  $25 \pm 2^\circ\text{C}$ . Dose and dye concentration are in optimum conditions. A handmade UV-light (NARVA-Germany UV-C, 18 W, 360 nm) set up was kept over the beaker as a source of high energetic photon. Total experimental set up was covered by a black cloth to protect the spreading of hazardous carcinogenic UV-rays to the premises (Fig. 1). Suspension was centrifuged at 9000 rpm (Remi, R-24) for 8 min after the completion of aging to separate the solid liquid phase. Supernatant was collected without any filtration to measure the dye concentration in effluent. Spectroscopic technique was adopted to quantify the dye concentration in the effluents using a UV-Visible spectrophotometer (UV-1800, Shimadzu, Japan). In IR, may have chance to degrade the organic on the precursors surfaces, but so slow that we consider the adsorption is predominant in dark.

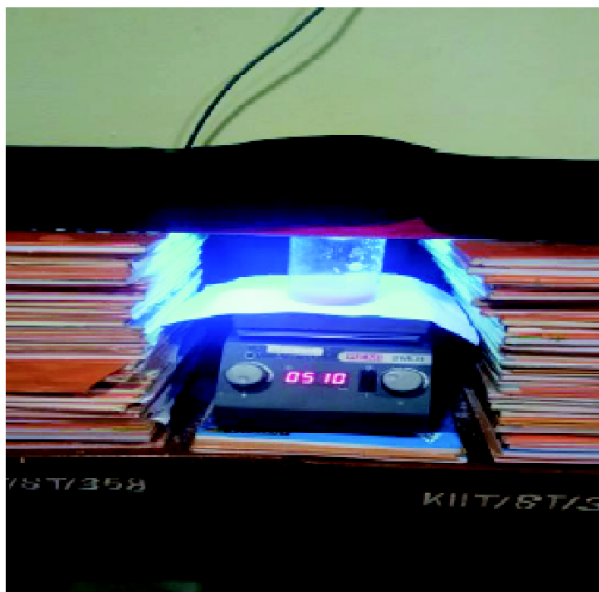


Fig. 1. UV-light set-up for photodegradation.

## Results and discussion

The positive charged sodium ions reside in between the edge-shared of  $\text{TiO}_6$  and octahedral layers of  $\text{Na}_2\text{Ti}_3\text{O}_7$ , during strong alkali treatment generated attractive force holds tightly sodium ions and  $\text{TiO}_6$  units together so strongly that the layer cannot be rolled to nanotubes. During hydrothermal heat treatment over a time, due to the large size of intercalated water molecules, enlarge the interlayer space to release the sodium ions and finally warped up and rolled into numerous nanotubes<sup>12,14</sup>. Fig. 2 shows the schematic mechanism of TNT formation.

To understand the crystallinity of the synthesized precursors, XRD data were recorded (Shimadzu XRD 6100,  $\text{Cu } K_\alpha$  radiation  $\lambda = 0.15406 \text{ nm}$ ) in the scan range of  $20^\circ\text{--}80^\circ$  ( $2\theta$ ) with a data acquisition rate of  $0.033^\circ$  per step. With some controversial issues it was understood that the formed nanomaterials are crystalline in nature<sup>12,13</sup>.

Variety of crystal modifications are reported between polytitanic acids,  $\text{H}_{2m}\text{Ti}_n\text{O}_{2n+m}$  and pure  $\text{TiO}_2$ <sup>14</sup>. It is really difficult to assign and describe the Miller indices in a particular axis for any nanomaterials during formation and warping as changes its crystallographic axis due to widening of peaks in a particular direction. Fig. 3 represents the X-ray diffraction patterns of both titanate nanotubes (sample 1) and hy-

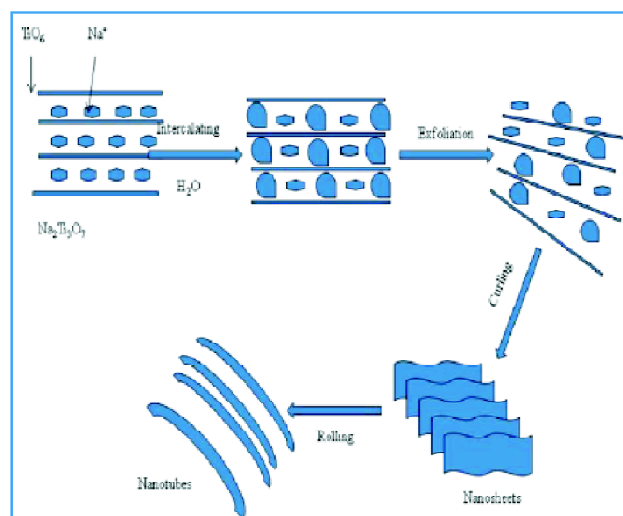


Fig. 2. Schematic diagrams for the synthesis of TNT.

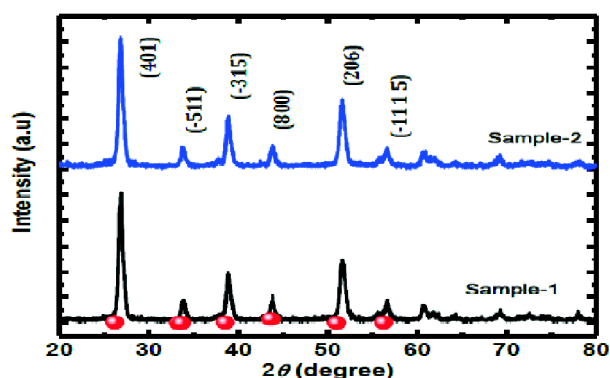


Fig. 3. X-Ray diffraction (XRD) pattern of Sample-1 and Sample-2. The (red) solid dots represent the peak positions corresponding to monoclinic  $\text{H}_2\text{Ti}_5\text{O}_{11}\cdot\text{H}_2\text{O}$  (JCPDF-00-044-0131).

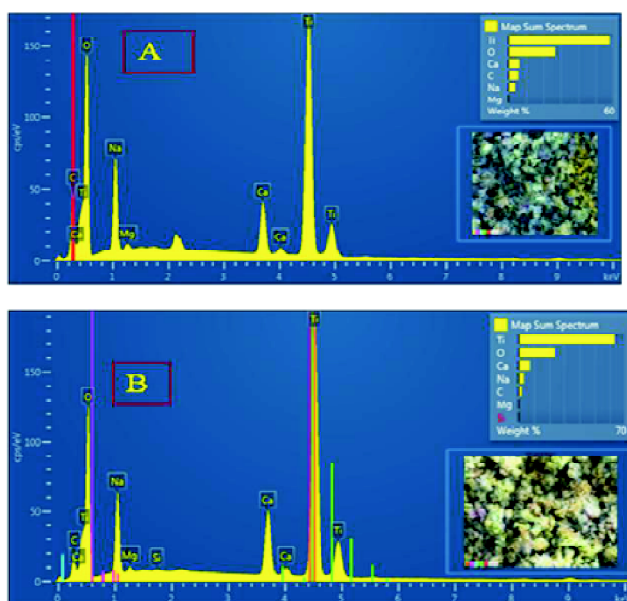
drogen titanate nanotubes (sample 2) showing the absence of any rutile or anatase phase of the synthesized precursors with a little change in peaks intensity, which can be correlated with the crystallographic series of  $\text{A}_2\text{Ti}_n\text{O}_{2n+1}$  with  $n = 5$  and  $A = \text{H, Na}$ <sup>14</sup>. Acid treatment of TNT with  $\text{HCl}/\text{H}_2\text{O}$  produces no extra/additional peaks except little changes in intensity, this helps to interpret the sample 2 originates from sample 1 only with the monoclinic structure of ( $C2/m$ )  $\text{H}_2\text{Ti}_5\text{O}_{11}\cdot\text{H}_2\text{O}$  and was analyzed by JCPDF-00-044-0131, well known software. Table 1 summarised the comparison of  $2\theta$  values with that of interplanar spacing ( $d_{hkl}$ ) along with the standards.

**Table 1.** Comparison of XRD data analysis of  $2\theta$  values and interlayer spacing  $D_{hkl}$ 

Sl. no.	Lattice planes	$2\theta$ (Degree)				$(d_{hkl})$ in Å	
		Standard	Experimentally measured		Standard	Experimentally measured	
			1	2		1	2
1.	(401)	26.197	26.87	26.92	3.399	3.315	3.310
2.	(-511)	33.640	33.80	33.67	2.662	2.649	2.659
3.	(-315)	38.525	38.87	38.96	2.335	2.315	2.310
4.	(800)	43.627	43.76	43.87	2.073	2.067	2.062
5.	(206)	51.008	51.70	51.50	1.789	1.766	1.773
6.	(-11 15)	56.253	56.59	56.60	1.634	1.625	1.625

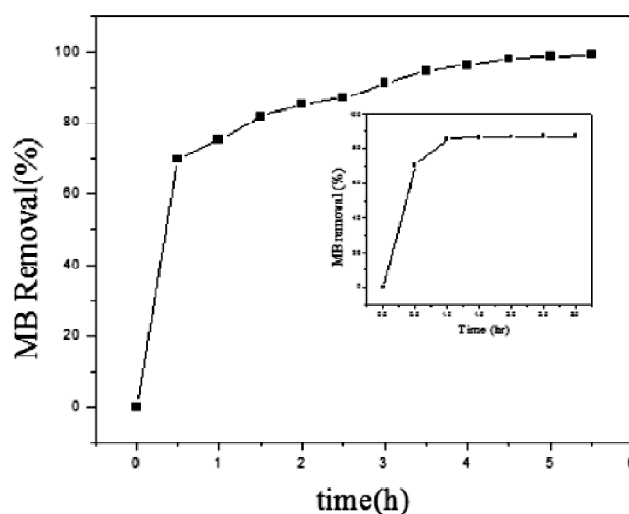
The atomic percentage compositions of both the synthesized materials were understood from the EDX spectrum (Figs. 4A and 4B). With some impurities, titanium is found to main component as anatase is ~99% pure. Remaining dye concentration in the treated effluents was determined spectrophotometrically at 663 nm ( $\lambda_{max}$  of MB) drawing a calibration curve in the concentration ranges of 0.0–8.0 mg/L, Absorbance = 0.202x (mg/L) + 0.0695 ( $R^2 = 0.997$ ).

Solute uptaking capacity by any kind of sorbents from


**Fig. 4.** EDX spectrum of TNT and HTNT (inset SEM image).

the solution is completely time dependent, though it depends on both the nature of solutes and sorbents. At the optimum conditions, initially the suspension was allowed to agitate in absence of UV-light to have the saturation point of adsorp-

tion. Result revealed within 1.5 h, saturated ~85% dye adsorbed, and after 4.5 h of photo-irradiation of the same sample, the final dye removal was achieved to ~98% (Fig. 5) with the optimal MB concentration of 10 mg/L. Acceleration of adsorption efficiency (%) was found till the numbers of photocatalyst sites ( $S_{BET} = 186.8 \text{ m}^2/\text{g}$ ) are being active in the beginning, unexposed minimum TNT sites, in the latter, in presence of sufficient oxygen, help to degrade the chemical moieties due to transition of electron(s) from VB to CB


**Fig. 5.** Kinetic study graph for photodegradation and adsorption (inset).

during impregnation of photon(s) in the suspension produced from UV-light. In complete photo-illumination study, photo-adsorption of solute molecules on sorbent surfaces, causes the high rate of photo-adsorption/degradation and slowly decreased with time due to the exhaustion of active surface sites of the used materials.

To understand the maximum affinity of MB towards precursor's sites, experiments carried out with different solute concentrations (6, 9, 10, 11 and 13 mg/L, dose 3 g/L) keeping all other experimental conditions fixed (photo-illumination study). The degradation efficiency was found varied from ~99% to ~80% and is obvious as the numbers of precursor's sites are same in all cases. Similarly dose variation study was also carried out (0.5–3 g/L) in the optimal operational conditions. Results revealed 3/L dose of sorbent can efficiently remove ~98% chemical moieties (here MB) when the initial organic concentration was maintained at 10 mg/L from aquatic environment and were used for further studies.

Isotherms namely Langmuir and Freundlich studies were carried out to interpret the adsorptive behavior of semiconductor photocatalyst adsorbent TNT towards the contaminant at constant temperature of 25±2°C. The study understood with the variation of doses at optimal conditions<sup>1</sup>.

Langmuir (1) and Freundlich (2) isotherms can be represented as:

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (1)$$

$$q_e = k_f C_e^{\frac{1}{n}} \quad (2)$$

Langmuir isotherm (Fig. 6A) drawn by plotting  $1/q_e$  vs  $1/C_e$  with the adsorptive capacity ( $Q_{\max}$ ) of 151.51 mg MB/g TNT, Freundlich isotherm (Fig. 6B), drawn by plotting  $\ln q_e$  vs  $\ln C_e$ . Affinity of organic moieties adsorption towards TNT was understood from adsorption intensity,  $n$  ( $1.01 > 1$ ) and found good. Dimensionless equilibrium parameter,  $R_L$  (Table 2) suggested the favorable adsorption and was evaluated by the following relation<sup>2</sup>.

$$R_L = \frac{1}{(1 + b C_0)} \quad (3)$$

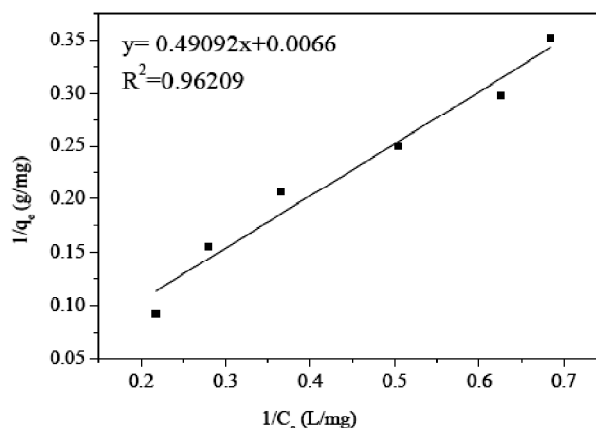


Fig. 6A. Langmuir isotherm.

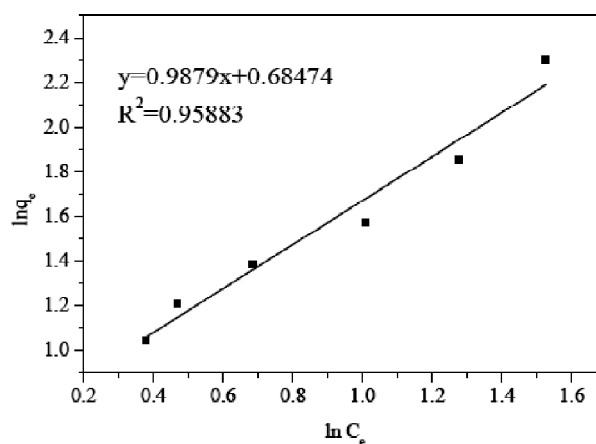


Fig. 6B. Freundlich isotherm.

Positive  $\Delta G^\circ$  value (10.752 kJ/mol) indicates the non spontaneous process, calculated using the following equation.

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G^\circ}{RT} \quad (4)$$

In synthetic solution, complete photodegradation (photo-adsorption) (6 h) study was conducted in order to understand

Table 2. Constant values of each isotherm

Synthetic sample	Temp. (K)	Isotherm constant (Langmuir)			Isotherm constant (Freundlich)			$R_L$	$\Delta G^\circ$ (kJ/mol)
		$Q_{\max}$ (mg/g)	$b$ (L/mg)	$R^2$	$n$	$k_f$ (mg/g)	$R^2$		
[MB] = 10 mg/L	298	151.51	0.013	0.96209	1.01	1.98	0.95883	0.008	10.752

the affect of MB removal efficiency in presence of different co-existing ions in optimum conditions as to look into the real dye bearing sample on TNT surfaces. The obtained results are summarized in Tables 3A and 3B. Degradation efficiency suppressed with increasing ion concentrations. Suppression or decolorisation was also noticed when study carried out in presence of ferrous ions (0.0–0.5 mg/L, ~95–67%). Decreasing removal efficiency (%) of organic in presence of some salts of common co-existing ions may due to coating on semiconductor photocatalyst surfaces rather soluble in aqueous media. This may help to prohibit the transition of negative charged electron(s) from the VB to CB to degrade the organic moieties<sup>15</sup>.

**Table 3A.** MB removal efficiency with co-existing ions

Concentration (mg/L)	Dye removal (%)			
	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>
0	~98	~98	~98	~98
50	~95	~95	~95	~95
100	~95	~95	~95	~85
150	~95	~95	~95	~71
200	~95	~95	~95	~69
250	~95	~95	~95	~61
300	~95	~95	~95	~55
400	~95	~95	~95	~45

\*Average of three replicates.

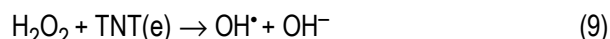
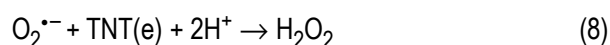
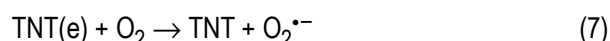
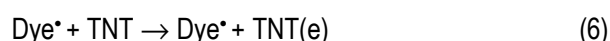
**Table 3B.** MB removal efficiency with different co-existing

Concentration (mg/L)	Dye removal (%)		
	PO <sub>4</sub> <sup>3-</sup>	SiO <sub>3</sub> <sup>2-</sup>	EDTA
0	~98	~98	~98
5	~89	~90	~95
10	~80	~87	~95
15	~75	~83	~91
20	~67	~77	~87
25	~61	~63	~80

\*Average of three replicates.

Dye molecules are converted into high energetic short-lived and active free radicals species due to the absorption of high energy photon produced from UV light source; transfer the negative charged electron(s) to semiconductor surfaces during contact time to CB from VB as the band gap is

low of 3.2 eV, may also transit through the nanotube channels as well as through produced free radicals also. The oxygen in the suspension may capture these generated electron(s) and produces O<sub>2</sub><sup>•-</sup> and HO<sup>•</sup> radical, among others. Finally an oxidation, reduction or both may have taken place due to the transition of electron(s) from HOMO to LUMO of the organic and mineralized<sup>12,16</sup> and can be represented as:



Dye<sup>\*</sup> + O<sub>2</sub> (or O<sub>2</sub><sup>•-</sup> or <sup>•</sup>OH) → Peroxylated or hydroxylated intermediates.

A complete photodegradation study was conducted at optimal conditions varying the pH from 2.0–10.0. Obtained result revealed the slight suppression within ±2.0% with pH, may be due to the change in structural property of MB<sup>15</sup>.

Spiked MB was tried to remove from tap and pond water using the developed technology with TNTs. The pre- and post treated water quality is shown in Table 4. It was found that at optimum conditions, MB removed ~92% and ~97%, respectively from pond water and tap water.

**Table 4.** MB removal efficiency in spiked water

Parameters	Treated tap water		Treated pond water	
	Before	After	Before	After
pH	~6.2	~6.8	~8.04	~8.30
EC (µs/cm)	~72	~100	~269	~305
Fe <sub>tot</sub> (mg/L)	~0.17	~0.17	~0.25	~0.25
Cl <sup>-</sup> (mg/L)	~170	~170	~120	~120
D.O. (mg/L)	~5.32	~4.76	~7.5	~6.2
TDS (mg/L)	~47	~48	~175	~178
Temp. (°C)	28±2	28±2	25±2	25±2
ORP (mV)	~140	~160	~64	~80
Alkalinity (mg/L)	–	–	0.68	~0.68
Hardness (mg/L)	~42	~42	~71	~71
Salinity (PSU)	~0.02	~0.08	~0.09	~0.15
[MB] = 10 mg/L	~97% removal		~92% removal	

\*Average of three replicates.

Regeneration and re-use of the spent material with suitable solvent is meaningful, which reduces the synthesis cost. Hence, to make the economy of the exhausted materials, the turnover study was performed. Two times turnover study of exhausted TNT was conducted (at optimum conditions) after successive washing with 100% EtOH (and dried) for six time agitating at 520–540 rpm till to procure ~85% of adsorbed MB only each and every time separately. The % MB up-take capacity was found to decrease gradually (~72% and ~54%). This may be un-availability of active precursor's surface sites (in photodegradation study).

### Conclusion

TNT/HTNT synthesized hydrothermally and characterized instrumentally. The prepared precursors used to remove MB from wastewater at room temperature. It was observed that removal of organic followed two kind mechanisms i.e. adsorption and photodegradation. In adsorption ~85% dye removed within 1.5 h of contact time with the sorbent whereas ~98% (final) removal achieved with another 4.5 h of photo-irradiation when the initial dye concentration was maintained to 10 mg/L with 3 g/L dose. The adsorptive capacity of the semiconductor photocatalyst was found to 151.51 mg MB/g TNT. Developed technology was implemented to remove MB from spiked tap water and pond water with water quality measures. Turnover studies revealed the suppression of degradation efficiency of the used precursors.

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