

**Adsorption/photodegradation of Congo Red on TNT surfaces: A kinetic study**Saismrutiranjana Mohanty^a, Sanjib Moulick^b and Sanjoy Kumar Maji^{*a}^aDepartment of Chemistry, ^bSchool of Civil Engineering,

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Hydrothermally synthesized titanate nanotubes (TNTs) were characterized and applied to remove Congo Red (CR) from synthetic as well as from the spiked tap and pond water under the optimized conditions at room temperature. Experimental results suggested that applying hydrothermally synthesized TNT at a dose of 4 g/L can remove to the tune of ~98% CR from the contaminated water medium with an initial concentration of 6 mg/L within 5.75 h. Removal followed both adsorption (0.75 h, removed ~86%) and photodegradation (5.0 h, ~98% final). The adsorptive capacity of TNT was found to be 12.04 mg/g from Langmuir isotherm with physical adsorption from D-R isotherm, favorable (R_L) and non spontaneous (ΔG°). Adsorption process followed pseudo-second order reaction model better than other three models. Like metals or metalloids, adsorption of CR did not follow either film diffusion or pore diffusion model. Study was also conducted to examine the effects of presence of coexisting ions in the removal of CR at different pH of media. Adsorption/degradation mechanism was proposed.

Keywords: Adsorption/photodegradation, dye, TNT, isotherm, kinetics.

Introduction

Due to fast population growth and rapid urbanization coupled with global warming, availability of fresh water has become a major concern particularly in regions with water scarcity. The urbanization majorly depends on industries in order to fulfil the requirements. These industries discharge their effluent in the surface water leading to contamination of surface as well as groundwater. The organic pollutants, especially dyes are discharged from different industries like rubber, dyes and pigments, cosmetic, textiles, tannery and from the synthetic industries. Due to the lack of rules and regulations, excess amount of dyes are used and discharged¹. The dyes are toxic and carcinogenic to the aquatic life and indirectly to the human beings^{2,3}.

In the present study, Congo Red (CR), a diazo dye, blue in acid solution and red in alkaline solution, a common dye used as a biological stain or as an indicator, used in textile and handloom industry to color the thread, is selected as a reference dye⁴. Commonly used treatment techniques include adsorption, flocculation, biological treatment, reverse osmosis, ultra- as well as nano-filtration and photo-catalysis⁵. Commonly used photocatalysts are TiO₂ (anatase, P25),

SnO₂, ZnO etc. The band gaps for TiO₂, SnO₂ and ZnO are 3.2 eV, 3.6 eV, and 3.37 eV, respectively. Among all the photocatalysts, TiO₂ is used more frequently as it transfers electron to molecular oxygen faster than the other available photocatalysts due to its low band gap. Furthermore, it is readily available, cheap, and eco-friendly in nature. In the present study, synthesized Titanate Nanotube (TNT) has been employed to remove Congo Red (CR) from aqueous media.

Materials and methods

Reagents: Used chemicals were of analytical reagent grade and used without further purification. Solutions were prepared using double distilled water. Synthetic Congo Red (CR) stock solution with a concentration of 500 mg/L was prepared using C₃₂H₂₂N₆Na₂O₆S₂ (molecular weight 697.00 g/mole, Himedia) and diluted as required.

Titanium dioxide (TiO₂, ~99% pure) was purchased from Loba Chemicals. Concentrated HCl, NaCl, NaOH, NaNO₃, Na₂HPO₄, Na₂EDTA.2H₂O, NH₄OH, NH₄Cl, Eriochrome black T, and 2-methoxy methanol were purchased from J. T. Baker. Appropriately diluted solutions were prepared as and when required.

Apparatus used were soaked in concentrated HNO_3 (Merck) for 24 h and washed in double distilled water followed by tap water, before being dried in a hot-air oven. Absorbance of different concentrations of dye measurements were carried out using a spectrophotometer (UV-1800, Shimadzu, Japan) equipped with 1-cm quartz cell. TEM measurement was done in a JEM-1400, JEOL (Japan) transmission electron microscope operating at 120 kV. FEI-SEM (Apreo LoVac) was used for SEM/EDX study. An electronic balance (Sartorius, BSA2245-CW) was used for weighing. Gilson micropipettes with disposable tips were used to add samples. Wensar, WPH-10, a digital pH meter was used to measure all pH values. Parameters of water samples were measured using titrimetric methods in our lab. A hand-made light set-up was used for the photodegradation of dye. Photon was emitted from the UV-light source of 360 nm of 18 W (UV-A, made in Germany). The total set-up was covered with a black cloth in order to protect the emission of hazardous UV rays to the surrounding (Fig. 1).

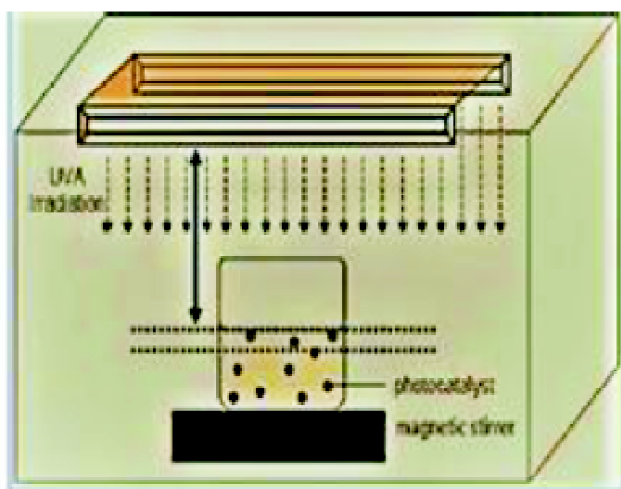


Fig. 1. Experimental set up.

Preparation of sorbent:

Titanate nanotube was synthesized hydrothermally at 150–160°C. Typically, 25 g of TiO_2 (P-25) was mixed with 100 mL of 10 M aqueous NaOH and stirred using a magnetic stirrer in a beaker at rpm of 520±20 for an hour at room temperature. After aging finished, the suspension was transferred to a stainless steel teflon-lined autoclave and put in a hot air oven for 24 h at 150–160°C and cooled to room temperature. The obtained reaction product was thoroughly

washed with large volumes of double distilled water repeatedly in order to achieve the neutral pH of ~7. Finally, obtained white cotton-batting-like solid was centrifuged (9000 rpm for 10 min) to separate TNT from the suspension and dried at 80°C for 6 h in a hot air oven and kept in a dry black box under dark condition for further use for adsorption/photodegradation of organic dye, CR from aqueous media.

The as-prepared TNT was characterized instrumentally with TEM, SEM/EDX. The as-prepared TNT was applied to remove the toxic organic dye CR from the aqueous media. Experimentally it was observed that the removal of dye from water medium followed two kinds of mechanism i.e. adsorption and photodegradation. The adsorption study was conducted in dark and the photodegradation study was understood by UV-irradiation. In experiment, 4 g/L dose of as-prepared TNT was dispersed in 50 mL of synthetic CR solution (500 mL beaker, 55.44 cm^2 , bed height from light source to the solution = 13.2 cm) with an initial concentration of 6 mg/L and at a pH of 6.8±0.2. The suspension was then put under a photocatalytic reactor and stirred at 520±20 rpm with a magnetic bar. Initially, the adsorption study was conducted in absence of UV-light. After achieving the saturation point of adsorption, the same suspension was photo-irradiated by UV-illumination in presence of sufficient amount of oxygen and stirred at the same rotational speed. The experiment was conducted at room temperature (~25±2°C). The total time for adsorption and UV-irradiation time was 5.75 h (0.75 +5.0 h). The suspension was then centrifuged (Remi-R 24) at 9000 rpm for 10 min in order to separate the solid and liquid phase from the experimental solutions. Collected supernatant liquid was used for the measurement of residual dye concentration present in effluent by a UV-Vis spectrophotometer at 498 nm (λ_{max}). It is important to mention here that during the time of adsorption of dye on TNT surface in dark (absence of UV-light), there might be a little chance of degradation in presence of IR. However, considering its rate to be very slow, this is not considered in the analysis.

Analytical method:

A standard linear calibration curve of CR ($\lambda_{\text{max}} = 498$ nm) was drawn in the concentration range of 0–10 mg/L (air as blank). and obtained as Absorbance (y) = 0.051x (mg/L) + 0.089, ($R^2 = 0.993$) and used for further quantification of dye concentrations remaining in the effluent.

Titanate nanotubes were synthesized in the laboratory from commercially available TiO_2 powder, following the developed previous methods⁶⁻⁹. When TiO_2 was treated with strong aqueous 10 M of NaOH, it is supposed to be the entrapment of positively charged Na^+ present in the suspension in between the edge-shared of TiO_6 and octahedral layers of $\text{Na}_2\text{Ti}_3\text{O}_7$. During entrapment, Na^+ and TiO_6 units tightly hold together; prohibiting the rolling into the nanotubes due to generated positive strong static attractive force between the two. Hydrothermal treatment, over a period of time, causes the gradual release of Na^+ with intercalated H_2O molecules into the interlayer space of TiO_6 sheets, due to the larger size of H_2O molecule than Na^+ . The size effect of those two chemical moieties helps to enlarge the interlayer distance during un-encapsulation/release of Na^+ , causing the weakening of attractive static interaction force existing between TiO_6 and octahedral layers. Layered $\text{Na}_2\text{Ti}_3\text{O}_7$ particle was then gradually exfoliated to form numerous sheet-shaped products^{10,11} and finally rolled to nanotubes. The nanotubes formation mechanism is shown in Fig. 2^{7,12}. TEM, SEM/EDX studies were performed to characterize the as-prepared TNT. However, by SEM, only surface morphology could be ascertained, but the actual shape and size of the precursor was not understood. TEM image (Fig. 3) clearly suggested the formation of TNT with an average diameter of 50 nm ($S_{\text{BET}} = 186.8 \text{ m}^2/\text{g}$). The sorret band (Fig. 4) of the TNT suggested the presence of titanium with other trace impurities as TiO_2 is only ~99% pure.

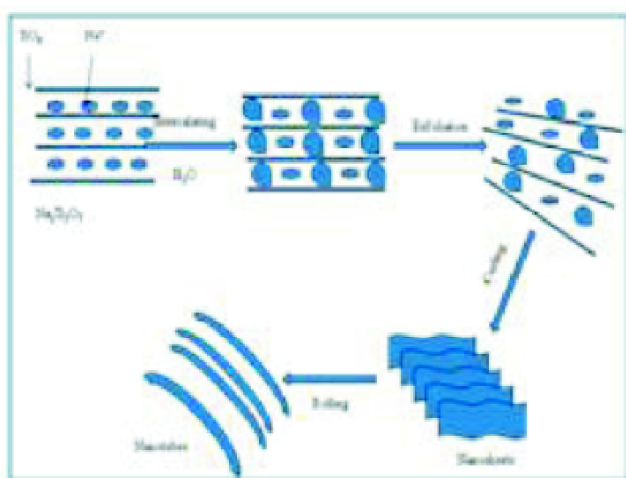


Fig. 2. Scheme of TNT synthesis.

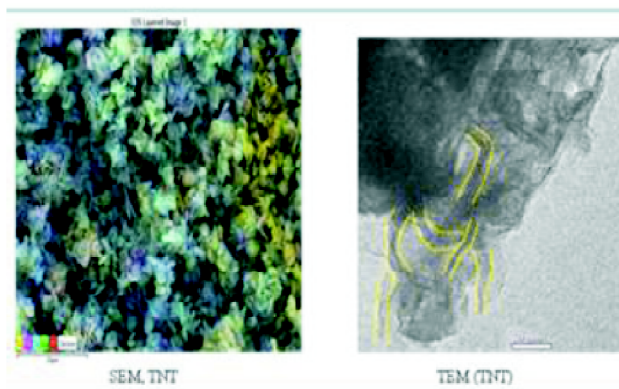


Fig. 3. SEM and TEM of TNT.

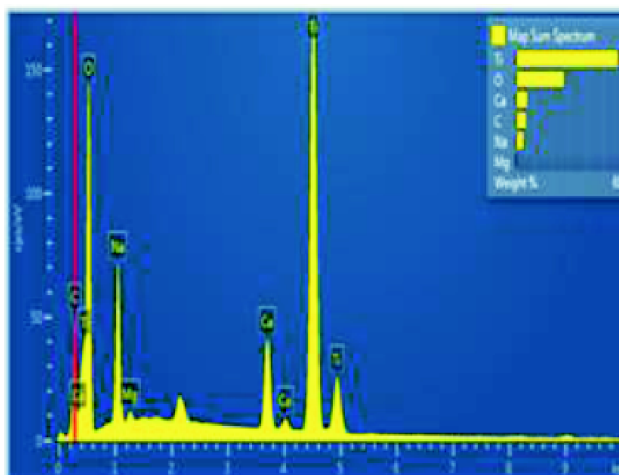


Fig. 4. Sorret band of TNT (EDX).

Results and discussion

Dose variation study:

Each and every chemical moiety (CR) has a tendency to accumulate on the sorbent surface in the maximum definite amount at a particular time of span. Hence, to fix the sorbent site, the study was conducted varying the semiconductor adsorbent TNT from 0.5–5 g/L at $25 \pm 2^\circ\text{C}$, 6.8 ± 0.2 pH, at aging speed of 520 ± 20 rpm. Complete photodegradation study suggested that 4 g/L of TNT can remove ~98% of CR with an initial concentration of 6 mg/L within the aging period of 5.75 h.

Concentration variation study:

Concentration variation study was conducted by varying the concentration of CR between 2 and 10 mg/L. Slowly the

suppression of removal efficiency was achieved with the increasing concentrations of the organic moiety. The result is obvious as adsorbent site is fixed in every case. However, obtained result revealed that 4 g/L dose of TNT can photodegrade ~98% of CR from the aqueous media with other fixed experimental conditions with an initial concentration of 6 mg/L.

Kinetics study:

Contact time between adsorbate and adsorbent is very important in order to achieve the maximum adsorbate removal efficiency. Under the same experimental conditions, i.e. TNT dose, concentration of CR, pH, aging speed, complete photo-irradiation study revealed that ~98% CR degraded within 5.75 h of aging. Now under the same experimental conditions, the study was conducted initially in absence of UV-light (in dark, adsorption), leading to the maximum saturation adsorption point within 0.75 h (~86%). The same suspension was treated with photo illumination using UV-A light source. The rest chemical moiety was degraded to ~98% (total) and mineralized due to the electronic transition between VB to CB of semiconductor adsorbent TNT (Fig. 5).

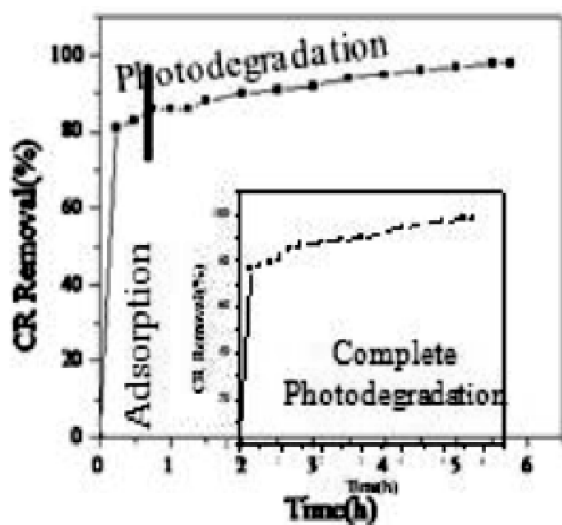


Fig. 5. Time variation study.

To understand the mechanism of solute adsorption on to the adsorbent, four kinetic models viz. first order reaction model based on the solution concentration, pseudo-first order model based on the solid capacity, second order reaction model based on the solution concentration and pseudo-second order reaction model based on the solid phase sorption were analyzed and a comparison of the best fit sorption mechanism were made^{13,14}. Four integrated linear equations were represented as:

(1) First order reaction model:

$$\ln C_t = \ln C_0 - k_1 t \tag{1}$$

(2) Pseudo-first reaction model:

$$\ln (q_1 - q_t) = \ln q_1 - k_s t \tag{2}$$

(3) Second order reaction model:

$$\frac{1}{C_t} - \frac{1}{C_0} = k_2 t \tag{3}$$

(4) The pseudo –second order reaction model:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{4}$$

h (initial sorption rate constant) = $k q_e^2$

Terms and symbols are as usual.

Based on the specific relation co-efficient (R^2), it can be inferred that the adsorption process followed the pseudo-second order reaction model (Table 1) (Fig. 6).

As dye removal followed adsorption and then photodegradation, it is important to determine the nature of process (pore/film diffusion) involved in the adsorption and the same was evaluated using the first order rate constant as follows:

$$t_{1/2} = 0.030 \frac{r^2}{D_p} \tag{5}$$

Table 1. Linear four kinetic equations

Dye	Model	Equation of linear fit line	R^2
[CR] = 6 mg/L	First-order reaction model	$\ln C_t = -0.0122 + 1.1805t$	0.9759
	Pseudo-first order reaction model	$\ln (q_1 - q_t) = -0.0336 - 0.8045t$	0.9585
	Second-order reaction model	$1/C_t = 0.0057t + 0.2839$	0.9601
	Pseudo-second-order reaction model	$t/q_t = 0.8456 + 5.1950t$	0.9875

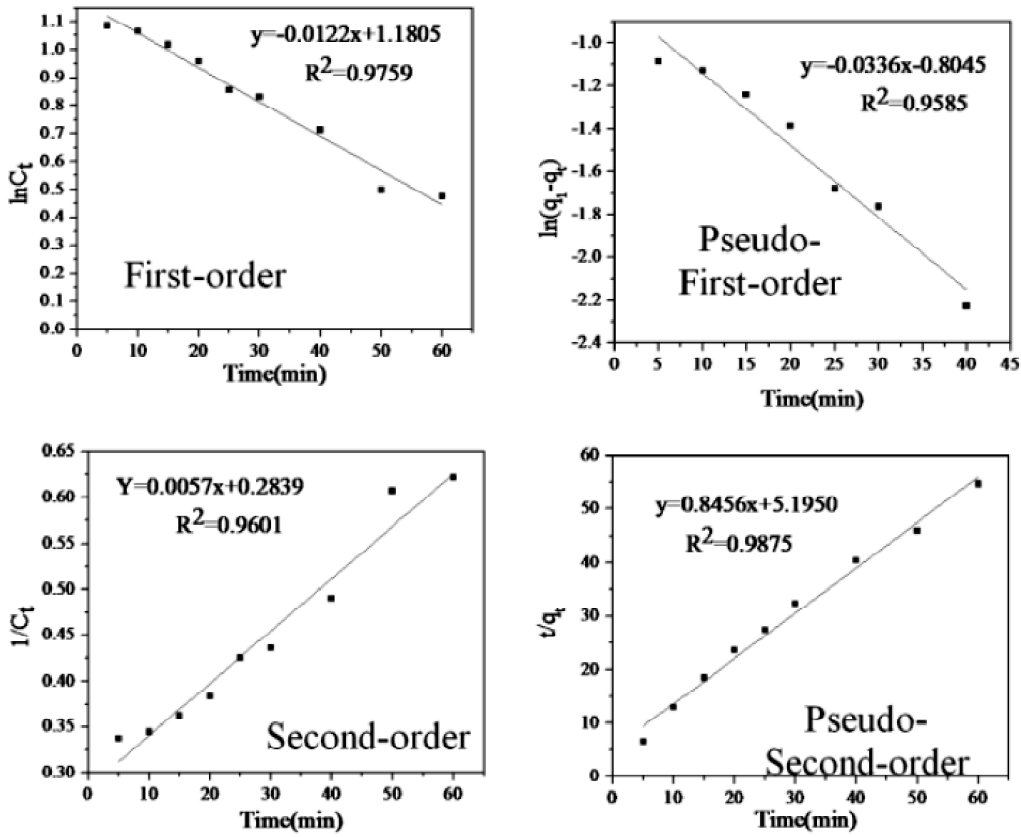


Fig. 6. Four kinetics curves.

$$t_{1/2} = 0.23 \frac{r\delta}{D_f} \times \frac{C_s}{C_e} \quad (6)$$

$t_{1/2}$ = half time, r = radius of the adsorbent particle (cm), D_p and D_f are pore diffusion and film diffusion coefficient (cm^2/s), C_s and C_e are the concentration of the adsorbate on the adsorbent and adsorbate in solution at equilibrium (mg/L) and δ = film thickness (0.001 cm). The $t_{1/2}$ can be calculated as

$$t_{1/2} = -\frac{\ln(0.5)}{k_1} \quad (7)$$

where k_1 is the first rate constant^{13,14}.

The calculated D_f and D_p values were found to be 10.77×10^{-13} and 5.94×10^{-17} cm^2/s^2 . Film diffusion becomes

the rate limiting step if D_f value is in the range of 10^{-6} to 10^{-8} cm^2/s^2 and for D_p , it should be in the range of 10^{-11} to 10^{-13} cm^2/s^2 . The obtained result suggested the adsorption did not follow either film diffusion or pore diffusion like heavy metal or metalloids (Table 2).

A complete photo-illumination study was conducted in the presence of some common co-existing ions in the aqueous media like, Cl^- , NO_3^- , PO_4^{3-} , EDTA, and pH. The obtained results revealed the suppression of CR removal efficiency on TNT surfaces. Presence of corresponding salts of those ions may coat on the TNT surfaces prohibiting the electronic transfer between VB to CB¹⁵. Increasing or decreasing pH of the media suppressed the CR removal efficiency. The pH_{ZPC} of TNT is 8.5. CR is an anionic dye. However, due to change in pH of the media, the structure of CR may change.

Table 2. Diffusion constant values

Initial dye	C_e (mg/L)	k_1 (1/s)	$t_{1/2}$ (s)	r (cm)	D_f (cm^2/s)	D_p (cm^2/s)
[CR] = 6 mg/L	~0.84	2.03×10^{-4}	3.4×10^3	26×10^{-7}	10.7×10^{-13}	5.9×10^{-17}

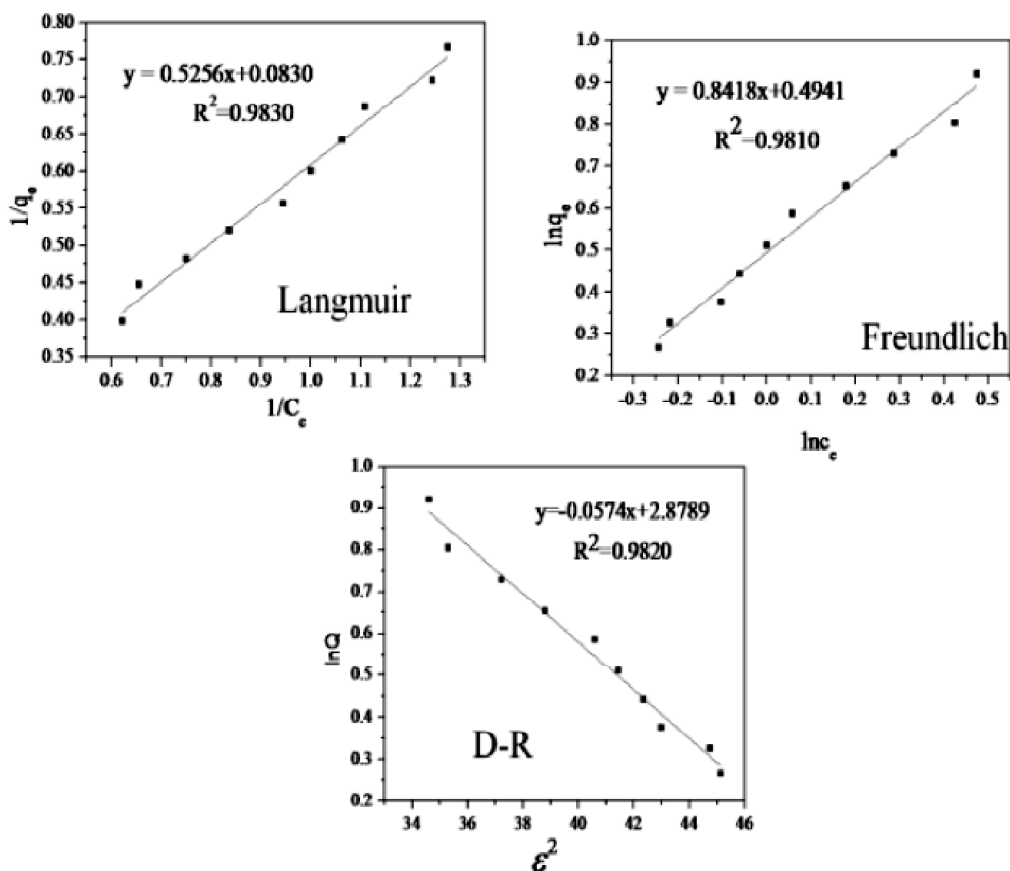


Fig. 7. Isotherms of CR on TNT surfaces.

Isotherm study:

During adsorption of dye on TNT surfaces at a particular time, due to weak van der Waals forces of attraction, the solute molecule gets attracted and adsorbed on to precursor's surface and in the same time there is little chance to desorp. Finally a dynamic equilibrium will be established between sorbate and sorbent. Hence, in the equilibrium, isotherm study was conducted to understand the solute (dye) up-take capacity of the adsorbent TNT at room temperature. The feasibility of the adsorption process was understood from D-R isotherm (Fig. 7) by calculating the mean free Energy (E). Favorability and the spontaneity of the adsorption process was understood from the dimensionless equilibrium parameter (R_L) and from the Gibbs free energy (ΔG°). The relationships are as follows^{1,5,6}:

$$\text{Langmuir Isotherm: } \frac{1}{q_e} = \frac{1}{Q_{\max}} + \frac{1}{bQ_{\max}} \left(\frac{1}{C_e} \right) \quad (8)$$

$$\text{Freundlich Isotherm: } \log q_e = \log k_f + \frac{1}{n} (\log C_e) \quad (9)$$

$$\text{D-R isotherm: } \ln Q = \ln Q_m - k\epsilon^2 \quad (10)$$

$$E = -(2k)^{-0.5} \quad (11)$$

$$R_L = \frac{1}{(1 + bC_0)} \quad (12)$$

$$\Delta G^\circ = RT \ln \left(\frac{1}{b} \right) \quad (13)$$

The isotherm constant values are shown in Table 3. The low removal efficiency of CR on TNT may be due to high molecular weight of chemical moiety of 697.00 g/mole.

Under the same experimental conditions, removal of CR was attempted from the spiked pond water (collected from Nimapara, a village of Puri District) and from tap water (School of Civil Engineering, KIIT DU). The obtained result revealed

Table 3. Isotherm constant

Parameter	Before treatment	After treatment	Before treatment	After treatment
	Tap water		Pond water	
	pH	6.2	6.8	8.04
EC ($\mu\text{s/cm}$)	72	100	269	305
Fe _{tot} (mg/L)	0.17	0.17	0.25	0.25
Cl ⁻ (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
Temperature (°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
[CR] = 6 mg/L	78% removed		81% removed	

that CR removal to the tune of ~81% (may be presence of different co-existing ions) and ~78%, from the corresponding pond water and tap water, respectively, were obtained using photo-irradiation (UV treatment) as the treatment measure. The water quality parameters pre- and post-treatment are presented in Table 4.

Impregnation of photon from UV light to the suspension, the activated CR molecules (dye) were converted into short-lived active transient free radicals species on contacting with TNT surfaces, transferred the produced negative charged electron(s) on it. This produced electron(s) can be injected into the conduction band of TNT connected through the nanotube channels. This injective process could also be directly performed by radical dye molecules. The injected electrons were captured by the surface adsorbed O₂ molecules

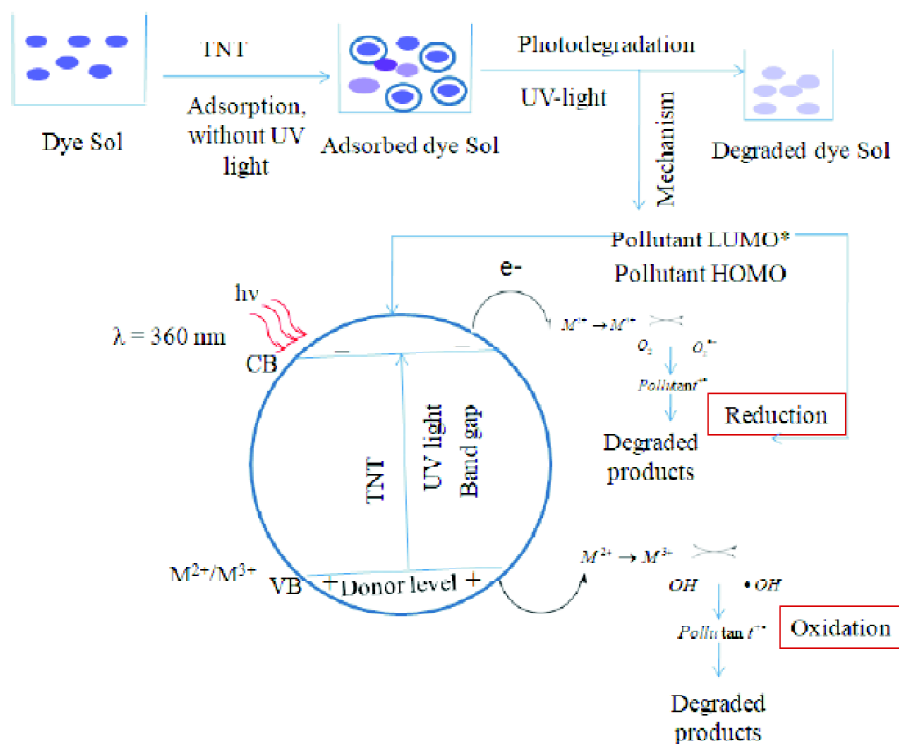
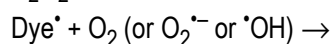
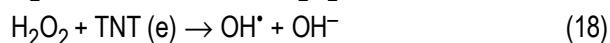
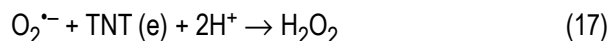
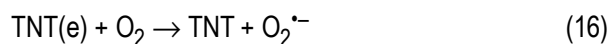
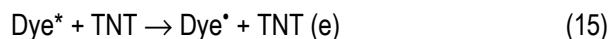


Fig. 8. Probable adsorption/photodegradation mechanism.

Table 4. Water quality parameters

Congo Red synthetic sample (6 mg/L) (298±2 K)	Langmuir isotherm		Freundlich isotherm		D-R isotherm	
	Q_{max} (mg/g)	B (L/mg)	n	k_f	E (kJ/mole)	Q (mg/g)
	R_L	R^2	R^2		R^2	
ΔG° (kJ/mole)	1.641	0.9830	0.9801		0.9820	

to yield $O_2^{\bullet-}$ and HO^{\bullet} radical, among others. Finally the dye molecules could be quickly demineralized by the radicals. The probable photo-degradation mechanism (Fig. 8) of dye under UV light using TNT is shown as follows^{7,16}:



Peroxylated or hydroxylated intermediates

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