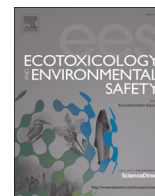




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# Adsorption of crystal violet onto functionalised multi-walled carbon nanotubes: Equilibrium and kinetic studies

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## ABSTRACT

Synthetic dyes present in effluent from textile, paper and paint industries contain crystal violet (CV), a known carcinogenic agent. This study investigates the modification of multiwalled carbon nanotubes by acid reflux method and equilibrium and kinetic behaviour of adsorption of CV onto functionalized multi-walled carbon nanotubes (fMWNTs) in batch system. High stability of the fMWNTs suspension in water indicates the hydrophilicity of fMWNTs induced due to the formation of functional groups that make hydrogen bonds with water molecules. fMWNTs were characterized by Fourier Transform Infra Red (FTIR) spectroscopy and the functional groups present on the fMWNTs were confirmed. Characteristic variation was observed in the FTIR spectra of fMWNTs after adsorption of crystal violet onto it. Adsorption characteristics were evaluated as a function of system variables such as contact time, dosage of fMWNTs and initial concentration and pH of the crystal violet solution. Adsorption capacity of fMWNTs and percentage removal of the dye increased with increase in contact time, adsorbent dosage and pH but declined with increase in initial concentration of the dye. fMWNTs showed higher adsorption capacity compared to that of pristine MWNTs. Data showed good fit with the Langmuir and Freundlich isotherm models and the pseudo-second order kinetic model; the maximum adsorption capacity was 90.52 mg/g. Kinetic parameters such as rate constants, equilibrium adsorption capacities and regression coefficients were estimated. Results indicate that fMWNTs are an effective adsorbent for the removal of crystal violet from aqueous solution.

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## 1. Introduction

Environmental contamination through the discharge of effluent containing synthetic dyes from textile, paper and paint industries has become a serious issue in recent years. Crystal violet (CV), also known as gentian violet, is a cationic dye used extensively in textile, paper and printing ink industries and also used as a biological stain, bacteriostatic agent in veterinary medicine, skin disinfectant in humans etc. It is a carcinogenic agent; it can cause skin and digestive tract irritation and can persist in the environment since it is poorly metabolised by microbes (Mittal et al., 2010). Out of the many physical, chemical, and biological treatment techniques such as coagulation, chemical precipitation, membrane filtration, adsorption, solvent extraction, reverse osmosis, photocatalytic degradation etc., adsorption is found to be the most versatile one, it yields the best results for the removal of dyes from effluents (Rafatullah et al., 2010). Numerous adsorbents and bioadsorbents such as treated ginger waste (Kumar and

Ahmad, 2011), NaOH-modified rice husk (Sagnik et al., 2011), bark powder of coniferous pines (Rais, 2009), teak (Satish et al., 2011), bottom ash (Puthiya et al., 2012), polyaniline/hollow manganese ferrite nanocomposites (Rahmatollah et al., 2010) etc. have been used for the removal of dyes from aqueous solution. Many researchers have reported the application of functionalized multi-walled carbon nanotubes for the removal of dyes (Mohammad et al., 2013; Yanhui et al., 2013), heavy metals (Yan-Hui et al., 2003; Li et al., 2014) etc. Functionalisation of carbon nanotubes increase the specific surface area and pore specific volume and generate more hydrophilic surface structures and oxygen containing functional groups. Functionalized multiwalled carbon nanotubes (fMWNTs) have been used for the adsorption of malachite green and the maximum uptake obtained was reported to be 142.85 mg/g (Yan-Hui et al., 2003). Alkali activated MWNTs were used for the enhanced removal of methyl orange and methylene blue (Jie et al., 2012). The individual and competitive adsorption capacities of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  by fMWNTs were studied. The estimated maximum sorption capacities by applying the Langmuir equation for single ion adsorption isotherms were 97.08 mg/g for  $Pb^{2+}$ , 24.49 mg/g for  $Cu^{2+}$  and 10.86 mg/g for  $Cd^{2+}$  (Yan-Hui et al., 2003). In an experimental investigation on the adsorption of  $Pb^{2+}$ ,

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$\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  onto carbon nanotubes (CNTs) with increasing wall number and amount of surface functional groups, CNTs exhibited more surface defects and higher adsorption capacity. In the present study, the effects of initial concentration of the dye, pH, adsorbent dosage, contact time and temperature on the adsorption of CV from aqueous solutions onto fMWNTs are investigated. Equilibrium sorption and kinetic characteristics of adsorption in batch systems are also studied.

## 2. Materials

Multiwalled carbon nanotubes (MWNTs, 93%) were purchased from Redex Nano Lab. Nitric acid ( $\text{HNO}_3$ , 70%) from Merck and crystal violet (MF:  $\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$ , MW:408,  $\lambda_{\text{max}}$ :580 nm) from SRL. All the chemicals were of analytical grade and used without further purification. MWNTs were modified by functionalisation using acid reflux method. Functionalized multiwalled carbon nanotubes (fMWNTs), used as the adsorbent were prepared by refluxing 200 mg of MWNTs in 50 mL of nitric acid for 12 h at 100 °C followed by washing and centrifugation until the pH of the washing became neutral. The centrifuged MWNTs were dried overnight in a hot air oven at 100 °C and stored. Stock solution of crystal violet (CV) was prepared by dissolving appropriate quantity of CV in distilled water. Working solutions of concentrations, 25 mg/L, 50 mg/L, 75 mg/L, 100 mg/L, 135 mg/L and 150 mg/L were prepared from the stock solution of CV.

## 3. Methods

Batch adsorption studies were performed with a working volume of 20 mL of CV solution of concentrations, 25 mg/L, 50 mg/L, 75 mg/L, 100 mg/L, 135 mg/L and 150 mg/L; the adsorbent dosage employed were, 0.25 g/L, 0.50 g/L, 0.75 g/L, 1.00 g/L and 1.25 g/L and pH 3, 6, 7 and 8. The samples were analysed for the residual concentration of CV every 5 min until equilibrium is reached using UV/vis spectrophotometer (Model Hitachi – 2800) at a wavelength of 580 nm. Percentage removal of the dye and the amount of dye adsorbed per unit mass of the adsorbent (mg/g) at equilibrium are obtained by Eqs. (1) and (2) respectively.

$$\text{Percentage removal (\%)} = \frac{C_i - C_t}{C_i} \times 100 \quad (1)$$

$$\text{Adsorption capacity (mg/g)} = \frac{C_i - C_e}{m} \times v \quad (2)$$

where  $C_i$  (mg/L),  $C_t$  (mg/L) and  $C_e$  (mg/L) are the concentrations of the dye initially, at time  $t$  and at equilibrium, respectively,  $m$  (g) is the mass of the adsorbent and  $v$  (L) is the volume of the dye solution. In order to compare the uptake of crystal violet from crystal violet solution using fMWNTs with the removal using pristine MWNTs, batch adsorption experiments were conducted with 0.5 mg/L of pristine MWNTs in solutions of crystal violet solutions with the concentration ranging from 50 mg/L to 150 mg/L.

Functional groups on the modified MWNTs after acid refluxing were identified from the FTIR spectra of the MWNTs obtained from the FTIR spectrophotometer (JASCO FT/IR-4100A) before and after modification. Functionalisation of MWNTs was also confirmed by the stability of the suspension of fMWNTs in water. MWNTs and fMWNTs were centrifuged at 8000 rpm for 10 min to check the stability of the suspension of MWNTs and fMWNTs in water.

Adsorption isotherm analysis was performed using Langmuir and Freundlich adsorption isotherm models. Pseudo-first order

and pseudo-second order kinetic models were employed for the adsorption kinetic analysis.

## 4. Results and discussion

The FTIR spectra of CV, pristine MWNT, fMWNT and crystal violet loaded fMWNT are presented in Fig. 1(a)–(c) respectively. The spectra of CV displays all characteristic peaks of the bonds in CV, namely  $1588.6 \text{ cm}^{-1}$  due to C=C stretching vibrations in aromatic nuclei,  $1367.8 \text{ cm}^{-1}$  due to C–H deformation in the methyl group,  $1176.5 \text{ cm}^{-1}$  due to C–H stretching vibrations in aromatic ring,  $2922.9 \text{ cm}^{-1}$  due to C–H stretching vibrations of the methyl group,  $1296.0 \text{ cm}^{-1}$  due to vibration of C–N and  $3455.9 \text{ cm}^{-1}$  due to the presence of O–H bonds of the water molecules adsorbed on CV.

The FTIR spectra of pristine MWNT does not present any characteristic peaks of functional groups. The FTIR spectra of the fMWNTs presented in Fig. 1(c) indicate the presence of main bands that represent the vibration of the functional groups of fMWNT like C=O and O–H bonds of COOH group attached to the MWNTs by sharp peaks at  $1750.3 \text{ cm}^{-1}$  and a broad peak at  $3446.2 \text{ cm}^{-1}$  respectively. This confirms the formation of functional groups permanently attached to the MWNTs by modification with acid oxidation. The FTIR spectra of the CV loaded fMWNT presented in Fig. 1(c) show characteristic changes in the FTIR spectra due to the adsorption of CV on to fMWNTs. The intensity of the peak representing the stretching vibrations of O–H group of fMWNTs decreased and the peak representing the stretching vibrations of the C=O group diminished in the spectra of CV loaded fMWNTs. This may be due to the formation of chemical bonds between C=O of fMWNTs and electrophilic  $\text{N}^+$  of CV.

## 5. Dispersion of fMWNTs

Pristine MWNT exhibits low dispersion in water due to its carbonic nature and the presence of van der Waals force between nanotubes. Fig. 2(a) and (b) presents the suspension of MWNTs and fMWNTs in water after centrifugation at 8000 rpm for 10 min. High stability of fMWNTs suspension in water indicates the hydrophilicity of fMWNTs induced due to the formation of O–H groups that make hydrogen bonds with water molecules. This also confirms the functionalisation of the MWNTs with the acid refluxing.

## 6. Effect of contact time

The effect of contact time on the adsorption capacity of fMWNTs and the percentage removal of CV from aqueous solution are presented in Fig. 3(a) and (b) respectively. Results indicate that the adsorption process is faster in the initial stages i.e., within the first 10 min, due to the presence of large number of vacant sites on the surface of the adsorbent; later, the percentage removal decreases and the adsorption process becomes slower due to more and more of these sites being occupied; equilibrium is reached within approximately 30–45 min. Occupation of the remaining vacant sites did not take place due to the high repulsive forces between the molecules of the dye at the adsorbent surfaces and in the bulk solution. The maximum dye uptake was obtained as 90.52 mg/g within 40 min. Complete removal was observed when adsorption experiments were conducted on aqueous solution of 25 mg/L CV concentration, the dosage of the adsorbent being 0.5 g/L. In this case, equilibrium was attained within 30 min. This may be because the number of

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