Journal of Molecular Liquids 212 (2015) 266–271

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

# Enhanced removal of toxic Congo red dye using multi walled carbon nanotubes: Kinetic, equilibrium studies and its comparison with other adsorbents

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ARTICLE INFO

*Article history:*
Received 10 August 2015
Received in revised form 14 September 2015
Accepted 16 September 2015
Available online xxxx

*Keywords:*
Adsorption
Multi walled carbon nanotubes (MWCNTs)
Congo red dye
Kinetics study

ABSTRACT

MWCNTs were used as an efficient adsorbent for rapid removal of hazardous Congo red dye (CR) from aqueous solutions; the whole adsorption process was well investigated and elucidated. The impact of several significant parameters such as contact time, pH, temperature and initial concentration were well studied and optimized. As a result of optimization the values of influential parameters such as contact time, pH, temperature, initial concentration and fixed adsorbent dose were found to be 60 min, 11, endothermic, 200 ppm and 0.05 g, respectively. The developed nano adsorbent shows an excellent potential ($q_e$, 352.11 mg/g; 92% of CR has been removed within 60 min) for removal of CR from the solvent phase. The adsorption kinetics and isotherm data were found to be well fitted and in good agreement with the pseudo-second order and Langmuir isotherm models, respectively. The efficient and rapid removal of the noxious CR dye using MWCNTs in a very short period of time, and the obtained maximum adsorption capacity of the developed adsorbent in comparison to the previously developed adsorbent establishes the significance of the work done.



## 1. Introduction

Various kinds of synthetic dyes appear in the effluents of several industries such as textiles, leather, paper, plastics, etc. The textile dyeing industry consumes large quantities of water during different stages of dyeing and finishing, among other processes. Since a very small amount of dye in water is highly visible and can be toxic to the biological creatures in water, the removal of dye from wastewater becomes environmentally important [1–3].

Considering the fact that the removal of these toxic dyes from wastewater is highly essential for the well-being of humans as well as biotic flora and fauna; various technologies have been used for rapid removal of such noxious dyes such as reduction, precipitation, adsorption and oxidation [4–7]. However, the adsorption process is known to be the most suitable method because of its high efficiency and for economic considerations [8–10]. Some adsorbents such as activated carbon, zeolites, biomaterials, nanoparticles, polymers, etc., have been extensively used for adsorption of toxic dyes [5–10]. Several other previously developed adsorbents such as carbon nanotubes [11–18], MWCNTs [19,20], nanoparticles and nanocomposites [21–25], rubber tires [26,27], and other low cost adsorbents, etc. [28–33] are extensively used for the rapid removal of noxious impurities from aqueous solutions. In this regard the removal of dyes remainders from the aqueous solution is one of the major global environment concern [34].

Carbon nanotubes (CNTs) have attracted keen attention in multidisciplinary areas due to their unique hollow tube structure and their many outstanding mechanical, electronic and optical properties [35] but the adsorption efficiency of such adsorbents has been reported to be very low. Therefore, it has become the center of attention of different research groups to search for more efficient adsorbents. In addition to the pioneering work carried out by Iijima [36] on the preparation of MWCNTs and SWCNTs using the arc evaporation method [37–39], other methods have been reported including laser ablation, chemical vapor deposition, electrolysis, flame synthesis, etc. It is worth mentioning

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http://dx.doi.org/10.1016/j.molliq.2015.09.027
0167-7322/

that the arc evaporation method, laser ablation and chemical vapor deposition are the most common techniques which are used broadly for synthesis of CNTs [40,41].

The aim of the present work was to evaluate the potential and effectiveness of MWCNTs for the removal of Congo red dye (CR) from aqueous solutions. The effect of various parameters such as contact time (t), pH, temperature, and initial dye concentration (C) on the adsorption process was well studied and optimized. The main objects of this work are as follows: (i) to study the feasibility of using MWCNTs as adsorbents for the removal of CR, (ii) to determine the applicability of various isotherm models (i.e., Langmuir, Freundlich and Temkin) to find out the best-fit isotherm equation, (iii) to evaluate kinetic parameters and explain the nature of adsorption, and (iv) to compare it with other adsorbents.

## 2. Experimental section

### 2.1. Material

MWCNTs were purchased from NanoAmor Nanostructured & Amorphous Materials, Inc., USA [purity > 95%, outer >50 nm, length 500–2000 nm, surface area ≈40 $m^2$/g, and manufacturing method catalytic chemical vapor deposition (CVD)]. Congo red dye (CR) is a red crystalline powder with a molecular weight of 696.665 g/mol and $\lambda_{max} = 498$ (nm) (Fig. 1) [5], was purchased from LABCHEM and used without any further purification. All working solutions were prepared with deviations of less than ±0.1% from the desired concentrations. All supplementary chemicals were of analytical grade and all solutions were mixed with deionized water. Their concentrations were measured by using UV-2550 UV–vis spectrophotometry (SHIMADZU, Japan).

### 2.2. Adsorption experiments

The experiment was carried out in 100 mL conical flasks containing 50 mL CR solutions in a water bath to elucidate the impact of the influential parameters i.e. pH (1–11), dye concentration (50–200 ppm), temperature (298 K), contact time (0–180 min), agitation speed (0–150 rpm) and 0.05 g of adsorbent. After each removal experiments, the samples were centrifuged (2000 rpm, 20 min) using a centrifuge (Hettich, EBA 21, Germany) for separation of adsorbent from dye solutions. The residual dye molecule concentration was analyzed by using a UV–vis spectrophotometer at 498 nm for CR. The adsorption study was performed by determining the removal conditions. The amount of dye adsorbed per unit adsorbent (mg dye per g adsorbent) was calculated according to a mass balance on the dye concentration using the equation:

$$q_t = V\,(C_o - C_t)/m \quad (1)$$

where $C_o$ is the initial dye concentration (mg/L), $C_t$ is the dye concentration in solution (mg/L) at time t, V is the volume of the solution (L), and m is the mass of the adsorbent (g). The percent removal (%) of dye was calculated using the equation:

$$\text{Removal}\ (\%) = ((C_o - C_e)/C_o) \times 100 \quad (2)$$

where $C_e$ is the concentration of dye solution (mg/L) at equilibrium. Microsoft Excel program was employed for data processing.

## 3. Results and discussion

### 3.1. Characterization of the MWCNTs

The surface textural and morphological properties of the developed adsorbent were carried out using SEM imaging. The obtained results are presented in Fig. 2. As shown in Fig. 2, the MWCNTs were entangled and some were in the form of agglomerates, and the length was several micrometers.

FT-IR was used to characterize the functional groups present on the surface of the adsorbent. Fig. 3 shows the FT-IR spectra of pristine MWCNTs. In Fig. 3, the peak at 1644 $cm^{-1}$ can be assigned to the C═C stretching, which indicates the graphite structure of MWCNTs.

### 3.2. Effect of contact time on the adsorption of CR onto MWCNTs

The time dependent behavior of CR adsorption was examined by varying the contact time between adsorbate and adsorbent in the range of 10–80 min. Fig. 4 reveals that 84% removal occurred in 10 min and 92% in 60 min. The adsorption process attained equilibrium within 40–70 min hence 60 min was taken as the equilibrium time in batch adsorption experiments. The adsorption of CR dye is rapid at the initial stage, and reaches the steady state position i.e. at equilibrium point it slows down and almost becomes constant. The obtained results can be ascribed to the facts that initially there are large numbers of vacant surface sites available for the adsorption, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to

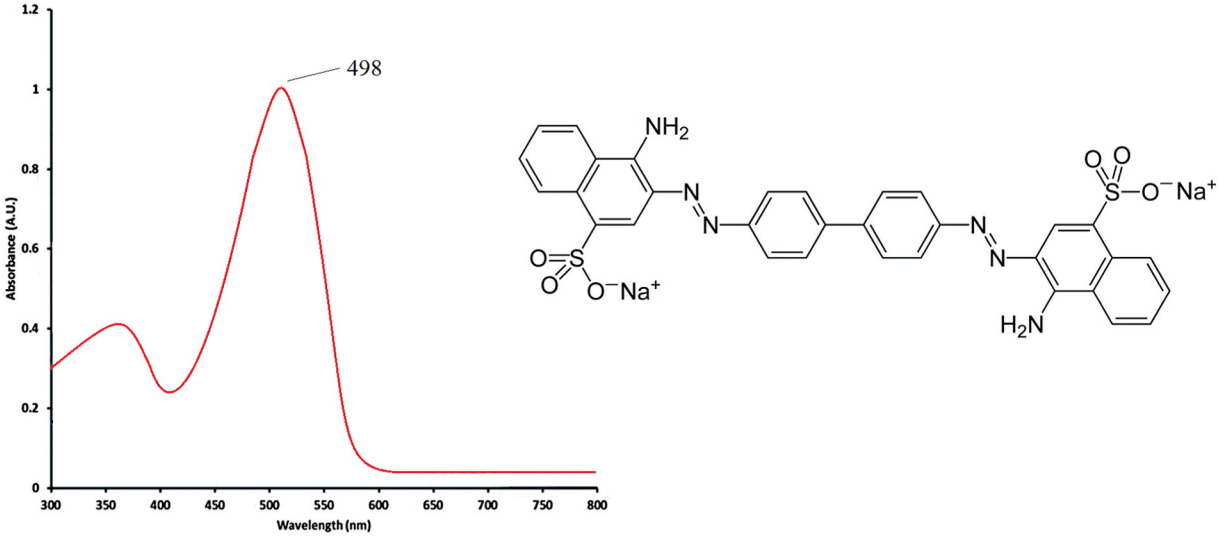


**Fig. 1.** Chemical structure and UV–vis spectra of Congo red dye.