Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Enhancing the adsorption performance of carbon nanotubes with a multistep functionalization method: Optimization of Reactive Blue 19 removal through response surface methodology

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ARTICLE INFO

Article history:
Received 3 May 2015
Received in revised form 21 July 2015
Accepted 10 October 2015
Available online 17 October 2015

Keywords:
Adsorption
Carbon nanotubes
Functionalization
Optimization
Reactive dye removal
Response surface methodology (RSM)

ABSTRACT

The main aim of present study was to enhance the adsorption capacity of Reactive Blue 19 (RB19) onto multi-walled carbon nanotubes (MWCNTs), pretreated in a multi-step functionalization process. The functionalization procedure consisted of microwave irradiation followed by sonication in dilute H_2SO_4. The properties of MWCNTs were investigated by X-ray diffraction, scanning electron microscopy, N_2 adsorption isotherms (Brunauer–Emmett–Teller surface area analysis), Raman spectroscopy and Fourier transform infrared spectroscopy. The effective addition of desired functional groups resulted in a considerable increase of dye removal efficiency and adsorption capacity. For pristine and functionalized MWCNTs, the maximum adsorption capacities were found to be 53.33 and 211.02 mg/g, respectively. In addition to the main aim of this research, a statistical/mathematical approach – response surface methodology – was utilized to simulate and determine the optimum conditions of RB19 removal by functionalized MWCNTs using three selected parameters (adsorbent dose, initial dye concentration and pH). High R^2-value (97.75%) and a good agreement between predicted R^2-value (89.11%) and adjusted R^2-value (95.72%) demonstrated an acceptable proportion of the experimental and predicted results. For maximum RB19 removal efficiency, eight optimum scenarios were also obtained and validated by further experiments.

1. Introduction

Reactive dyes usually have a synthetic origin and complex aromatic structures, making them stable and difficult to biodegrade (Won et al., 2008). Untreated disposal of effluents contaminated by reactive dyes may result in adverse effects on human/aquatic life (Ozcan et al., 2007). Reactive Blue 19 (RB19) dye is commonly used in the textile and leather industry and may be mutagenic and toxic because of the presence of electrophilic vinylsulfone groups (McCallum et al., 2000; Siddique et al., 2011). High efficiency, simplicity and low cost in addition to high solubility of reactive dyes in water, have made the adsorption process preferable among the other conventional methods for removal of reactive dyes from aqueous solutions (Wu, 2007).

Carbon nanotubes (CNTs) have been proven to possess a great potential as exceptional adsorbents for removing dyes because of their large specific surface area, small pore size, layered and hollow structures (Wang et al., 2012). Raw CNTs usually contain different impurities reducing their structural and electrical properties (Chen et al., 2004), which could affect dye removal efficiency. Multi-walled carbon nanotubes

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http://dx.doi.org/10.1016/j.psep.2015.10.007

(MWCNTs) produced by chemical vapor deposition (CVD) procedure contain impurities of amorphous carbon, graphite particles and metal catalysts (Chen et al., 2002). There are several ways to purify and functionalize MWCNTs such as ultrasonication (Rossell et al., 2013), microwave acid digestion (MacKenzie et al., 2011) and acid oxidation (Aviles et al., 2009). Each of these methods may have undesirable effects, such as time/energy consumption, excessive loss of CNTs and morphological damage (Hou et al., 2008).

Although there are several studies in which MWCNTs, prior to be used as adsorbent, were treated by the aforementioned methods (Lu et al., 2008; Rosenzweig et al., 2014; Yao et al., 2010), to the best of our knowledge, using a multistep procedure consisting of irradiation in a modified domestic microwave followed by sonication in dilute acid has not been studied yet. Therefore, in this study, this combined pretreatment method is applied to achieve the desired functionalization of MWCNTs and minimize some adverse effects of the other intense methods. Furthermore, the adsorption process of RB19 dye onto pristine and functionalized MWCNTs is investigated to demonstrate the considerable enhancement of adsorption performance. Finally, to simulate and optimize the adsorption process using functionalized MWCNTs, response surface methodology (RSM) is applied to develop a mathematical correlation between the selected parameters including adsorbent dose, initial dye concentration and pH in RB19 removal procedure.

2. Materials and methods

2.1. *Multistep functionalization of MWCNTs*

Raw MWCNTs fabricated by CVD method (length (10–20 μm) and diameter (30–50 nm)) was purchased from Neutrino Corporation, Iran. First, 0.1 g of pristine MWCNTs were put onto a quartz plate and irradiated in a modified domestic microwave (Samsung, ME201—Malaysia) for 10 min with power of 100 W under a constant airflow of 1000 mL/min and was cooled afterwards to room temperature. Most of MWCNT surface oxidation activity occurs within the first hour of sonication in acid (Xing et al., 2005), therefore, the irradiated MWCNTs were mixed in 100 mL of 3 M H_2SO_4 and sonicated for 1 h in a conventional ultrasonic bath (Sonoswiss, 90 W, 50/60 Hz—Switzerland). Finally, the slurry was vacuum filtered through 0.2 μm PTFE filters (Sartorius-Germany) and thoroughly washed with distilled water.

2.2. *Characterization of MWCNTs*

The structure of samples was investigated by X-ray diffraction (XRD) analysis on Inel-Equinox 3000 (France) using CuK_α radiation ($\lambda = 1.5406$ Å) at 40 kV. The 2θ ranged from 10 to 80 degree, where θ is the diffraction angle. The morphology of MWCNTs was observed by scanning electron microscopy (SEM) on a Philips-XL30 (Holland) operating at 25 kV. The specific surface area of MWCNTs were also determined by N_2 adsorption/desorption isotherms (BET analysis) at 77 K using a Quantachrome Autosorb 1 analyzer (USA). Raman spectroscopy was performed on an Almega Thermo Nicolet Dispersive Raman spectrometer (USA) with a laser power of 100 mW at 523 nm, in a spectral range of 1000 to 3000 cm^{-1}. The Fourier transform infrared spectroscopy (FT-IR) analysis was conducted with a Thermo Nicolet, Nexus 670 (USA) in the spectral range from 4000 to 800 cm^{-1} on KBr discs.

2.3. *Adsorption procedure of RB19*

RB19 was provided by the Alvan Sabet Company, Iran. The general properties and chemical structure of RB19 are presented in Table 1. pH of the solution was adjusted with H_2SO_4 and NaOH (Merck-Germany) and measured using a 340i/SET pH meter (WTW-Germany). The effect of different pH values (2–12) on RB19 stability was also investigated and it was observed that this dye is stable in this range.

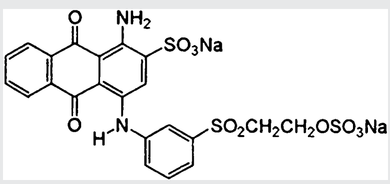
For adsorption batch experiments, 150 mL of RB19 solution and the desired dosage of MWCNTs were placed in 250 mL flasks. To disperse pristine and functionalized MWCNTs, the solution was sonicated for 5 min, then it was agitated at 150 rpm on a standard shaker (Edmund Buhler, Germany). Afterwards, the sample was centrifuged at 6000 rpm for 10 min prior to the analysis (Hettich, EBA 21-Germany). RB19 concentration was quantified using a HACH spectrophotometer DR/4000 (USA) at a wavelength corresponding to the absorbance of 592 nm (λ_{max}). The adsorption studies were carried out at 25 ± 2 °C. The amount of RB19 adsorbed on the MWCNTs per unit mass of adsorbent, q (mg/g) and percentage of dye removal was calculated by the following equations:

$$\text{Dye removal efficiency}\,(\%) = \frac{\left(C_0 - C_f\right)}{C_0} \times 100 \tag{1}$$

$$q = \frac{\left(C_0 - C_f\right) V}{M} \tag{2}$$

where C_0 is the initial dye concentration (mg/L), C_f is the dye concentration at the end of adsorption procedure (mg/L), q is the amount of adsorbed dye on MWCNTs (mg/g), V is the volume of the dye solution (L) and M is the mass of MWCNTs (g).

Table 1 – The general properties and chemical structure of RB19.

Characteristics	Values	Chemical structure
Molecular formula	$C_{22}H_{16}N_2Na_2O_{11}S_3$	
λ_{max} (nm)	594	
Molecular weight (M_W)	626.54	