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Amine functionalized multi-walled carbon nanotubes: Single and binary systems for high capacity dye removal

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HIGHLIGHTS

- Simplified novel production method for amino dendrimer CNTs.
- Exceptional high adsorption capacities for dyestuffs removal-over 500 mg/g.
- Exceptionally fast contact time to reach equilibrium.
- Equilibrium data fitted Langmuir model; rate data fitted pseudo-second order model.

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ABSTRACT

The aim of this study was to develop a feasible and cost effective method to produce amine functionalized multi-walled carbon nanotubes (CNT-NH_2) and investigate the ability of this CNT-NH_2 material to adsorb anionic dyes in single and binary (mixture of dyes) systems. For this purpose, pristine CNTs were functionalized by primary and secondary functional groups namely (-NH2) and (-NH), respectively. Acid Blue 45 (AB45) and Acid Black 1 (AB1) were used as anionic dye models for adsorption. FTIR, SEM, BET, Raman Spectra, and Zeta potential measurements have been employed for characterizing the synthetic nanocomposite and these techniques indicated that the amino functionalized CNTs have been favorably synthesized. The effects of different operational parameters including pH, initial dye concentration, adsorbent dosage, and salt on dye removal were evaluated. The dye adsorption isotherm and kinetics were also studied. The results of this study indicated that the stronger interactions between CNT-NH_2 and AB1 suggest a higher adsorption of AB45 compared to AB1 in both single and binary dye systems. Moreover, the maximum adsorption capacities of the studied functionalized nanotube in single dye solutions, for AB45 and AB1 were 714 and 666 mg g^{-1}, respectively. These capacities are exceptionally high for the removal of acid dyes. It was found that AB45 and AB1 adsorption on the CNT-NH_2 followed the Langmuir isotherm model and pseudo-second order kinetics model in both single and binary systems. According to the results of this study the CNT-NH_2 were an effective adsorbent to remove anionic dyes from single and binary systems.

1. Introduction

Water is the main and fundamental part of the environment for the basic requirement of human life. Unfortunately, in recent years, a significant quantity of wastewater has been generated by a large range of industries, including: printing, textile, dyestuff, paper, plastic and other products [1–4]. The discharge of wastewaters with large amounts of color and high levels of suspended and dissolved solids, organic pollutants into the ecosystems inflicts significant environmental hazards because it is difficult to clean-up dye contaminants because of their non-biodegradability and polluting nature [5–8]. Moreover many dyes are toxic for animal and human life cycles because they affect the nervous issues. Therefore the removal of dyes from industrial wastewater is very important [9,10].

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For the benefits of health and environmental safety, new techniques to eliminate dyes from the colored wastewaters are urgently required and they should be cost effective, efficient and eco-friendly. Among several chemical, physical and biological methods for dye removal, adsorption is the most efficient system because of its low expenditure, high performance and easy exploitation. So far, several adsorbents have been investigated, however, the application of some adsorbents has some intrinsic limitations including long contact time and low efficiency. Therefore, discovering novel adsorbents with easy preparation, great adsorption efficiency and relatively inexpensive, is required. Among the different types of carbon products which have been synthesized and applied for dye adsorption are carbon nanotubes (CNTs) [11]. CNTs include two types: single-walled and multi-walled. These novel materials have been attracting considerable attention because of their great electrical, physical, chemical, mechanical and optical properties. Nevertheless, the usage of CNTs has been considerably limited by their negligible suspension into aqueous solution due to the powerful intermolecular van der Waals bonds between tubes that cause the formation of agglomerations [12]. To enable the dispersion of CNTs, researchers have used different types of methods to prepare novel functional groups on the surface of CNTs [13]. The application of amine groups and their ability to chelate with metal ions and dye is well established [14,15]. From these approaches, amine modified CNTs have been studied since the amine group has a great reactivity and can interact with many materials. In this research, amine modified carbon nanotubes (CNT-NH_2) were synthesized and analyzed by Fourier-transform infrared spectroscopy (FTIR) analysis, X-ray diffraction (XRD), Raman, Brunauer, Emmett, and Teller specific surface area measurement (BET) analyses and zeta potential measurements. This study presents a novel procedure to synthesize CNT-NH_2 using a new easy production technique. Its adsorption capability was studied using Acid Blue 45 (AB45) and Acid Black 1 (AB1) removal as model color pollutants; the isotherms and kinetics of AB45 and AB1adsorption onto CNT-NH_2 have been studied.

2. Experimental

2.1. Materials

Anionic dyes, Acid Black 1 (AB1) and Acid Blue 45 (AB45) were obtained from Ciba Co., Iran and their structure and characteristics are tabulated in Table 1. The pristine CNT were supplied by the Nanocyl SA. (Sambreville, Belgium). All ingredients used for surface fictionalization of CNTs (such as diethylenetriamine (DETA), maleic anhydride (Man), dibenzoyl peroxide, xylene, etc.) were provided by Merck Company. The dyes and all chemicals in this study were used without further purification.

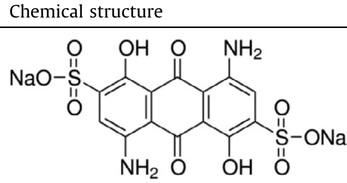
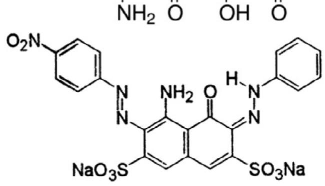
2.2. CNT-NH_2 synthesis and characterization

The production of functionalized carbon nanotubes was carried out in two steps. First unsaturated monomers with functional groups -NH and -NH_2 were synthesized by the reaction of (Man) and (DETA). Thus, equimolar amounts of unsaturated monomers i.e. DETA (0.1 mol, 10.3 g) and Man (0.1 mol, 9.8 g) were heated from ambient temperature to 80 °C and stirred in 60 mL water for 60 min. Thereafter, 10 g of MWCNTs was added to the amine-containing monomer solution and refluxed with xylene at 140 °C for 4 h. In this step, free radical polymerization of anhydride precursor onto the surface of CNTs was conducted using benzoyl peroxide (0.3 g) and Sb_2O_3 (0.15 g) as initiator and catalyst, respectively. As a result imide rings were formed, which potentially speedup free radical homo polymerization of amine functionalized monomer [16]. The final step was to dry the amine-functionalized MWCNTs in a vacuum oven at 80 °C for 4 h and grind it (Scheme 1). The morphological properties of pristine and modified MWCNTs were analyzed using scanning electron microscopy (SEM, JEOL, JSM 5800) coupled with energy dispersive X-ray analysis (EDAX) with 20 kV at 2500 times magnification for comparison of the effect of pretreatment. The Fourier transform infrared (FTIR) spectra were taken as KBr pellets using a Tensor 27 spectrometer (Bruker Optik GmbH, Germany) in the wavenumber range of 500–4000 cm^{-1}. Zeta-potential values of pristine and functionalized CNTs were measured using a Zeta sizer Nano ZS system (Malvern, UK) equipped with a standard 628 nm laser. Raman spectra were determined using a Raman spectrometer (RAM HR) with the 486 nm line of an Ar ion laser. BET specific surface area measurements were conducted using surface area analyzer (Nova 2000, Quantachrome Instruments, FL and USA) and nitrogen as the adsorbing gas. The sample was slowly heated to 300 °C for 4 h under a nitrogen atmosphere. Digimizer software version 4.1.1.0 was used in order to determine the mean diameter and particle size distribution of pristine and modified MWCNTs.

2.3. Adsorption procedure

Dye adsorption experiments were performed by mixing known amounts of CNT-NH_2 in 250 mL of dye solution in jar sat 25 °C. The effects of pH (2–10), initial dye concentrations (25–100 mg/L), inorganic salts (0.01 M) and CNT-NH_2 dosages (0.02–0.15 g/L) on CNT-NH_2 adsorption capacity were investigated. The solution samples were taken at known time intervals during the adsorption process. The residual dye concentrations were determined by Shimadzu UV/vis-1700 spectrophotometer at the maximum wavelength of 595 and 618 nm for AB45 and AB1, respectively. The effects of adsorption parameters in single and binary systems were

Table 1
The characteristics of used dyes.

Dye	Chemical structure	Molar mass (g/mol)	Dye purity	Molecular formula	λ_{max} (nm)
Acid Blue 45		474.33	99%	$C_{14}H_8N_2Na_2O_{10}S_2$	595
Acid Black 1		616.490	99%	$C_{22}H_{14}N_6Na_2O_9S_2$	618