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Effect of electrostatic interaction on the methylene blue and methyl orange adsorption by the pristine and functionalized carbon nanotubes

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HIGHLIGHTS

- Multi-walled carbon nanotubes were functionalized with cysteamine groups.
- The adsorption of methylene blue and orange dyes was investigated on these surfaces.
- The effect of temperature, contact time and initial concentration was considered.
- The optimal contact time was found to be about 60 min.
- Kinetic of the adsorption process was explored.

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were functionalized with cysteamine groups by several percentage of mass as adsorbents, then kinetics adsorption capacity was investigated for methylene blue (MB) and methyl orange (MO) as anionic and cationic dyes adsorbate molecules, respectively. The effect of temperature (from 283 to 303 K), contact time and initial concentration of the MB and MO dyes in a solution (10 to 40 ppm) was considered. The optimal contact time was found to be about 60 min. Some kinetics model such as pseudo-first-order, pseudo-second-order, intra-particle diffusion and the Elovich were tested. The adsorptions of MB dye on the pristine and functionalized MWCNT surfaces were found to be the intra-particle diffusion and the pseudo-second-order kinetic model, respectively and for adsorption of MO dye by the pristine and low functionalized MWCNTs and highly functionalized tubes, found to be the pseudo-second-order and intra-particle diffusion kinetic model, respectively, based on the chi-square statistic (X^2) and also high correlation coefficient (R^2) values.

1. Introduction

One of the most environmental concerns is dyes as wastewater of industries. Today industries use a lot amount of dyes for production of food, leather, paper, cosmetics, and textiles. Several of dyes and their derivatives are not readily biodegradable and have a carcinogenic, toxic, or mutagenic efficacy on mankind and animals. So, a significant area of applied and basic research is the removal of dyes pollution from wastewater of industries [1]. Effluents from the textile industry contain various kinds of synthetic dyestuffs, and there has been increasing scientific interest in regard to decolonization of these effluents in the last few decades [2]. Dyes can cause allergy, dermatitis, skin irritation [3–7], and also provoke cancer [8], and mutation in humans [9].

Methylene blue (MB) dye is one of the cationic dyes that used as a material for dyeing wood, cotton, and silk. Also, MB dye is not classified to be a high toxic dye [10]. Therefore, removing MB from wastewater before discharge is an essential task. Methyl orange (MO) also is one of the anionic dyes that used in the textile industry and in the titrations as well as a pH indicator because of its clear and distinct color change. Methyl orange is commonly used in titrations for acids because it changes color at the pH of mid-strength acid [11].

Nanostructured materials are knows as proper adsorbents due to their high surface to volume ratio [12–19]. Carbon nanotubes

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(CNTs) have attracted high attention in interdisciplinary areas because of their unique empty tube structure, and outstanding electronic, optical, and mechanical properties [20–23]. An application of CNTs is as adsorbent which are used alone or in combination with other substances as nanocomposite. In comparison with classical adsorbents such as clay and activated carbon, the CNTs are more attractive because of its physicochemical favorable stability, structural and diversity high selectivity [24,25]. Extensive experiments have been conducted on the adsorption of organic or inorganic contaminants on CNTs such as dioxin [26], Cd^{2+} [27], Zn^{2+} [28], Cr^{6+} [29], Cu^{2+} [30], fluoride [31], Pb^{2+} [21], and toxic gases.

One of the main goals of this work is the investigation of the effect of electrostatic interaction on the adsorption process. So, surface of MWCNT-COOH functionalized by cysteamine groups was prepared with different percentages of mass, namely, MWCNT (0%), MWCNT-SH_1 (1%), MWCNT-SH_3 (3%), and MWCNT-SH_5 (5%) as nanocomposite adsorbents. In the MWCNT-COOH [12], negative surface charge was increased with increasing the percentage of the cysteamine groups in nanocomposite adsorbents. Also, MB and MO were selected as anionic and cationic dyes, respectively. The capacity in the adsorption of MB and MO at 298 K and pH 6 was calculated. The effect of temperature, contact time and initial dye concentrations was investigated on the adsorption process. Scanning electron microscope (SEM), Fourier transforms infrared (FT-IR) and Raman spectroscopic techniques were used for characterization surface of adsorbents.

2. Materials and methods

2.1. Materials

2.1.1. Multi-walled CNT functionalized with carboxyl (MWCNT-COOH) and cysteamine

MWCNTs were providing equipment from Modern Technology Development Institute, Iran (CVD, Spin Coater and Spray Coater), then MWCNT-COOH was provided with a purity of over 95%. Average diameter 1–2 nm; length 5–30 nm and SSA ~400 m^2/g were prepared by catalytic chemical vapor deposition (CVD) from Modern Technology Development Institute, Iran. Cysteamine was provided from the Sigma-Aldrich Co. (Germany) with a purity of over 98% for synthesis the following specifications.

2.1.2. Methyl orange and blue dyes

Methyl orange and blue dyes were provided from the Sigma-Aldrich Co. (Germany) with empirical formula $C_{14}H_{14}N_3NaO_3S$, and $C_{16}H_{18}ClN_3S$, respectively, as shown in Fig. 1.

2.2. Preparation of nanocomposite MWCNT functionalized with thiol (MWCNT-SH)

For preparing the nanocomposite *MWCNT* functionalized with thiol (MWCNT-SH), 80 mg of dry powder of *MWCNT-COOH* with 80 mg of cysteamine hydrochloride were solved in ethanol, and the solution was shacked until becomes evenly. Also, 50 mg of 1-ethyl (3, 3 dieamino-propel acetate) carobo amide 99% (EDC) was used for better reaction between graphene oxide and glycine (with purity ≥99% provided by Aldrich company). Afterward, 30 mg of N-hydroxyl Svsynamyd (NHS) 99.9% (Aldrich Company) was added to the solution. The reaction between *MWCNT-COOH* and cysteamine hydrochloride was shown in Fig. 2. After completion of the reaction, nanocomposite MWCNT-SH was separated by micro filter and washed with deionized water and ethanol for several times. The pH of output water was neutralized. Then the resulting mixture placed in the oven at 80 °C for 48 h until its moisture taken completely.

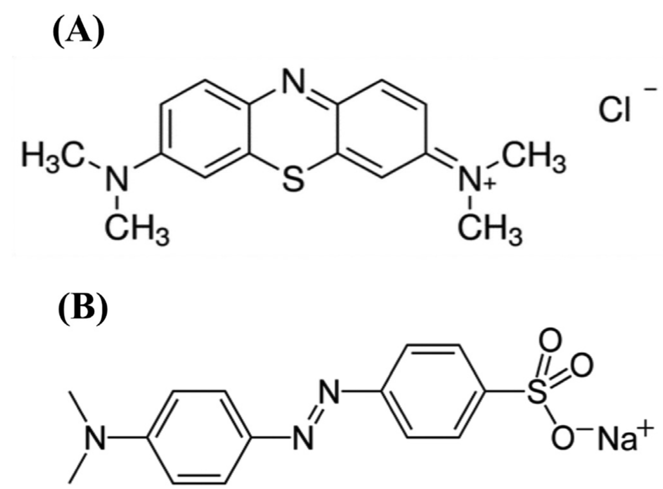

Fig. 1. Structure of (A) methyl orange (MO) and (B) methylene blue (MB).

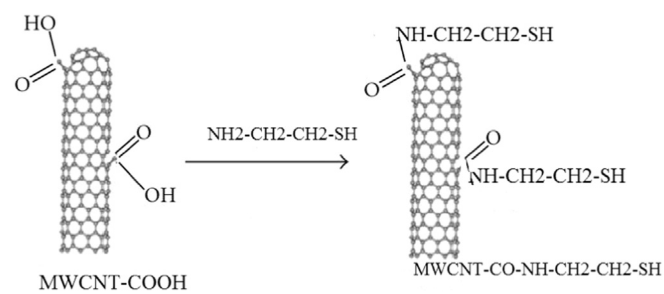

Fig. 2. Preparation of nanocomposite: the reaction between multi-walled carbon nanotubes functionalized by carboxyl with cysteamine hydrochloride.

3. Results and discussion

3.1. Characterization of nanocomposite MWCNT-SH

We have synthesized adsorbents and the results of the FTIR, TGA and Raman spectroscopic studies are in good agreement with the results of the Robati et al. [32]. Results of the SEM for MWCNT-COOH, and MWCNT-SH are shown in Fig. 3. It can be found that the active particles are dispersed on the surface of MWCNT-COOH, and nanocomposite formation is observable.

3.2. Adsorption study

With the rotation speed of 200 rpm the samples transferred into100 mL glass flasks. Then 20 mg of MWCNT, MWCNT-SH_1, MWCNT-SH_3, and MWCNT-SH_5 adsorbents were added into 20 mL of MB and MO dyes solution with known concentration of MB and MO dyes (10 mgL^{-1}) at 298 K and pH 6. The optimum time for the adsorption process selected to be 60 min since the removal of MB and MO did not changed after this time. Remaining MB and MO dyes in the samples were specified by using the UV–vis spectrophotometer furnished by Varian (Cary 100 Bio) (London-England). The maximum wavelengths were 615 and 480 nm for MB and MO dyes, respectively. The following equation was used to calculate the adsorption rate and the concentration of MB and MO for both before and after adsorption [33]:

$$q_e = \left(\frac{C_e - C_0}{W}\right) \times V \quad (1)$$

where C_e (in milligrams per liter) is initial concentrations of MB or