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Enhanced adsorption of Congo red dye by functionalized carbon nanotube/mixed metal oxides nanocomposites derived from layered double hydroxide precursor

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HIGHLIGHTS

- Novel CNT/Mg(Al)O nanocomposites were synthesized from a LDH precursor.
- The surface of the CNT is functionalized with abundant —OH and COO— groups without any further modification.
- The CNT/Mg(Al)O nanocomposites exhibit rapid adsorption rate and high adsorption capacity in the removal of Congo red with the maximum adsorption capacity enhanced to 1250 mg/g.
- Adsorption mechanism mainly involves complexation and electrostatic interaction.

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ABSTRACT

Functionalized carbon nanotube/mixed metal oxides (CNT/MMO) nanocomposites composed of CNT and Mg(Al)O nanoparticles have been synthesized by pyrolysis of a terephthalic intercalated layered double hydroxide (LDH) precursor. The chemical composition and morphology of this nanocomposites were investigated by XRD, SEM, and TEM measurements. FTIR characterization shows that the surface of the prepared CNT is functionalized with abundant oxygen-containing groups without further modification. As a novel adsorbent, the as-prepared functionalized CNT/Mg(Al)O nanocomposites exhibit very high performance in the removal of Congo red (CR) dye from aqueous solutions. The initial pH of dye solution and dosage of adsorbent have an important influence on the adsorption property of the CNT/Mg(Al)O nanocomposites. The adsorption isotherm obeys the Langmuir model, with the maximum adsorption capacity greatly enhanced to 1250 mg/g, exhibiting potential applications in wastewater treatment. A adsorption mechanism that involves (i) strong interactions between the functional groups on the surface of CNT and CR molecules and (ii) electrostatic interactions between positively charged reconstructed LDH layer and negatively charged CR molecules, was proposed.

1. Introduction

In recent years, increasing concern for public health and environmental quality has led to a growth of special interest in developing and implementing various methods of removing potentially toxic organic and inorganic pollutants from water. Especially, the dye-contaminated wastewater is one of the most serious environmental problems due to its deep color, complex component, and low biodegradable [1]. Congo red (CR) is a popular anionic dye and has been widely used in many industries including directly textiles, printing and dyeing, paper, rubber plastics and so forth. Wastewaters containing CR have to be treated adequately before discharge into the environment, because it can be metabolized to benzidine, a human carcinogen [2]. Therefore, the development of cost-effective methods for removal of CR from waste effluents is of considerable environmental importance.

Various physical and chemical methods of treatment of dye-contaminated wastewater including coagulation/flocculation [3], biological treatment [4], ozone treatment [5], chemical oxidation [6], membrane filtration [7], ion-exchange [8], as well as

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photocatalytic degradation [9] have been suggested. However, most of these methods present several disadvantages like chemical requirements, low efficiency and usually produce large amounts of sludge which can add other environmental problems. As one alternate effective process, adsorption technology has been regarded as one of the most promising and widely used methods due to its effectiveness, efficiency, economy and no secondary pollution. A number of materials including metal oxides and hydroxides [10], zeolites [11], active carbon [12], graphene oxide [13], as well as many other carbonaceous materials derived from solid waste [14,15] have been reported to be capable of adsorbing dyes from wastewater.

As an important carbon material, carbon nanotube (CNT) has received great interest in water treatment due to its small size, high aspect ratio, large accessible specific surface area, well-developed mesopores, as well as easily modified surfaces. Large surface area and high porosity provide enough adsorption sites for harmful contaminations present in wastewater. High aspect ratio of CNT makes it a possible candidate for water purification. In recent years, great efforts have been made to remove various organic pollutants and metal ions in wastewater by CNT [16,17]. To further improve their adsorption performance, various CNT composites have been synthesized and widely used to remove dye pollutions from wastewater. For example, Gao et al. reported that the adsorption capacities of CNT/polymer nanocomposites for anionic azo dyes orange II, sunset yellow FCF and amaranth were enhanced after the incorporation of poly(1-glycidyl-3-methylimidazolium chloride), with the maximum values calculated to be 68, 86 and 47 mg/g, respectively [18]. Madrakian et al. have investigated the removal of cationic dyes crystal violet, thionine, janus green B, and methylene blue from water by magnetic-modified CNT with maximum adsorption capacities of 228, 250, 36 and 48 mg/g, respectively [19]. Mishra et al. reported the adsorption of azo dye direct CR on the functionalized multi walled CNT and the maximum adsorption capacity was about 148 mg/g [20]. Chatterjee et al. successfully obtained CNT/chitosan hydrogel beads, which could adsorb CR with a maximum adsorption capacity of 450.4 mg/g [21]. However, these adsorption capabilities are not entirely satisfactory and it is still a challenge to explore novel CNT composites adsorbents with high adsorption capacity, short adsorption time as well as low cost for practical utilization.

Mixed metal oxides (MMO) derived from layered double hydroxide (LDH) precursors have drew tremendous interest in both theoretical and technological fields in recent years. Especially, by virtue of their low-cost, minimum environmental impact, as well as their high adsorption properties based on the unique property of LDH material known as "memory effect", the MMO materials have been demonstrated to be an efficient adsorbent for removal of various pollutants such as oxyanions, heavy ions and organic dyes [22–24]. Therefore, the integration of CNT and MMO to forming novel CNT/MMO nanocomposites may potentially offer the viable solutions to the limitations faced by the adsorbents mentioned above. However, there are few reports about such nanocomposites.

In our previous work, functionalized CNT with C—OH and COO—M groups on the surface was successfully synthesized by pyrolysis of CoAl LDH precursor containing salicylate anions and exhibited high performance in the removal of CR dye with the maximum adsorption capacity as high as 882 mg/g [25]. Herein, nanocomposites of functionalized CNT and Mg(Al)O nanoparticles (CNT/Mg(Al)O nanocomposites) were synthesized via the facile pyrolysis process using CoFeMgAl LDH containing terephthalic anions (TA) as precursor. The structures and properties of the prepared CNT/Mg(Al)O nanocomposites were characterized by XRD, SEM, TEM and FT-IR measurements. As an example of the potential applications of the resulting functionalized CNT/Mg(Al)O nanocomposites, they were used as adsorbent to remove CR from aqueous solution. The influences of parameters on adsorption property including initial pH of dye solution and dosage of adsorbent have been investigated. To study the adsorption mechanism, the CNT/Mg(Al)O nanocomposites after adsorption of CR were also investigated in detail.

2. Materials and methods

2.1. Synthesis of CNT/Mg(Al)O nanocomposites

2.1.1. Synthesis of CoFeMgAl-TA LDH precursor

All chemicals were of analytical reagent grade and used as received without further purification. The CoFeMgAl-TA LDH precursor was prepared by a simple coprecipitation method. In a typical procedure, a mixture of $Co(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ with Co/Fe/Mg/Al ratio of 2.0/1.0/2.0/1.0 was dissolved in 50 mL of deionized water to form a clear mixed salt solution ($[Co^{2+}] + [Fe^{3+}] + [Mg^{2+}] + [Al^{3+}] = 1.2$ M). Another mixture of terephthalic acid (0.04 mol) and NaOH (0.08 mol) was dissolved in 100 mL of deionized water to prepare sodium terephthalic solution. A three-fold excess of terephthalic above the necessary stoichiometric amount required for charge neutrality was used in the reaction mixture to reduce the probability of incorporating competing nitrate and carbonate anions into the product LDH. Then, the as-prepared mixed salt solution and another 100 mL of NaOH solution ($[OH^-] = 2$ M) were simultaneously added dropwise to sodium terephthalic solution with the pH maintained at 7 during the whole process. The obtained suspension was transferred into a Teflon-lined autoclave and crystallized at 100 °C for 24 h. The resulting solid product was separated by centrifugation, washed with deionized water several times until pH = 7, and dried in an oven at 60 °C for 12 h to collect the solid powder CoFeMgAl-TA LDH.

2.1.2. Synthesis of CNT/Mg(Al)O nanocomposites

The CNT/Mg(Al)O nanocomposites were prepared by pyrolysis of the CoFeMgAl-TA LDH precursor under N_2 atmosphere. In a typical process, the CoFeMgAl-TA LDH precursor was placed in a ceramic boat which was placed in a furnace and purged with N_2 for 2 min to exclude the air in the furnace. Under a continuous flow (60 mL min^{-1}) of N_2 gas, the furnace temperature was raised to 650 °C at a ramping rate of 5 °C min^{-1} and then kept for 2 h. After slow cooling down naturally to room temperature, CNT/Mg(Al)O nanocomposites powder was obtained.

2.2. Characterization

The as-synthesized CNT/Mg(Al)O nanocomposites were characterized by X-ray diffraction (XRD, Shimadzu XRD-6000 diffractometer with Cu Kα1 radiation, $\lambda = 0.1541$ nm, 40 kV, 30 mA), Fourier transform IR (FT-IR, Bruker Vector-22), scanning electron microscopy (SEM, Hitachi S-4700), and transmission electron microscopy (TEM, Hitachi H-800). The zeta potential of CNT/Mg(Al)O nanocomposites suspensions were measured using a Zeta Meter 3.0 (Zeta Meter Inc.) equipped with a microprocessor unit in a pH range of 2–10.

2.3. Adsorption studies

The adsorption experiments were conducted by adding 30 mg CNT/Mg(Al)O nanocomposites adsorbent to 100 mL of CR ($C_{32}H_{22}N_6O_6S_2Na_2$) solution with the concentration fixed at 100 mg/L under vigorous stirring at room temperature. At different time intervals, approximately 3 mL of aliquots were taken from the