



Co-precipitation of magnetic Fe₃O₄ nanoparticles onto carbon nanotubes for removal of copper ions from aqueous solution



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ABSTRACT

The removal of copper ions by magnetic Fe₃O₄/carbon nanotube (CNT) composite adsorbents, prepared by co-precipitation method, in aqueous solution has been investigated. The influence of magnetite loading (35.5–64.1 wt.%) onto oxidized CNT support on the adsorption capacity and regeneration efficiency is investigated. The adsorption isotherms of Cu²⁺ ions are well characterized by Langmuir, Freundlich, and Dubinin–Radushkevich models within the temperature range of 303–323 K. The decoration of magnetic Fe₃O₄ significantly enhances the removal efficiency, equilibrium rate constant, and adsorption capacity, as analyzed by these models. The appropriate loading of magnetite nanoparticles on the CNT supports not only increases adsorption capacity but also facilitates regeneration efficiency. Accordingly, the Fe₃O₄/CNT composite can be used as an effective adsorbent for rapid removal of Cu²⁺ ions from aqueous solution.

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1. Introduction

Heavy metal ions such as Cu²⁺ have been recognized for their high toxicity and non-biodegradability in environment, which even in trace amount can accumulate in living organisms through food chains [1]. The pollution by disposal of heavy metal contaminated wastewater into the ecosystem is causing worldwide concern [2–4]. The toxic effects of heavy metals on human health have been widely reported, showing correlation between presences of heavy metals and high blood pressure, speech disorders, fatigue, sleep disabilities, aggressive behavior, memory loss, and so on [5]. Thus, the removal of heavy metal ions from wastewater has become a crucial issue. A number of methods have been developed to remove heavy metal ions or other pollutants such as chemical precipitation [6], ion-exchange [7], flocculation [8], electrolysis [9], membrane separation [10], adsorption [11–13] and photocatalysis [14–24]. As compared with the others, adsorption is one of the most potential processes owing to its easy operation, high removal efficiency, and compatibility with various contaminants [25–32].

It is well known that activated carbon and activated carbon fabric are popular adsorbents because of their high porosity and vast

specific surface area, thus showing superior ability for removing liquid-phase contaminants such as organic compounds and colors [33–38]. More recently, an alternative carbon adsorbent, carbon nanotube (CNT), has attracted lots of attentions due to its one-dimensional structure and intriguing physical properties. So far, CNTs have been considered as a promising adsorbent for the removal of different heavy metals from drinking water or wastewater, e.g., lead [39], mercury [40], zinc [41], chromium [42] and copper [43]. The above achievements have confirmed the adsorption performance of heavy metals on CNT adsorbents. This can be attributed to the fact that CNTs act as contaminant-carriers, offering strong affinities to pollutants in liquid phase [44–50]. However, separation and regeneration of the spent CNTs after water purification or treatment process is still a challenge attracting extensive attention. One route to efficient separation of spent CNTs from aqueous solution is anchoring magnetic magnetite (*i.e.*, Fe₃O₄ nanoparticles) to CNTs, thus forming magnetic Fe₃O₄/CNT composite adsorbents [12,51]. Accordingly, the magnetic separation method is capable of rapidly separating the Fe₃O₄/CNT adsorbents from aqueous solution.

Within the above scope, this work aims at well dispersion of magnetic Fe₃O₄ nanoparticles onto CNTs, using a co-precipitation method. Copper ion (*i.e.*, Cu²⁺), a frequent constituent in industrial and agricultural effluents, was used as adsorbate [2]. It is generally recognized that copper ions are highly toxic and can be

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released into environment from many sources including electroplating, battery manufacturing, mechanical mining, textile, plastic, and semiconductor industries [25,52]. The weight loading of Fe_3O_4 nanoparticles on CNT support serves as a crucial factor to determine the adsorption capacity and regeneration efficiency. Herein we report a series of adsorption/desorption experiments and the resulting adsorption isotherms are systematically interpreted by using Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) models. The merit of the present work is to shed some lights on (i) the robust design of magnetic CNT adsorbents for removal of Cu ions from aqueous solution and (ii) the optimal ratio of Fe_3O_4 to CNT on the improved adsorption/regeneration efficiency. The influence of Fe_3O_4 /CNT ratio on the removal efficiency, equilibrium rate constant, and adsorption capacity are systematically investigated. The separation method involving magnetic CNT adsorbent is capable of offering a scalable process for industrial applications due to its facile operation, high removal/regeneration performance and usage of low-cost adsorbents.

2. Experimental

2.1. Synthesis of magnetic CNT adsorbents

The CNT sample was synthesized by catalytic chemical vapor deposition method, using Ni oxide and ethylene as catalyst and carbon source, respectively. The CNTs were of multi-layered structure with several micrometers in length and 50 nm in average diameter. Prior to the decoration of magnetite, the CNT sample was chemically oxidized in 4 M nitric acid. The chemical oxidation process was conducted in an ultrasonic bath for 6 h. The CNT slurry was then water-washed several times until the pH value of the slurry reached 5. After filtering, the oxidized CNTs were dehydrated at 80 °C in oven overnight.

One co-precipitation method was employed to synthesize magnetic Fe_3O_4 nanoparticles, which could be briefly described as follows. First, we prepared an aqueous mixture containing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with a molar ratio of $\text{Fe}^{3+}:\text{Fe}^{2+}=2:1$. After that, sodium dodecyl sulfate (SDS, chemical formula: $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$) powder was carefully added to the F-containing solution. The SDS powder used here acted as a dispersing agent to avoid the inter-particle aggregation. Finally, the oxidized CNT powders were carefully put into the solution, forming uniform CNT slurry. The chemical oxidation treatment using nitric acid enabled the implantation of surface functionalities including carbonyl, carboxyl, and hydroxyl groups to both end and sidewall of CNT adsorbent. The presence of surface functionalities displays strong affinity to iron ions or their hydration molecules, beneficial for the robust formation of magnetite/CNT composite adsorbents for liquid-phase adsorption. The temperature of CNT slurry was raised to 50 °C and maintained at this temperature under N_2 atmosphere for 1 h. Then we added ammonia into the CNT slurry. The dropping process was stopped once the pH value of the slurry reached 10. After water washing several times, the resultant Fe_3O_4 /CNT composites were placed in a vacuum oven at 80 °C overnight. Herein CNT/ Fe_3O_4 ratios were set at 1:0.5, 1:1, and 1:2, designated as CF1, CF2, and CF3, respectively.

2.2. Batch adsorption and regeneration

Batch adsorption experiments were carried out by adding appropriate amount of Fe_3O_4 /CNT adsorbent to 20 mL aqueous solution with Cu^{2+} concentration ranging from 100 to 900 mg/L. The batch adsorption experiments were performed in a constant-temperature bath at different temperatures (i.e., 303, 313, and 323 K) with a shaker speed of 75 rpm. Preliminary experiments indicated that the adsorption process reached equilibrium in

2.5 h for all Fe_3O_4 /CNT adsorbents employed in this work. After reaching adsorption equilibrium, one UV/visible spectrophotometer (Shimadzu, Model UV-2550) was adopted to analyze the Cu^{2+} concentrations in the residual solutions at appropriate wavelength (i.e., 810 nm). The adsorption capacities for all adsorbents could be calculated using mass balance equations. After the adsorption process, NaOH solution was used as a regeneration agent to extract Cu^{2+} ions from the spent Fe_3O_4 /CNT adsorbents. The regeneration agent was carefully titrated in the spent adsorbents until the pH value of the slurry increased to 10. Four cycles of adsorption/desorption tests were carried out to identify the regeneration efficiencies. The adsorption experiments of regenerated Fe_3O_4 /CNT adsorbents were conducted at 303 K. The schematics for the formation of magnetic Fe_3O_4 /CNT adsorbents and the adsorption/desorption cycle of Cu^{2+} ions in aqueous solution could be illustrated in Fig. 1.

2.3. Materials characterization of Fe_3O_4 /CNT adsorbents

Fourier transformed infrared (FT-IR) spectroscopy was employed to characterize surface functional groups on each adsorbent. The FT-IR spectra were carried out with Nicolet Avatar 360 FT-IR spectrometer. The spectral ranges were recorded with a resolution of 4/cm. X-ray photoelectron spectroscopy (XPS) was adopted to analyze chemical composition of Fe_3O_4 /CNT composites, using Fison VG ESCA210 spectrometer with Mg-K α radiation. The deconvolution of XP spectra was conducted by using a non-linear least squares fitting program with a symmetric Gaussian function. The weight percentage of magnetite nanoparticles on CNT support was estimated by a thermogravimetric analyzer (TGA, Perkin Elmer Pyris 1 TGA). Herein the TGA analysis was performed under a steady air flow with a heating rate of 10 °C/min within the temperature range of 30 – 800 °C. Field-emission scanning electron spectroscopy (FE-SEM, JEOL 6701F) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100) were used to observe the morphology of Fe_3O_4 /CNT adsorbents. The crystalline structure of as-prepared Fe_3O_4 /CNT adsorbents was determined by X-ray diffraction (XRD) with Cu-K α radiation, using an automated X-ray diffractometer (Rigaku, D/MAX 2500).

3. Results and discussion

3.1. Morphology and structure of magnetite/CNT composites

Representative XRD patterns of as-prepared magnetite and magnetite/CNT composite (i.e., CF1 sample) are illustrated in Fig. 2. For comparison, diffraction pattern of fresh CNT is presented (i.e., oxidized CNT), showing a typical diffraction peak at 26.1° as a result of $d_{(002)}$ interlayer distance of 0.340 nm, confirming the presence of graphite-like crystalline structure. After the deposition of magnetite, the peaks of CF1 sample appear at 30.0° (2 2 0), 35.2° (3 1 1), 42.9° (4 0 0), 56.9° (5 1 1), and 62.5° (4 4 0), which are well identical with the standard XRD data for cubic phase Fe_3O_4 (JCPDS, Card No.: 89-4319) with a face-centered cubic structure [53]. The additional peak at around 26°, assigned to the CNT support, can also be observed, evidencing the formation of a composite composed of crystalline Fe_3O_4 and CNT. TGA curves of different Fe_3O_4 /CNT composites are illustrated in the Supporting Information (see Figure S1). The curves clearly show that the maximal weight loss occurs at approximately 500 °C for all composites, assigned to the gasification reaction of carbon in the presence of oxygen. After 650 °C, the weight loss curves tend to be stabilized. The residual weight mainly originates from the Fe_3O_4 deposits onto the CNT support. As expected, the residual weight is found to have an order as CF3 (64.1 wt.%) > CF2 (48.2 wt.%) > CF1 (35.5 wt.%), which is in good agreement with the Fe_3O_4 loading onto CNT support in the co-precipitation preparation.

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