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Facile synthesis of alumina-decorated multi-walled carbon nanotubes for simultaneous adsorption of cadmium ion and trichloroethylene

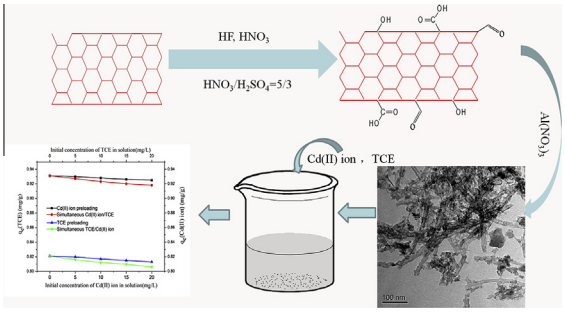
Jie Liang *, Junfeng Liu, Xingzhong Yuan *, Haoran Dong, Guangming Zeng, Haipeng Wu, Hou Wang, Jiayu Liu, Shanshan Hua, Shuqu Zhang, Zhigang Yu, Xiaoxiao He, Yan He

College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China

HIGHLIGHTS

- Hybrid alumina-decorated multi-wall carbon nanotubes (MWCNTs) were synthesized.
- Alumina (Al_2O_3) was "soldered" by slow pyrolysis on MWCNTs.
- The hybrids were used to simultaneously remove Cd(II) ion and TCE from groundwater.
- The nanocomposites showed higher adsorption capacity than MWCNTs and Al_2O_3.
- The Al_2O_3 could significantly restrain aggregation of functionalized MWCNTs.

GRAPHICAL ABSTRACT



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ABSTRACT

An adsorbent was prepared by decorating alumina onto the surface of multi-wall carbon nanotubes (MWCNTs) for simultaneous removal of cadmium ion (Cd(II) ion) and trichloroethylene (TCE) from groundwater. Structural characterization demonstrated that the nanocomposites was successfully synthesized and exhibited large surface area and restrained aggregation property. Batch experiments were conducted under various conditions (i.e., different pH, the presence of other groundwater constituents) to investigate the removal of Cd(II) ion or/and TCE by the alumina-decorated multi-walled carbon nanotubes (Al_2O_3/MWCNTs) and the underlying mechanisms. The adsorption kinetics of Cd(II) ion and TCE followed the pseudo-second-order kinetic model and exhibited 3-stage intraparticle diffusion mode. Equilibrium data of Cd(II) ion and TCE were best fitted by Langmuir and Freundlich model, respectively. The adsorption mechanisms of Al_2O_3/MWCNTs toward Cd(II) ion and TCE mainly involved in the electrostatic interactions, the hydrogen bond interactions and the protonation or hydroxylation of Al_2O_3. The maximum adsorption capacities of Al_2O_3/MWCNTs for TCE and Cd(II) ion were 19.84 mg/g and 27.21 mg/g, respectively, which were higher than that of Al_2O_3, MWCNTs and the functionalized MWCNTs. The results suggested that the Al_2O_3/MWCNTs could be considered as an effective and promising adsorbent for simultaneous removal of Cd(II) ion and TCE from groundwater.

1. Introduction

Groundwater pollution has become a critical environmental and economic issue in the worldwide [1]. Heavy metal ions such as cadmium ion (Cd(II) ion) are the main contaminant of groundwater and soils at the metal plating industry and the solid waste

* Corresponding authors at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China. Tel.: +86 731 88821413; fax: +86 731 88823701.
E-mail addresses: liangjie@hnu.edu.cn, liangjie82@163.com (J. Liang), yxz@hnu.edu.cn (X. Yuan).

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landfill site [1]. Due to its nonbiodegradable nature, Cd(II) ion can accumulate in the environment and enter the food chain, causing adverse effects to human health and ecological receptors and resulting in osteoporosis, anemia and renal damage [2]. Because of the improper storage and disposal of the spent solvents, groundwater contamination by chlorinated solvents (mainly trichloroethylene) at many industries and solid waste landfill sites has been discovered and can influence the human central nervous system, causing symptoms such as dizziness, headaches, confusion, euphoria, facial numbness, and weakness [3,4]. Therefore, the US EPA recommends permissible limit in drinking water to be 5 μg/L for both Cd(II) ion and TCE [5,6]. It should be noted that there is a high possibility that Cd(II) ion and TCE coexist in the environment, such as groundwater contaminated by the landfill leachate [7,8]. Thus, there is a need to find an effective approach to remove the excess Cd(II) ion and TCE from groundwater simultaneously.

Several methods have been applied for the removal of Cd(II) ion or TCE from aqueous solution, e.g., precipitation, ion exchange, coagulation, and adsorption [9]. Among these methods, adsorption is one of the most popular and widely used techniques for groundwater depuration, and shows a robust operating configuration, high reliability and economic advantages [10]. Various adsorbents like magnetic mesoporous carbon [11], carbon [2], activated alumina [12], activated carbon [13], sustainable organic mulch [10], acid/basic oxygen furnace slag [3], pine needle biochars [14] were used for the removal of Cd(II) ion/TCE. However, many of these adsorbents have low adsorption capacity and slow process kinetics. Hence, it is quite necessary to develop some useful adsorbents.

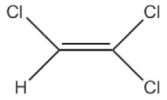
Carbon nanotubes (CNTs), including single-wall (SWCNTs) and multi-wall (MWCNTs), have attracted significant attention in environmental protection. Unlike many adsorbents, MWCNTs possess different features that contribute to the excellent removal capacities; such as fibrous shape with high aspect ratio, large accessible external surface area, light mass density, easily modified surfaces and well developed mesopores [15–17]. However, the strong intermolecular interactions between the tubes can lead to the formation of aggregates, decreasing their accessible surface area and hindering the application of MWCNTs [18]. In order to solve this problem, the uses of MWCNTs as support of CeO_2 [19], iron oxides [20], TiO_2 [21], tungsten oxide [22], chitosan [23], cellulose [24], graphene [25] and MnO_2 [26] have been reported. Saleh et al. [27] synthesized the nanocomposite MWCNT/alumina via hydrothermal treatment and investigated the possible chemical bond formation between functionalized carbon nanotubes and alumina. Previous studies also synthesized the amorphous alumina supported on carbon nanotubes, the granular carbon nanotubes/alumina hybrid and the nanofloral clusters of carbon nanotubes/activated alumina to remove fluoride and lead [9,28], diclofenac sodium and carbamazepine [29] and Cr(VI) and Cd(II) ion [12], respectively. This composites not only possess large surface area, a better orientation degree [30], but also exhibit excellent characteristics and high adsorption capacities for contaminants. But most current researches focused on the adsorption of heavy metal or organic contaminants and failed to consider the potential interactions between heavy metal and organic contaminants in a coexisting system. To the best of our knowledge, there are no reports about the synthesis of nano-sized Al_2O_3/MWCNTs composites and its application in the simultaneous removal of Cd(II) ion and TCE from groundwater.

In the present work, we synthesized a new Al_2O_3/MWCNTs adsorbent with an improved approach and investigated the feasibility and mechanisms of simultaneous adsorption of Cd(II) ion and TCE from contaminated groundwater. The influences of solution pH and groundwater constituents on the adsorption properties were evaluated. The kinetics of Cd(II) ion and TCE adsorption were analyzed using a pseudo-second-order kinetic model. The adsorption equilibrium was analyzed using Langmuir and Freundlich models. The effects of Cd(II) ion on the sorption of TCE and vice versa were also investigated. Finally, the feasibility of Al_2O_3/MWCNTs for Cd(II) ion and TCE removal was examined in the synthetic groundwater to simulate the situation in the practical application.

2. Materials and methods

2.1. Materials

MWCNTs (purity: >95 wt%; ash: <1.5 wt% outer diameter: 10–20 nm; length: 10–30 μm) were purchased from Chengdu Organic Chemistry Co. Ltd, Chinese Academy of Sciences. TCE was purchased from Sigma–Aldrich Chemical Co, and used directly as received. Different initial concentrations of Cd(II) ion solutions were prepared by dissolving $Cd(NO_3)_2{\cdot}5H_2O$ in ultrapure water. The initial TCE solution was prepared by dilution of the TCE-in-methanol mixture. Stock solutions were prepared daily. Glassware was kept overnight in a 10% (v/v) HNO_3 solution. The synthetic groundwater containing 230 mg/L Na^+, 32 mg/L Ca^{2+}, 234 mg/L Cl^-, 183 mg/L HCO_3^-, 96 mg/L SO_4^{2-} was used as the background electrolyte in this study, which was within the typical concentrations of natural groundwater [31].



The chemical structure of TCE

2.2. Synthesis of Al_2O_3/MWCNTs

The preparation of Al_2O_3/MWCNTs was accomplished according to the previous literature with some modification [9,29]. All glassware was cleaned by aqua regia freshly prepared prior to use. The purification of the MWCNTs was accomplished by adding 2.5 g MWCNTs into 50 mL concentrated nitric acid (67% by weight) at 70 °C for 24 h, followed by filtering and washing with ultrapure water, and then adding into 50 mL HF (40% by weight) at 70 °C for 24 h. After that, the turbid liquid was filtered and washed with ultrapure water until the pH approach 7.0, and then drying at 105 °C for 6 h. Then, the purified MWCNTs were functionalized by refluxing with nitric acid (67% by weight) and sulfuric acid (96% by weight) (volume ratio 5:3) [32] at 140 °C for 2 h under stirring conditions (50 rpm). The product was filtered and rinsed with ultrapure water until the pH approach 7.0, coupled with drying overnight in the oven. Typically, 2.5 g functionalized MWCNTs were dispersed into ultrapure water and magnetically agitated 6 h at which acceptable level of dispersion was observed. Afterwards, 7.835 g $Al(NO_3)_3{\cdot}9H_2O$ was properly dissolved in ultrapure water. The $Al(NO_3)_3$ solutions were drop wised added into dispersed functionalized MWCNTs. During consecutive drops, appropriate time should be left for the aluminum to reach, appropriately disperse and engage to the surface of functionalized MWCNTs. After that, the suspension was dried at 105 °C. The obtained material was heated up to 400 °C for 2 h, where the pyrolysis process resulted in the alumina formation decorated onto the surface of functionalized MWCNTs, and sealed in glass containers for subsequent testing.

2.3. Characterization methods

The morphologies and sizes of the Al_2O_3/MWCNTs were analyzed by the S-4800 field emission scanning electron microscope