Journal of Molecular Liquids 260 (2018) 149–158

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Multiwalled carbon nanotubes incorporated with or without amino groups for aqueous Pb(II) removal: Comparison and mechanism study

Kunlun Yang [a], Zimo Lou [a], Ruiqi Fu [a], Jiasheng Zhou [a], Jiang Xu [a,b], Shams Ali Baig [c], Xinhua Xu [a,*]

[a] Department of Environmental Engineering, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310058, People's Republic of China
[b] Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh 15213, USA
[c] Department of Environmental Sciences, Abdul Wali Khan University, Mardan 23200, Pakistan

ARTICLE INFO

Article history:
Received 21 January 2018
Received in revised form 13 March 2018
Accepted 20 March 2018
Available online 26 March 2018

Keywords:
Amino-functionalized
Multiwalled carbon nanotube
Co-condensation
Pb(II) adsorption
Complexation

ABSTRACT

A novel amino-functionalized multiwalled carbon nanotube (MWCNTs @SiO_2-NH_2) was prepared via co-condensation using etraethyl orthosilicate and 3-aminopropyl trimethoxysilane for effective removal of Pb(II) from water. The Pb (II) adsorption efficiencies of MWCNTs and MWCNTs@SiO_2-NH_2 were compared and the change of morphology features was assessed in batch adsorption experiments. The characterization analysis like XRD, FITR and XPS revealed that amino groups were successfully grafted on the MWCNTs. Adsorption results demonstrated that the best TEOS/APTMS loading ratio was about 10:3 based on their solution volume ratio. Compared to the poor Pb(II) adsorption capacity of pristine MWCNTs, the maximum adsorption capacity of MWCNTs@SiO_2-NH_2 was greatly improved to 147 mg/g after amination treatment. Pb(II) adsorption onto MWCNTs@SiO_2-NH_2 was strongly pH-dependent and the optimal aqueous pH was about 5. Moreover, the pseudo-second-order kinetics model and Langmuir isotherm model could well describe the Pb(II) adsorption process by MWCNTs@SiO_2-NH_2. Thermodynamics analysis illustrated that the Pb(II) adsorption was spontaneous and endothermic. FTIR and XPS analysis of MWCNTs@SiO_2-NH_2 after adsorption demonstrated the complexation between amino groups and Pb(II) played a vital role in the adsorption mechanism. Findings from the present study suggested that successful Pb(II) removal could be achieved using such novel adsorbent composite with optimized process.

1. Introduction

Lead (Pb) is one of the most widely distributed toxic heavy metal pollutants in the environment, which can exist in the atmosphere, water and soil. The main sources of lead contaminant are mining, metal smelting, alloys formation, battery manufacturing and pigments [1,2]. With rapid industrialization and urbanization, more and more lead contaminant is discharged into the aqueous environment and enables to accumulate as lead ion (Pb(II)) in the wastewater [3]. Due to the toxic effects of Pb(II) to humans organs such as the central nervous system, digestive system and hematopoietic system etc. [1,4], the effective treatment and removal of Pb(II) have received considerable attention. The conventional methods for Pb(II) treatment include chemical treatment (chemical precipitation, coagulation and ion-exchange), physical treatment (adsorption, evaporation and membrane filtration) and biological treatment [5]. Among them, adsorption method has more advantages including high efficiency, strong renewability and versatile, low operating cost and less sludge production [6], which make it more attractive. However, the traditional adsorbents like activated carbons and zeolites suffer from low adsorption capacity, poor mechanical strength and lack of structural and functional tenability [7], seriously affecting their practical application in real large scale. Hence, novel efficient adsorbents are necessary for Pb(II) removal from wastewater.

Carbon nanotubes (CNTs) have received considerable attention due to their unique electronic, chemical, mechanical properties and potential applicability in various fields such as material science and biological system. Recently, CNTs have also been applied in the removal of some heavy metal pollutants (i.e. mercury, cadmium and chromium) [8–13], which have been proved to be superior adsorbents because of their large surface areas and the capability to establish (π–π) electrostatic interactions [14]. From these researches, it could be found that the functional groups on CNTs are very important, which can improve the dispersion and homogeneity of the CNTs, provide active sites and efficiently enhance the interaction of pollutants and CNTs [15]. Up to now, amino groups (-NH_2), hydroxyl (–OH), thiol (-SH) and carboxyl (–COOH) have been introduced onto CNTs to increase the adsorption capacity, selectivity and removal efficiency of heavy metals [16–19]. Among these functional groups, the amino groups show an excellent ability for further functionalizing and improving the adsorption properties of CNTs. Due to the high nucleophilicity and special chemical

* Corresponding author.
E-mail address: xuxinhua@zju.edu.cn (X. Xu).

https://doi.org/10.1016/j.molliq.2018.03.082

versatility, amino groups can improve the solubility of CNTs in some solvents and become useful chelating sites for some heavy metals or organic molecules [20]. The strong binding ability of amino groups to some metals such as mercury, cadmium and copper has been reported so far [8–12]. However, the reported preparation methods of functionalized CNTs were complex, including acidification, activation, oxidation of CNTs and grafting of functional groups [9,10,12]. Moreover, researches about the application of pristine CNTs and the amino-functionalized CNTs for Pb(II) removal are very limited [21,22].

In this study, a facile one-pot co-condensation method without acidification and oxidation procedure was used for the preparation of novel amino-functionalized multiwalled carbon nanotube (MWCNTs@SiO_2-NH_2) through coupled reaction. In such amination process, the tetraethyl orthosilicate (TEOS) was used as the cross-linker and 3-aminopropyl trimethoxysilane (APTMS) was used as the –NH_2 groups' provider. Characterization analysis of pristine MWCNTs and MWCNTs @SiO_2-NH_2 were performed and compared to verify if the amino groups were successfully grafted on the MWCNTs. The change of Pb(II) capacity for MWCNTs incorporated with or without amino groups was also investigated through batch adsorption experiments. Furthermore, the influences of TEOS/APTMS ratios, solution pH, co-existing interferences and temperature on Pb(II) removal were studied. The possible Pb(II) adsorption mechanism were evaluated from the kinetics, isotherms and thermodynamics and further explored through the characterization of MWCNTs @SiO_2-NH_2 after adsorption.

2. Materials and methods

2.1. Materials

Ammonia, polyethylene glycol 4000 (PEG4000), ethylene glycol, tetraethoxysilane, NaCl, KCl and $MgCl_2$ were purchased from the Sinopharm Group Chemical Reagent Co., Ltd., China. $Pb(NO_3)_2$, sodium alga acid, humic acid and 3-aminopropyl trimethoxysilane were produced by Aladdin Reagent Co., Ltd., China. Multiwalled carbon nanotube (MWCNTs,0–40 nm) was supplied by Shenzhen Nanotech Port Co., Ltd., China. All chemicals were of analytical grade and used without any purification.

2.2. Synthesis of MWCNTs @SiO_2-NH_2 composites

MWCNTs @SiO_2-NH_2 was prepared by a one-pot co-condensation method. The specific steps were as follows: 0.5 g MWCNTs were dispersed into 150 mL mixed solution contained alcohol and ultrapure water with the volume ratio of 12:1, and then ultra-sonicated in the ultrasonic cleaner for about 30 min. Afterwards, the suspension was kept stable at about 30 °C and 3 mL ammonium hydroxide was added dropwise into the suspensions. After the mixed suspension was mechanical stirred for 30 min, 1 mL TEOS and 0.25 mL APTMS were sequentially added, then the co-condensation reaction was carried out at 30 °C for 4 h under continuous stirring. After that, the suspension was filtrated and washed repeatedly with ultrapure water to remove residual reagents. At last, the desired products were obtained after vacuum drying at 60 °C for 12 h.

2.3. Adsorbent characterization

The specific surface area and pore size were measured by Brunauer–Emmett–Teller (BET) method (3H-2000PS2, China).The morphological structures were analyzed by TEM (JEM11230, JEOL, Japan) and SEM (Hitachi S-3000N, Japan). XRD (X-ray diffraction, X'pert PRO, analytical B.V., Netherlands) was tested to describe the crystal structures. The functional groups and surface elemental of MWCNTs@SiO_2-NH_2 before and after Pb(II) adsorption were characterized by Fourier transform infrared spectrometer (FTIR, IR Prestige-21, Japan) and the X-ray photoelectron spectroscopy (Kratos Axis Ultra DLD, SHIMADZU, Japan). Zetasizer 3000 HAS (Malvern Instruments Ltd., Worcestershire, UK) was used to measure the zeta potential of adsorbents at various pH from 2 to 10.

2.4. Batch adsorption experiments

Most batch adsorption tests were performed in 100 mL conical flasks in a shaker (SKY-110WX, China) with 180 rpm at the temperature of 30 °C by using water bath. In a typical procedure, 20 mg of adsorbents were added into the conical flasks containing 25 mL of 100 mg/L Pb(II) solutions.

The adsorption kinetics experiments were conducted under such conditions: Pb(II) of 100 mg/L, pH of 5.2 ± 0.1 and temperature of 303 K. The samples were taken at 1, 5, 15, 30, 60, 120, 240, 480, 720, 1080, 1440 min and then determined after filtered by 0.45 μm membrane. For all adsorption isotherms, the Pb(II) concentrations were increased from 20 to 250 mg/L under the natural pH of 5.2 ± 0.1. Then the suspension was shaken at 303 K for 24 h and the residual Pb(II) was tested after filtration. In addition, the analysis of adsorption thermodynamics was studied at the temperatures of 293, 303, 313, 323 and 333 K. The effect of different initial pH (from 2.0 ± 0.1 to 6.0 ± 0.1) on the removal of Pb(II) was analyzed, which was adjusted by 0.1 M NaOH or HNO_3 solutions. The influence of normal interferences including K^+, Na^+, Mg^{2+}, SA (sodium alginate) and HA (humic acid) were investigated too.

2.5. Analytical method

The concentration of Pb(II) in the water was analyzed in the atomic absorption spectrophotometer (AA-6300, Shimadzu, Japan). Lead nitrate was used to prepare the stock and working solutions of standard Pb(II), which was dissolved in the 2‰ nitric acid solution. Then 0, 0.5, 1, 3, 5, 10 mg/L of Pb(II) were used for the standard curve. The samples were diluted to the standard range after filtered through a 0.45 μm membrane.

3. Results and discussion

3.1. Characterization of adsorbent

3.1.1. Surface morphology and crystal structure

The SEM and TEM images of MWCNTs and MWCNTs@SiO_2-NH_2 are shown in Fig. 1. The images exhibited that carbon tubes in MWCNTs twined each other, generating the abundant network structure of MWCNTs. Moreover, the surfaces of carbon tubes in MWCNTs were relatively smooth, which was possibly unfavourable for the Pb(II) adsorption and the grafting of amino groups. Due to TEOS could synthesized three-dimensional network structure by themselves, MWCNTs was first wrapped with SiO_2 by using TEOS to roughen the surface and facilitate the grafting of amino groups. After the amination treatment, the surfaces of MWCNTs@SiO_2-NH_2 were covered by a layer of nanoparticles, becoming rougher than that of MWCNTs. TEM images revealed the diameter of carbon tubes increased from 25 to 40 nm to 55–60 nm after amination, suggesting that the surface of MWCNTs@SiO_2-NH_2 was densely covered by SiO_2 and amino groups. Table 1 presents the BET-N_2 results of MWCNTs, MWCNTs@SiO_2 and MWCNTs@SiO_2-NH_2 and proved such process. After the MWCNTs were treated with TEOS, the specific surface area (S_a) of MWCNTs@SiO_2 became a little larger than that of MWCNTs. At the same time, S_a and total pore volume of MWCNTs@SiO_2-NH_2 were the smallest among the three materials' test. The reason was that massive hydrophilic groups like -NH_2 covered on the surface of MWCNTs@SiO_2-NH_2 after amination, even filling part of the three-dimensional network structure and resulting the significant decrease of the S_a and total pore volume detected by BET-N_2. This result confirmed the hydrophilic amino groups was successfully grafted on the MWCNTs@SiO_2-NH_2.