Journal of Colloid and Interface Science 448 (2015) 347–355

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

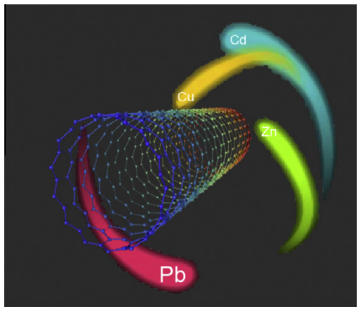
www.elsevier.com/locate/jcis

Competitive adsorption of heavy metal ions on carbon nanotubes and the desorption in simulated biofluids

Xin Ma [a,1], Sheng-Tao Yang [b,1], Huan Tang [c], Yuanfang Liu [a,c], Haifang Wang [a,*]

[a] Institute of Nanochemistry and Nanobiology, Shanghai University, Shanghai 200444, China
[b] College of Chemistry and Environment Protection Engineering, Southwest University for Nationalities, Chengdu 610041, China
[c] Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 January 2015
Accepted 13 February 2015
Available online 23 February 2015

Keywords:
Carbon nanotubes
Adsorption
Desorption
Biofluid
Toxicity
Synergistic effect

ABSTRACT

Carbon nanotubes (CNTs) had meaningful adsorption capacities for Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}, while Pb^{2+} showed the highest adsorption in the competitive adsorption evaluations. The desorption behaviors of heavy metal ions were completely different in various biofluids, where the desorption was significantly influenced by pH and the presence of proteins/other cations. The desorption was most effective in simulated stomach juice, and much less effective in other simulated biofluids. More Pb^{2+} stuck to CNTs than others, resulting in less desorption. Interestingly, the competitive desorption behaviors of four ions were largely changed comparing to the individual desorption behaviors. The implications to the biosafety evaluations and synergistic effects of CNT are discussed.

1. Introduction

Carbon nanomaterials have attracted great interests for their unique structure and fascinating properties [1,2]. In particular, sp^2 carbon nanomaterials, such as carbon nanotubes (CNTs), fullerene and graphene, have lots of attractive applications in many important fields, including energy [3], electronics [4], material [5], biomedical area [6] and environment [7,8]. For instance, CNTs have been used for drug delivery [9], bioimaging [10], biodefense [11], photothermal treatment [12]. The applications of CNTs as adsorbents in water treatment have also been widely investigated, showing very high adsorption capacity for various pollutants [13–16]. Due to the valuable applications and great potential, the biosafety of carbon nanomaterials has been widely concerned [17–19].

Recently, the synergistic toxicity of CNTs and heavy metals has aroused great interest [20–22]. Several studies showed that CNTs could worsen the toxicity of heavy metal ions. Kim et al. reported

* Corresponding author. Fax: +86 21 66135275.
E-mail address: hwang@shu.edu.cn (H. Wang).
[1] The authors contributed equally.

http://dx.doi.org/10.1016/j.jcis.2015.02.042
0021-9797/

that CNTs could interact strongly with normal organic matter to release the binding Cu^{2+}, which induced toxicity to *Daphniamagna* [23]. They also found that CNTs enhanced the toxicity of Cu^{2+} to *Daphniamagna* by improving the bioavailability of Cu^{2+} [24]. Martinez et al. reported that CNTs enhanced the toxicity of Pb^{2+} to freshwater fish [25]. It was speculated that the adsorption of Pb^{2+} on CNTs was related to the enhanced toxicity. Qin et al. reported that CNTs enhanced the toxicity of Pb^{2+} to *Daphniamagna*, in particular at higher pH values [26]. However, the available studies mainly focused on describing the synergistic effects rather than the underneath mechanism. To fully understand the underneath mechanism, the first step is to investigate the competitive adsorption and desorption of heavy metals on CNTs in biological systems.

Herein, we systematically evaluated the adsorption/desorption behaviors of heavy metal ions on oxidized CNTs in simulated biofluids. The adsorption isotherms and kinetics of Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} on CNTs were measured. The competitive adsorption of the four ions on CNTs was evaluated. The desorption behaviors of Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} from CNTs in simulated biofluids were investigated one-by-one and also in a competitive way. Our results clearly showed that CNTs adsorbed heavy metal ions fast and effectively. The desorption of heavy metal ions from CNTs was influenced by pH and the presence of proteins/cations in biofluids. Pb^{2+} showed higher affinity to CNTs and lower desorption. The competitive desorption of four ions showed quite different behaviors from individual desorption. The implications to the biosafety evaluations and synergistic effects of CNT are discussed.

2. Materials and methods

2.1. Materials

MWCNTs with outer diameters of 10–20 nm and lengths of 5–15 μm were purchased from Shenzhen Nanotechnologies Port Co. Ltd., China. Uric acid, glucosaminhydrochloride, mucin (from porcine stomach), pepsin (from porcine gastric mucosa), pancreatin (from porcine pancreas), lipase (from porcine pancreas) were obtained from Sigma, and glucuronic acid was obtained from Alfa Aesar. Dlbecco's modified eagle medium (DMEM) were purchased from Hangzhou Gino Biological Pharmaceutical Engineering Co. Ltd., China. Bovine serum albumin (BSA) was obtained from Dingguo Biotechnology Co. Ltd., China. Bovine serum was bought from Sijiqing Biological Engineering Co. Ltd., China. All other chemicals were of analytical grade and supplied by Sinopharm Chemical Reagent Co. Ltd., China. The simulated gastric juice and intestinal juice were prepared following the recipes listed in Table 1, which was given by Peters et al. [27].

2.2. Oxidation of MWCNTs

MWCNTs (1.0 g) were dispersed in 400 mL of concentrated H_2SO_4/HNO_3 mixture (V:V = 3:1) and sonicated for 6 h. After cooling to room temperature, MWCNTs were washed with deionized water to near neutral. MWCNTs were then centrifuged at 20,000*g* for 15 min and the sediment was dried at 70 °C for 24 h to obtain the O-MWCNTs. O-MWCNTs were characterized with infrared (IR) spectrometer (Avatar 370, Thermo Nicolet, USA) and transmission electron microscopy (TEM, JEM-200CX, Hitachi, Japan).

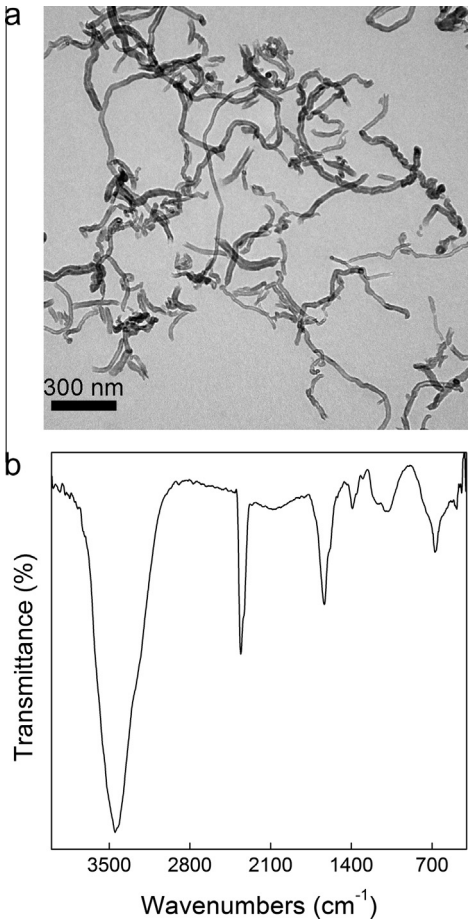


Fig. 1. Representative TEM image (a) and IR spectrum (b) of O-MWCNTs.

2.3. Adsorption behaviors

We firstly investigated the adsorption behaviors of Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} on O-MWCNTs individually. In the kinetics study, 5 mg of O-MWCNTs were added to 6 mL of heavy metal solution separately (Pb^{2+}: 140 mg/L; Cu^{2+}: 40 mg/L; Zn^{2+}: 40 mg/L; Cd^{2+}: 40 mg/L; pH = 5). The mixture was shaken at 25 °C and collected for metal concentration determination at different time intervals. The mixtures were centrifuged at 30,000*g* for 10 min before the inductive coupling plasma-atomic emission spectrometer (ICP-AES, Prodigy, Leeman Labs, USA) measurement. The kinetics data of heavy metals were fitted to pseudo-second-order model (Eq. (1)). In the isothermal adsorption study, 5 mg O-MWCNTs were added to 6 mL of heavy metal solution (Pb^{2+}: 0–200 mg/L; Cu^{2+}: 0–60 mg/L; Zn^{2+}: 0–80 mg/L; Cd^{2+}: 0–60 mg/L; pH = 5). The mixture was shaken at 25 °C for 2 h and collected for metal

Table 1
Recipes of simulated gastric and intestinal juice for 1 L.

	Inorganic constituents	Organic constituents
Gastric juice (pH 1.3 ± 0.1)	2752 mg NaCl, 824 mg KCl, 306 mg $NaH_2PO_4{\cdot}H_2O$, 302 mg $CaCl_2$, 650 mg glucose, 20 mg glucuronic acid	85 mg urea, 3 g mucin, 330 mg glucosaminhydrochloride, 1 g BSA, 2.5 g pepsin
Intestinal juice (pH 8.1 ± 0.1)	7012 mg NaCl, 80 mg KH_2PO_4, 564 mg KCl, 50 mg $MgCl_2{\cdot}6H_2O$, 151 mg $CaCl_2$, 3388 mg $NaHCO_3$, 180 μL HCl (37%)	100 mg urea,1 g BSA, 1.5 g lipase, 4.5 g pancreatin