Effect of acid and alcohol network forces within functionalized multiwall carbon nanotubes bundles on adsorption of copper (II) species

Shirley Rosenzweig [a], George A. Sorial [a,*], Endalkachew Sahle-Demessie [b], James Mack [c]

[a] Environment Engineering Program, School of Energy, Environmental, Biological, and Medical Engineering, University of Cincinnati, P.O. Box 210012, Cincinnati, OH 45221-0012, USA
[b] U.S. Environmental Protection Agency, Office of Research and Development, NRMRL, 26 W. Martin Luther King Drive, MS 443, Cincinnati, OH 45268, USA
[c] Department of Chemistry, University of Cincinnati, 301 Clifton Court, Cincinnati, OH 45221-0172, USA

HIGHLIGHTS

► Network forces in oxygen functionalized MWCNTs are contributors to adsorption capacity.
► Alcohol functionalized MWCNTs have better adsorption capacity than acid functionalized MWCNTs.
► Adsorption capacity acid functionalized MWCNT can be improved by strong-base washing.
► Removal of impurities did not improve the effect of initial concentration.
► The constant electronegativity of functionalized MWCNT makes them good sorbents.

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ABSTRACT

The adsorptive capacity of multiwall CNTs for copper species in water depends on the type of functional group present on their surface. The alcohol (OH) and acid (COOH) network forces formed by van der Waals bonds within the CNT bundles can define their aggregate state and available sites for copper adsorption. Copper is attracted to different oxygen radicals on the surface and within the bundles of CNTs. The effect of initial concentration shown on isotherm curves was investigated as an impact of different network forces and the presence of impurities leached from as-received CNTs. Deprotonation of CNTs reduced the COOH network forces, improved adsorption capacity and removed the effect of initial concentration. Impurities leached from CNTs under the effect of pH were less than 1 mg g^{-1} for each metal, which was insignificant compared to copper in solution. Pristine CNTs were acid washed and purified (Ox-CNTs), improving their adsorption capacity, but the effect of initial concentration was still present. Adsorption of copper is stronger for OH-functionalized CNTs, followed by deprotonated COOH-functionalized CNTs, as-received COOH-functionalized CNT, Ox-CNTs and finally pristine CNTs. FTIR, XPS and zeta potential measurements were used to identify and quantify the different surface functional groups present on CNTs.

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1. Introduction

The contamination of copper (II) species in drinking water is the result of corrosion of the domestic and commercial plumbing materials in the water distribution system, erosion of natural deposits and industrial discharge. U.S. Environmental Protection Agency (USEPA) established regulating limits for copper in drinking water when copper levels exceed 1.3 mg L^{-1}. Ingestion of copper can cause depression, gastrointestinal and central nervous irritation if consumed above the action level for long periods. The corrosion reactions depend on type of minerals present in the water that form different metal species, stagnation of the water in the pipes, age of the pipes, the acidity and temperature of the water. In many cases, the pH of water in the distribution systems drops below the pH at which the water left the treatment plant (USEPA, 1993). Fluctuation of pH can cause disruption of copper passivation films and pitting of copper pipes, causing metal precipitation or dissolution, introducing other contaminants in the water stream (Schock et al., 1995; Dartmann et al., 2010). Therefore, controlling the levels of copper when it reaches the households is of ultimately importance. There is an increasing interest in finding cost-effective materials that can be applied in the domestic water systems that keep levels of pollutants under safe limit. Among current methods for removing copper from water are adjusting pH with addition of corrosion inhibitors and chemical precipitation.

* Corresponding author. Tel.: +1 513 556 2987; fax: +1 513 556 4162.
E-mail address: george.sorial@uc.edu (G.A. Sorial).

However, the most popular, effective removal method, for many low level pollutants, is adsorption (Li et al., 2004).

Adsorption of metals on carbon nanotubes (CNTs) has important applications in sensors, membranes and water treatment. CNTs have been studied for their capacity on removing copper from water (Rao et al., 2007; Sheng et al., 2010), and new applications are popular due to CNT nanosize advantages over other carbon sorbents. In most cases, pristine CNT is modified by acid-wash or plasma treatment which can add some functional groups to the surface and improve copper adsorption, as reported by Shao et al. (2010). There is no reliable method that can quantify which type of oxygen groups prevail on the CNT surface, which is fundamental for realistic applications. Commercially CNT functionalization processes are more efficient than laboratory methods. Most articles evaluated the pH effect by buffering water (Stafiej and Pyrzynska, 2007; Gao et al., 2009). It is well known that copper will precipitate in solutions above pH 6 (Wu, 2007). Any study that included pH variation through buffer addition should have considered that copper would form other complexes in water (Shock et al., 1995; Dartmann et al., 2010). A conclusion that adsorption of copper on CNTs is enhanced at higher pHs is incorrect if not have mentioned the complexation effect, considering that there is no removal of copper by adsorption but yet by precipitation (Wu, 2007).

Adsorption capacity is investigated under the effect of acid (COOH) and alcohol (OH) network forces within the bundles based on the different surface groups present on CNTs. CNTs are different from many commonly used carbon sorbents due to their unique pore formation based on the entanglement of a large number of individual nanotubes (Rao et al., 2007). CNTs adhere to each other because of the van der Waals attraction forces (Rao et al., 2007; Stafiej and Pyrzynska, 2007; Upadhyayula et al., 2009), creating a peculiar aggregation state. Due to these specific structure and morphology of CNTs, there are many possible sites available for adsorption (Rakov, 2006; Upadhyayula et al., 2009). The active sites for copper adsorption on ideal defect-free CNTs are the sites in the interstitial channels between the bundles (mesopores) and in the grooves at the periphery of the bundles. There are limited possibilities of adsorption happening in the internal cavity of open CNTs, because of the filled internal structure, such as with coaxial tubes and nanopeas (fullerenes) structures, or closed ends (Fischer, 2006; Rakov, 2006). The oxygen groups on the surface can act as specific sites for adsorption of metal cations (Kuo, 2009). CNT suspension stability in water is highly dependent on the oxygen functions present on the CNT surface, and it is an important property on sorbents (Upadhyayula et al., 2009; Chen et al., 2010; Cho et al., 2010).

Several factors can affect the adsorption capacity of CNTs, including speciation of metals in water (Rao et al., 2007; Gao et al., 2009). The prospective of new applications for CNT has increased the interest on their manufacturing, competing to offer commercial functionalized CNT at low cost, high quality and purity. However, there can be traces of metal impurities on CNTs left from the synthesis process, and one needs to be cautious that CNTs will not leach more impurities than removing pollutants from water. Impurities on as-received CNTs could affect their toxicological hazard assessment of potential human exposure to CNT (Kennedy et al., 2008). Residual metals of environmental interest can be measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. Transmission Electron Microscope (TEM) images show a thin layer around the CNTs that were identified as amorphous oxidized carbon (Naseh et al., 2010). The presence of amorphous carbon impurities and the effect of preconditioning CNTs using acid and base washes are also investigated here.

Plasma and wet functionalization methods are used commercially to add functional groups to CNT surfaces and to reduce impurities associated with the synthesis process (Rakov, 2006; Cho et al., 2010). However, the purification effectiveness of these methods is limited by their side effects. (Djordjevic et al., 2006; Pumera, 2007). Acid-wash functionalization has limitations on adding oxygen groups to the CNT walls, and can damage the CNT structure, affecting the consistency of the sorption results (Kuo, 2009). On the other hand, plasma functionalization methods will add few hydroxyl groups (Naseh et al., 2010).

The main objective of this study is to investigate the adsorptive properties of selected CNTs under different aspects as-received and conditioned CNTs. Equilibrium isotherm and kinetic studies are conducted to measure and compare these effects. In this study, the association of spectrometry analysis and zeta potential measurements can give a good idea of which oxygen groups are prevalent on the surface. In order to move on towards realistic applications of CNTs, it is important to understand properties of CNT and how they affect the CNTs behavior in water.

2. Material and methods

2.1. CNTs

Alcohol functionalized (OH–CNT), acid functionalized (COOH–CNT) and pristine CNTs were obtained from Sun Innovation, Inc., EUA. All three types of CNT have similar dimensions (20–30 nm outer diameter; 5–10 nm inner diameter; 10–30 μm length), purity 95% and specific surface area (>110 m^2 g^{-1}). The CNT powders were dried in an oven set at 105 °C to remove humidity, stored in sealed glass containers at room temperature until further use.

2.2. Copper stock solutions and standards

All copper stock solutions were prepared from reagent grade Cu(NO$_3$).2.5H$_2$O (Sigma–Aldrich, USA). Distilled autoclave water without buffering additions was used at pH 5.1–5.3. After adding copper nitrate, the pH of water remained unchanged. Each stock solution was prepared in conical flasks and stirred for 45 min. Samples taken from stock solution were diluted to create standard solutions for calibration curves of 1–5 mg L^{-1}-Cu(II). AAS (Atomic Analyzer Analyst Spectrometer 300, Perkin Elmer, USA) with flame method was used to determine the concentration of copper. The method detection limit was 0.15 mg L^{-1}-Cu(II).

2.3. Characterization

The size and morphology of the CNTs were analyzed using a TEM (CM200 TEM, Philips, Netherlands) operating at 200 kV. Two sets of CNT solutions were prepared. First solution used 2 wt.% of sodium dodecyl sulfate surfactant, while the second solution used N-methylpirrolidone and dimethyl formamide solvents added 1:1. Both solutions have different effects on solubility of CNTs, creating different visual effects to facilitate image analysis (Moore et al., 2003).

The functional groups were characterized using an AVATAR 360 E.S.P. FTIR Spectrometer (Nicolet Instrument Corporation, USA) equipped with a DTGS KBr detector and controlled by EZ OMNIC 5.0 software. Spectra were acquired in the 4000–400 cm^{-1} range, and 64 scans at a resolution of 4 cm^{-1} (Wu, 2007; Gao et al., 2009; Kuo, 2009). The background spectrum of KBr was recorded at the same conditions. Baseline correction was applied to correct the spectra automatically.

The specific surface area was measured using a BET AutoChem II 2920 (Micromeritics Instrument Corporation, USA). The characterization used single point specific surface area technique with