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## **Chemical Engineering Journal**

Chemical Engineering Journal

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

# Effect of natural organic matter (NOM) on Cu(II) adsorption by multi-walled carbon nanotubes: Relationship with NOM properties

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#### HIGHLIGHTS

- ▶ Effect of NOM characteristics on the Cu adsorption by MWCNTs was investigated.
- ► Cu adsorption by MWCNTs increased with increasing NOM concentration.
- ▶ The aromaticity is a key factor for NOM sorption on MWCNTs.
- ▶ O-containing functional groups play critical roles in NOM effect on Cu adsorption.

#### ARTICLE INFO

Article history: Received 5 April 2012 Received in revised form 25 June 2012 Accepted 26 June 2012 Available online 2 July 2012

Keywords: Natural organic matter Cu(II) Multi-walled carbon nanotubes Adsorption

#### ABSTRACT

The effect of natural organic matter (NOM) on Cu(II) adsorption by multi-walled carbon nanotubes (MWCNTs) was investigated. Particular attention was paid to the relationship between NOM properties and NOM adsorption and their effects on the Cu(II) adsorption by MWCNTs. The results showed that the NOM adsorption data were well fit to the Freundlich isotherm model, and the MWCNTs that had higher oxygen content had lower  $K_F$  (Freundlich constants) values. The  $K_F$  values for the different types of NOM varied greatly and were proportional to the aromatic carbon content, the specific ultraviolet absorbance at 275 nm, and the TOC-normalized fluorescence intensity of the F3 peak at ~460 nm. In contrast, they had negative linear correlations with the absorbance ratios at 250 nm and 365 nm and the TOC-normalized fluorescence intensity of the F3 peak at  $\sim$ 460 nm. System the Cu(II) adsorption by the MWCNTs increased with increasing NOM concentrations due to the complexing of Cu(II) with the adsorbed NOM. This was confirmed by XPS and FTIR spectra. The increased degree of Cu(II) adsorption was positively correlated with the carboxyl carbon content, carboxyl group content, and the polarity index of the NOM. The findings in this study highlight that the NOM characteristics are responsible for controlling the NOM adsorption and its effects on heavy metal sorption by MWCNTs.

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#### 1. Introduction

Carbon nanotubes (CNTs), which are categorized into two main species, single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs), are allotropes of carbon that possess exceptional physicochemical, optical, and mechanical properties [1,2]. They have been studied widely with regard to their potential environmental application as effective adsorbents of heavy metals [3–8] and organic chemicals [9] during solid-phase extraction and water treatment. Due to extensive applications, CNTs have inevitably been released into the environment. As a result, there are serious concerns over their health and environmental risks [10,11] with increasing evidence of the toxicity of CNTs [12]. The adsorption of toxic substances by CNTs may enhance the toxicity of CNTs and further affect the fate and transfer of toxic substances in the environment [9]. Therefore, an investigation of the adsorption behavior of CNTs is needed to evaluate the environmental and health risks of CNTs.

Natural organic matter (NOM) is a complex and heterogeneous mixture of a diverse group of molecules [13]. Humic acid (HA) and fulvic acid (FA) are its main components, accounting for, on average, 10% and 40%, respectively, of dissolved organic carbon [14]. NOM is ubiquitous in the natural environment. Manufactured CNTs will inevitably interact with NOM after they are released into the environment [15–17]. Moreover, due to the aromatic, carboxylic

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