Colloids and Surfaces A: Physicochem. Eng. Aspects 419 (2013) 69–79

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

# Coating carbon nanotubes with crystalline manganese dioxide nanoparticles and their application for lead ions removal from model and real water

Mohamed Abdel Salam*

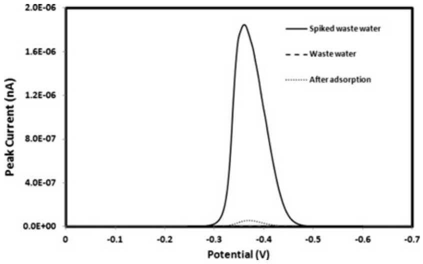
*Chemistry Department, Faculty of Science, King Abdulaziz University, P.O Box 80200-Jeddah 21589, Saudi Arabia*

## HIGHLIGHTS

- The MWCNTs/$MnO_2$ nanocomposite were synthesized and characterized.
- The results showed that MWCNTs were coated with 10.2% of the crystalline $\alpha$-$MnO_2$.
- The MWCNTs/$MnO_2$ used for the removal of lead ions from model and real water sample.
- The adsorption was studied kinetically and thermodynamically.
- The adsorption was spontaneous, endothermic, and chemical in nature.

## GRAPHICAL ABSTRACT

This graph shows the differential pulse anodic stripping voltammetry measurements for the removal of lead ions from spiked waste water sample by MWCNTs/$MnO_2$ nanocomposite.



## ARTICLE INFO

*Article history:*
Received 16 September 2012
Received in revised form 8 November 2012
Accepted 25 November 2012
Available online 4 December 2012

*Keywords:*
Carbon nanotubes
$MnO_2$
Lead ions
Kinetic
Thermodynamic
Real water

## ABSTRACT

Multi-walled carbon nanotubes/manganese oxide (MWCNTs/$MnO_2$) nanocomposite was synthesized, characterized, and used successfully for the removal of lead ions from an aqueous solution and waste water sample. The characterization techniques showed that MWCNTs were coated with 10.2% of the crystalline $\alpha$-$MnO_2$ (w/w percent). The adsorption process was optimized, and the results showed that most of the lead could be removed from a solution with 10 mg MWCNTs/$MnO_2$ nanocomposite, at a pH between 7.0 and 9.0, and within a few min. The adsorption was studied kinetically, and the results revealed that the adsorption of lead ions by a MWCNTs/$MnO_2$ nanocomposite from an aqueous solution could be described well by a pseudo-second-order model and the Elovich model. The mechanism of adsorption showed that the adsorption process was complex and involves a different step, but it was mainly controlled by a liquid film diffusion mechanism. The thermodynamic parameters were calculated, and the adsorption was found to be chemical, spontaneous, and endothermic in nature with positive entropy. The MWCNTs/$MnO_2$ nanocomposite was used for the removal of lead ions from a spiked waste water sample, and the results showed that all the lead ions were removed.

## 1. Introduction

Environmental pollution as a result of rapid technological development is a serious concern for ecology. Heavy metals are major pollutants of some ground and surface waters and are often present in industrial or urban waste waters. These metals are harmful to humans, animals, and other living creatures. Lead, for example, is the second most hazardous substance according to the Agency of Toxic Substances & Disease Registry (ATSDR, 2007) [1]. Lead in the environment arises from both natural and anthropogenic sources. Exposure can occur through drinking water, food, air, soil, and dust from old paint containing lead. It is a very toxic element and human exposure can result in a wide range of biological effects, depending on the level and duration of exposure. High levels of exposure to lead may result in toxicity in humans, which causes problems in the synthesis of hemoglobin; has an effect on the kidneys,

---

* Tel.: +966 541886660; fax: +966 2 6952292.
*E-mail address:* masalam16@hotmail.com

0927-7757/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2012.11.064

gastrointestinal tract, joints, and reproductive system; and causes acute or chronic damage to the nervous system. Chronic exposure to lead can affect the central nervous center or urinal system and leads to kidney damage and death. The potential sources of lead are the manufacture of batteries, metal products, paints, and ceramic glazes. Classical physicochemical techniques for the removal of lead from aqueous solutions are ion exchange, chemical precipitation, oxidation, reduction, and reverse osmosis [2]. These methods are either costly, difficult to implement or produce by-products that require further treatment. The adsorption process, on the other hand, is cost-effective and efficient even at very low concentrations of lead.

Currently, different types of adsorbents used for the removal of lead from water include zeolites [3], metallic oxides such as manganese oxides [4], activated carbon [5], ion exchange resins [6], and different biosorbents [7,8]. There is a crucial need for new adsorbents for the efficient removal of lead from water. Carbon nanotubes (CNTs) are emerging nanomaterials that captured the attention of the scientific world after their discovery in 1991 [9]. Many research studies have shown the capability of CNTs in the adsorption and removal of different organic pollutants from water such as aniline [10,11], resorcinol [12], polyhalogenated compounds [13–15], benzene and its derivatives [16], and inorganic pollutants such as heavy metals [17–19], especially lead ions [20,21]. Previous studies confirm that the adsorption efficiency and capability of CNTs could be improved significantly by the modification of carbon nanotubes, especially for the removal process of lead ions from water [22–25]. Previous studies showed that coating common adsorbents with manganese oxides enhanced greatly their adsorption abilities and removal efficiency for different pollutants [26,27], especially lead (II) [28,29]. Manganese oxides were used previously to coat carbon nanotubes for different applications such as energy storage [30], electrochemical capacitor [31], and catalysis [32], but only one study focused on the removal of lead (II) from an aqueous solution by carbon nanotubes coated with amorphous manganese oxide [33]. More work is needed to explore the effect of coating MWCNTs with manganese oxide and their potential application as efficient adsorbents for lead (II) removal.

This work studies the synthesis of a nanocomposite made of well-known adsorbents: multi-walled carbon nanotubes (MWCNTs) and manganese dioxide ($MnO_2$). The produced MWCNTs/$MnO_2$ nanocomposite was characterized using different characterization techniques such as x-ray diffraction, scanning electron microscopy, surface area analyzer, as well as zeta potential. The produced MWCNTs/$MnO_2$ nanocomposite was used for the removal of lead ions, as an example of heavy metals ions, from solution. The effect of different parameters such as removal time, adsorbent mass, and solution pH, which affect the removal process, will be optimized. The removal of lead ions from the solution by MWCNTs/$MnO_2$ nanocomposite was studied kinetically using different kinetic models to understand the adsorption mechanism. Finally, the MWCNTs/$MnO_2$ nanocomposite was used for the removal of lead ions from a waste water real sample.

## 2. Materials and methods

### 2.1. Materials

Multi-walled carbon nanotubes with an average diameter of 110–170 nm were obtained from Sigma–Aldrich. Analytical grade lead nitrate (Fluka, Ion Solution, 1000 mg/L) was employed to prepare stock solutions each containing 100 mg/L of lead ions. The stock solutions were further diluted to the desired ion concentrations. All other chemicals were analytical grade and were obtained from Sigma–Aldrich. The experiments were performed using ultrapure water with resistivity not less than 18.2 MΩ cm obtained with a Millipore Milli-Q system (Billerica, USA).

### 2.2. Preparation of MWCNTs/$MnO_2$ nanocomposite

The MWCNTs/$MnO_2$ nanocomposite was prepared as follows: 5.0 g of MWCNTs was added to 250 ml of 0.5 M potassium permanganate solution, and the mixture was heated to 70 °C and stirred at 500 rpm using a heater with a magnetic stirrer. 200 ml of 0.025 M manganese sulfate and 100 ml of 0.025 M sodium hydroxide were added drop wise using two separate burettes to the potassium permanganate solution. The produced brown suspension of the manganese oxide was stirred for one hour at 70 °C. The suspension was then filtered, washed with distilled water, and dried in an oven at 110 °C. The $MnO_2$ was formed according to the following equations:

$$MnSO_4 + 2NaOH \rightarrow Mn(OH)_2 + Na_2SO_4$$

$$3Mn(OH)_2 + 2KMnO_4 \rightarrow 5MnO_2 + 2KOH + 2H_2O$$

### 2.3. Characterization techniques

FEI-Field Emission Scanning Electron Microscope (FISEM) Quanta FEG 450, Netherlands was used to characterize the morphological structure of the MWCNTs/$MnO_2$ nanocomposite. The specific surface areas of the MWCNTs/$MnO_2$ nanocomposite were determined from nitrogen adsorption/desorption isotherms measured at 77 K using Nova 2000 series, Chromatech. Prior to analysis, the samples were outgased at 250 °C for 4 h. X-ray diffraction (XRD) patterns were recorded for phase analysis and crystallite size measurement on a Philips X pert pro diffractometer, operated at 40 mA and 40 kV by using Cu$K_\alpha$ radiation and a nickel filter, in the $2\theta$ range from 2 to 70° in steps of 0.02°, with a sampling time of one second per step. Thermal properties were investigated using Shimadzu Thermal Analyzer with a scan rate 10.0 °C/min in air atmosphere. Zeta potential of the MWCNTs was measured by a Malvern zetameter (Zetasizer 2000). The pH values of MWCNTs solution were adjusted from 2.0 to 10.0 by adding 0.1 M hydrochloric acid or sodium hydroxide solution to the glass beaker at 25 °C.

### 2.4. Analytical measurements

The lead ions concentration was determined by voltammetric measurement using a Metrohm, 797 VA computrace (Switzerland) with a three electrode system, including hanging mercury as the working electrode, a platinum plate as the counter electrode, and Ag/AgCl (3.0 mol $L^{-1}$ KCl) as the reference electrode. The lead ions determination was evaluated by differential pulse anodic stripping voltammetry (DPASV) at −0.363 V. This analytical method was developed and used extensively in previous studies [25,34–36].

### 2.5. Adsorption experiments

Kinetic experiments were carried out to establish the effect of time and temperature on the adsorption process and to identify the adsorption rate. The experimental procedures are described as follows: (1) A series of 10 ml solutions containing 10 mg/L of lead nitrate were prepared in a 250 ml glass bottle and kept at a certain temperature; (2) the pH of the solution was adjusted to 7.0 using a universal pH buffer (Britton–Robinson buffer); (3) the ionic strength was adjusted to 0.01 M using a 0.10 M $KNO_3$ solution; (4) a certain amount of the solid adsorbent was added to the solution; (5) the solution was shaken continuously for a certain period of time; (6) after the completion of preset time intervals, the solution