



# As-synthesized multi-walled carbon nanotubes for the removal of ionic and non-ionic surfactants



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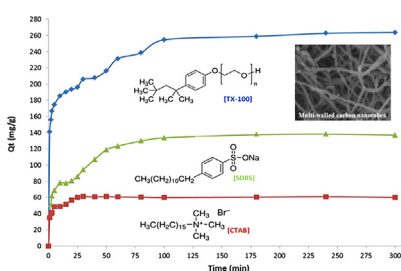
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## HIGHLIGHTS

- Necessity of removing surfactants from aquatic environments.
- Carbon nanotubes very promising adsorbent for this task.
- Maximum removal for non-ionic surfactant (360 mg/g).
- Ultrasonication helped double the removal performance for ionic surfactants.
- Hydrophobic, along with electrostatic, interactions were the main mechanisms.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This research deals with the application of untreated multi-walled carbon nanotubes (MWCNT) in their agglomerates form for the removal of non-ionic (TX-100), cationic (CTAB) and anionic (SDBS) surfactants from aqueous media. In order to optimize the removal process, the influence of several key parameters was investigated including contact time under different solid/liquid ratios, initial solution pH, temperature, along with ultrasonication assistance and desorption assays.

Experimentations revealed that pH variation enhanced the removal capacities at optimum values of 6, 2 and 8 for TX-100, SDBS and CTAB, respectively, and that hydrophobic interaction is a major adsorption factor, especially for non-ionic surfactant with possible electrostatic interactions occurring for the ionic ones. As well, removal efficiencies peaked for an optimum temperature range between 35 and 45 °C. As for the ultrasonication assistance, it enhanced the overall removal capacities, especially that of the ionic surfactant, with an enhancement of 52% for the case of SDBS after 1 h of treatment. The modeling results revealed that the pseudo-second order model provided the best correlation of the dynamic data and that the process was controlled by intraparticle diffusion phenomena. At equilibrium, and under optimized experimental conditions, untreated MWCNTs showed promising removal capacities with 359, 312 and 156 mg/g for TX-100, SDBS and CTAB, respectively.

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## 1. Introduction

The need for the decontamination of waters, wastewaters and aquatic environment, is becoming an urgent matter to be dealt

with. Besides, between 2010 and 2050 the world population is expected to increase by 34% to reach 9 billion and with the cultivable lands becoming more and more scarcer [1], tremendous pressure will be put on three vital supplies: food, water and energy. Humanity already witnessed (and still do) the murderous conflicts and huge amount of corruptions linked to energy resources like oil and gas around the world. Therefore, let us just think of the possible

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scenarios if such conflicts will be around the most precious supply on this earth: Water.

Obviously, the word “vital” takes all its meanings when related to water. That is why human endeavor in the field of water treatment, with scientists and researchers at its vanguard, are very important and involve diverse disciplines, and therefore different treatment techniques including adsorption [2], advanced oxidation process [3] membrane separation [4], photocatalytic degradation [5] and bioremediation [6].

The objective of this study is to focus on emerging pollutants in order to anticipate the application of the adsorption technique in future water treatment procedures targeting this kind of pollution. Thus, synthetic surfactants were targeted as pollutants of emerging concern. Indeed, several studies revealed that detergents and other tensioactive compounds may modify environmental equilibrium by contaminating lakes and groundwater [7], therefore harming fish and other aquatic organisms by affecting their respiratory gaseous exchanges [8]. As well, surfactants present a synergistic binding effect on pharmaceuticals, thus increasing their impact on both humans and animals [9]. Such eco-toxicological threat posed by surfactants is magnified by their extensive use (12 M tonnes annually [10]) in modern life and in major industrial fields including paints and leather production [11].

First discovered by Iijima [12], carbon nanotubes have attracted (and still do) tremendous attention in various research and development fields considering their interesting physical, chemical, electrical and structural properties [13]. One of the main applications of carbon nanotubes is water treatment [14]. However, there are two major limitations for their wide application in water treatment technologies: (i) their hydrophobicity [15] and (ii) production cost [16].

The bulk of the research work involving both carbon nanotubes and surfactants is related to the dispersion and stabilization of the nanotubes via surfactant addition in aqueous phase. In the field water treatment however, and as pollutants of emerging concern, surfactants should be removed from aqueous media and not added to it.

Therefore, the objective of this research is the use carbon nanotubes to remediate surfactant-related pollution in aqueous media via adsorption. The main aim is to optimize the operating conditions affecting the adsorptive removal of ionic and non-ionic surfactants for aqueous solutions using as-synthesized and untreated MWCNTs.

## 2. Materials and methods

### 2.1. Carbon nanotubes

MWCNTs, produced via catalytic chemical vapor deposition, were purchased from Sigma–Aldrich, with 5  $\mu\text{m}$  average tube length and purity above 95%. The as-received nanomaterial were thoroughly washed with ultra-purified water, then dried at 80 °C for 24 h and stored in desiccators.

The choice of this kind of carbon nanotubes was made based on several considerations. First, the economical one since the MWCNTs used in this work were among the cheapest manufactured nanotubes from the Sigma–Aldrich catalogue (around 6.45 euros per gram). As for the choice to work with the raw carbonaceous nanomaterial without prior treatment (i.e., thermal carbonization and/or chemical purification), it was made in order to monitor the removal behavior of the raw nanotubes and to avoid any extra cost, especially that for the case of surfactants (macromolecular sized contaminants), the internal pore of MWCNTs would not be available for endohedral interactions. As well, it is worth experimenting these MWCNTs in their manufactured form (i.e., agglomerates).

Indeed, carbon nanotubes tend to aggregate and form interesting porous network due to the entanglement of thousands of individual tubes adhered to each other as a result of Van–der–Waals forces of attractions [17].

### 2.2. Surfactants

Three synthetic surfactants were experimented in this study: *anionic* sodium dodecyl benzene sulfonate (SDBS) and *cationic* Cetyl Trimethyl Ammonium Bromide (CTAB), purchased from Sigma–Aldrich. *Nonionic* Octylphenoethoxylate (TX-100) was supplied by BDH Chemicals. Synthetic solutions for each surfactant were prepared separately by dissolving accurately weighed amounts of powdered (SDBS and CTAB) or liquid (TX-100) surfactants in ultra-purified water and subsequently diluted to obtain the required concentrations. Spectrophotometric scanning of dilute solutions was performed and absorbance maxima for each surfactant were identified as 200 nm for CTAB, 224 nm for SDBS and 225 nm for TX-100.

### 2.3. Characterization analyses

#### 2.3.1. BET (Brunauer, Emmett and Teller) method

The BET surface area and porous properties of the studied MWCNT were assessed via nitrogen adsorption experiments. The nanomaterials were characterized by  $\text{N}_2$  adsorption at 77 K using a Micromeritics® surface area and porosimetry analyzer (model Gemini 2380 V1.00). The sample was degassed to remove any moisture and the built-in software provided BET surface area ( $S_{\text{BET}}$ ) by applying the BET equation to the adsorption data. The pore size distribution was estimated using the Barrett–Joiner–Halenda (BJH) equation during the desorption phase [18].

#### 2.3.2. Point of zero charge (PZC) determination

The PZC was estimated using a previously reported technique [19]. Two series of vials filled with 20 mL ultrapure water were prepared with initial pH ranging from 2 to 12. The pH values were adjusted using 0.1 M hydrochloric acid and sodium hydroxide. Then, 3 mg of the dried and untreated MWCNTs were placed in each vial and left overnight ( $\approx 14$  h) to reach equilibrium at 25 °C. The equilibrium (final) pH was then measured and plotted against the initial pH using the average of the two series. The PZC value is therefore obtained from the point at which the initial pH vs final pH curve crossed the  $y = x$  line on the graph.

#### 2.3.3. SEM (scanning electron microscopy) analysis

A scanning electron microscope (SEM) equipped with an energy dispersive X-ray microanalysis (Hitachi SEM/EDS S-4800) was used to determine the surface of the MWCNTs and the porous structure of the agglomerated network. The sorbent nanomaterials were firstly mounted on an aluminum stub and the microscope was operated at an accelerating voltage of 20 kV.

### 2.4. Sorption experimental procedure

All adsorption experiments were carried out by stirring the desired amount of untreated MWCNTs with 10 mL of the pollutant solution in 15 mL round bottom glass tubes in a thermo-regulated oscillatory shaker. The removal efficiency was investigated under various initial surfactant concentrations (5–150 mg/L), pH values (2–12), temperatures (25–55 °C), MWCNTs concentration (0.1 to 1 g/L) and ultrasonic assistance (0 to 3 h using an ultrasonic frequency of 40 kHz).

After a pre-determined time interval (for kinetics) or at equilibrium time (for isotherms), a solution sample was extracted, filtered (using a 0.2  $\mu\text{m}$  syringe filter) and analyzed for residual surfactants

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