

# Oxidized Carbon Nanotubes Filters For Iron Removal From Aqueous Solutions

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**Abstract:** CNT-based filters have a prospective advantage in comparison to the commercial filters already in operation because they are lightweight and do not require electricity to operate. In this work, oxidized multiwall carbon nanotubes (MWCNTs) Taunit were used as a novel filter for removing Fe (II) from aqueous solution. The removal efficiency of iron by oxidized MWCNTs was studied as a function of pH, iron concentration in aqueous solution, MWCNT mass. From these investigations, the removal efficiency of iron could reach 52% for concentration 50 ppm, suggesting that Taunit is an excellent adsorbent for iron removal from water. A significant increase in iron removal efficiency at a pH of 8. The effect of oxidation on the structural of MWCNTs was characterized by SEM and EDS techniques to investigate the functionalization with oxygen-containing and outer diameter distribution. The adsorption mechanisms are mainly attributable to chemical interactions between metal ions and surface functional groups of the CNTs. It was found that functionalized CNT-based filters are more efficient to remove iron from aqueous solutions. Oxidized MWCNTs may be a promising candidate for heavy metal ions removal from industrial wastewater.

**Keywords:** Functionalization, Iron, MWCNT, Taunit.

## I. INTRODUCTION

The pollution of water resources due to the disposal of heavy metals was causing worldwide concern. Water crisis is one of the greatest challenges of our time. Water demand is growing rapidly as a result of increasing population and rapid urbanization. However, water resources are limited in populated areas and arid regions. The shortage of water resources calls for efficient technologies for waste water reclamation and sea water desalination [1]. Heavy metal pollutants like iron have been a major preoccupation for many years because of its toxicity toward aquatic-life, plants, animals, human beings and the environment [2], [3].

Iron is one of the most abundant metals of the Earth's crust. It occurs naturally in water in soluble form as the ferrous iron or complex form like the ferric iron, or have an industrial origin; mining, iron and steel industry, metals corrosion. Commonly iron is blamed for much of the water-quality problems, as it makes the water's aesthetic appearance undesirable, gives a metallic taste to water making it unpleasant for consumption. It can also be at the origin of corrosion in drains sewers, due to the development of microorganisms and the ferrobacteries. Iron bacteria do not cause health problems, but cause odors, corrode plumbing equipment, reduce well yields [4]. Following the above-mentioned facts, higher concentrations of iron in water

cause failure of water supply systems operation, water quality deterioration and the reduction of pipe flow cross-section [5].

The common methods for removing metals from water like ion exchange, reverse osmosis, and electro dialysis have proven to be either too expensive or inefficient to remove heavy metal ions from aqueous solutions [6]-[8]. At present, chemical treatments are not used due to disadvantages like high costs of maintenance. The advent of nanotechnology for water purification brought a lot of hope. The success of CNTs membranes as a filter is based on their unique properties which include high surface areas, and good mechanical and thermal stability [9], [10]. Despite having smaller pores, CNTs have high permeability and less pressure is required to pump water through the filter, possibly due to smooth CNT interiors [11]. The main advantage of this is reduced costs through energy savings. So their applicability for removal of hazardous pollutants from aqueous streams have been studying extensively [12], [13]. The surface of carbon nanotubes is originally inert and solvophobic, thus the practical effect of the application of CNTs, especially in filtration of solutions, is lower than expected [14]. A possible solution to this problem is to modify the surface of carbon nanotubes by oxidation. The amorphous carbon and catalyst particles introduced by the CVD preparation process were removed during the course of oxidation treatment. The functionalization of CNTs surfaces with oxygen containing groups in the present study was carried out by treatment with concentrated nitric acid oxidation technique [15]. Multi-walled carbon nanotubes (MWCNT) were previously used for removal of metal ions, such as lead, copper, cadmium, silver, nickel [16]. Kandah and Meunier found that the adsorption of Ni<sup>2+</sup> by oxidized CNTs is 1.24 times greater than commercial activated carbon [17]. The objectives of present work are (a) to investigate the process of purification and functionalization of MWCNTs using ultrasonic process in nitric acid oxidation; (b) to study the filtration efficiency of iron by MWCNT (Taunit-filter) as a function of iron solution pH, ionic concentrations and CNTs dose.

## II. METHODS

### A. Characterization of the filter

The material of the present study is an industrial carbon nanotubes Taunit. "Taunit" CNTs produced by "Nanotech Center" (Tambov, Russia). This material is a loose black powder, composed of grainy agglomerates of MWCNTs with a size of several micrometers. Their geometric parameters

and some physical properties are shown in Table . MWCNT filters were prepared by sandwiching of compressed “Taunit”

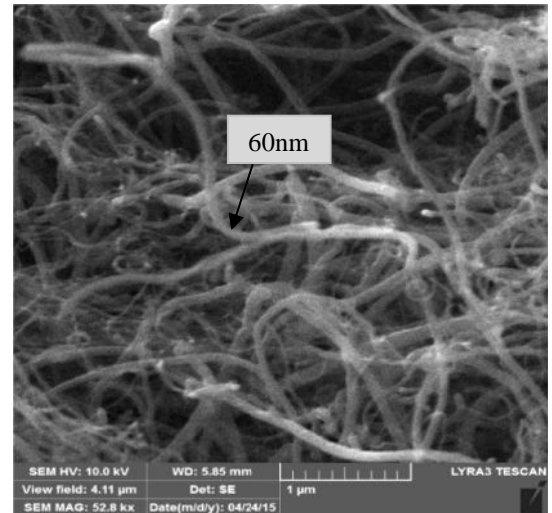
**Table** Characteristics of MWCNT in this work.

Parameter	“Taunit” CNTs
External diameter, nm	(20-70)
Internal diameter, nm	(5-10)
Length, $\mu\text{m}$	2 and more
Specific surface area, $\text{m}^2/\text{g}$	(120-130 )
Bulk density, $\text{g}/\text{cm}^3$	(0.4-0.6)

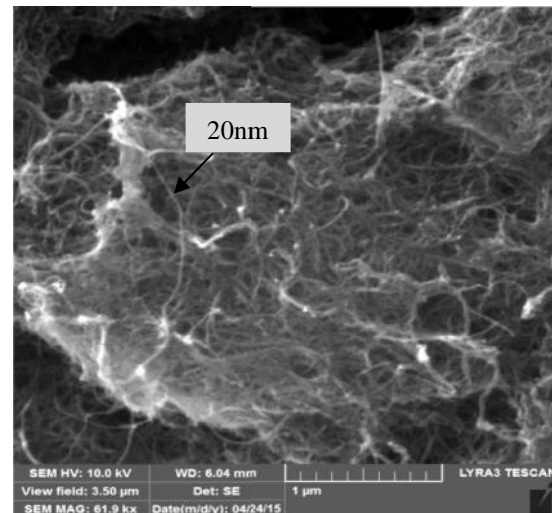
CNTs between two pieces of glassy fiber filter and putted into a syringe.

#### B. Iron Stock Solution Preparations

In order to make iron stock solution, 0.18 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is taken into 1000 ml of distilled water. The prepared stock solution made is of the concentration of 1000 ppm and diluted to desired concentration.



(a)



(b)

**Fig. 1** SEM images of MWCNTs showing the outer diameter (a) pristine, (b) after oxidation.

#### C. Chemical Functionalization of “Taunit” using Nitric Acid

The surface functionalization was carried out using the ultrasonic method. 0.5 g of “Taunit” was added into 100 ml of concentrated nitric acid. Then the mixture solution was sonicated in water bath at  $80^\circ\text{C}$  for 10 hours. Afterwards, the mixture was filtered and washed several times with deionized water until its pH reaches 7. The functionalized MWCNTs had been dried in oven at  $80^\circ\text{C}$  for overnight.

#### D. Experimental design

Table shows the experimental parameters and their variations. The removal efficiency (R) is defined as follows:

$$R = \frac{K_o - K}{K_o} \times 100 \quad (1)$$

Where  $K_o$  and  $K$  are the aqueous solution conductivity, initial and after filtration ( $\mu\text{S}/\text{cm}$ ),  $K=C$ , is the molar conductivity in  $\mu\text{S}/(\text{cm} \cdot \text{mol})$  and  $C$  is the concentration of ions in the solution in  $\text{mol}^{-1}$ .

### III. RESULTS AND DISCUSSION

#### A. Surface analysis of oxidized MWCNTs

Morphology of the pristine and oxidized MWCNTs was characterized by SEM (TESCAN). A clear decrease in nanotube diameters was observed as shown in Fig. 1. It follows from EDS analysis that the oxygen content was increased after oxidation Fig. 2 (b). Also, it is clearly seen the iron deposition after filtration process, Fig. 2 (c).

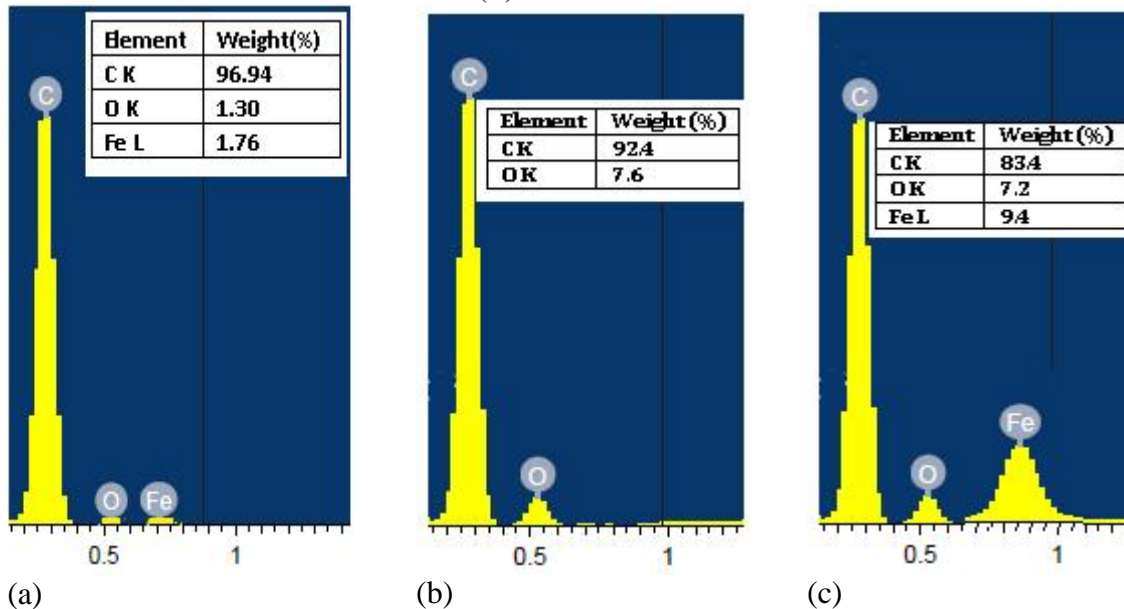
#### B. Effect of iron concentration in aqueous solution

A comparative study of the filtration efficiency of raw and oxidized Taunit is performed for iron removal as a function of iron concentration in aqueous solution. From Table , one can see, with an increase in initial concentration of iron in aqueous solution the removal efficiency (R) decreases. At 200 ppm concentration, R is only 8.75% for 0.3 g raw Taunit but for the same amount of oxidized Taunit the efficiency is 22%. Whereas at low concentration of 50 ppm, R of oxidized Taunit is around 52%. This may indicate that the adsorption interaction between the oxidized MWCNTs and Fe (II) ions

was mainly of ionic interaction nature which is in agreement with an ion exchange mechanism, as illustrated in Fig. 3. High concentration of iron limits its transfer to oxidized MWCNT surfaces.

**Table** Experiment parameters and its variation.

Parameter	Variation		
	Low	Medium	High
1. Iron concentration in solution (ppm)	50	100	200
2. pH of iron aqueous Solution	3	6	8
3. Filter dosage (g/50ml)	0.1	0.2	0.3



**Fig. 2** EDS analysis of Taunit: (a) pristine, (b) after oxidation, (c) oxidized Taunit after filtration of iron solution.

#### C. Effect of pH of iron aqueous solutions

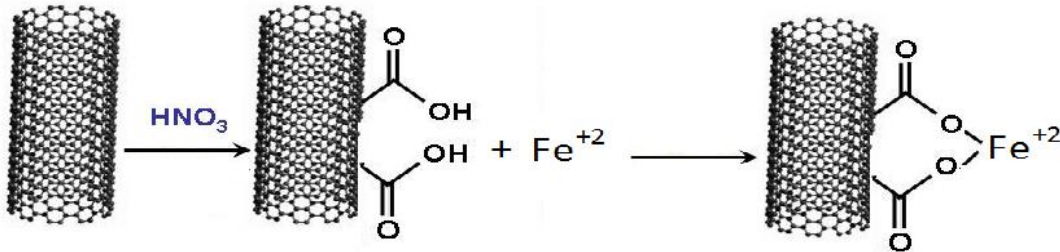
As the pH of the solution increases, the surface charge of CNTs becomes more negative probably because of the deposition of more hydroxide ions [18], which increasing iron ion exchange. From an electrostatic interaction point of view, filtration of iron was favored at high pH. In the present investigation, filtration data are obtained in the pH range from 3 to 8, for iron initial concentration of 200 ppm and with 0.3 g raw and oxidized Taunit. From Fig. 4, the removal efficiency of iron is increased as pH is increased. The graph reveals that for oxidized Taunit at pH=3, R is around 5%, whereas at pH=8, R increases to 32%.

#### D. Effect of Dosage of raw and oxidized Taunit

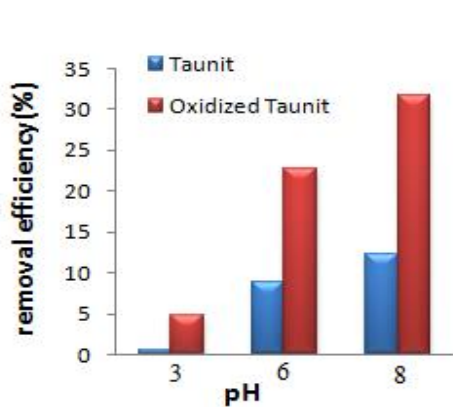
Fig. 5 shows an increase of the removal efficiency of Fe (II) with the increase of MWCNT mass. This phenomenon implied that the filtration depended on the availability of binding sites. The oxidation treatment had evident impact on the MWCNT removal efficiency of Fe (II). It is also clear that the removal efficiency of oxidized MWCNTs was higher than that of raw MWCNTs. Oxidized MWCNTs had larger specific surface area than the untreated MWCNTs. It is known that oxidation of carbon surface can offer not only a higher specific surface area, but also a larger number of oxygen-containing functional groups, which increases the ion exchange capacity of carbon materials.

**Table** Variation in removal efficiency with initial concentration of iron in aqueous solution (C) with raw (T) and oxidized Taunit (OT) at pH of 6.

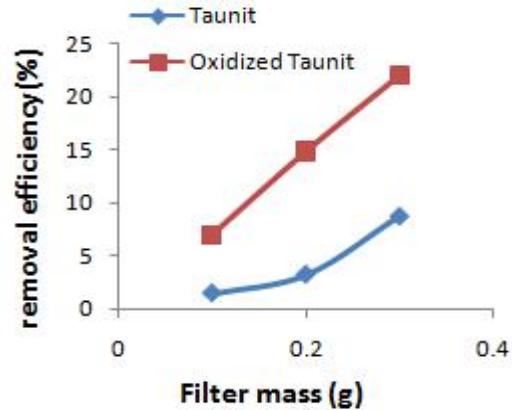
C (ppm)	K (μS) before filtration	K (μS) after filtration (T)	K (μS) after filtration (OT)	Removal efficiency (T) (%)	Removal efficiency (OT) (%)
200	560	511	433	8.75	22.68
100	284	252	192	11.27	32.39
50	148	126	71	14.87	52.02



**Fig. 3** Schematic diagram for the interaction of iron cation with oxidized MWCNTs.



**Fig. 4** Variation in removal efficiency with pH of iron aqueous solution.



**Fig. 5** Variation in removal efficiency of iron with dosage of Taunit at pH=6 and C=200 ppm.

#### IV. CONCLUSION

The application of carbon nanotubes for the removal of heavy metal ions from liquid solutions is one of the pioneer studies. In this study the application of both raw and oxidized CNTs were investigated as potential filters to remove iron from solutions. Some parameters were found important to determine the removal efficiency; the concentration of metals in aqueous solution, pH and the filter mass. All of the parameters used in the filter experiment were significant and have direct impacts on the removal efficiency which was identified from the regression analysis. Basing on the data obtained, the predominant ion exchange mechanism involving surface functional groups of oxidized MWCNTs was presumed. From the characterization of the Taunit-filter, it was found that the interaction of iron with oxidized CNTs is higher compared to raw CNTs. This is due to the fact that oxidation provides oxygen containing groups, reduce diameter of carbon tubes and remove impurities. It was also

noted that the key factors that favor the removal efficiency of iron, high pH and low initial concentration. Thus, MWCNTs provides high expectations on the development of wastewater treatment and environmental contamination reduction.

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