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Enhanced Removal of Ni(II) From Aqueous Solutions by Effective Acid Functionalization of Carbon Nanotube Based Filters

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Abstract

Multiwalled carbon nanotubes (MWNTs) have shown a promising efficiency as an adsorbent, owing to their large surface area and affinity for heavy metal ions. Nevertheless, the effective functionalization of the MWNT is essential to enhance the surface reactivity towards heavy metal removal. In order to elucidate this functionalization, acid treatment of mixture of HNO_3/H_2SO_4 followed by H_2SO_4/H_2O_2 for etching process was conducted. The acid functionalized MWNTs (F-MWNTs) were characterized with SEM, EDS, BET surface area and FTIR. The obtained results confirm the formation of oxygen groups attached to the surfaces of treated nanotubes (e.g. carboxyl) which alter their physicochemical properties and enhance the surface reactivity. The removal of Ni(II) from aqueous solutions by using immaculate and functionalized MWNT-filters (F-MWNTs) was studied as a function of pH, initial concentration of Ni(II), MWNT mass and contact time. F-MWNT filters showed an enhancement of the removal efficiency of Ni(II) up to 99.8% for concentration 10 ppm with exceptionally high adsorption capacity that could reach 333.3 mg/g. The adsorption isotherm is well fitted by the Langmuir equation. The ion exchange mechanism between F-MWNTs and Ni(II) ions is suggested as well-situated mechanism. It was found that F-MWNT filters can be reused through many cycles of regeneration with high performance. Our investigation demonstrated that F-MWNT filters are effective and can be appreciably considered as resourceful and economical adsorbent for heavy metal removal from wastewater.

Keywords: CNT functionalization, Ni (II) filtration, Removal efficiency, adsorption mechanism, Ion exchange mechanism

Introduction

Wastes that contain metals are considered to be perilous to both human life and the environment due to their keen toxicity, even when the heavy metals are present at hint concentrations [1, 2]. Water resources are polluted by various sources such as metallurgical, withdrawal, tannery, chemical manufacturing, fossil fuel refineries, battery manufacturing industries and production of plastics, involving the use of metal compounds, particularly as heat stabilizers, and so forth [3, 4]. Removal of toxic metals is one of the major challenges in ensuring safe water for all as well as protecting the environment [5-7]. Excessive amounts of heavy metals such as cadmium, chromium, copper, lead, Ni(II), mercury and zinc in the aqueous environment may cause serious concern due to their toxicity and carcinogenicity, which may cause damage to various systems of the human body [8]. Ni(II) (II) is a toxic metal ion present in wastewater. Approximately 50% of Ni(II) produced is used in steel factories, in Ni(II) batteries, and in the construction of some alloys, which causes an increase in the Ni(II) burden on the ecosystem and deterioration of water quality [9]. Many methods have been developed and investigated to remove metal ions from contaminated water such as ion exchange, reverse osmosis, and electrodialysis have proven to be either too expensive or inefficient to

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remove heavy metal ions from aqueous solutions [10]. Increasingly rigorous standards regarding the quality of drinking water have stimulated a mounting effort in the exploitation of new highly efficient methods. CNT filters, particularly those that are functionalized have been recommended as a potential adsorbent for the removal of heavy metals in contaminated water. In consequence of their unique structure and remarkable properties, CNTs have emerged as novel materials for applications in a variety of fields such as super capacitors [11], photovoltaic devices [12], hydrogen storage [13], conducting polymer composites [14], aircraft structures [15], wastewater treatment [16-18] and cancer treatment [19]. However, the chemical inertness and amphiphobic nature of the raw CNTs has impeded the apprehension of full potential towards variety of applications [20]. The extremely pitiable reactivity and dispersibility properties of raw CNT can lead to self-aggregation among the CNTs tubules, and also the difficulty of CNTs filtration properties. To overcome these constraints, surface change of CNT is important to completely exploit their novel properties by adjusting their surface properties [21].

Numerous examinations have announced the surface modification procedures, such as acid oxidation treatment [22], impregnation with metal or metal oxides [23], coating with surfactant [24], and natural organic matter [25]. CNTs expel overwhelming metals by complexation or by electrostatic fascination of metal particles to different surface oxygen-containing functional groups [26]. The performance of removal depends on the morphology of the nanotubes which depends on the type of treatment used to enhance the filtration efficiency. Several techniques can be used to modify carbon nanostructures aiming at the maturity of materials peculiar physicochemical properties [27]. The most commonly used functionalization methods are acid oxidation method due to its effortlessness of preparation and efficiency [28]. Acid oxidation method can be achieved by chemical treatment of CNTs by using oxidizing agents such as potassium permanganate ($KMnO_4$), nitric acid (HNO_3), sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and hydrogen peroxide [29]. Acid treatment of CNTs has shown to be very valuable in increasing reactivity of CNTs by introducing these functional groups, such as carbonyl, hydroxyl and carboxyl groups. There were several studies have been conducted on the acid functionalization of MWNTs [30, 31]. However, to the best of our knowledge, there is limited study that evaluates the performance of functionalized MWNTs (F-MWNTs) on the effect of acid type and concentration, amount of MWNTs, operating temperature, treatment methods and durations. The present study is to optimize acid treatment conditions that could provide the best F-MWNTs, with highest attachment of oxygen-functional groups on the surface and enhances the filtration efficiency. Although different chemical treatments are routinely used nowadays for modifying CNTs, the application of their effects has not yet been fully studied especially for water purification.

In this study, we report an effective acid functionalization of CNTs by mixture of HNO_3/ H_2SO_4 followed by etched treatment of H_2SO_4 /H_2O_2 solution can produce clear changes in the morphology of the surface, introduce functional groups, change diameter of the tubes. We explore the enhancement in the filtration efficiency of Ni(II) by F-MWNTs filters compared with the pristine one. The functionalization effects and element deposition on the CNT filter are characterized using scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). The effect of pH, concentration, contact time and mass on the removal efficiency of Ni(II) was studied. The filtration enhancement and adsorption mechanism due to acid functionalization are discussed.

Experimental Methods

Acid functionalization of MWNTs

The material for the current study was the multiwalled carbon nanotube Taunit-M (TM), produced by “Nanotech” (Tambov, Russia) in a form of powder, composed of granular agglomerates of MWNTs with a length of several micrometers, average external diameters (12-25) nm, and specific surface area (BET) 221.8 m^2/g, as provided by the manufacturer. TM was compressed using high pressure piston to the form of circular tablet with the diameter 10 mm, the thickness of 4 mm and masses from 0.1 to 0.3 g as optimum lower and higher filter masses. To perform our effective acid functionalization of MWNTs, first a 300 mg of pristine TM was mixed directly with mixture of 10 mL of 8 M HNO_3 and 60 mL of 8 M H_2SO_4 in a 250 ml open flask. Afterwards, the mixture was sonicated in water bath at 60°C for 3 h, using ultrasonic vibrations. Finally, the resulting suspension was filtered and the samples etched for half an hour with a 4:1 H_2SO_4 (98%)/H_2O_2 (30%) solution to remove all carbon particles produced by the first reaction. After that, the solution was filtered and washed several times with deionized water until it reaches pH 7. The functionalized MWNTs had been dried in oven at 100°C for 12 h.

The physical morphology and the surface investigation of pristine (P-TM) and ozone functionalized F-TM tablets, was examined using powerful tools. A scanning electron microscope (*SEM, TESCAN*) with the Digitizer software is applied to quantify the average diameter of the tubes. To account for the oxygen content and the surface functional groups of F-TM, Energy dispersive X-ray (EDS), and Fourier-transform infrared (FTIR) spectra (*IFS 66 V/S, Bruker*) were conducted. The specific surface area of pristine MWNTs used in this investigation was determined using nitrogen adsorption method was found to be 226.5 g/m^2.

Filter design and Experimental procedure

MWNTs filters were prepared by sandwiching of filter tablets between two pieces of twine membrane, and putted into a syringe [16]. The1000 ppm Ni(II) stock solution was prepared by dissolving 1.8 g of $NiSO_4 \cdot 7H_2O$ in 1000 ml of distilled water afterwards diluted to accomplish the ideal concentration. The chemicals utilized in the trials were bought in high expository virtue. The pH of the stock solutions is adjusted by 0.1 M HNO_3 or 0.1 M NaOH. The entirety of the bunch tests were conducted in a 50 ml syringe filtering arrangement. In each filtration examination, various filter tablets mass, from 50 to 150 mg, were inserted into the syringe and the 50 ml of Ni(II) solution with initial Ni concentrations of 10 to 100 ppm were added. The effect of initial concentration and filter dosage were examined at different values of pH varying from 4 to 10. Table 1 shows the parameter variations. Before and after each experiment, the Ni(II) concentration was measured spectrophotometrically using a UV/Vis spectrophotometer, as well as the solution conductivity and removal efficiency (*R*), defined as

$$R(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_O and C are the Ni(II) concentrations in aqueous solutions, initial and after filtration. Increasing the filtration volume and time the concentration, *C*, and the removal efficiency, *R*, shall approach a certain saturation values *Cs* and *Rs* when a vacant adsorption sites will be exhausted and filtration process enters a dynamic equilibrium stage. The adsorption capacity *qs* (mg/g) can be estimated from, [16]:

$$q_s = \frac{V \cdot C_s \cdot R_S}{m} \tag{2}$$

where *m* (in g) is the mass of the adsorbent and *V* (in l) is the volume of the liquid solution, for Ni (II) concentration of 100 mg/l which considered the saturation concentration and the volume of Ni (II) solution 500 ml at pH=10 and 0.15 g filter mass, using Eq (2), the adsorption capacity can be estimated as 333.3 mg/g for F-MWNTs.

To estimate the filter regeneration possibility, 50 ml of water, NaOH and HNO_3 are examined as effective solutions for desorption process.

TABLE 1: Experiment parameters and its variation

Parameter	**Variation**		
Concentration of Ni (II) in initial aqueous solution (ppm)	**10**	**50**	**100**
The pH of Ni (II) in aqueous solution	**3**	**7**	**100**
MWNT filter dosage (in mg per 50 ml of solution)	**50**	**100**	**150**

Results

Effect of initial Ni(II) concentration in aqueous solution

A comparison study of the filtration efficiency of P-MWNT and F-MWNT filters is performed for Ni(II) removal as a function of Ni(II)concentration in aqueous solution. From Fig. 1, it is apparent that the increase in the initial concentration of Ni(II) in aqueous solution leads to a drop in the removal efficiency (*R*). At 10 ppm, *R* of F-MWNT is around 99.8%. This may designate that the adsorption interaction between the F-MWNT filters and the Ni(II) ions was principally of ionic interaction nature which is in accordance with the ion exchange mechanism [26], proving that the removal efficiency of F-MWNT is better than P-MWNT filters. For Ni(II) concentration of 100 mg/l (the saturation concentration), and 150 mg filter quantity, using Eq. (2), the adsorption capacity can be estimated as 243.33 mg/g for P-MWNTs and 333.3 mg/g for F-MWNTs, which is high compared to the other adsorbents, [32-35]. This suggests that the F-MWNTs are efficient heavy metal adsorbents. Functionalized Taunit-M has smaller average diameters and higher specific surface area, as proved by SEM analysis, sec 4.1, compared with the pervious published work related to CNT applications as filters. Also the chemical treatment using mixture of HNO_3/H_2SO_4 followed by H_2SO_4/H_2O_2 enhancing the functionalization which in turn increases the adsorption sites and the filtration efficiency of the filter. Moreover, CNT-based filters showed high removal efficiency of heavy metals like chromium, cadmium, and Nickel. For example, these membranes showed high removal efficiency for chromium, that could reach 97% [17], and for Ni (II) is about 85% [16]. The adsorption capacity of Ni (II) on the P-MWNT and F-MWNT filters were fitted by applying the Langmuir isotherm model [18]. Langmuir equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature and adsorption is limited to monolayer coverage, and intermolecular forces decrease with the distance from the adsorption surface. From Fig.2, for Ni (II) concentration of 100 mg/l the sorption capacity of P-MWNTs and F-MWNTs, respectively, are 240.5, 315.5 mg/g. The R_L value, [18], in the present investigation was found to be 0.852 for F-MWNTs, showing that the adsorption of Ni (II) ion on F-MWNTs is favorable.

Effect of pH and filter mass of Ni(II) aqueous solution

The pH influences the surface charge of the adsorbent, the degree of ionization and the species of the filter. So pH is an important factor controlling the process of adsorption. The effect of pH on the removal of Ni(II) is investigated by testing three values of pH (4, 7 and 10) and Ni(II) concentration 10 ppm with filter mass 150 mg. Figure 3 shows that the maximum removal of Ni(II) occurs at the pH range of 10, as the removal efficiency (*R*) could reach 99.8% for F-MWNT filters, whereas *R* is about 65% at pH =4. From Fig. 3, the removal of Ni(II) from aqueous solution to F-MWNT filters is more efficient than P-MWNT [36]. The solution pH affected the surface charge of F-MWNT, the quantity of ionization, and the speciation of the surface functional groups. In low pH, the surface of F-MWNTs became positively charged and Ni(II) ions could be barely adsorbed on the surface of F-MWNTs because the Ni(II) ions are hydrated cations. Summarizing, the enhance in the Ni(II) removal as the pH increases could be explained on the basis of a reduction in competition between protons and Ni(II) ions for the same adsorption sites and by the decrease in positive surface charge, which resulted in a lower electrostatic repulsion between the surface and Ni(II) ions.

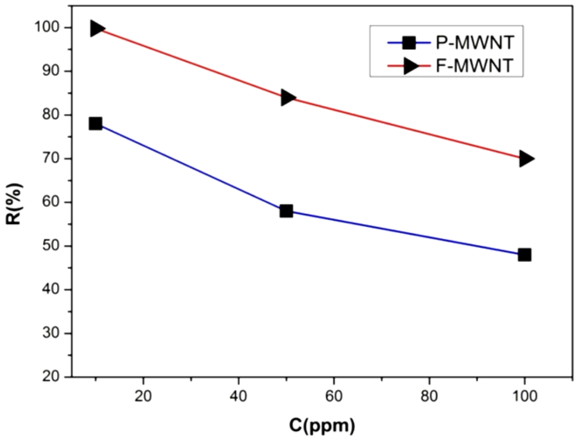


Fig. 1 Variation in removal efficiency with the initial concentration of Ni(II) in aqueous solution (*C*) with P-MWNT and F-MWNT filters at pH of 10.

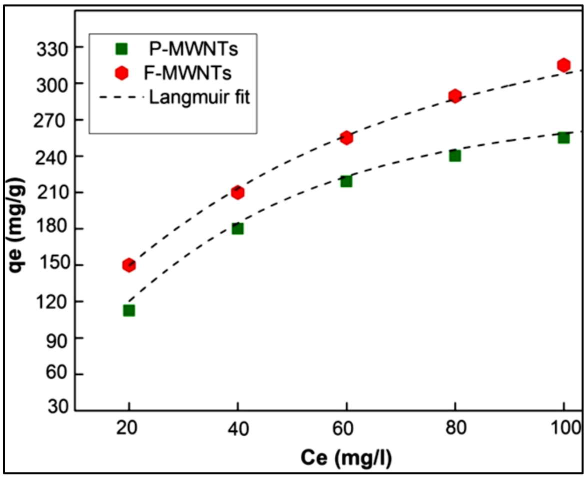


Fig.2 Langmuir isotherms model of P-MWNT and F-MWNT filters

Figure 4 shows the removal efficiency enhancement of Ni(II) with the increase of MWNT filter mass. This phenomenon implied that the filtration depended on the availability of binding sites. The functionalization had evident impact on the MWNT removal efficiency of Ni(II); *R* of F-MWNT filter was systematically higher than that of P-MWNT. It is worth to note that functionalized filters had smaller diameter and larger specific surface area compared with the untreated MWNTs as evidenced by Fig. 5.

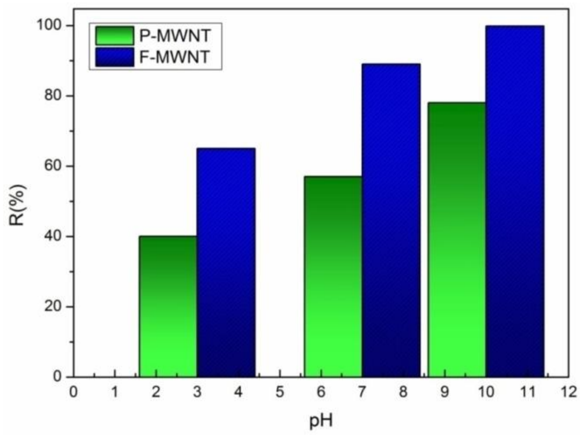


Fig. 3 Variation in removal efficiency with pH of Ni(II) solution for P-MWNT and F-MWNT filters

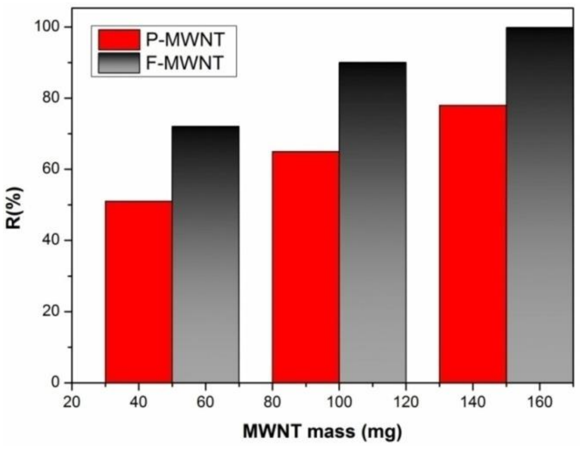


Fig. 4 Variation in removal efficiency of Ni(II) from aqueous solution with P-MWNT and F-MWNT filter mass.

Removal efficiency of Ni(II) and contact time

The removal efficiency is correlated to the contact time between Ni(II) ions in the solution and the CNTs in the filter. The contact time and the solution flow rate calculated by [16, 26]. In our experiment, Ni(II) (II) solution concentration was 10 ppm with pH =10, and filter mass was 150 mg. The filtration time, solution flow rate, contact time and the removal efficiency of Ni(II) for P-MWNT and F-MWNT filter are listed in Table 2. Contact time of 0.87 min was required to remove 78% of Ni(II) by P-MWNT filter. Even at 0.42 min contact time, the removal efficiency by F-MWNT filter was high and could reach 99.8%. Also the flow rate of the solution through the filter in the case of F-MWNT filter was higher than P-MWNT one. The short contact time of the F-MWNT filter, further supports the application of functionalized MWNTs as effective sorbents.

Effect of solution pH on the filter regeneration

Metal desorption from loaded sorbents is essential for making the filtration process competitive; this depends on the cost of the sorbent and the value of the metal [37, 38]. To regenerate the TM filters we applied a treatment by HNO_3 and NaOH solutions in addition to pure water treatment. Figure 5 shows the recovery of F-MWNT filter at three different pH. It is apparent that the recovery percentage due to Ni(II) desorption from the filter increased with pH reduction. H^+ is the main compound lead Ni(II) being recovered from adsorbent surface. At high and neutral pH, the concentration of H^+ is lower than acidic solutions, so the filter recovery is lower. Therefore, HNO_3 solution was selected as the regeneration solution for effective Ni(II) desorption. This in agreement with the results discussed in the report [37]. The recovery of 150 mg of F-MWNT filter after absorbing 99.8% of 10 ppm Ni(II) concentration by 50 ml HNO_3 solution is low cost process. About 98% of the sorbed Ni(II) ions is released within 12 min, indicating that the desorption is even faster than the sorption process. Five successive sorption/desorption cycle runs were performed using 50 mL of HNO_3. The F-MWNT filter shows quite high stability in both sorption and desorption performance along the five cycles. After regeneration, the MWNT filter was again carefully washed with distilled water to become ready for the following run of uptake. The regeneration performance for each cycle was found to be slightly decreased from 98% in the first cycle to 93% in the fifth run.

Discussions

SEM and EDS characterization and enhancement mechanism of acid functionalized MWNT-based filters

SEM and EDS analysis were conducted to identify the morphology of P-MWNT and F-MWNT filter samples. Figure 6 shows SEM images of the pristine TM, Fig. 6a, and acid functionalized TM, Fig. 6b, of MWNT filter Functionalized TM shows the same bundling structure, which bear a resemblance to the pristine MWNTs.

TABLE 2: The estimation for time of filtration, flow rate, contact time, and the removal efficiency of Ni(II) for P-MWNT and F-MWNT.

Parameter	Filtration time (min)	Flow rate (cm/min)	Contact time (min)	Removal efficiency (%)
P-MWNT	25	0.65	0.87	78
F-MWNT	18	0.93	0.42	99.8

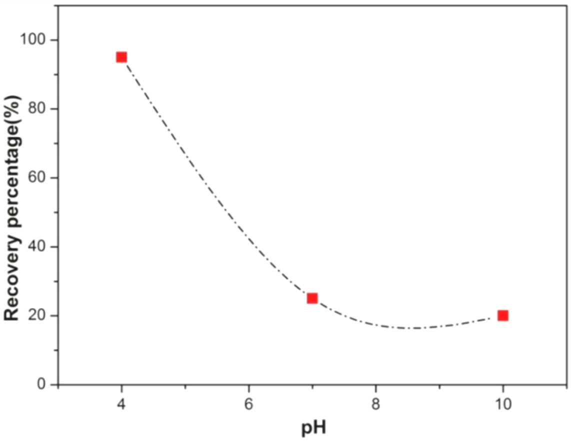
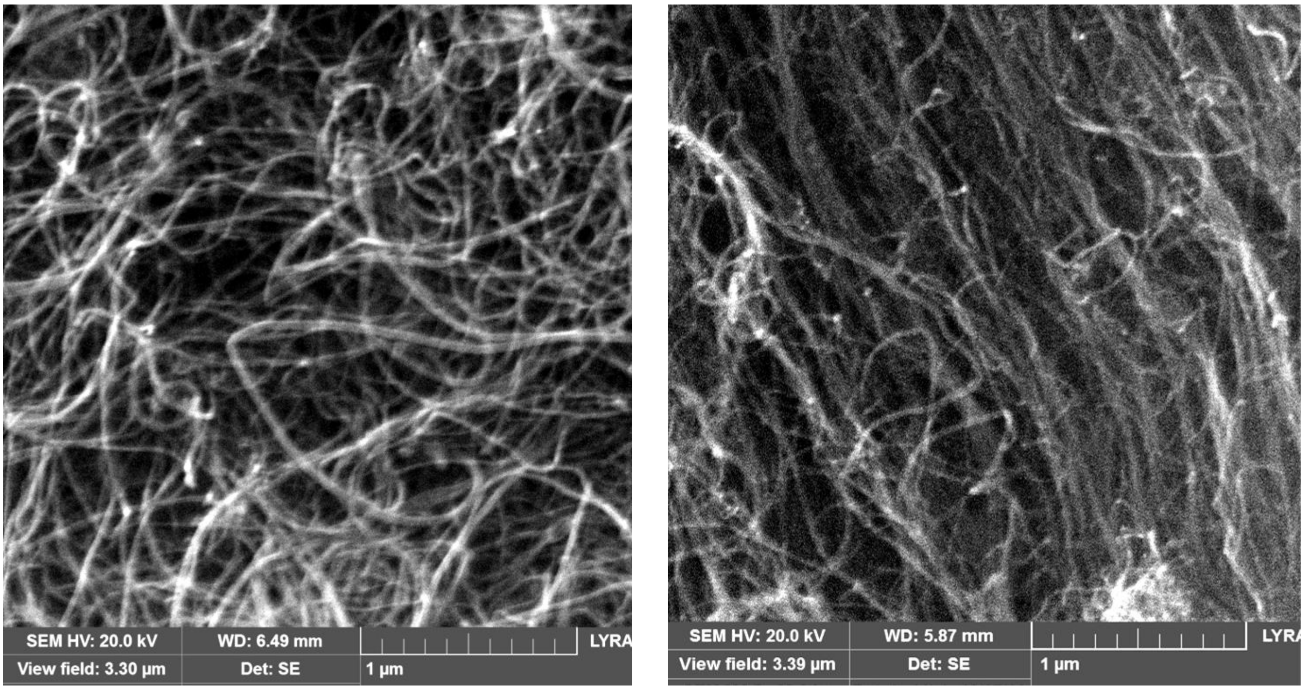


Fig. 5 Effect of solution pH on desorption of Ni(II) from functionalized TM filters.

This demonstrated that after acid treatment, the structure of long, hollow tube is still preserved. We measure the outer diameters of the tubes in both pristine and functionalized samples. The average diameter values are around 25 nm for P-MWNT, Fig. 6a, and 17 nm for F-MWNT, Fig. 6b. These numerical estimations show that the functionalized MWNTs, on the average, have lost their outermost walls formed in amorphous structure during the functionalization process. The mechanism for this diameter reduction discussed in [38].The dwindling of nanotube diameters indicates that the acid functionalization induced some changes in the periphery of MWNTs, either dissolving a significant fraction of amorphous carbon or that reduce the constituent part size and develop the adsorption proficiency. The specific surface area of MWNTs after acid treatment was about 284.7 g/m^2 which are high comparable with pristine one. The EDS analysis offers a quantitative study of the oxygen content of the functionalized MWNTs. Attaching carboxylic groups by acid treatment enhances the reactivity of CNT walls for adsorption of substantial metal particles from fluid arrangements. This enhancement is proved by EDS analysis that offers a quantitative study of the metal content of the pristine and functionalized MWNTs. Figures 7a and 7b show the element content on the surface of pristine and functionalized MWNT filters after filtration, which shows Ni(II) deposition on these CNT filters. It is obvious that the Ni(II) fraction deposition on F-MWNT higher than P-MWNT, in a good correspondence with enhancement of removal efficiency by MWNTs filters after functionalization, as reported in Sec. 4.2. Also, the oxygen enhancement after ion irradiation was revealed by EDS analysis, Figures 7c and 7d. One can see that the degree of functionalization, represented by the increase of the oxygen content, for F-MWNT is somewhat higher than that of P-MWNT. For investigations by FTIR spectrometry, the pristine and functionalized MWNTs samples were readied onto KBr crystals using utilizing simplified strategy [16]. Figure 8 summarizes the behavior of the functional groups observed via FTIR spectroscopy. The acid treated MWNTs shows new peaks in comparison with pristine MWNTs, which lack the hydroxyl and carbonyl groups, Fig.8a. Figure 8b shows more intense peaks for F-MWNTs at 3445 cm^{-1}, 1635 cm^{-1} and 1150 cm^{-1} that correlated with O–H, – COOH and C=O, respectively. Similar observations of the FTIR spectra for MWNT-COOH was reported by and Wu et al. [39]. It is recommended that the adsorption of heavy metals onto the F-MWNTs are mainly controlled by the strong interactions between the metal ions and hydrophilic surface functional groups, especially carboxyl and hydroxyl groups [24]. Comparison of the FTIR spectra of MWNTs before and after Ni(II) filtration confirmed this mechanism (Fig. 8c). Contrasted with the first FTIR range, the adsorption of Ni(II) particle on the functionalized MWNTs brought about varieties of FTIR peaks which could be attributed to the interactions between metal particles and the functional groups on the tube surface.

Mechanism of MWNT filters efficiency enhancement by acid functionalization

The announced outcomes above have shown the nearby relationship between the efficiency enhancement, Fig. 1, and Ni concentration increase in the CNTs, Fig.6, which indicates that the heavy metal adsorption is the dominating mechanism for water purification by CNTs filtering.



(a) Average diameter = 25 nm (b) Average diameter = 17 nm

Fig. 6 SEM images showing the surface morphology and the average outer diameter distribution of P-MWNT (a) and F-MWNT filter (b).

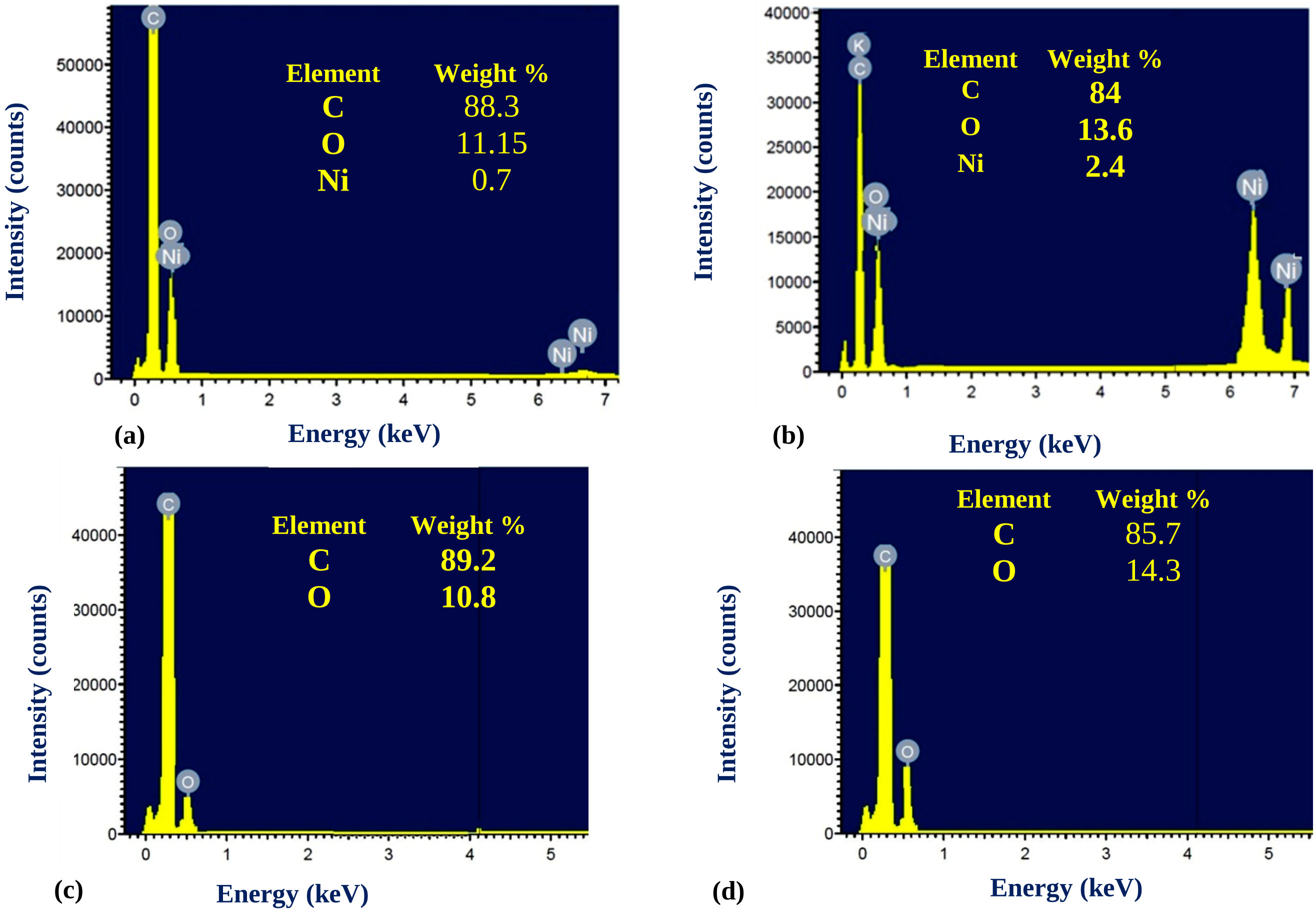


Fig. 7 The EDS analysis shows the Ni(II)content onto the surface of P-MWNT (a) and F-MWNT parts of filter (b) after filtration, and the oxygen-content enhancement for P-MWNT (c) and F-MWNT (d).

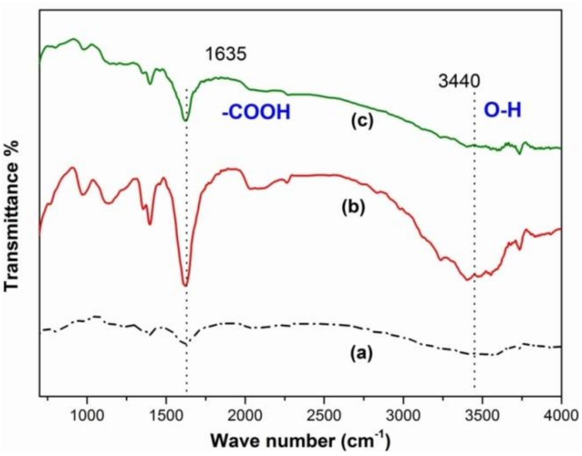


Fig. 8 FTIR spectra of pristine MWNTs (a), functionalized MWNTs before filtration (b) and the acid functionalized MWNTs after filtration (c).

Evidently, functionalization process introduces defects on the wall of MWNTs which enhances the adsorption of Ni(II). This mechanism could be related to the uptake of Ni(II) ions from solution to the places with larger functional groups sites that could be illustrated by the ion exchange mechanism model. These groups can be involved in chemical bonding and are responsible for the cation exchange capacity of F-MWNT. Also the physical adsorption plays a critical role in the adsorption of Ni(II) on the MWNTs filter, that the magnetite ion could be attached directly to the surface of CNT. This will be the possible mechanism for the uptake of Ni(II) from aqueous solutions by P-MWNTs. Figure 8 shows another mechanism is due to the functionalization of the MWNTs walls with carboxylic (-COOH) groups after acid treatment as shown in EDS analysis (Fig. 6c, d) and FTIR spectrum, Fig.7.

According to this mechanism, the adsorption interaction between the functionalized MWNTs and Ni(II) ions is due to the ion exchange and complexation mechanisms [26].

Follow these consequences; the high removal efficiency of F-MWNT that could reach 100% for concentration of 10ppm due to the fact that, the F-MWNT has higher concentrations of function groups which serves as pinning places for the adsorption of the metal from filtering solution.

Conclusions

In this study the application of both pristine and ion beam functionalized MWNTs were investigated as prospective filters to remove Ni(II) from aqueous solutions. MWNT samples were functionalized by mixture of HNO_3/ H_2SO_4 followed by etched treatment of H_2SO_4 /H_2O_2 solution to remove all carbon particles. Some parameters were found important to determine the removal efficiency; the concentration of metals in aqueous solution, pH, contact time and the filter mass. Prevailing techniques, SEM, EDS and FTIR were used to investigate the MWNT filter structure, the Ni(II) deposition in both pristine and functionalized filters. Both, EDS and FTIR, show the increase of Ni adsorption in the functionalized samples. Direct filtering experiments gave a significant enhancement of removal efficiency which was referred to defect formation introduced by functionalization treatment.

It was noted that, the key factors favoring the removal efficiency are high pH and low initial concentration.

At pH=10 and Ni concentration of 10 ppm the removal efficiency could reach 99.8% in the functionalized CNT filter.

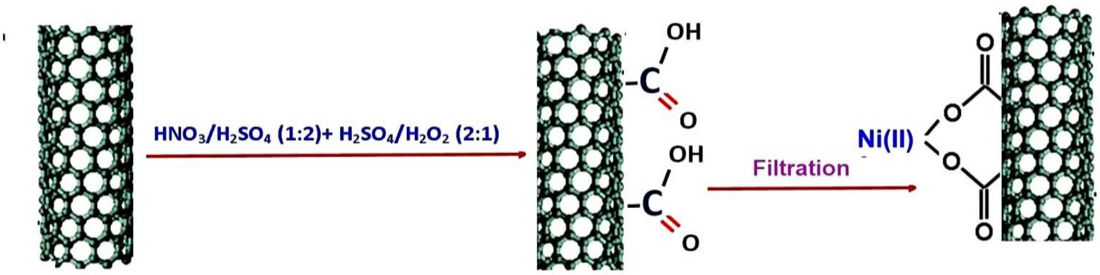


Fig. 9 Schematic shows the functionalization filtration mechanism of Ni by CNT-based filters showing the ion exchange mechanism. Detailed functionalization process with nitric acid was reported in [16].

The ion exchange mechanism is postulated. We conclude that these filters are efficient for heavy metal removal and could be an alternative kind of profitable filters for waste water management.

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