Surface functionalization of multi-walled carbon nanotubes by ozone and the enhancement of their environmental applications

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Abstract
Selective functionalization of multiwalled carbon nanotubes (MWNTs) is essential for many prospective applications of such materials. In the present study, MWNTs grown by chemical vapor deposition are functionalized by ozone treatment at room temperature. Through this environmental and functionalization method, the chemical reactivity of MWNTs can be altered and tuned. Ozone functionalized MWNTs (F-MWNTs) were characterized by Raman spectroscopy, SEM, EDS, BET surface area, XPS, and FTIR. The results obtained confirm the formation of oxygen groups attached to the surface of ozone-treated nanotubes (e.g. carboxyl), which modify their physicochemical properties and boost the surface reactivity. The F-MWNT filters showed 99.5% manganese removal efficiency at 20 ppm concentration in the solution, which is higher than the efficiency reported earlier. The optimal parameters for Mn adsorption by F-MWNTs were studied. Possible mechanisms of F-MWNT adsorption processes are also discussed.

1. Introduction

Owing to their toxicity, waste with heavy metals, even in very small concentrations, is hazardous to humans and the environment [1]. Heavy metals are one of the most well-known types of poisons in groundwater due to their high lethality, prevalence, and non-degradability [1]. Manganese is one of the most abundant metals in nature. It is a crucial metal for the human system and enzymes activation. It is present in the atmosphere as suspended particulates resulting from industrial emission, soil cloting, and volcanic emissions [2]. Manganese affects the appearance and taste of water, and it can be considered as a source of corrosion in drain sewers, due to the development of microorganisms and bacteria. These pathogens do not cause health problems; however, they cause scent, corrode plumbing equipment, and reduce well yields section [3]. Due to the toxicity and non-degradability of metallic species, scientists all over the world have carried out extensive work to remove them from aqueous solutions and industrial effluents. A removal process should be simple, effective and inexpensive [4]. Membrane filtration [5], chemical deposition [6], ion exchange [7], silica [8], and the adsorption on activated carbon [9], are among the most commonly used methodologies for this purpose. However, most removal processes have disadvantages, such as continuous injection of chemicals, high costs, and even incomplete metal removal [10].

Carbon nanotubes (CNTs) possess many exceptional electrical, optical, thermal, and mechanical properties [11]. They have low weight, high aspect ratio, extremely high rigidity, and maintain large elastic deformation [12]. Multiwalled carbon nanotubes (MWNTs) are composed of concentric layers of single-walled carbon nanotubes. A large amount of proposed applications of CNTs depend on their functionalization, the need for which is due to the hydrophobicity and inertness of pristine CNTs, which limits their potential use. Fixing certain chemical radicals on their surface is a way to overcome this drawback. Due to their special configuration and outstanding properties, MWNTs have emerged as innovative material for applications in a variety of fields, such as super-capacitors [13], photovoltaic devices [14], hydrogen storage [15], conducting polymer composites...
The preliminary material of the current study was the commercial multiwalled carbon nanotube Taunit-M. Ozonation of the MWNTs followed by HCl demineralization to eliminate the carbonaceous particles and transition metals. As grown MWNTs in mixture about 100 mg l$^{-1}$ of an ozone-oxygen mixture using ozone concentration 1 of an ozone-oxygen mixture using ozone concentration 1 for reaction time 6 h at room temperature which are the optimal conditions for the enhancement of oxygen-containing functional groups. CNTs remove heavy metals by complexation or electrostatic attraction of metal ions to various surface oxygen-containing functional groups. It has been demonstrated that acidizing of CNTs is indeed important for increasing the reactivity of the tube surface and providing the useful functionality by attaching carboxyl and hydroxyl groups. However, these acid treatments require either long processing times or, as a rule, an oversized installation. The ozone oxidation is an alternative treatment that has been shown to oxidize nanotubes at room temperature and can be performed on individual nanotubes with a low capital cost and high processing sustainability. Ozone improves surface properties of carbon nanotubes by increasing the specific surface area, pore volume, and enriching the surface with functional groups. Numerous studies have reported on methods of filtration enhancement of ozone functionalized MWNTs. The effect of pH, concentration, contact time and the mass on the removal efficiency of manganese were studied and confirmed by Langmuir isotherm. This technique is dry and less time consuming than other chemical oxidation methods.

2. Material and methods

2.1. Ozone functionalization of the MWNTs

The preliminary material of the current study was the commercial multiwalled carbon nanotube Taunit-M (TM) produced by chemical vapor deposition technique (CVD), with the catalytic composition (Co, Mo)/MgO–Al$_2$O$_3$, and the technical grade propane & butane as the carbon source. The process of CVD synthesis was performed for 45 min at 700 °C in the manufacturing reactor of CNT synthesis (Nano-Tech Center, Tambov-Russia). The MWNTs produced in these conditions are in the form of hollow cylinders, figure 2, composed of granular agglomerates of MWNT with a nanotube length 98.5% and the remaining 1.5% includes amorphous carbon and of metallic catalysts. As grown MWNTs followed by HCl demineralization to eliminate the carbonaceous particles and transition metals. Purified MWNTs (TM) were compressed using high pressure piston to the form of circular tablet with the diameter 20 mm, the thickness of 5 mm, and masses from 0.1 to 0.3 g. Pristine and ozone functionalized MWNT tablets were controlled identically. In order to perform the ozone functionalization of TM tablets, a flow of diluted ozone was generated by an ozone generator with pure oxygen as the gas source. The MWNT tablet was placed in a quartz U-type reactor and treated in a stream 12 l h$^{-1}$ of an ozone-oxygen mixture using ozone concentration in mixture about 100 mg l$^{-1}$ for reaction time 6 h at room temperature which are the optimal conditions for ozone treatment.

The physical morphology and the surface investigations of pristine (P-TM) and ozone functionalized F-TM tablets were examined using powerful tools. Scanning electron microscope (SEM, TESCAN) with the Digitizer software was performed to quantify the average diameter of the tubes. To confirm the enhancement of oxygen content and the surface functional groups of F-TM, Energy dispersive x-ray (EDS), x-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectra (IFS 66 V/S, Bruker) were conducted. The specific surface area of P-TM used in this investigation was determined using nitrogen adsorption method was found to be 223.5 g m$^{-2}$. The adsorbed content on the MWNT filter was characterized by micro Raman...
INTEGRA Spectra system with an excitation laser of 473 nm wavelength in backscattering geometry, 100× confocal microscope, and a laser spot diameter of 2 μm.

2.2. Filter design and manganese stock solution preparation

Figure 1 shows the filter design and the filtration mechanism that will be discussed in detail in the upcoming sections [18]. The manganese solution used in the experiments was prepared by diluting a solution of 1000 mg l⁻¹ KMnO₄ in deionized water to achieve the desired concentration. The chemicals used in the experiments were purchased in high analytical purity, and used without further purification. 0.1 M HNO₃ or 0.1 M NaOH is used to adjust the pH of the stock solutions.

All of the batch experiments were conducted in 50 ml syringe filtering system. In each experiment, various filter tablets mass, from 100 to 300 mg, were put into the syringe and the 50 ml of manganese solution with initial Mn concentrations of 20 to 200 ppm were added. The effect of the solution concentration and the filter dosage were investigated at different pH varying from 4 to 10. Before and after each experiment, the manganese concentration was measured spectrophotometrically using a UV/vis spectrophotometer, and the removal efficiency (R), defined as in equation (1) [19]:

\[
R(\%) = \frac{C_0 - C}{C_0} \times 100
\]  

where \(C_0\) and \(C\) are the Mn concentrations in the aqueous solutions, before and after the filtration process, was estimated as a function of Mn concentration in the initial solution. As the filtration process approach certain saturation values \(C_s\) and \(R_s\), the adsorption capacity \(q_s\) (mg g⁻¹) can be estimated from equations (2), (3) [19]:

\[
q_s = \frac{V(C_0 - C_s)}{m}
\]

\[
q_s = \frac{V \cdot C_s \cdot R_s}{m}
\]

where \(m\) (in g) is the mass of the adsorbent and \(V\) (in l) is the volume of the liquid solution, to evaluate the desorption of manganese adsorption and filter regeneration, after manganese filtration at \(\text{pH} = 4\) and concentration 20 ppm, F-TM with adsorbed manganese were used as a filter to 50 ml of water, NaOH and HNO₃ solutions, in order to determine the effect of pH of regeneration solution on desorption process.
3. Results and discussion

3.1. Surface analysis of pristine and ozone functionalized MWNTs filters

Morphology of pristine (P-TM) and ozone functionalized F-TM filters was characterized by SEM and EDS analysis. Figure 2 shows the SEM images of the P-TM, figure 2(a), and F-TM filters, figure 2(b). F-TM shows the same worm-like bundling structure, which resembles the P-TM. This demonstrated that after ozone treatment, the structure of long, hollow tube is still preserved. The average diameter values are approximately 26 nm for P-TM, figure 2(a), and 15 nm for F-TM, figure 2(b). The mechanism for this diameter reduction was discussed in [36]. The decreasing of the tube diameters indicates that the ozone functionalization induced some changes in the periphery of MWNTs that reduce the particle size and enhance the adsorption efficiency. The specific surface area of F-TM was about 318 g m\(^{-2}\) which are high comparable with P-TM. Attaching carboxylic groups by room temperature ozone treatment enhances the reactivity of CNT walls for adsorption of heavy metal ions from aqueous solutions. The reactivity enhancement was demonstrated by the EDS investigation that offers a quantitative study of the metal content of the pristine and ozone functionalized MWNTs. Figures 3(a) and (b) illustrate the deposition of Mn on the surface of P-TM and F-TM filters after the filtration process. It is obvious that the manganese fraction deposition on F-TM higher than P-TM filters, in a good correspondence with enhancement of removal efficiency by MWNTs filters after functionalization, as reported in section 3.6. Also, the oxygen enhancement after ozone process was revealed by EDS analysis, figures 3(c), and (d).

For investigations by FTIR spectrometry, P-TM and F-TM filters were prepared onto KBr crystals using drag and drop method [18]. Figure 4 shows the behavior of the functional groups observed via FTIR spectroscopy. The ozone treated MWNTs shows new peaks in comparison with pristine MWNTs, which lack the oxygenated groups, figure 4(a), [37]. It is recommended that the adsorption of heavy metals onto the F-MWNTs is mainly controlled by the strong interactions between the metal ions and hydrophilic surface functional groups [27]. Comparison of the FTIR spectra of MWNTs before and after manganese filtration confirmed this mechanism, figure 4(c). Compared to the original FTIR spectrum, the adsorption of manganese ion on the functionalized MWNTs resulted in variations of FTIR peaks which could be attributed to the interactions between metal ions and carboxyl groups, figures 4(b), and (c). The shifts in the vibrational frequencies of C–O, –COOH and –OH from 1115 cm\(^{-1}\) to 1085 cm\(^{-1}\), 1630 cm\(^{-1}\) to 1620 cm\(^{-1}\) and 3415 cm\(^{-1}\) to 3445 cm\(^{-1}\) respectively, that can be attributed to the interactions between the metal ions and the functional groups on the tube surface.

XPS is a common surface technique to obtain the distribution of the surface oxygen species on the outer walls of MWNTs. Figure 5 shows the effect of the ozone reaction time on the percentages of the three oxygen functionalities C–O, C=O and O=C–OH. It seems that the oxidation for the three paths depending on the experimental conditions. It is evident that the number of O=C–O groups increase for longer treatment times, that agree with the reported mechanism [38]. According to this mechanism, C–O groups are the primary functions produced by the ozone functionalization. A further treatment results in the transformation of these primary functions onto C=O and later on into O=C–O. It is clearly seen that the optimum reaction time for the ozone treatment is 6 h, which produce an enhancement of the O=C–OH groups that could reach 7% of the total oxygen content.
3.2. Raman spectra of pristine and ozone functionalized MWNTs filters

RS of P-TM and F-TM excited by 473.8 nm blue laser were recorded in the 200–3200 cm$^{-1}$ region, as shown in figure 6. Three characteristic peaks, the D band (disorder band), the G band (graphite band and the G’ band (second overtone of the defect induced D band and is related to the three dimensional order) appeared at 1340, 1580 and 2700 cm$^{-1}$, respectively. These peaks are significant for investigating the graphitic nature and structural ordering of the tubes [39]. The data obtained from the experiment shows an increasing ID/IG ratio from 0.61 to 0.8 after ozone functionalization, figures 6(a), (b), indicating increasing of defects and vacancies in

Figure 3. The EDS analysis shows the element content for of P-TM (a) and F-TM filter (b) after filtration, and the oxygen enhancement for P-TM (c) and F-TM (d).

Figure 4. FTIR spectra show the functional groups onto the surface of P-TM (a), F-TM before filtration (b) and F-TM after filtration (c).
the functionalized samples due to attaching oxygen content like carboxylic groups [40]. The other band $G'$ is indicative of long-range order in a sample and account for the purity of MWNTs. The variation of the intensity of the $G'$ band supports our explanation: the higher intensity of $G'$-band accounts for fewer defects in P-TM; in contrast the reduction of this band, figure 6(b), correlates with the defect formation in walls of MWNTs. The manganese deposition on the MWNT filter before and after functionalization was further investigated using RS as shown in figures 6(c), (d). Raman band located at approximately 629 cm$^{-1}$ for the MnO$_4^-$ content are in good agreement with the major vibrational features of the MnO$_4^-$ compounds previously reported by [41]. This band
acts as an independent indicator for the filter absorption capacity. After filtration a slightly change in ID/IG ratio indicates that the filter conserve its structure after filtration process, figures 6(c), (d). The ozone functionalized MWNT filter shows a high intensity of a magnetite peak compared with the pristine one. Thus, the results of the RS correlate with the functional groups formation during the functionalization process, figure 4.

3.3. Effect of manganese concentration in aqueous solution on the removal performance
A comparative study of the filtration efficiency of P-TM and F-TM filters is performed for manganese removal as a function of manganese concentration in aqueous solution. From figure 7(a), with an increase in the initial concentration of manganese in aqueous solution, it can be seen that the removal efficiency, R, decreases. At 200 ppm concentration, R is about 52% for 300 mg for P-TM filter but for the same amount of the filter the efficiency of F-TM is 82%, whereas, at low concentration of 20 ppm, R of F-TM is around 99.5%. This may suggest that the adsorption interaction between functionalized MWNTs and manganese ions was mainly of an ion interaction nature consistent with an ion exchange mechanism [29], demonstrating that the removal efficiency of F-TM is better than P-TM. For manganese concentration of 200 mg l\(^{-1}\) and 300 mg filter mass, using equations (2), (3), the adsorption capacity can be estimated as 173.33 mg g\(^{-1}\) for P-TM and 273.33 mg g\(^{-1}\) for F-TM. These values are relatively high compared to the previous materials used as adsorbents, table 1. This suggests that the F-MWNTs are efficient heavy metal adsorbents. MWNT-based filters showed high removal efficiency of heavy metals like nickel, chromium, iron, and cadmium. For example, these membranes showed high removal efficiency for chromium, that could reach 97% [19], and for nickel is about 85% [20].

3.4. Effect of pH of manganese aqueous solution and the filter mass on the removal performance
The pH influences the surface charge of the adsorbent, the amount 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 manganese is investigated by testing three values of pH (4, 7 and 10) and manganese concentration 20 ppm with filter mass 300 mg. Figure 7(b) shows that the maximum removal of manganese occurs at the pH range of 4, as the removal efficiency (R) could accomplish 99.5% for F-TM filters, whereas R is about 65% at pH = 10. Figure 2(b) demonstrates that the removal of manganese by F-TM filters is more efficient than P-TM. The negatively charged MnO\(_4^-\) is easily to be adsorbed to F-TM at low pH values due to the complexation mechanism,
\[ \text{C}_x\text{OH} + \text{H}^+ \leftrightarrow \text{C}_x\text{OH}_2^+. \] At high pH values, the higher the valence of the adsorbed anions the more negative the surface becomes, hence inhibiting the further adsorption of anions [46].

Figure 8(a) shows an increase of the removal efficiency of manganese with the increase of MWNT filter mass. This phenomenon indicated that the filtration relied on the availability of the reactive sites. The functionalization had evident impact on the MWNT removal efficiency of manganese; R of F-TM filter was systematically higher than that of P-TM. It is worth to note that functionalized filters had smaller diameter and larger specific surface area compared with the untreated MWNTs as evidenced by figure 2.

3.5. The contact time and the regeneration of MWNTs filters

The filtration performance is correlated to the contact time between manganese ions in the solution and the CNTs in the filter. Significant parameters such as filtration time, flow rate, and contact time can be roughly estimated using previous report, [18]. In our experiment, manganese solution concentration was 20 ppm with pH = 4, filter mass was 0.3 g, thickness and active area of the filter were 0.4 cm and 3 cm\(^2\), respectively. From table 2, even at 0.43 min contact time, the removal efficiency by F-TM filter was high and could reach 99.5%. Also the flow rate of the solution through the filter in the case of F-TM filter was higher than P-TM one. The short contact time of the F-TM filter, further supports the application of ozone functionalized MWNTs as effective sorbents.

To account for the regeneration ability of the TM filters we applied a treatment by HNO\(_3\) and NaOH solutions in addition to pure water. Figure 8(b) shows the recovery of F-TM filter at three different pH. It is apparent that the recovery percentage due to manganese desorption from the filter increased with increasing pH. Therefore, NaOH solution was selected as the regeneration solution for effective manganese desorption. This in agreement with the results discussed in the report [47]. The recovery of 0.3 g of F-TM filter after absorbing 99.5% of 20 ppm manganese concentration by 50 ml NaOH solution is a low cost process.

3.6. Effect of ozone functionalization on MWNTs filters and the removal enhancement mechanism

As the surface of MWNTs attacked by the ozone molecules, caps and wall defects are etched away to a large extent and the surface of F-TM filters becomes functionalized by carboxylic groups. The ozone functionalization process enhances significantly the oxygen content and further alters the surface charges in agreement with existing literature [18]. The reported results above have demonstrated the close correlation between the efficiency enhancement, figure 7(a), and the heavy metal concentration increase in the MWNTs, figure 3, which indicates that the Mn adsorption is the dominating mechanism for water purification by CNTs filtering. It was also shown that the adsorption correlates with the functional groups increased by the reported ozone
functionalization as indicated by RS, figure 6. Evidently, this mechanism could be related to the uptake of
manganese ions from solution to the places with larger functional groups sites. This can be explained by the ion
exchange and complexation mechanism models. Also the physical adsorption plays a significant role in the
adsorption of manganese 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 manganese from aqueous solutions, figure 1. Ozone
functionalization of the TM filters with oxygenated groups, which serves as pinning sites for adsorption of
the metal from filtering solution, as indicated in EDS analysis (figures 3(c), (d)) and FTIR analysis, figure 4,
supports the ion exchange and complexation mechanisms [29]. Summarizing these observations; the ozone
functionalization procedure, enhances the reactivity and the uptake of manganese. The high removal efficiency
of F-TM filters that could exceed 99.5% for concentration of 20 ppm manganese concentration is explained by
the fact that, the F-TM/manganese reactivity enhancement could be interpreted by physical adsorption and ion
exchange mechanisms, figure 1. The advantage of the ozone process is that it is a ‘dry’ and, hence, more
environment friendly technology compared with wet chemical acids.

3.7. Adsorption isotherm model for Mn removal
The adsorption capacity ($q_e$) of manganese on the P-TM and F-TM were fitted by applying the Langmuir
isotherm model [48], figure 9.

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{4}$$

Where $q_e$ (mg g$^{-1}$) is the specific equilibrium amount of manganese adsorbed, $C_e$ (mg l$^{-1}$) is the equilibrium
concentration of manganese in aqueous solution, $q_m$ (mg g$^{-1}$) is the maximal adsorption capacity, and $k_L$ is the
Langmuir constant (l mg$^{-1}$). This adsorption model gives a representation of the adsorption equilibrium
between manganese in solution and the surface active sites of the ozone treated MWNT filters. Langmuir
equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid
surface and is limited to monolayer coverage. From table 3, the value of $q_m$, which characterize the adsorption
capacity is significantly enhanced after the ozone functionalization of MWNTs, which could be attributed to the
increase of surface oxygen groups. The constant $k_L$ has the same trend as $q_m$, indicating that F-MWNTs have a
higher affinity for manganese adsorption than P-MWNTs, figure 8. A dimensionless constant called separation
factor or equilibrium parameter ($R_L$), which is expressed by the following relationship, [49],

| Adsorbents | $q_m$ (mg g$^{-1}$) | $k_L$ (l mg$^{-1}$) | $R_L^2$ |
|------------|--------------------|--------------------|---------|
| P-TM       | 180.5              | 4.01E-5            | 0.972   |
| F-TM       | 291.5              | 1.92E-4            | 0.991   |
where $C_i$ is the initial concentration. The value of $R_L$ indicated the type of Langmuir isotherm to be unfavorable ($R_L > 1$), or favorable ($0 < R_L < 1$) [49]. The $R_L$ value in the present investigation was found to be 0.761 for F-MWNTs, showing that the adsorption of manganese ion on F-MWNTs is favorable.

### 4. Conclusions

This study examined the use of both primary and ozone-functionalized MWNT-based filters as promising adsorbents for the absorption of manganese from aqueous solutions. The MWNT samples were purified and functionalized at room temperature using an ozone-oxygen mixture to remove amorphous carbon particles and to attach oxygen-containing groups to the tube surface. Advanced techniques such as Raman spectroscopy, SEM, XPS and EDS have been used to study the MWNT configuration and manganese content of the original and ozone functionalized filters. The development of sites of reactivity activated by functional groups on the nanotube walls was associated with a significant increase in the intensity ratio of the D and G bands in Raman spectra, in addition to a decrease in the intensities of the G′ bands in the functionalized MWNT filters. Raman analysis, FTIR and EDS techniques confirmed the enhancement of Mn adsorption by functionalized filters. It is worth noting that low pH and low initial concentration are the main factors behind removal efficiency. Significant improvement was found in the removal efficiency of F-MWNT filters, which can reach 99.5% at 20 ppm Mn and pH = 4. The controlled adsorption of manganese was in good agreement with Langmuir’s model. Two conceivable mechanisms include the uptake of manganese molecules from an aqueous solution; ion exchange and physical adsorption. We have concluded that F-MWNT filters are efficient for removal of heavy metals and may be an alternative category for reliable wastewater filters. It is assumed that the controlled ozone functionalization of CNTs will be useful for future work on nanostructures.

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### References

[1] Zhang K, Cheung W H and Valix M 2005 Roles of physical and chemical properties of activated carbon in the adsorption of lead ions Chemosphere 60 1129–40
[2] Forstner U and Wittmann G T W 1981 Metal Pollution in the Aquatic Environment. 66 (New York, Tokyo: Springer-Verlag, Berlin, Heidelberg) p 277
[3] Akpomie K G and Dawodu F A 2014 Simultaneous adsorption of Ni(II) and Mn(II) ions from aqueous solution unto a Nigerian kaolinite clay Journal of Materials Research and Technology 3 129–41
[4] Ahn C K, Woo C H and Park J M 2008 Enhanced sorption of phenanthrene on activated carbon in surfactant solution Carbon 46 1401–10
[5] Bessbousses H, Rhalou T, Verchere J F and Lebrun L 2008 Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containing poly(ethylenimine) in a poly(vinyl alcohol) matrix J. Membr. Sci. 307 249–59
[6] Gonzalez-Muno M J, Rodriguez M A, Luque S and Alvarez J R 2006 Recovery of heavy metals from metal industry wastewaters by chemical precipitation and Nanofiltration Desalination 200 742–4
[7] Kiefer R, Kalintchev A and Holl W H 2007 Column performance of ion exchange resins with aminophosphonate functional groups for elimination of heavy metals React. Funct. Polym. 67 1421–32
[8] Passos C G et al 2008 Use of 7-amino-4-azahexysilsilica and 10-amino-4 azadecysilsila xerogels as adsorbent for Pb (II). Kinetic and equilibrium study Colloids Surf. (A) 316 297–306
[9] Amuda O S, Giwa A A and Bello I A 2007 Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon Biochem. Eng. J. 36 174–81
[10] Minceva M, Markovska L. and Meshko V 2007 Removal of Zn^{2+}, Cd^{2+} and Pb^{2+} from binary aqueous solution by natural zeolites and granulated activated carbon Maced. J. Chem. Chem. Eng. 26 125–134
[11] Bouazzza M and Zenkour A M 2020 Vibration of carbon nanotube-reinforced plates via refined nth-higher-order theory Arch. Appl. Mech. 90 1755–69
[12] Bouazzza M, Amara K, Zidour M, Abdellouahed T and El Abbas A B 2014 Thermal effect on buckling of multilayered carbon nanotubes using different gradient elasticity theories Nanosci. nanotechnology 4 27–33
[13] He S et al 2017 Biocompatible carbon nanotube fibers for implantable supercapacitors Carbon 122 162–7
[14] Bhata R and Ujjain S K 2017 Soluble single-wall carbon nanotubes for photocatalysts Mater. Lett. 190 165–8
[15] Mohammadi M, Khoshnevisan B and varshoy S 2016 Electrochemical hydrogen storage in EPD made porous Ni-CNT electrode Int. J. Hydrogen Energy 41 10311–5
[16] Khatoon H and Ahmad S 2017 A review on conducting polymer reinforced polyurethane composites J. Ind. Eng. Chem. 53 1–22
[17] Gohardani O, Eiola M C and Elizetxea C 2014 Potential and prospective implementation of carbon nanotubes on next generation aircraft and space vehicles: a review of current and expected applications in aerospace sciences Prog. Aerosp. Sci. 70 42–68
[18] Elshey E and Elshey M 2016 Characterization of functionalized multiwalled carbon nanotubes and application as an effective filter for heavy metal removal from aqueous solutions Chinese J. Chem. Eng. 24 1695–8
[19] Elshey E, Al-Ameen A, Chechenin N G, Makunin A V, Motaweh H A and Leksina E G 2017 Functionalized carbon nanotubes based filters for chromium removal from aqueous solutions Water Science & Technology 75 1564
[20] Elshey E, Al-Ameen A and Motaweh H 2020 Antimicrobial activity of functionalized carbon nanotubes against pathogenic microorganisms IET Nanobiotechnol. 14 457–464
[21] Sheikhpour A, Golbabaie A and Kasaean A 2017 Carbon nanotubes: a review of novel strategies for cancer diagnosis and treatment Materials Science and Engineering: C 76 1289–304
[22] Saffuddin N, Razia A and Junia A 2013 Carbon nanotubes: a review on structure and their interaction with proteins Journal of Chemistry 2012 18
[23] Atif R and Inam F 2016 Reasons and remedies for the agglomeration of multilayered graphene and carbon nanotubes in polymers Beilstein J. Nanotechnol. 7 1174
[24] Zhang Z, Pfefferle L and Haller G L 2014 Comparing characterization of functionalized multiwalled carbon nanotubes by potentiometric proton titration, NEXAFS, and XPS Chin. J. Catal. 35 836–63
[25] Hannula P M et al 2017 Observations of copper deposition on functionalized carbon nanotube films Electrochim. Acta 232 495–504
[26] Qiao M, Ran Q and Wu S 2018 Novel star–like surfactant as dispersant for multi-walled carbon nanotubes in aqueous suspensions at high concentration Appl. Surf. Sci. 433 973–82
[27] Xie J et al 2018 A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: preparation, application, and mechanism Chemosphere 195 351–64
[28] Elshey E M and Elshey M 2016 Removal of iron and manganese from aqueous solutions using carbon nanotubes filters Water Science & Technology: Water Supply 16 347–53
[29] Kis A et al 2004 Reinforcement of single-walled carbon nanotube bundles by intertube bridging Nature Mater 3 153–7
[30] Elshey E, Chechenin N G, Makunin A V, Shemukhin A A and Motaweh H A 2018 Enhancement of cont-based filters efficiency by ion beam irradiation Radiat. Phys. Chem. 146 19–25
[31] Ahmed D S, Haider A J and Mohammad M R 2013 Comparison of functionalization of MultiWalled carbon nanotubes treated by oil olive and nitric acid and their characterization Energy Procedia 36 1111–8
[32] Wesensk K A, Smith B A, Schrote K E, Wilson H K, Diegelmann S R and Fairbrother D H 2011 Surface and structural characterization of multi-walled carbon nanotubes following different oxidative treatments Carbon 49 26–36
[33] Sham M L and Kim J-K 2006 Surface functionalities of multi-wall carbon nanotubes after UV/Ozone and TETA treatments Carbon 44 768–77
[34] Hemraj-Benny T, Bandosz T J and Wong S S 2008 Effect of ozonolysis on the pore structure, surface chemistry, and bundling of single-walled carbon nanotubes J. Collid Interface Sci. 317 375–82
[35] Ling X, Wei Y, Zou L and Xu S 2013 The effect of different order of purification treatments on the purity of multiwalled carbon nanotubes Appl. Surf. Sci. 276 159–66
[36] Wu D C et al 2010 Multi-walled carbon nanotube/polyimide composite film fabricated through electrophoretic deposition Polymer 51 2155–60
[37] Morales-Lara F, Perez-Mendoza M J, Altmajer-Vaz D, Garcia-Roman G, Melguizo M, Lopez-Garzon F and Domingo-Garcia M 2013 Functionalization of multiwall carbon nanotubes by ozone at basic pH. Comparison with oxygen plasma and ozone in gas phase J. Phys. Chem. C 117 1647–55
[38] Dresselhaus M S, Dresselhaus G, Saito R and Jorio A 2005 Raman spectroscopy of carbon nanotubes Phys. Rep. 409 47–99
[39] Osvald S, Havel M and Gogotsi Y 2013 Monitoring oxidation of multiwalled carbon nanotubes by Raman spectroscopy J. Raman Spectros. 44 378–386
[40] Bernardini S, Bellatreccia F, Municchia A C, Ventura G D and Sodo A 2019 Raman spectra of natural manganese oxides J. Raman Spectros. 50 1–16
[41] Ucer A, Uyanik A and Aygun S F 2006 Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilized activated carbon Sep. Purr. Technol. 47 113–8
[42] Rajic N, Stojaokvic D, Jevtic S, Logar N Z, Kovac J and Kaucic V 2009 Removal of aqueous manganese using the natural zeolitic tuff from the Vranjska Banja deposit in Serbia J. Hazard. Mater. 172 1450–7
[43] Zhenze L, Shiyoyoshi I, Takushi K, Toru I, Xiaoowu T and Qingtang T 2010 Manganese removal from aqueous solution using a thermally decomposed leaf J. Hazard. Mater. 177 501–7
[44] Vijayaraghavan K, Heng W, Yun N and Balasubramanian R 2011 Biosorption characteristics of crab shell particles for the removal of manganese(II) and zinc(II) from aqueous solutions Desalination 266 195–200
[45] Ganesan P, Kamajar R, Sozhan G and Vasudevan S 2013 Oxidized multiwalled carbon nanotubes as adsorbent for the removal of manganese from aqueous solution Environ Sci. Pollut. Res. 20 987–96
[46] Samia A K, Al-Zhrai G and Abdel Salam M 2012 Removal of heavy metals from aqueous solutions by multi-walled carbon nanotubes modified with 6-hydroxyquinoline Chem. Eng. J. 181 159–68
[47] Langmuir I 1916 The constitution and fundamental properties of solids and liquids J. Am. Chem. Soc. 38 2221–9
[48] Mittal A and Kurup L 2006 Column operations for the removal and recovery of a hazardous dye ‘acid red 270 from aqueous solutions, using waste materials bottom ash and deoiled soya Ecol Environ Conserv Paper 12 181–6