Removal of Lead Ions from Aqueous Solution Using Multi-Walled Carbon Nanotubes: The Effect of Functionalization

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ABSTRACT

This study evaluates the lead adsorption efficiency of pristine multi walled carbon nanotubes (raw-MWCNTs), oxidized multi-walled carbon nanotubes (o-MWCNTs) and functionalized multi-walled carbon nanotubes with Tris (2-aminoethyl) amine (MWCNTs- TAA) from aqueous solution. Functionalization reactions were accomplished using acid treatment. MWCNTs- TAA and o-MWCNTs were characterized using scanning electron microscopy (SEM), Fourier transform infrared (FTIR), Raman spectroscopies, and thermal gravimetric analyzer (TGA). The results indicated that the oxidation and functionalization reactions successfully occurred. The adsorption of Pb(II), onto nano particles were investigated using batch equilibrium adsorption experiments and determined by the flame atomic absorption spectrometry (FAAS). The effects of pH, contact time, initial Pb(II) ions concentration, and adsorbent dosage on the adsorption process were studied. The obtained results revealed that removal of Pb(II) ions from water strongly depends on the pH of the sample solution. Maximum adsorption capacities of Pb(II) ions under the optimal conditions were 6.7, 27.8, 71 mg/g for raw- MWCNTs, o-MWCNTs and MWCNTs-TAA respectively. This means that oxidation and functionalization reactions leads to higher adsorption capacity in comparison to raw- MWCNTs. Regarding to desorption experimental, regenerated MWCNTs can be reused over four times without considerable loss of adsorption capacity. The obtained data were fitted with the Langmuir and Freundlich isotherm adsorption models. It was found that the Langmuir equation can satisfactorily explain the experimental data obtained for Pb(II) for all of the used sorbents.
KEYWORDS: Oxidized multi-walled carbon nanotubes; functionalized multi-walled carbon nanotubes; Adsorption isotherm models; Flame atomic absorption spectrometry.

1. INTRODUCTION

Lead is the most pollutant entering human life through industrial waste water and causes different illness. The main source of lead pollution in the water is originated from industrial process. Since this pollutant is non-biodegradable, it remains in the environment and causes serious illness such as nervous system damage, kidney disease, mental retardation and cancer[1-3].

There are various methods including chemical precipitation, ion exchange, membrane filtration and adsorption for lead removal from waste water [4-7]. Due to the simplicity, efficiency, and widespread application; adsorption process has been considered by scientists [8]. In addition, adsorption process is sometimes reversible and adsorbents can be regenerated using proper desorption process.

Many attempts have been done for application of nanoparticles such as carbon nano tubes in adsorption processes [9-11]. Because of unique properties such as high ratio of surface to volume, light weight, strength, large external surface area, internal sites nanotubes, and capability of π-π electrostatic interaction; these materials can be good candidates for adsorption process [12]. However, performance of these nanoparticles is limited because of their agglomeration and poor dispersion, which result from the van der Waals bonds among the graphene sheets. This drawback can be overcome by surface functionalization [13-15]. Different methods for functionalization of carbon nanotube have reported in the literature such as non-covalent functionalization [16], covalent functionalization [17], and defect functionalization [18].

The most common and the simplest method is defect functionalization. In this method, under the oxidized treatment by various reagents (e.g.,nitric acid, sulfuric acid , ammonium hydroxide and hydrogen peroxide), functional containing oxygen groups such as carboxylic, carbonyl,and hydroxyl are created on the surface of the nanoparticles [19-20]. Many researchers have been reported defect functionalization of carbon nanotubes for uptake of pollutants such as cadmium [21], zinc [22], hexavalent chromium [23], nickel [24], lead [25], copper [26], herbicide [27], and phenols [28]. Regarding to above reports, the o-MWCNTs can be a good sorbent for organic and inorganic pollutants.

Another technique to enhance dispersion of carbon nanotubes is covalent functionalization, which generates functional groups on the surface of nano particles. In general, defect modifications on the surface of carbon nanotubes are firstly made by strong acid and further modifications are accomplished by various molecules that can be grafted through creation of amide, ester, and amine bonds. 1-(2-pyridylazo)-2-naphtol [29], thiosemicarbazide [30], 2-aminobenzothiazole [31], phenyl-iminodiaceticacid [32],ethyenediamine[33], diethylenetriamine,triethylenetetrami [34], poly(2-aminothiophenol) [35], and tris(2-aminoethyl)amine [36] are the typical molecules which have reported in the literature as functionalization agents.

The main goal of this study is the assessment of lead adsorption efficiency of raw-MWCNTs, o-MWCNTs and MWCNTs-TAA from aqueous solution. The oxidation and functionalization reactions were monitored using SEM, FTIR, Raman spectroscopies and TGA analyzer. FAAS was used to determine lead concentration in samples. The effects of pH value, sorbent dosage, and contact time on the adsorption process were studied. Adsorption capacity was measured via the batch method. Adsorption mechanism was also studied for three types of sorbent. To better understanding the adsorption process, the obtained data were simulated by Langmuir and Freundlich isotherm models.

2. EXPERIMENTAL

2.1. Materials
High purity reagents from Sigma Aldrich and Merk were used for the preparation of all solutions.MWCNTs was purcheased from Cheaptubes Inc. (USA) with 10-20 nm in outer diameter, 30 nm in length, and >95% purity. Other reagents including concentrated HNO_3, thionyl chloride ($SOCl_2$), dimethyl formamide (DMF), dichloromethane (DCM), triethylamine, and tris(2-aminoethyl) amine were from Sigma Aldrich.

Lead stock solution (1000 mgL^{-1}) was prepared by dissolving its an appropriate amount nitrate salt (analytical grade) in deionized water. The solution was then diluted to the required concentrations for the sorption measurements. Laboratory glassware used were repeatedly washed with 5% v/v HNO_3 and rinsed with deionized water.

2.2. Instruments and apparatus
The morphology of MWCNTs was observed by Tescan VEGA-II scanning electron microscope. A Varian Model spectra AA.200 atomic absorption spectrometer equipped with single element hollow cathode (HCL) lamps, deuterium background correction, and air-acetylene was used for Pb(II) measurements. Lead HCL was used as the radiation sources at the wavelength of 217nm. The instrumental parameter adjustments were those recommended by the manufacturer.

TGA thermograms were obtained by a TGA-7HT from Perkin Elmer (USA) under N_2 and in the range of 25-700 °C by ramp of 10 °C/min.

The functional groups on the surface of carbon nanotubes were detected by an EQUINOX 55 FTIR spectrometer. The pH values were adjusted with a Metrohm digital pH meter. The structural information of nano particles was evaluated by a Raman Spectrometer; Model Almega Thermo Nicolet Dispersive Raman Spectrometer.

2.3. Sorbents preparation
The MWCNTs and 250 mL HNO_3 were dispersed for 45 min in an ultrasonic bath (35 KHz, 70 W). The reaction flask equipped with a reflux condenser, a magnetic stirrer and a thermometer was mounted in the oil bath. The suspension was stirred at 110 °C for 48 h and 50 mL of sulfuric acid and hydrogen peroxide mixture were then added to the solution and sonicated for 10 min. The mixture was cooled to the room temperature and was vacuum filtered. The mixture was then washed with deionized water until a neutral pH of the filtrate was reached. The o- MWCNTs were dried in a vacuum oven at 105 °C overnight. In the next steps, the 300 mg of obtained o-MWCNTs was suspended in 20 mL thionyl chloride and stirred at 70 °C for 24 h. Using DCM, the mixture was diluted and filtered under vacuum condition. Washing by DCM was continued until the filtrate became colorless. The obtained solid filtrate (MWCNTs-COCl) was dried in a vacuum oven at 40 °C. The dried MWCNTs-COCl was dispersed into 50 mL anhydrous DMF, and then 15 mL tris(2-aminoethyl) amine and 3 mL triethylamine were added. The mixture left to stir at 50°C for 36 h. The mixture was filtered through an appropriate filter. To eliminate of the unreacted materials, the filtrate was washed by DMF until the colorless DMF was observed. Finally, the filtrate was rinsed using ethanol and put under vacuum oven at 80 °C for 12 h [19,36]. In all aforesaid processes due to applied mild conditions, the structure of MWCNTs was not changed.

2.4. Procedure
The adsorption experiments were performed in the polyethylene test tubes using batch method. A portion of the sample solutions (10 mL) including Pb(II) ions, transferred into tubes. The desired pH values were adjusted with addition of HNO_3 or NaOH (0.1-0.01 mol L^{-1} concentration). 10 mg of the adsorbent was then added to the solution and the mixture was shaken at 160 rpm for 45 min. To separate of the adsorbent, after centrifuge at 1600 rpm for 15 min the mixture was filtered using 0.45 μm membrane filters. The concentration

of Pb(II) ions in the solution was determined by FAAS.The percentage of removed Pb(II) ions (R) was determined as follows [27,37]:

$$\% \ R = (C_0 - C_t)/C_0 \times 100 \qquad\qquad (1)$$

where C_0 is the initial concentration of Pb(II) ions in mg L^{-1}, C_t is the concentration of Pb(II) ions at time t in mg L^{-1}.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of functionalized MWCNTs

SEM micrographs of raw- MWCNTs and o- MWCNTs are demonstrated in Figure 1. It is obvious that the separated carbon nanotubes have cylindrical shape with the external diameters in the range of 20-30 nm. Some aggregations can be detected in this micrograph because of intermolecular forces among the MWCNTs with different shapes and directions. It seems the acidic treatment has no significant effect on the shape and size of MWCNTs and only a smoother surface is obtained.
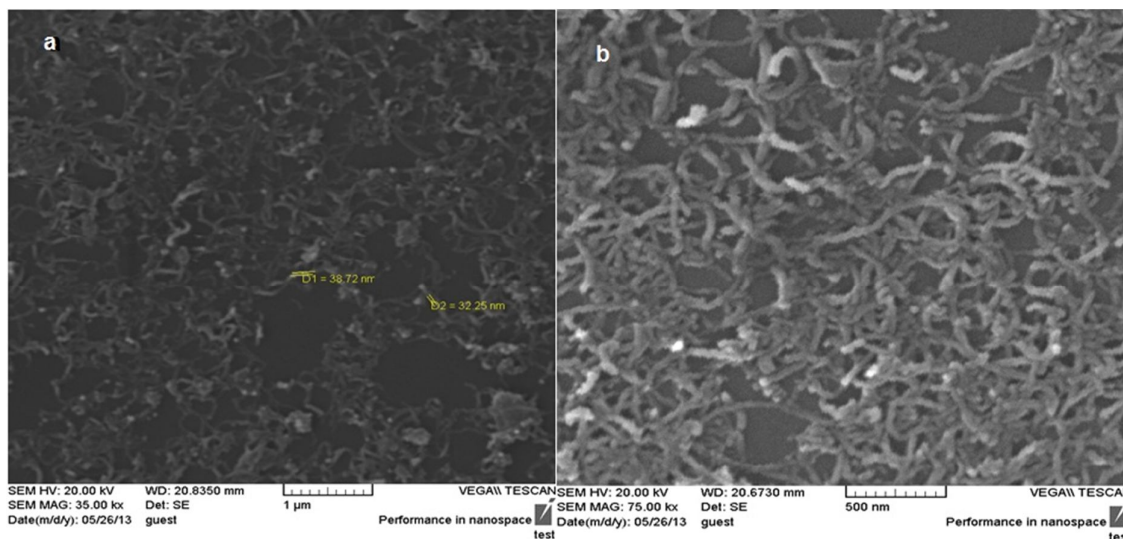

Figure1: SEM micrographs of a) raw-MWCNT b) O-MWCNT

The FTIR spectra of raw- MWCNTs, o-MWCNTs and MWCNTs–TAA are compared in Figure 2. In the FTIR spectrum of o-MWCNTs, the bands at 1400 and1710cm^{-1} can be attributed to the stretching vibrations of O-H and C=O bending of carboxyl groups, while the band at 1080 cm^{-1} is assigned to the – CO - stretching vibration of ester group. Moreover, existence of broad peak in 3450 cm^{-1} implies to OH group, which means that oxidation of the MWCNTs have induced functional groups such as carboxyl and hydroxyl on the surface of nano particles. In the FTIR spectrum of MWCNT-TAA a peak appears at 1580 cm^{-1}, which is originated from C-N stretching and N –H bending vibration [36]. Presence of this bond indicates grafting of TAA on the surface of o-MWCNTs.
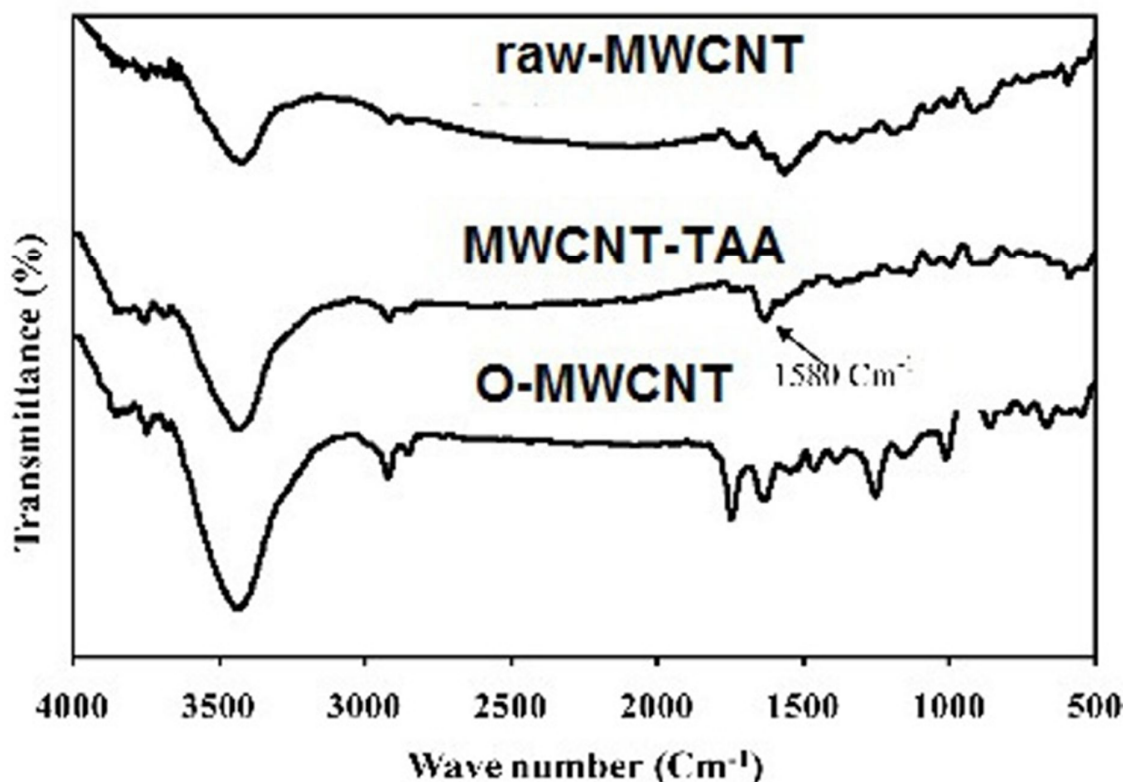
Figure 2: FTIR spectra of the samples

TGA analysis present useful information about the functionalization reactions due to thermal instability of organic groups in the samples. Thermograms of the samples are shown in Figure 3. As can be seen, raw-MWCNTs is stable and hardly decompose below 700°C while the weight of o-MWCNTs and MWCNTs-TAA decrease. Decomposition of o-MWCNTs occurs gradually in the applied range of test. The first weight loss about 100°C was related to elimination of physically adsorbed water. The further weight loss (6%) in the thermogram was related to organic functional groups which is an confirmation for oxidation reaction. The trend of weight loss for MWCNTs-TAA is moderate and faster than that of o-MWCNTs up to 450 °C due to decomposition of TAA. Above 450 °C, the decomposition rate of MWCNTs-TAA is slow and may be attributed to degradation of unreacted - COOH groups. Residuals of the o-MWCNTs and MWCNTs-TAA at 450 °C were 6 and 9 wt. %, respectively.
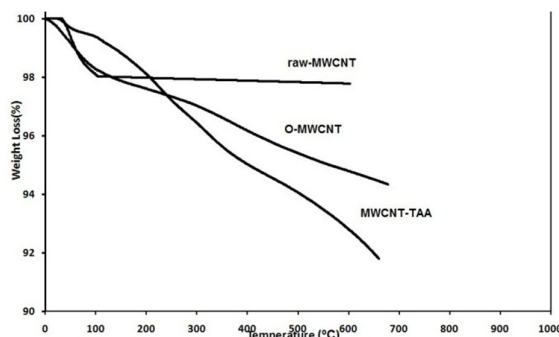
Figure 3: TGA thermograms of the samples

Another method for assessment of functionalization reaction is Raman spectroscopy.[38-39]. Figure 4 shows the Raman spectra of the samples. Two main peaks in the Raman spectra were appeared in the samples at 1339 and 1580 cm^{-1} which are known as D and G bonds, respectively. D band is related to disordered carbon atoms of MWCNTs corresponding to sp^3-hybridized and G band shows the sp^2-hybridized of carbon atoms in

the graphene sheets. Area ratio of the D to G bands (I_D/I_G) can be used to assess the amount of defects in nano particles structure.

This ratio was decreased for o-MWCNTs (I_D/I_G =1.27) in comparison to raw- MWCNTs (I_D/I_G =1.46) because of elimination of amorphous carbon during acid treatment. In other words, I_D/I_G is balanced by two factors which the functionalization reaction leads to higher I_D/I_G ratio while the purification in oxidation reaction lowers this ratio. I_D/I_G ratio was increased for MWCNT-TAA (I_D/I_G=1.5) which approves the successful conversion of o-MWCNTs to MWCNTs-TAA. In the absence of amorphous carbon, the increase of I_D is related to increase of carbon containing sp^3-hybridized and implies to successful functionalization reaction.
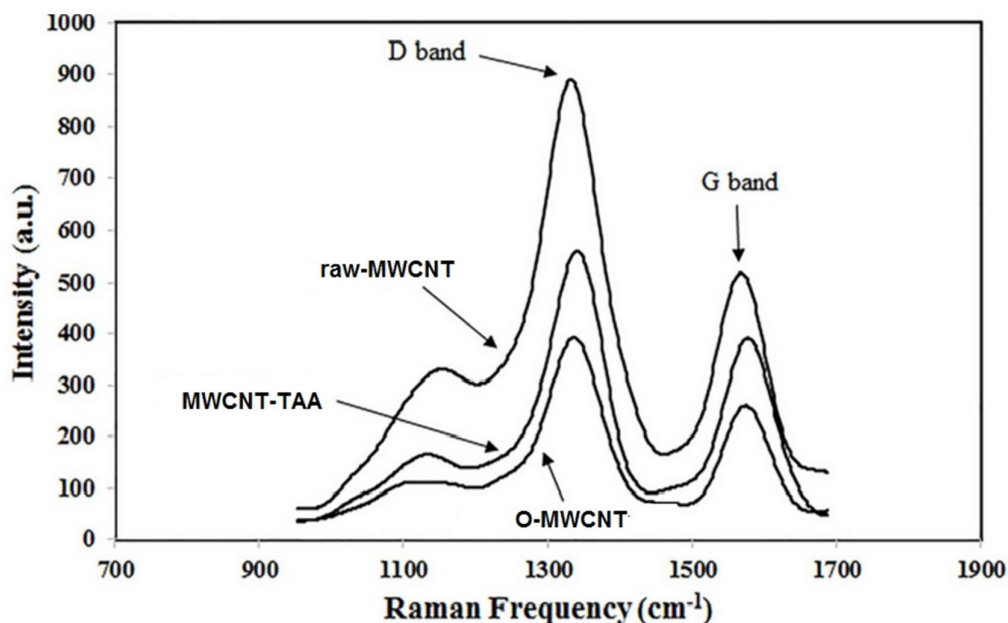

Figure 4: Raman spectra of the samples

3.2. Evaluation of adsorption

The adsorption behavior of Pb(II) on raw- MWCNTs, o-MWCNTs and MWCNTs–TAA was studied at pH values in the range of 2-11 using either NaOH (0.01-0.1mol L^{-1}) or HNO$_3$ (0.01- 0.1mol L^{-1}) for pH adjustment and is shown in figure 5.
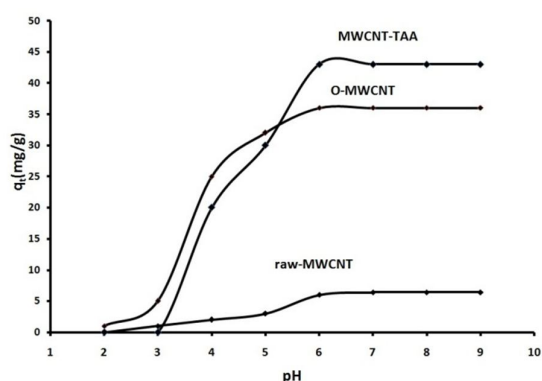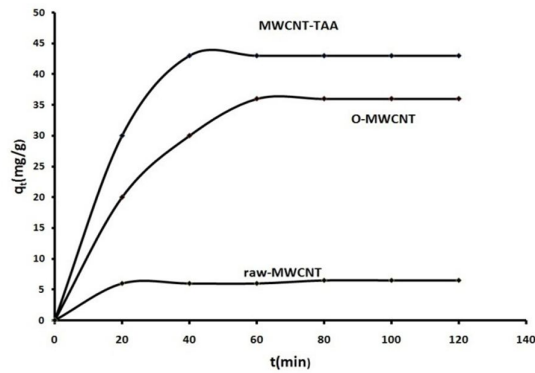

Figure 5: Adsorption capacity of lead ions at various pH values

There are four probable forms of lead at different pH values: Pb^{2+}, $Pb(OH)^{+1}$, $Pb(OH)_2$, and $Pb(OH)^{3-}$ [40]. At pH<6, the most of the lead is Pb^{2+} while with increase of pH, other forms are appeared. Therefore, sorption initiates from pH=3 and there is no adsorption below this pH value. This trend can be attributed to competition between H^+ and Pb^{2+} ions for capturing the active sites. It is clear that sorption of the lead on the nano particles is strongly depended on the pH value of the solution owing to its effect on solubility of Pb(II), surface charge adsorbent and degree of protonation of binding sites of the chelating molecules on adsorbate during the reaction [41-42]. As can be seen, the adsorption of lead on the raw-MWCNTs is not strongly affected by pH value. It is

well known that in pH values above point of zero charge (pH$_{pzc}$), the adsorbent surface charge is negative. Therefore, the Pb^{2+} was attracted on the adsorbent surface. The low adsorption of lead ions in acidic solutions on o- MWCNTs can be attributed to the low dissociation of the oxygen containing   groups and competition between H$^+$ and metal ions on the same sorption sites. In the removal of lead ions from aqueous solution by MWCNTs-TAA, the favorite mechanism is reaction between lone electron pair in nitrogen of the TAA groups and metals ion, which results in formation of metal complex. While in acidic solution (pH<3), the active sites of TAA (electron lone pair) is protonated and inhibited from reaction with Pb^{2+}.

Dependency of the lead ions removal from solution versus time is depicted in Figure 6. This parameter is an important factor as it affects the adsorption performance. The amounts of sorbent, temperature, and pH value were kept constant under the optimal condition. Different contact times from 15 to 120 min were considered according to the batch method. As can be seen, the adsorption on to all three types of sorbents increase very rapidly with contact time up to 45 min and remain fixed. It seems, in this time the equilibrium of the adsorption process is obtained; thus, for all the experiments contact time of 60 min was chosen.


Figure 6 : Removal percentage of lead ions at various times

3.3 .Adsorption capacity

For determination of adsorption capacity, 10 mL of the lead ion solutions at its initial conditions (2-80 mg/L and pH 5.7-6) was prepared and 10 mg of each type of sorbents were added to the solution. After 60 min of shaking, the solutions were separated from the adsorbent and lead ion were determined by FAAS. The amount of adsorbed metal ions per gram of the adsorbent at time t (q_t in mg g^{-1}) is plotted versus the initial concentration (C_0 in mg L^{-1}) in Figure 7. q_t was calculated according to the following equation [37].

$$q_t = (C_0 - C_t)V/M \qquad (2)$$
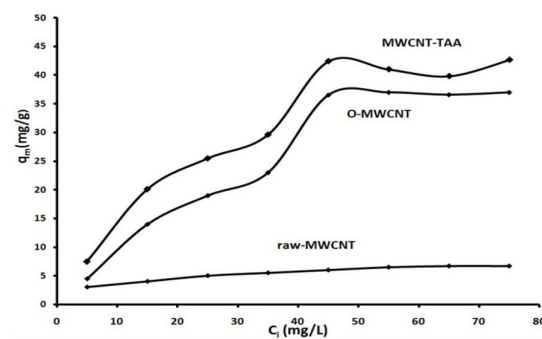
Figure 7 : Adsorption capacity of lead ions on sorbents

where C_t is the equilibrium concentration of Pb^{+2} ions in mg L^{-1} at time t, M the adsorbent mass in g, and V is the volume of lead ion solutions in L. After addition of raw-MWCNTs into lead solution , hydrogen bonds between π- electron of raw-MWCNTs and water released hydrogen ions are formed. On the other hand, there is a competition between lead and hydrogen ions for formation of hydrogen bonding with π- electrons. At lower pH, due to high concentration of hydrogen ions the probability of hydrogen ions interaction with π- electron is higher and lead adsorption is lower occurred. With increase of pH, the dominant reactions with π- electrons are belonged to lead ions. Measurement of pH at the end of experiments confirmed the decrease of pH which is a confirmation for ion exchange mechanism for lead adsorption on raw-MWCNTs. In the case of o-MWCNTs,

adsorption capacity was increased dramatically. The main reason for this trend is ionization of oxygen containing functional groups. It should be considered that ionization of oxygen containing functional groups is accomplished above pH_{pcz}. In other words, the electrostatic attraction is formed between lead ions and negative charge of nano particle surfaces which leads to extracting lead ions from the solution. The presence of amine groups in the MWCNTs-TAA changes the mechanism of adsorption with higher efficiency. The surface complexation between non bonding ion pair of amine groups and lead ions is occurred and caused to increasing of adsorption capacity via chelating interaction. It is important to note that there is another physical adsorption mechanism in all aforesaid sorbents which is related to nano particles structure. In this mechanism, the leads ions enter to interior channels of nano particles structure which can be intensified with increase of contact time. It can be concluded that lead adsorption mechanism is very complex and is a combination of physisorption and chemisorptions with different contributions.

3.4. Adsorption Isotherm

The most common models for explanation the distribution of metal ions between adsorbent and liquid phase are Langmuir and Freundlich isotherm models [47,48]. The main assumption in Langmuir model is that adsorption occurred by monolayer coverage of the adsorbate on the adsorbent surface, without additional interaction between adsorbate molecules. The Langmuir equation is given:

$$qe = \frac{bq_mCe}{1+bCe} \qquad (3)$$

Equation 3 can be expressed in linear form as:

$$\frac{Ce}{q_e} = \frac{1}{bq_m} + \frac{Ce}{q_m} \qquad (4)$$

where C_e is the equilibrium concentration of lead ions in the solution, q_e is the value of lead ions adsorbed on adsorbent after equilibrium, q_m is the maximum amount adsorbed, and b is the Langmuir constant that indicates the affinity of binding sites on the adsorbent surface. q_m and b are determined from intercept and slope of $1/q_e$ versus $1/c_e$. The Freundlich model describes that adsorption is performed by multilayer coverage on the heterogeneous surface. The Freundlich model is:

$$q_e = K_f \, C_e^{1/n} \qquad (5)$$

Equation 5 can be expressed in linear form as:

$$\ln q_e = \ln k_f + n \ln C_e \qquad (6)$$

K_f and n are the Freundlich constants that are related to the capacity and power of adsorption, respectively. The adsorption isotherms of Pb^{2+} on raw- MWCNTs, o- MWCNTs and MWCNTs-TAA at pH value of 5.7- 6 are shown in Figure 8. All parameters of the isotherms were determined by fitting the adsorption equilibrium data to the isotherm models and depicted in Table 1.
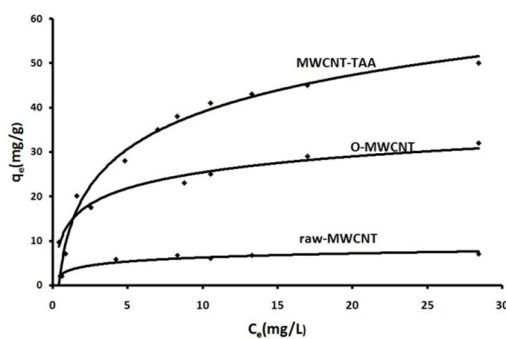
Figure 8: Adsorption isotherms of lead ions on sorbents

It is obvious that correlation coefficient for the Langmuir model are more than those of the Freundlich model. This indicates that the Langmuir model better describes adsorption of Pb^{2+} on nano particles. In addition, the obtained values for n from the isotherms were larger than unity, which indicates desirable adsorption on sorbents.

Table 1. Langmuir and Freundlich isotherm parameters for Pb^{+2} adsorption on raw-MWCNTs, o-MWCNTs, MWCNTs-TAA.

Freundlich model					Langmuir model			
	χ^2	K_f	n	r^2	χ^2	K_L	$q_{max(mg/g)}$	r^2
raw-MWCNTs	0.8	4.76	7	0.98	0.037	3.71	6.71	0.961
o- MWCNTs	44.2	12.8	3.42	0.899	2.785	1.33	27.8	0.931
MWCNTs-TAA	144	8.34	1.43	0.993	11	0.13	71	0.945

In the raw- MWCNTs case, the experiment data were well fitted to both isotherm models ($R^2>0.96$). In order to choose the best isotherm model for raw- MWCNTs, the data was analysed using the Chi square test [49]. The Chi square test calculated using the following equation :

$$\chi^2 = \sum \ (q_e - q_{em} \ )^2 /q_{em} \qquad (7)$$

Where q_e is the value of lead ions adsorbed on the adsorbent after equilibrium obtained from the experimental data and q_{em} is the adsorption capacity obtained from the isotherm model. This statistical test was applied for Pb^{2+} . χ^2 values obtained are given in Table 1. As seen, χ^2 values of the Langmuir model for Pb^{2+} are smaller than χ^2 values of the Freundlich model. Therefore, according to the results, the Langmuir isotherm model agrees well with the equilibrium experimental data.

The maximum lead adsorption capacities calculated by applying the Langmuir equation for MWCNTs-TAA, o-MWCNTs , raw-MWCNTs were 71, 27.8, and 6.71 $mg.g^{-1}$, respectively. In Table 2 Pb^{2+} adsorption capacities of o - MWCNTs and MWCNTs-TAA were compared with other sorbents that published in literature.

Table 2. Comparison of various adsorbents with this study

Adsorbent	Adsorption capacity(mg/g)	Reference
Chelating resin	7.38	43
Activated carbon	13.05	44
Silica gel/gallic acid	12.63	45
Modified nanometer sio2	6.7	46
MWCNTs-TAA	71	This work
Oxidized- MWCNT$_S$	27.8	This work

3.5. Application of MWCNTs for real samples

The real samples were tap water of Tehran and Babolsar river in Iran. In each experiment, four samples containing 0, 5, 10, and 15 ppm of Pb^{2+} ions were spiked. According to batch method, 10 mg of the adsorbent was added to Pb^{2+} ions solution. Finally, the adsorptions were determined for Pb^{2+} ions. The adsorbent was added to the samples and their adsorptions were determined. All the experiments were performed in triplicate and the mean values were reported. The results are listed in Table 3. It is clear that adsorption of Pb^{2+} ions mentioned is not affected by the presence of other ions in the real water samples; thus, o - MWCNTs and MWCNTs-TAA have great potential for removal of Pb^{2+} in water solutions.

3.6. Reusability experiment

Desorption of the loaded nanoparticles was performed by washing the lead adsorbed MWCNTs using 0.1 mol L^{-1} HNO_3 solutions. For this purpose sorption experiments were conducted at initial Pb^{+2} ions concentration of 30 mgL^{-1} (similar to the batch method described). MWCNTs was dried at 60°C for 2 h and then dispersed in 0.1 mol L^{-1} HNO_3 solutions. After sonication, Pb^{+2} removed from MWCNTs were filtrated and measured by FAAS. After regeneration of the sorbent, it was washed with deionized water and used in further adsorption-desorption tests. These procedures were repeated four times and the results revealed that the sorbent capability after regeneration did not significantly change.

Table 3. Removal percentage after treating 10 mL of water with 10 mg adsorbent.

Sample	Adsorbent	Added Pb^{2+} ions(mgL^{-1})	Removal%	RSD%
Tap water	**o-MWCNTs**	0	-	0.12
		5	97 .2	0.22
		10	95.5	0.35
		15	95.2	0.19
River water	**o-MWCNTs**	0	-	0.14
		5	96.2	0.26
		10	95.7	0.19
		15	96.4	0.38
Tap water	**MWCNTs-TAA**	0	-	0. 11
		5	99.1	0.33
		10	97	0.21
		15	96.6	0.17
River water	**MWCNTs-TAA**	0	-	0.14
		5	98.3	0.22
		10	96.2	0.19
		15	95.9	0.34

4. Conclusion

The adsorption of Pb^{2+} by raw- MWCNTs, o-MWCNTs and MWCNTs-TAA was studied.
The solution pH value played a critical role in removal of Pb^{2+} from water solutions .The main reason for adsorption of Pb^{2+} on the surface of the raw-MWCNTs and o- MWCNTs was originated from ion exchange reaction. While for lead adsorption on the surface MWCNTs-TAA was from sharing of lone ion pair of amine groups to lead ions. It can be concluded that adsorption of Pb^{2+} on MWCNTs is a complex phenomenon and cannot be easily explained by one mechanism. Adsorption-desorption cycles applied for 4 times by MWCNTs, which means the ability of the sorbent was not exhausted. Adsorption experiments of real samples showed that the o- MWCNTs and MWCNTs-TAA have a favorable potential for removal of Pb^{+2} from aqueous solution. The Langmuir isotherm model could suitably explain the experimental data for Pb^{2+}. Regarding the Langmuir equation, the maximum adsorption capacity values for Pb^{2+} onto raw-MWCNTs, o-MWCNTs and MWCNTs-TAA were 71, 27.8, and 6.91 mg.g^{-1}, respectively.

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