Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal

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ABSTRACT

Alumina-coated multi-wall carbon nanotubes were synthesized and characterized by scanning electron microscopy, X-ray diffraction, and FTIR. They were used as an adsorbent for the removal of lead ions from aqueous solutions in two modes, batch and fixed bed. In the batch mode, experiments were carried out to investigate the effect of contact time, agitation speed, adsorbent dosage and solution pH on the removal of lead. The coated nanotubes exhibit better removal ability over uncoated. For fixed-bed columns, thickness of the layer and flow rate were investigated. Increasing the thickness and decreasing the flow rate enhanced the removal of lead. The prepared adsorbent displayed the main advantage of separation convenience when a fixed-bed column was used compared to the batch adsorption treatment.

1. Introduction

Production and consumption of lead is increasing worldwide. According to International Lead and Zinc Study Group (2010) excessive amounts of lead reaching up to 8.757 million tonnes were used and consumed worldwide. The major industrial sources of lead released into the environment are battery manufacturing, acid metal plating and finishing, ammunition, tetraethyl lead manufacturing, ceramic and glass industries printing, painting, dying, and other industries. Contamination could occur also when water flows through lead-containing pipes [1] though the use of lead for water piping is forbidden. On the other side, it could enter the food chain through drinking water and crop irrigation which is considered to be a widespread problem. Lead is non-biodegradable and tends to bio-accumulate in cells of the living things [2]. Lead has been recognized for its negative effect on the environment where it accumulates in living systems. Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain. According to US Environmental Protection Agency, the maximum contaminant level for lead is 0.015 mg/L and the maximum contaminant level goal is zero [3].

To achieve this goal, several methods have been applied for removal of lead from wastewaters. This includes precipitation, solvent extraction, ion exchange, coagulation and floatation [4]. However, most of these methods present several disadvantages like chemical requirements, low efficiency and usually produce large amounts of sludge which can add other environmental problems. One alternate effective process is the adsorption which relies on the utilization of solid adsorbents with no chemical degradation. It is attractive due to its merits of effectiveness, efficiency and free-sludge [5]. Several adsorbents have been used for removal of heavy metals. Natural zeolite has been used for the removal of lead [6,7]. Aquatic plant was also used for removal of lead and zinc ions from wastewater [8]. Fly ash sub grades were also used for removal of lead ions from wastewater [9]. Ion exchange columns packed with Amberlite IR-120 resin was used for removal of ionic alkyl-lead compounds from aqueous solution [10]. Granular activated carbon columns were used in removing lead and cadmium ions from aqueous waste streams [11]. Gupta et al. have used different adsorbents, such as bagasse fly ash, a sugar industry waste material, for removal of lead [12,13], duolite C-433: a synthetic resin for removal of lead [14], green algae Spirogyra species [15], activated carbon [16], and red mud, an aluminum industry waste, for removal of lead and chromium [17]. Other adsorbents, bottom ash and de-oiled soya [18] and crown ethers [19] have been used for different pollutants removal. Alternatives to carbon have been used for adsorption of various pollutants [20], basic dye [21] and lead [22] from aqueous solution.

Adsorbents such as alumina, silica and zirconia are well known by their high surface area, high mechanical properties and good resistivity to thermal degradation, and they exist in several struc-

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tures and amphoteric properties. Alumina has been used for removal of nickel [23], lead and cadmium [24]. Activated alumina is considered as one of the common adsorbent used for heavy metal removal, pre-concentration and separation of trace amounts of elements in flow injection—inductively coupled plasma [25].

Due to a large specific surface area and small, hollow, and layered structures, carbon nanotubes (CNTs) have already been investigated as promising adsorbents for various organic pollutants and metal ions and can be easily modified by chemical treatment to increase their adsorption capacity [26]. CNTs have been used for the treatment of heavy metals contaminated aqueous solutions. CNT adsorption technology has the potential to be used for the removal of pollutants. Unlike many adsorbents, CNTs possess fibrous shape with high aspect ratio, large accessible external surface area, and well-developed mesopores, all contribute to the superior removal capacities. CNT has been used for removal of lead from water [27,28]. The uses of CNT as support of metallic oxides have still been reported. The advantages of this chemistry are that materials with higher sorption capacity, larger surface area and supported metallic oxides with better orientation degree with regard to net metallic oxides can be obtained. Composite of carbon nanotube and alumina was used as a new sorbent for nickel pre-concentration from water samples, using a flow injection system coupled to flame atomic absorption spectrometry [29].

In most wastewater flowing systems, because the contact time is not sufficiently long for the attainment of equilibrium, it is required to perform equilibrium studies using columns. Fixed-bed column tests have been widely used to predict the performance of full-scale fixed-bed absorbers and to evaluate the mass transport parameters of many contaminants [30–34]. Short bed adsorber column, is a fixed-bed column with a bed of sufficiently short length that immediate concentration breakthrough occurs. Activated carbon [35], zeolite [36], cellulose [37] were used as packing materials in a fixed-bed column for the removal of lead.

This work aims to investigate the adsorption behavior of alumina supported on carbon nanotube for the treatment of lead aqueous solutions. For this purpose MWCNT/Al_2O_3 composites were synthesized and characterized. The effect of contact time, dosage of adsorbent and agitation speed was studied and the relationship between pH and removal efficiency was analyzed. For comparison purposes, the same study was carried using functionalized uncoated MWCNTs. We were further interested in preparing a column filled with Al_2O_3-coated MWCNTs composite. Different parameters, such as composites layer thickness and flow rate were investigated.

2. Experimental

2.1. Materials

Nitric acid, lead nitrate and aluminum nitrate were all obtained from Sigma–Aldrich. Stock solutions were prepared daily by dissolving in distilled water. Lead solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions. In order to prevent metal contamination from laboratory glassware, glassware was kept overnight in a 10% (v/v) HNO_3 solution. All other chemicals were of analytical grade.

2.2. Synthesis of Al_2O_3-coated MWCNTs

The multi-wall carbon nanotubes (MWCNTs) used in this study as a building block, were of more than 95% purity and procured commercially. Further purification of the MWCNTs was accomplished by stirring them in concentrated nitric acid at 70 °C for

12 h, followed by filtering and washing with distilled water, and then drying at 110 °C for 6 h. Then, the MWCNTs were oxidized by refluxing with 50% nitric acid at 120 °C for 12 h under stirring conditions. The product was then filtered and rinsed with doubly distilled water and dried overnight in the oven.

The preparation of Al_2O_3/MWCNT composites was accomplished as follows: All glassware was cleaned by aqua regia freshly prepared prior to use. Typically, some amounts of MWCNTs were dispersed into deionized water and magnetically agitated 6 h at which acceptable level of dispersion was observed. A specific amount of aluminum nitrate was properly dissolved in deionized water. Carefully, the aluminum nitrate solution was drop wise added into dispersed MWCNTs. Between consecutive drops, there should be an appropriate time for the aluminum to reach, appropriately disperse and engage to the MWCNTs' surface. After that, the suspension was dried at 110 °C. The obtained material was heated up to 400 °C for 90 min, where the pyrolysis process resulted in alumina formation supported onto the MWCNTs' surface.

2.3. Characterization methods

The size and morphology of the synthesized composites were characterized by scanning electron microscopy analysis using a Field Emission Scanning Electron Microscope (FESEM, FEI Nova-Nano SEM-600, Netherlands).

The structure phases and average size of the synthesized adsorbents was analyzed by X-ray powder diffraction (Shimadzu XRD 6000). Infrared absorption spectra were measured at room temperature on a FTIR spectrometer. 10 mg of sample was lyophilized, gently mixed with 300 mg of KBr powder and compressed into discs at a force of 17 kN for 5 min using a manual tablet presser.

2.4. Adsorption experiments

The contact time of lead is an important factor for lead ion removal. Adsorption experiments were conducted by preparing 50-mL Erlenmeyer flasks containing 10 mg of the adsorbent and 25 mL of 20 ppm Pb^{2+} at a fixed pH. The glass bottle was placed on a slow-moving platform shaker and aliquots were taken from the suspension at different time intervals of the reaction. The concentration of Pb^{2+} in effluent solutions were analyzed by inductively coupled plasma spectrometer and removal or adsorption (%) versus reaction time was determined according to the following procedure. Adsorption experiments were performed in 50-mL glass pyramic bottles containing 25 mL of different concentrations of lead. To investigate the effect of adsorbent dosage, different doses of adsorbents were added to each bottle. The influence of solution pH values on lead removal was also studied by adding defined amount of the MWCNT adsorbents into the glass pyramic bottles containing 25 mL of different lead solution with pH values ranging from 3 to 7. All batch experiments were carried out at ambient temperature (25 ± 2 °C) and all the suspensions were shaken on a rotary shaker at 200 rpm for 24 h. The fixed-bed system, the column was packed with the synthesized composites. The lead (II) solutions were passed through the bed to study their adsorption capacity. The different layer thickness of the adsorbent and the flow rate of the solutions were used as specified for each experiment.

The metal uptake capacity (amount of removal of lead ion) and the adsorption capacity (percentage of lead ion removal) were calculated using the following equations:

Metal Uptake Capacity = Initial lead ion concentration – Final lead ion concentration.

Adsorption Capacity or Lead Removal (%) = (Metal Uptake Capacity × 100)/Initial lead ion concentration.
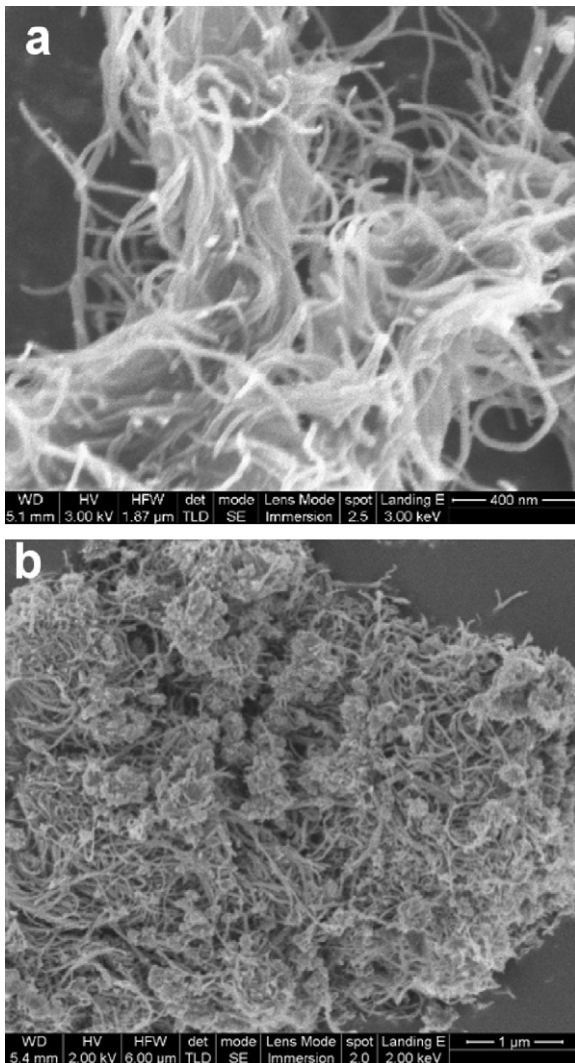
Fig. 2. X-ray diffraction of (a) uncoated MWCNTs and (b) Al$_2$O$_3$-coated MWCNTs.

NTs and synthesize Al$_2$O$_3$-coated MWCNTs were performed for a better comprehension of the structure and composition of these materials. An absorption band revealing the vibrational properties of Al–O bond is observed for in around 500 cm^{-1}. This band is mainly assigned to the stretching vibrations of Al–O (υAl–O). The broad absorption peaks in the range of 3410–3465 cm^{-1} correspond to –OH group, indicating of existence of the hydroxyl groups on the surface of the composites or it can be attributed to the adsorption of some atmospheric water during FTIR measurements. Those at 1500–1650 cm^{-1} are the C=O stretching mode of the functional groups on the surface of the MWCNTs or arising from the absorption of atmospheric CO$_2$ on the surface of the composites. The peak at 3420 cm^{-1} is attributed to the stretching vibration of O–H band. The two peaks at 2920 and 2854 cm^{-1} correspond to the C–H stretch vibration, originated from the surface of tubes, Fig. 3(a), are obviously weak in Fig. 3(b), which suggests that the surface of MWCNTs has been covered by Al$_2$O$_3$.

3. Results and discussion

3.1. Characterization of Al$_2$O$_3$-coated MWCNTs

The morphologies of MWCNTs and synthesized MWCNT/alumina adsorbent were obtained by SEM, Fig. 1(a) and (b). It is well known that after the acidification of MWCNTs, their surface presents polar groups, such as hydroxyl or carboxyl groups (as shown in Fig. 3) which are able to interact, by hydrogen bonding with Al$_2$O$_3$ surface. It was observed that aluminum oxide nanoparticles were successfully coated on the surface of MWCNTs to form multi-wall carbon nanotube aluminum oxide composites, as depicted in Fig. 1(b).

Fig. 2(a) and (b) shows the XRD patterns of MWCNTs and MWCNT/alumina composites. It was observed that the two peaks corresponding to the structure of MWCNTs (Fig. 2(a)) also exist in the XRD pattern of the MWCNT composites (Fig. 2(b)). The broad peak of MWCNT in XRD was seen narrow in the XRD of the composite because MWCNT in the composite was coated with alumina. The observed XRD of the synthesized Al$_2$O$_3$-coated MWCNTs was in convenience with that reported for the synthesis of alumina carbon nanotube composite using thermal pressure method [38].

FTIR measurements are used in order to confirm the formation alumina on the surface of MWCNTs. FTIR spectra of uncoated MWC-
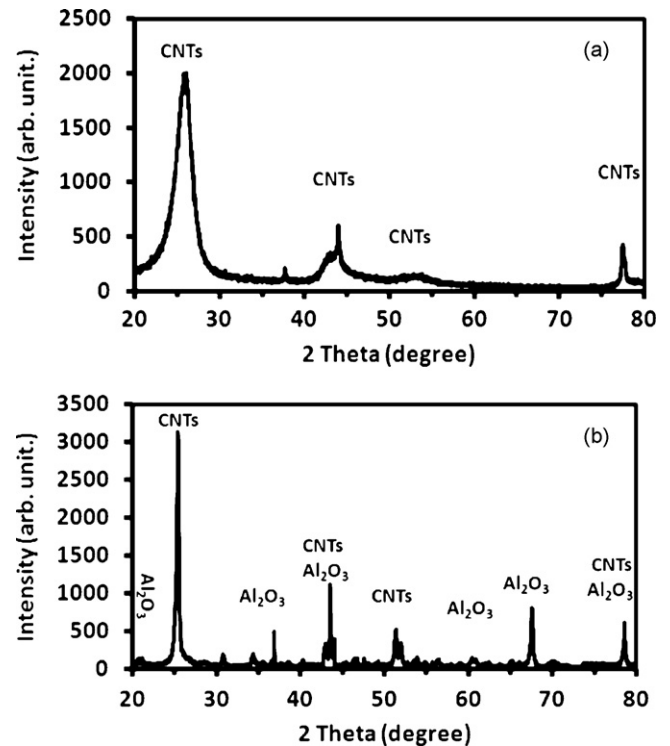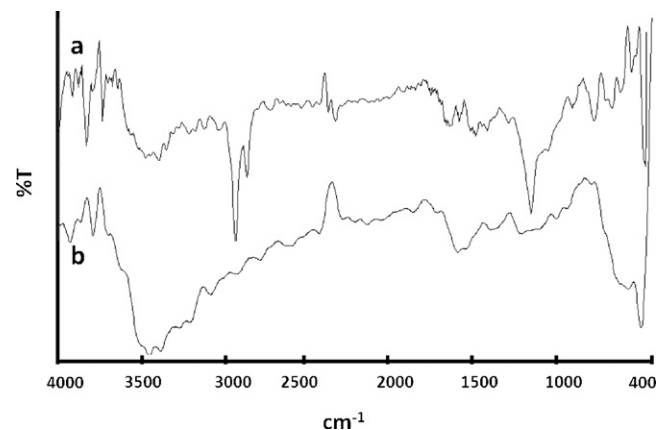

Fig. 1. SEM photograph of (a) uncoated MWCNTs and (b) Al$_2$O$_3$-coated MWCNTs.

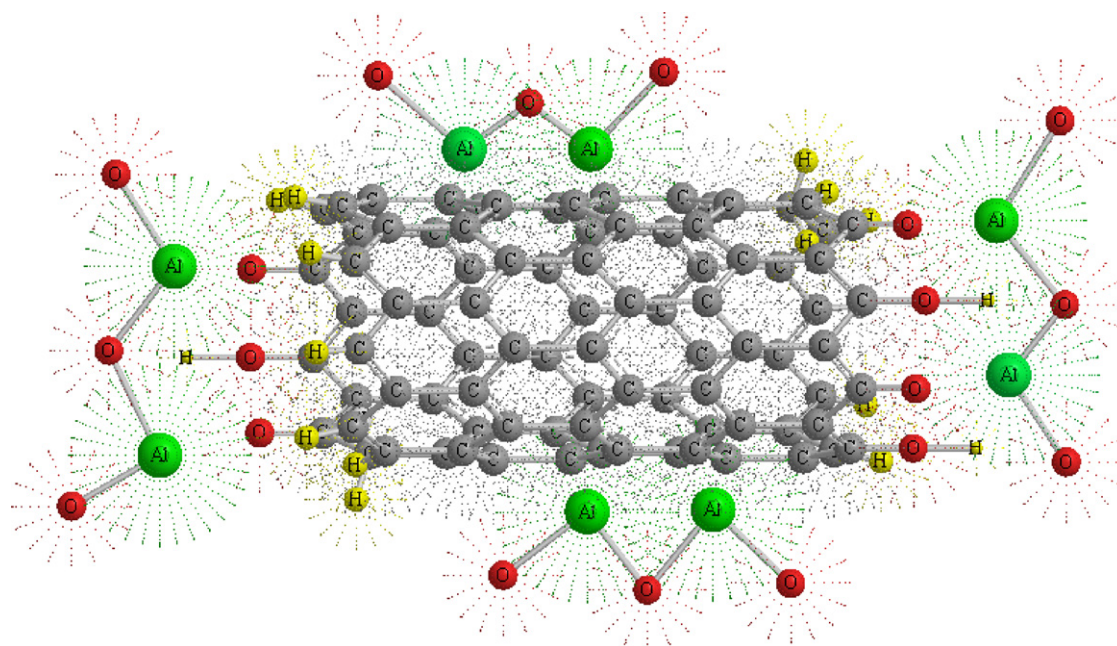Fig. 3. FTIR spectra of (a) uncoated MWCNTs and (b) alumina-coated MWCNTs.

Fig. 4. Cylindrical bonds representative diagram of alumina-coated MWCNTs.

Based on the characterization results, XRD, SEM and FTIR, a schematic diagram of structural nature of alignment of Al_2O_3 on the surface of MWCNTs is depicted in Fig. 4. One explanation is based on the assumption that aluminum atom of alumina is aligned closer to the oxygen atom of the carbonyl group (C=O) of MWCNTs which enhanced by the affinity of aluminum atom to interact with the pair of electrons on the oxygen. The oxygen atom of Al_2O_3 is aligned close to the hydrogen atom of hydroxyl group of MWCNTs due to the hydrogen bond formation. In addition the attractive van der Waals forces are expected to play a role.

3.2. Batch experiments

3.2.1. Effect of contact time

The effect of contact time on the removal of lead ions by the uncoated MWCNT and alumina-coated MWCNTs is depicted in Fig. 5. In both adsorbents, a rather fast adsorption of the lead ions occurs during the first hour of the adsorption process followed by a slower stage as the adsorbed amount of lead reaches its equilibrium value. Thus, 60 min were sufficient for the sorption equilibrium to be achieved. Coated MWCNT has higher capacity for adsorption toward lead comparing with uncoated MWCNT, as can be seen in Fig. 5.

3.2.2. Effect of pH

pH is one of the most important parameters controlling the metal ion adsorption process. Thus, the influence of pH on adsorption capacity was studied over a range of pH values from 3 to 7 and not more than 7 for avoiding lead precipitation. As depicted in Fig. 6, it was observed that lead adsorption increased when pH increased from 3 to 7. This may be attributed to the contributions of MWCNTs adsorption toward lead ions resulted from electrostatic attraction between the negatively charged MWCNTs adsorbent surface and the positively charged cationic lead.

The pH is a significant factor for determining the form of the metallic species in aqueous media. It influences the adsorption process of metal ions, as it determines the magnitude and sign of
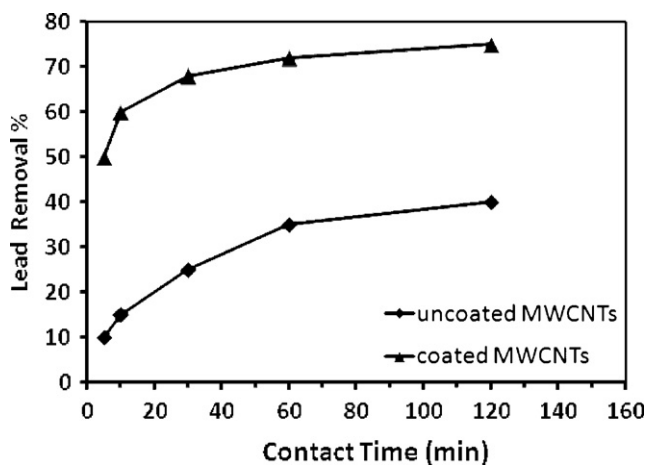

Fig. 5. Effect of contact time on the percent removal of Pb(II) by uncoated MWCNTs and the alumina-coated MWCNTs. pH = 5.5, agitation speed = 150 rpm, adsorbent dosage = 10 mg.
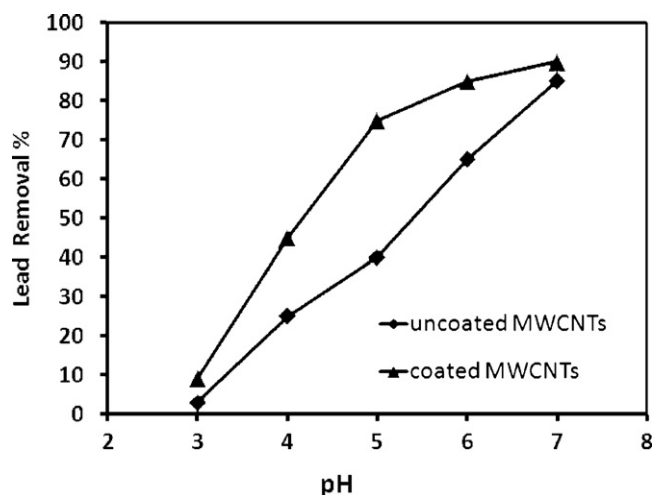

Fig. 6. Effect of pH on the adsorption of Pb(II) ions. Initial Pb(II) conc. Agitation speed = 150 rpm, adsorbent dosage = 10 mg, contact time 120 min.
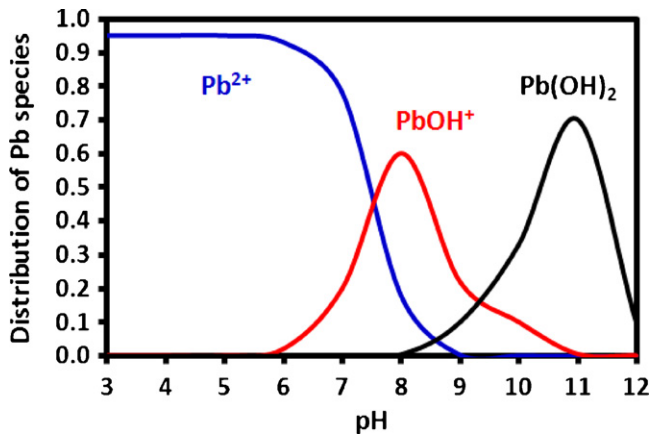
Fig. 7. Speciation diagram of lead as a function of pH.

the charge on ions. Fig. 7 gives the distribution of lead species as a function of pH. In case of low pH (<6), positively charged lead (II) species are dominant. In case of high pH values (pH = 7–11), however, there are several lead species with different charges. This includes $Pb(OH)^+$ and $Pb(OH)_2$ and thus the removal of Pb is possibly accomplished by simultaneous precipitation of $Pb(OH)_2$ and sorption of $Pb(OH)^+$.

3.2.3. Effect of composite dosage

As depicted in Fig. 8, it was observed that the percentages of lead adsorbed increased as the composite dosage was increased over the range 1–50 mg. The removal of approximately 100% was achieved when 50 mg of the coated MWCNTs was soaked in 25 mL of 20 ppm lead solution comparing with 85% removal when 50 mg of uncoated MWCNTs was used. Thus, the mechanism of composite adsorption toward cationic lead may be derived from three reasons. One reason might be based on van der Waals interactions occurring between the hexagonally arrayed carbon atoms in the graphite sheet of MWCNTs and the positively charged lead ions. The second one might be due to the electrostatic attraction between the positive cationic lead and the negative charged MWCNTs adsorbent surface. The third one might be due to the electrostatic attraction between the pairs of electrons on the oxygen atoms of alumina and the positive cationic lead. The first two reasons are supported by the removal ability of unmodified carbon nanotube, as depicted in Fig. 8. The third reason is supported by improvement in removal when alumina modified carbon nanotube was used for removal of lead, comparing the adsorption ability of carbon nanotube only.
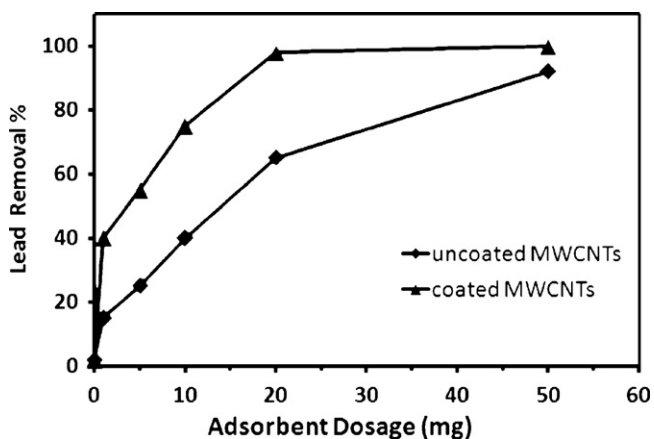

Fig. 8. Effect of adsorbent dosage on adsorption of Pb(II) ions. Initial agitation speed = 150 rpm, pH = 5.5, contact time 120 min.
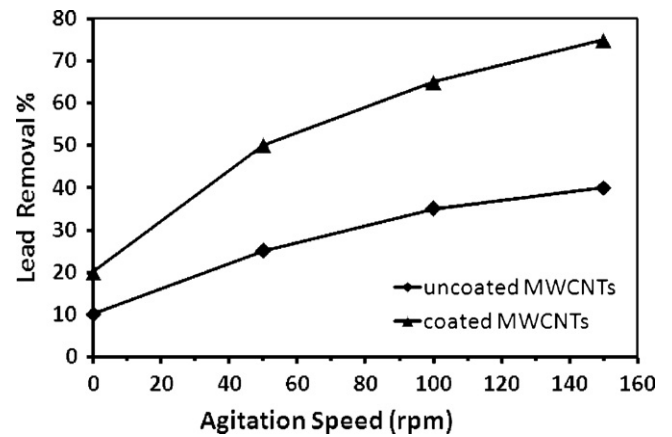

Fig. 9. Effect of agitation speed on adsorption of Pb(II) ions. pH = 5.5, contact time 120 min, adsorbent dosage = 10 mg.

3.2.4. Effect of agitation speed

The agitation speed plays an important role in the adsorption process. It was observed that the percentages of lead adsorbed increased as the agitation speed was increased up to 150 rpm. The removal ratio of lead increased from 20% to around 99% when the synthesized $MWCNT/Al_2O_3$ composites were used and from 10% to 50% in case of MWCNTs adsorbent. The adsorption capacity was greatest when 150 rpm speed was used, as shown in Fig. 9.

3.3. Fixed-bed column experiments

3.3.1. pH dependence

The solution pH is an important factor in adsorption equilibrium and kinetics of metal ion. The curve for the percentage removal, adsorption of lead ions, at different initial pH values is shown in Fig. 10.

3.3.2. Effect of layer thickness

Fig. 11 shows the percentage removal of lead by coated MWCNT of different thickness and at a flow rate of 7 mL/min. Increasing the thickness of the layer produces an increase in the adsorption of lead ions. This may be due to an increase of the surface area of adsorbent that provided more binding sites for adsorption of lead with a thicker layer and the efficiency is increased by allowing sufficient time for the lead adsorbate to diffuse into the whole mass of the adsorbent.

3.3.3. Effect of flow velocity

To investigate the effect of flow rate on the adsorption of lead ions into the synthesized composites, both the metal concentration
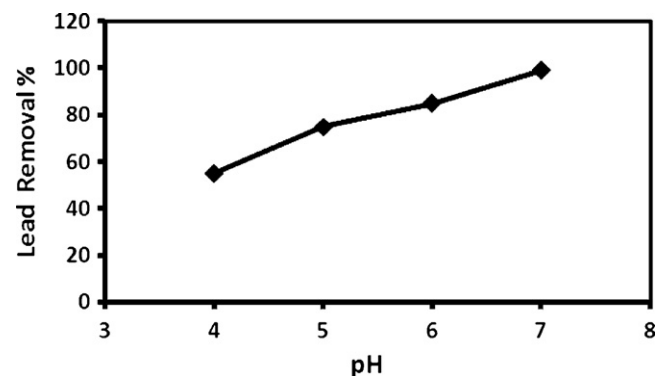

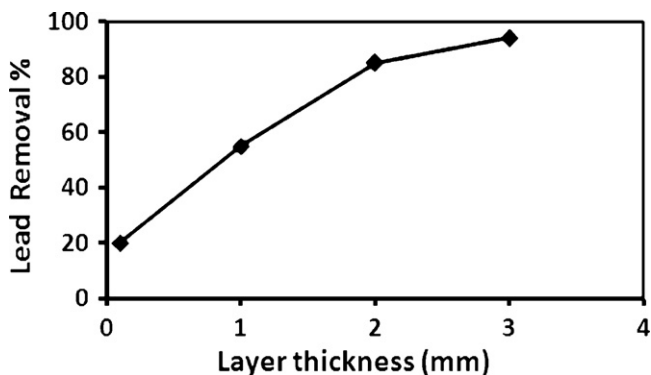Fig. 10. Effect of pH on adsorption of Pb(II) ions, in fixed-bed system.

Fig. 11. Effect of layer thickness on adsorption of Pb(II) ions, in fixed-bed system.
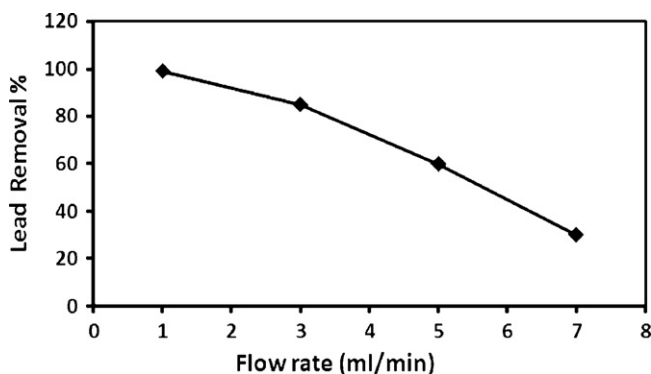

Fig. 12. Effect of flow rate on adsorption of Pb(II) ions, in fixed-bed system.

in the feed solution and the layer thickness were kept constant, whereas the flow rate was changed from 1.0 to 7.0 mL/min. The results are given in Fig. 12, where the uptake of lead ions decreased with an increase in flow rate. This is because the time required to reach an equilibrium state is much longer than the time allowed by the flow rate. Therefore, increasing the flow velocity causes shorter retention time. The maximum adsorption efficiency was obtained at a flow rate of 7 mL/min.

3.3.4. Breakthrough curve

The breakthrough curves for an initial Pb(II) concentration of 20 ppm are depicted in Fig. 13 for a bed depth of 1 cm at flow rates of 1, 3 and 5 mL/min. The results show that when the volumetric feed rates were decreased from 5 to 1 mL/min more favorable adsorption conditions were achieved. The effluent solution concentration reached to 5% of its feed concentration (breakthrough points) at 80, 200, 340 min residence times for 5, 3 and 1 mL/min, respectively.
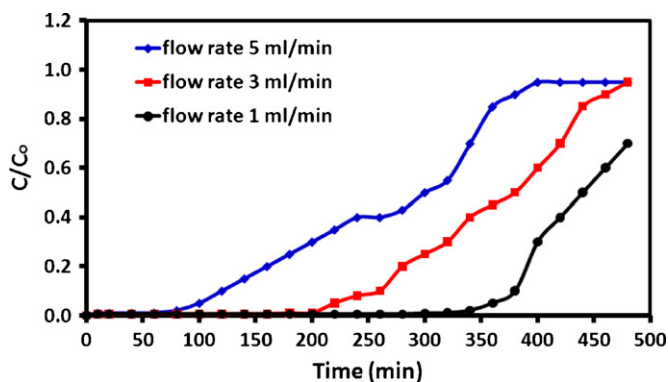

Fig. 13. Breakthrough curves of Pb(II) on the composite for three different flow rates.

4. Conclusions

An alumina-coated multi-wall carbon nanotube material was synthesized. SEM, XRD and FTIR indicated that MWCNTs were coated with alumina. The materials were found to be an effective adsorbent for the removal of lead ions from aqueous solution. With an increase in influent pH between 3 and 7, the percentage of lead removed increased. By increasing agitation speed, contact time and adsorbent dosage the amount removed was increased. In the fixed-bed mode, by decreasing the flow rate, the percentage of lead removal increased. However, the removal was increased when the bed thickness was increased. This study shows that the reported composite can be used in an industrial wastewater treatment for removal of lead.

References

[1] Y.Y. Luo, A. Hong, Oxidation and dissolution of lead in chlorinated drinking water, Adv. Environ. Eng. 1 (1997) 84–97.
[2] L. Yan-Hui, Z. Yanqiu, Z. Yimin, W. Dehai, L. Zhaokun, Different morphologies of carbon nanotubes effect on the lead removal from aqueous solution, Diamond Relat. Mat. 15 (2006) 90–94.
[3] U.S. Environmental Agency, Drinking Water Contaminants, Available from: http://www.epa.gov/safewater/contaminants/index.html, July 27, 2010.
[4] C. Quintelas, Z. Rocha, B. Silva, B. Fonseca, H. Figueiredo, T. Tavares, Removal of Cd(II), Cr(VI), Fe(III) and Ni(II) from aqueous solutions by an E. coli biofilm supported on kaolin, Chem. Eng. J. 149 (2009) 319–324.
[5] H.C. Chu, K.M. Chen, Reuse of activated sludge biomass. II. The rate processes for the adsorption of basic dyes on biomass, Process Biochem. 37 (2002) 1129–1134.
[6] H. Faghihian, M. Ghannadi, H. Kazemian, The use of clinptilolite of radioactive cesium and strontium from nuclear waste water and lead, nickel, cadmium, barium from municipal waste water, Sep. Sci. Technol. 34 (1999) 2275–2292.
[7] M Pansini, C. Collella, Dynamic data on lead uptake from water by chabazite, Desalination 78 (1990) 287–295.
[8] R.K. Srivastav, S.K. Gupta, K.D.P. Nigam, P. Vasudevan, Use of aquatic plants for the removal of heavy metals from waste waters, Int. J. Environ. Stud. 45 (1993) 43–50.
[9] M.T. Laumakis, P.J. Martin, S. Pamucku, K. Owens, Proceeding of the International Conference on Hazard Waste Management, New York: ASCE, 1995, pp. 528–535.
[10] C.N. Hewitt, P.J. Metcalfe, R.A. Street, Method for the sampling and removal of ionic alkyl-lead compounds from aqueous solution using ion-exchange media, Water Res. 25 (1991) 91–94.
[11] B.E. Reed, S. Arunachalam, B. Thomas, Removal of lead and cadmium from aqueous streams using granular activated carbon columns, Environ. Program 13 (1994) 60–64.
[12] V.K. Gupta, D. Mohan, S. Sharma, Removal of lead from wastewater using bagasse fly ash-a sugar industry waste material, Sep. Sci. Technol. 33 (1998) 1331–1343.
[13] V.K. Gupta, A. Imran, Removal of lead and chromium from wastewater using bagasse fly ash-a sugar industry waste, J. Colloid Interface Sci. 27 (2004) 21–28.
[14] V.K. Gupta, P. Singh, N. Rahman, Adsorption behavior of Hg(II), Pb(II) and Cd(II) from aqueous solution on duolite C-433: a synthetic resin, J. Colloid Interface Sci. 275 (2004) 398–402.
[15] V.K. Gupta, A. Rastogi, Biosorption of lead from aqueous solutions by green algae Spirogyra species: kinetics and equilibrium studies, J. Hazard Mater. 152 (2008) 407–414.
[16] V.K. Gupta, S.K. Srivastava, D. Mohan, S. Sharma, Design parameters for fixed bed reactors of activated carbon developed from fertilizer waste for the removal of some heavy metal ions, Waste Manag. 17 (1997) 517–522.
[17] V.K. Gupta, M. Gupta, S. Sharma, Process development for the removal of lead and chromium from aqueous solutions using red mud-an aluminum industry waste, Water Res. 35 (2001) 1125–1134.
[18] V.K. Gupta, A. Mittal, L. Krishnan, J. Mittal, Adsorption Treatment and Recovery of the Hazardous Dye, Brilliant Blue FCF, Over Bottom Ash and De-Oiled Soya, J. Colloid Interface Sci. 293 (1) (2006) 16–26.
[19] V.K. Gupta, P. Kumar, Cadmium (II) - selective sensors based on dibenzo-24-crown-8 in PVC matrix, Anal. Chim. Acta 389 (1999) 205–212.
[20] V.K. Gupta, P.J.M. Carrott, M.M.L. Ribeiro Carrott, Suhas, Low cost adsorbents: Growing approach to wastewater treatment – A review, Critical Reviews in Environmental Science and Technology 39 (2009) 783–842.

[21] V.K. Gupta, Suhas, Application of low cost adsorbents for dye removal- A review, J. Environmental Management 90 (2009) 2313–2342.

[22] I. Ali, V.K. Gupta, Advances in Water Treatment by Adsorption Technology, Nature Protocols 1 (6) (2007) 2661–2667.

[23] S. Rengaraj, Y. Jei-Won, K. Younghun, K. Won-Ho, Application of mg-mesoporous alumina prepared by using magnesium stearate as a template for the removal of nickel: kinetics, isotherm and error analysis, Ind. Eng. Chem. Res. 46 (2007) 2834–2842.

[24] K.N Tarun, K.B. Ashim, K.D. Sudip, Adsorption of Cd(II) and Pb(II) from aqueous solutions on activated alumina, J. Colloid Interface Sci. 333 (2009) 14–26.

[25] Y. Jun, J. Zucheng, C. Gang, H. Bin, Simultaneous on-line preconcentration and determination of trace metals in environmental samples by flow injection combined with inductively coupled plasma mass spectrometry using a nanometer-sized alumina packed micro-column, Anal. Chim. Acta 540 (2005) 333–339.

[26] C.L. Chen, X.K. Wang, M. Nagatsu, Europium adsorption on multiwall carbon nanotube/iron oxide magnetic composite in the presence of polyacrylic acid, Environ. Sci. Technol. 43 (2009) 2362–2367.

[27] Y.H. Li, Z. Di, J. Ding, D. Wu, Z. Luan, Y. Zhu, Adsorption thermodynamic, kinetic and desorption studies of Pb^{2+} on carbon nanotubes, Water Res. 39 (2005) 605–609.

[28] S Anna, P. Krystyna, Adsorption of heavy metal ions with carbon nanotubes, Sep. Purif. Technol. 58 (2007) 49–52.

[29] R.S. Amais, J.S. Ribeiro, M.G. Segatelli, I.V.P. Yoshida, P.O. Luccas, C.R.T. Tarley, Assessment of nanocomposite alumina supported on multi-wall carbon nanotubes as sorbent for on-line nickel preconcentration in water samples, Sep. Purif. Technol. 58 (2007) 122–128.

[30] D.W. Hand, J.C. Crittenden, D.R. Hokanson, J.L. Bulloch, Predicting the performance of fixed-bed granular activated carbon adsorbers, Water Sci. Technol. 35 (1997) 235–241.

[31] D.R. Knappe, V.L. Snoeyink, P. Roche, M.J. Prados, M.M. Bourbigot, The effect of preloading on rapid small-scale column test predictions of atrazine removal byGAC adsorbers, Water Res. 31 (1997) 2899–2909.

[32] P. Westerhoff, D. Highfield, M. Badruzzaman, Y. Yoon, Rapid small-scale column tests for arsenate removal in iron oxide packed bed columns, J. Environ. Eng. 131 (2005) 262–271.

[33] A. Sperlich, A. Werner, G. Genz, E. Amy, E. Worch, M. Jekel, Breakthrough behavior of granular ferric hydroxide (GFH) fixed-bed adsorption filters: modeling and experimental approaches, Water Res. 39 (2005) 1190–1198.

[34] E.H. Smith, W.J. Weber, Evaluation of mass-transfer parameters for adsorption of organic-compounds from complex organic matrices, Environ. Sci. Technol. 23 (1989) 713–722.

[35] L. Moo-Yeal, S. Hyun-Jae, H.L. Sung, M.P. Jong, Y. Ji-Won, Removal of lead in a fixed-bed column packed with activated carbon and crab shell, Sep. Purif. Technol. 33 (1998) 1043–1056.

[36] M. Turan, U. Mart, B. Yüksel, M.S. Celik, Lead removal in fixed-bed columns by zeolite and sepiolite, Chemosphere 60 (2005) 1487–1492.

[37] Z. Dao, Z. Lina, Z. Jinping, G. Shenlian, Development of a fixed-bed column with cellulose/chitin beads to remove heavy-metal ions, J. Appl. Polym. Sci. 94 (2004) 684–691.

[38] C.N. He, F. Tian, S.J. Liu, A carbon nanotube/alumina network structure for fabricating alumina matrix composites, J. Alloys Compd. 478 (2009) 816–819.