Original Article

Efficiency determination of single-walled carbon nanotubes on adsorption of copper ions from synthetic wastewater

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ABSTRACT

Aims: The ability of single-walled carbon nanotubes (SWCNT) for copper adsorption from synthetic wastewater was evaluated.
Materials and Methods: The batch adsorption studies were performed under various laboratory conditions with initial Copper concentrations of 1, 5, 10, and 50 mg/l, adsorbent dose of 0.1-0.4 mg/L, contact time of 1-60 min and pH of 5-8. The solution was mixed with a mechanical shaker with 150 r.p.m. at 20°C. The suitability of the adsorbent was evaluated using Langmuir, Freundlich isotherm models.
Results: The optimum pH for the copper removal was 6-7. The capacity of copper adsorption at equilibrium conditions increased by increasing the concentration of the adsorbate. On increasing the initial concentration of the Cu solution, copper removal reduced. The maximum removal of copper was obtained in dose 0.4 mg/L SWCNTs, 10 mg/L concentration of copper, pH: 7 and 10 min contact time, which were equal to 94%. The Both on Freundlich and Langmuir isotherm models gave the appropriate accordance to the adsorption data ($R^2 > 0.99$). The maximum copper adsorption capacity obtained 1.33 mg/g by SWCNTs.
Conclusion: The adsorption rate of the copper ions from synthetic wastewater in optimal conditions was quick. In these conditions, the SWCNTs were able to adsorb copper ions from the synthetic wastewater, effectively.

Key words: Adsorption, isotherm, single-walled carbon nanotubes, synthetic wastewater

INTRODUCTION

One of the major challenges is the gradual raise of the heavy metals in the environment. They accumulate in the living creatures while this increase is a consequence of both human and natural sources. The main distinctiveness of the heavy metals is their non-biodegradability and their tendency to accumulate in biological materials.[1]

Some of the deleterious effects of these metals on the human body include damage to the nervous system and kidneys and cause tumors.[2] Copper is one of the most prominent heavy metals in nature through water sources. A tint and a bitter, unpleasant taste in water caused by the copper ion concentrations greater than 5 mg/l Hence, the maximum permissible concentration of copper in drinking water is

Access this article online

Quick Response Code:

Website:
www.ijehe.org

DOI:
10.4103/2277-9183.170707

This article may be cited as:
Sadeghinya A, Bina B, Mahvi AH, Esrafili A, Dehghanifard E, Takanlu LK. Efficiency determination of single-walled carbon nanotubes on adsorption of copper ions from synthetic wastewater. Int J Env Health Eng 2015;4:40.

1 ppm.[3] The main source of this metal in the national industrial sewage relates to metal cleaning processes, plating tubs, and pickle ponds. The other potential sources include pulp and paper mill plants, petroleum refining, paint production, motor vehicles plating parts, etc. The copper concentration in the effluent for each of these industries may be on average 50-1000 mg/l, for which this amount of copper may pollute a wide range of the underground waters and the wastewater in vicinity of the manufacture.[4-6]

So far, various methods are used to remove heavy metals from water, while some methods can be mentioned: Reverse osmosis,[7] electrolysis,[8] chemical precipitation,[9] surface adsorption,[10] etc., as each has its own advantages and disadvantages, so that studies, results consider surface adsorption the most useful method for metals removal from aqueous solutions.[1,6] One of the new adsorbents in nanotechnology is carbon nanotubes proffered by the Japanese researcher, Sumio Iijima, in 1991, and it was discovered by chance when studying carbon electrode arc discharge.[11,12] In fact, the carbon nanotubes are the carbon atom sheets, moving inside a roller-form via high surface area, high reactivity, thermal and mechanical resistance and unique chemical and physical properties at these materials.[11,13,14] These materials can be divided into two major categories based on building type and number of carbon layers in their structures:

1. Single-walled carbon nanotubes (SWCNTs),
2. Multi-walled carbon nanotubes (MWCNTs).[11,12]

The SWCNTs have smaller diameter and length than the MWCNTs, thus could not produce in mass quantities due to the small size, but could be easier used than the MWCNTs.[6,13]

The SWCNTs are one of the new adsorbents in nanotechnology, and they are efficient for the environmental contaminant removal in several studies. Concerning the expansion of nanotechnology in various environmental aspects, the aim of the present study was to determine the efficiency of the new technology of the SWCNTs for the removal of copper ions from synthetic wastewater.

The mechanisms of heavy metal ion adsorption on CNTs are very complicated and appear attributable to physical adsorption, electrostatic attraction, precipitation and chemical interaction between the heavy metal ions and the surface functional groups of CNTs. Among these, chemical interaction between the heavy metal ions and the surface functional groups of CNTs is the major adsorption mechanism.[13]

Several factors, such as surface charge, speciation of heavy metal ions in solution and experimental conditions, affect the adsorption of heavy metal ions on CNTs, which leads to a dependence of the adsorbed amount on the point of zero charge of CNTs (pHpzc:a pH value, called 'point of zero charge', at which the net surface charge is zero), isoelectric point, and experimental conditions, such as ionic strength, pH, foreign ions, CNT mass, contact time, initial metal ion concentration, and temperature.[5,14]

MATERIALS AND METHODS

The used materials in this study were the SWCNTs, copper nitrate, hydrochloric acid, nitric acid, and sodium hydroxide. All of the used materials in this study except SWCNTs were prepared from Merck Co, Germany. The stock solution of copper was obtained by 500 ml dissolved salt in distilled water, and the required concentrations were obtained by diluting the stock solution. This study was performed at the laboratory scale and SWCNTs with 5 nm diameter and 100 nm average length, which were purchased from the Iranian Research Institute of Petroleum Industry, are used for the removal of copper ions from the synthetic waste water [Figure 1].

The effective parameters in the adsorption process include pH, copper ions concentration, concentration of SWCNTs added to the synthetic wastewater, and contact time.

Primarily, the synthetic wastewater samples were prepared by defined concentrations in different conditions in the laboratory. Then a certain amount of the SWCNTs contacted in a shaker with 150 rpm in terms of pH and contact time, and finally the adsorbent containing solution was passed from 0.2 μ PTFE filter, which could measure the final concentration of copper ions by atomic adsorption spectrophotometer, model Perkin Elmer A Analyst 200 that each test was repeated three times to determine the accuracy.

In this study the copper ions adsorption from synthetic wastewater with SWCNTs and the impact of changes in various physical, chemical, and operational parameters, which is pH initial concentration of copper ions, the concentration of SWCNTs, and contact time impact on adsorption rate also was studied.

In this regards, 50 ml of solution containing copper ions, was poured into the flask with 4 concentration levels of 1, 5, 10, and 50 mg/l, then a certain dose of SWCNTs in 4 levels of 0.1, 0.2, 0.3, and 0.4 mg/l was added and 4 levels of pH in the range of 5 to 8 at 7 time levels from 1 to 60 min was studied on copper

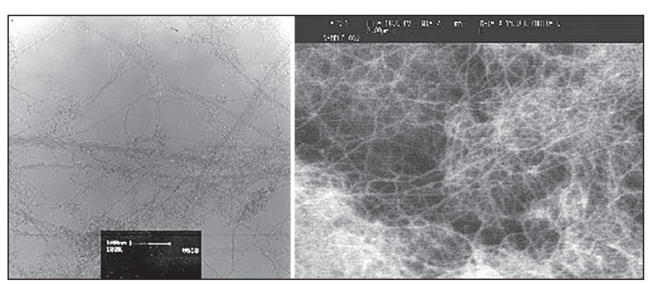

Figure 1: SEM and TEM images of single-walled carbon nanotubes

adsorption using atomic adsorption spectroscopy. All tests were carried out by mixing rate of 150 rpm. The percentage of the copper ions removal was calculated by Equation 1.[6,15]

$$U_p\ 100 \times \left(1 - \frac{C_e}{C_i}\right) \quad \text{(Eq. 1)}$$

Where, C_i and C_e, are the primary and the equilibrium concentration of copper ions in ppm, respectively. The copper ions removal percentage is equal to the reduction rate after the initial adsorption rate.[12]

RESULTS

Effect of pH on adsorption of copper ions

As can be seen in the Figure 2, by increasing pH from 5 to 7, the adsorption rate increased from 67% to 94%. In further testing until pH 8, there was observed 7% reduction in adsorption.

Effect of initial concentration on copper ions adsorption

Figure 3 display that, by increasing the initial concentrations of copper ions, the adsorption reduction was evident. Therefore, by increasing the initial concentration from 1 to 50 mg/l, the adsorption rate decreased from 96% to 86%. In regard of the concentration of 10 mg/l, 94% of the copper ions were removed and then by increasing the concentration from 10 to 50 mg, 11% reduction was observed in adsorption, thereof the concentration of 10 mg was chosen as the optimal concentration and further tests were performed on this concentration.

Effect of single-walled carbon nanotubes doses on adsorption

Figure 3 show that, by increasing the nanoparticle dose from 0.1 to 0.4 mg, the adsorption rate of copper ions was increased from 48% to 83%.

Effect of contact time on adsorption rate

The results indicated that the maximum adsorption per 10 min was about 94%. The tests continued for 60 min, as the adsorption rate reduced from 95% to 62% during 10-60 min, which indicates desorption of the copper ions. Thus, the contact time of 10 min was chosen as the optimal time, and the further tests were performed at 10 min [Figure 4].

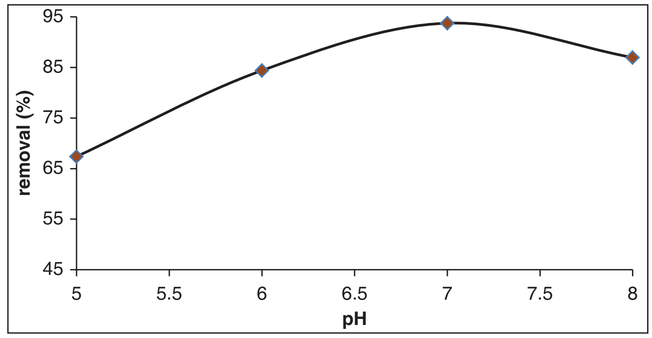

Figure 2: Effect of pH on copper adsorption

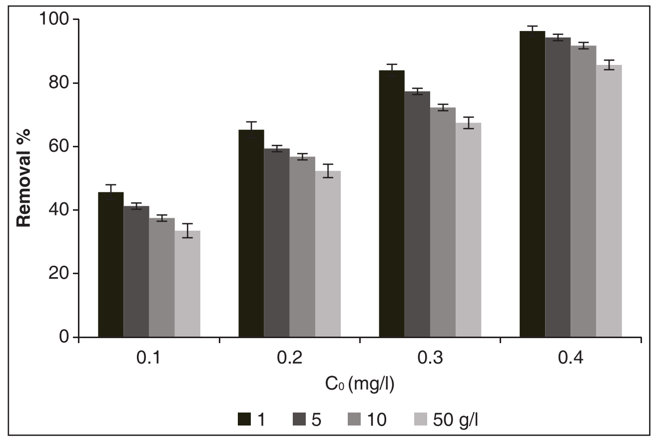

Figure 3: Effect of initial concentration and adsorbent dose on adsorption rate

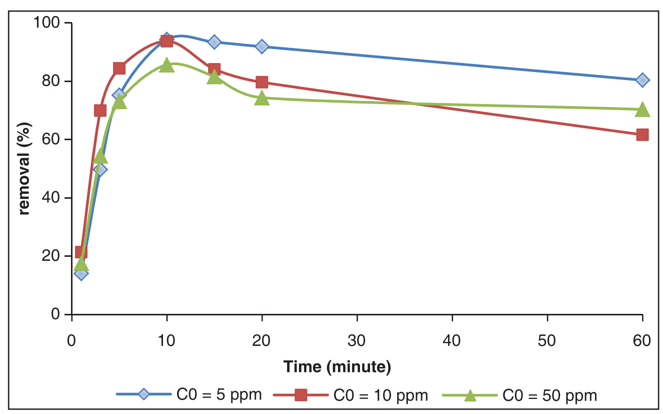

Figure 4: Effect of contact time on adsorption

DISCUSSION

The carbon nanotubes are well capable for the removal of copper metal ions. The major divalent copper ions removal process reacted at the initial moments and the first 10 min. This phenomenon indicates the rapid rate of the copper adsorption process by the carbon nanotubes. By increasing the concentration rate of the heavy metal ions, on one hand, the adsorption rate per unit mass of adsorbent increases and, on the other hand, the removal rate decreases. In fact, the higher initial concentration between the solution and solid phase has the driving force to overcome all transference obstacles of heavy metal ion contamination. Thus, the adsorption rate increased per unit mass of adsorbent. On the other hand, due to the increase of the heavy metal ions in the solution and the saturation state at equilibrium, the removal percentage reduced. Further, the other variables were examined, so the initial concentration of 10 ppm was chosen as the optimum initial concentration. The results indicated that adsorption occurred in the initial concentration rates of 5, 10, and 50 mg/l of copper ions in the first 10 min of the process, while the concentration values reduced at 0.285 mg/l, to 0.624, and 7.165 mg/l. The pH of the solution affects the surface charge of the nanoparticles. The distribution of the functional groups, that is, carboxyl and hydroxyl, can be calculated as the pH factor through the basic acid titration. The pH_{pzc} was measured according to the sources, and about five was obtained.[12,14] At $pH > pH_{pzc}$, the positively charged heavy metals may be adsorbed onto the negatively charged CNTs. Therefore, the heavy metal adsorption increases, when pH increases.[8,14] In an acidic environment due to the vicinity of H^+ ions, the activity of carbonyl, carboxyl and hydroxyl factors decreases, which are the heavy metal ion factors on the adsorbent surface. As a result, the copper ions adsorption decreases due to the lack of the proper adsorption. As pH increase to 6.5-7, the increase of the surface negative charge occurs due to the negative charge factors at increased adsorption rate.[5] The less adsorption in the acidic solution occurs due to the competition between hydrogen ions and metal ions adsorption onto CNTs adsorption sites.[8]

Since the adsorption conflict occurs at alkaline pH due to the formation of the hydroxide deposits and heavy metal ions removal from solution, the range of tested pH is chosen in the range of 4-8. The removal percentage difference indicates the essential role of pH on the removal rate. Whereas the copper adsorption percentage in various pH rates is different, the copper adsorption increases as the pH of the solution were increased from 4 to 7. The reason for this issue is the oxidation of CNTs with oxidized acid, which may generate highly active groups, that is, hydroxyl, carbonyl, and carboxyl on the surface of CNTs. The decrease of the removal rate in pH above 7 indicates the reduction in the negative surface charge density of the CNTs. Thus, the negative charge on the surface of CNTs is the main reason for the copper adsorption in the studied pH range.

Acidic surface sites give a negative zeta-potential, whereas basic sites give a positive zeta-potential. This implies that at low pH, a significant amount of basic groups, which are able to induce a positive surface charge, are present on the surface.

Therefore, large amounts of basic groups are able to induce a positive surface charge at lower surface pH rate. Atieh *et al*. used carbon nanotubes for lead removal with the highest removal rate at pH = 5.5.[15] Pyrzynska *et al*. studied several heavy metals removal by carbon nanoparticles, as the maximum metal ions removal rate was found at pH = 6. For copper ions, pH = 7, is compared with the other heavy metal ions with more tendency and competition in the adsorption of the carbon nanoparticles, which is related to the metal ions electro-negativity and the primary stable metal hydroxide.[16] Tang *et al*. found the highest copper adsorption rate by the MWCNTs at pH = 6.[5] As the examination of the initial concentration change of the copper ions concluded that, by the increase of the copper concentration, the adsorption rate reduces. In regard of the fixed adsorbent dose and the limited number of the available adsorption sites, the reduction percentage of the corresponding contamination removal increases rationally the concentration of the input pollutant.[19,20]

The carbon nanotubes concentration showed that the higher nanotubes concentration increases the copper adsorption rate due to the increased adsorption on the surface free sites or the nanotubes surface area.[21]

The copper adsorption increases by increasing the adsorbent dose with the maximum adsorption at 0.4 mg. The effect of the contact time change on adsorption was studied for 60 min and it was found that the adsorption rate increased by the increased exposure time to 10 min and after 10 min, there were slight effects on the copper ions adsorption. The adsorption was very fast to reach equilibrium for about 10 min. This is due to the high effective level of the carbon nanotubes, which released of the copper ions from the solution to the present active sites at the solid surface of the carbon nanotubes.[6,14]

Adsorption isotherms

The adsorption isotherms are used to define of the mass absorbed per unit mass of the adsorbent material. Among the isotherm models, Freundlich and Langmuir isotherms are more widely used. In the present study, Freundlich and Langmuir isotherm models are used to plot adsorption data.[19,22] Langmuir and Freundlich adsorption isotherm curves are shown in Figure 5.

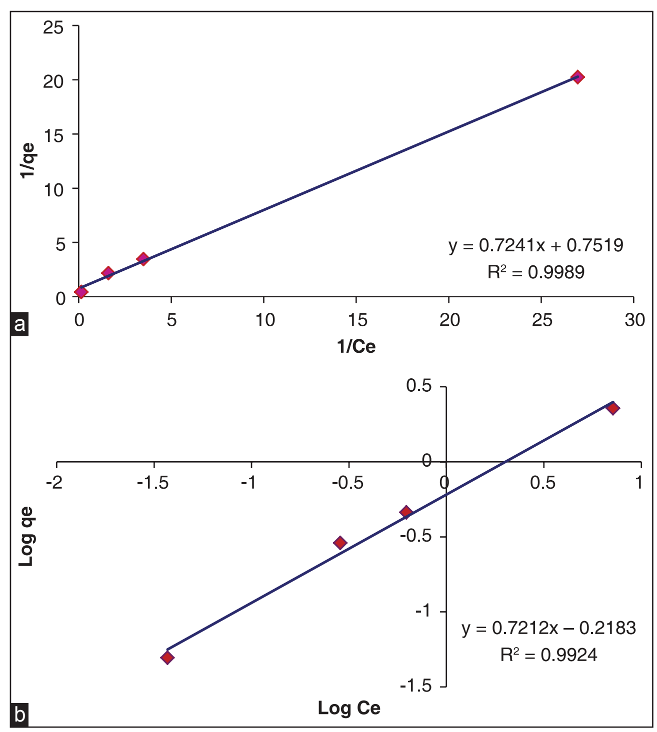

Figure 5: (a) Langmuir isotherm curve, (b) Freundlich isotherm curve

According to the Langmuir equation:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad \text{(Eq. 2)}$$

The values of K_l, $q_{max,}$ and R^2 calculated equal to 1.038, 1.33 and 0.999, respectively, and the following equation is obtained,

$$q_e = \frac{q_{\max}(1.038C_e)}{1 + (1.038C_e)} \quad \text{(Eq. 3)}$$

In this equation, C_e is the equilibrium concentration of Cu (ppm), and K_l represents adsorption capacity (dm^3/mol) and q_{max} represents the maximum adsorption rate (mol/m^2).

According to Freundlich equation:

$$\log(q_{eq}) = \log(K_f) + \frac{1}{n}\log(C_{eq}) \quad \text{(Eq. 4)}$$

The values of K_f, n, R^2 are calculated equal to 0.6, 1.387 and 0.992, respectively, and the following equation is obtained,

$$q_e = 0.6C_e^{0.721} \quad \text{(Eq. 5)}$$

Where, C_e is the equilibrium concentration of Cu (ppm) and K_f represents the absorbent capacity (dm^3/mol) and n represents the adsorption intensity. The isotherm parameters of Langmuir and Freundlich are reported in Table 1. According to the results of the plotted adsorption isotherms, it was found that Langmuir adsorption isotherm equation has higher and more proper correlation coefficient than Freundlich isotherm and thus it is consistent with the adsorption of Langmuir model. Since the adsorption isotherms of Freundlich and Langmuir indicate the monolayer adsorption versus the double-layer isotherm adsorption, which could conclude that the adsorption of the copper ions are performed by the monolayer carbon nanotubes.[19,22,23] In conclusion using SWCNTs for removal copper ions in appropriate condition is quick and efficient.

CONCLUSIONS

The most proper performance values for the copper adsorption in pH = 7 were 10 min contact time, initial concentration of copper of 10 mg/l, and the concentration of carbon nanotubes of 0.4 mg. The adsorption was highly dependent on the initial pH and initial concentration of copper ions in the solution, while it was increased by the higher concentration of the carbon nanotubes and it was decreased by the higher metal ion concentration. The copper removal had been well performed as a model of metal ions in wastewater by adsorption onto the carbon nanotubes.

Table 1: The parameters of the used isotherm models

Model	K_f	K_l=b (L/mg)	Q_m (mg/g)	R^2	*n*
Freundlich	0.6	—	—	0.9924	1.386
Langmuir	—	1.038	1.33	0.9989	—

ACKNOWLEDGMENT

This article is the result of MSc thesis approved in the Isfahan University of Medical Sciences. The authors are grateful to them for financial support.

REFERENCES

1. Tofighy MA, Mohammadi T. Adsorption of divalent heavy metal ions from water using carbon nanotube sheets. J Hazard Mater 2011;185:140-7.
2. Pyrzyńska K, Bystrzejewski M. Comparative study of heavy metal ions sorption onto activated carbon, carbon nanotubes, and carbon-encapsulated magnetic nanoparticles. Colloids Surf A Physicochem Eng Asp 2010;362:102-9.
3. Bystrzejewski M, Pyrzyńska K. Kinetics of copper ions sorption onto activated carbon, carbon nanotubes and carbon-encapsulated magnetic nanoparticles. Colloids Surf A Physicochem Eng Asp 2011;377:402-8.
4. Ge F, Li MM, Ye H, Zhao BX. Effective removal of heavy metal ions Cd2+, Zn2+, Pb2+, Cu2+ from aqueous solution by polymer-modified magnetic nanoparticles. J Hazard Mater 2012;211-212:366-72.
5. Tang WW, Zeng GM, Gong JL, Liu Y, Wang XY, Liu YY, *et al*. Simultaneous adsorption of atrazine and Cu (II) from wastewater by magnetic multi-walled carbon nanotube. Chem Eng J 2012;211-212:470-8.
6. Mobasherpour I, Bafrooei BH, Ebrahimi M. Determination of Adsorption Capacity and Thermodynamic Parameters of Cu2+ Removal from Aqueous Solution by γ–Al2O3/CNT Nano-composite. J Sep Sci Eng 2011;4:57-68.
7. Zhao G, Wu X, Tan X, Wang X. Sorption of heavy metal ions from aqueous solutions: A review. Open Colloid Sci J 2011;4:19-31.
8. Fu F, Wang Q. Removal of heavy metal ions from wastewaters: A review. J Environ Manage 2011;92:407-18.
9. Wan Ngah WS, Hanafiah MA. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. Bioresour Technol 2008;99:3935-48.
10. Demirbas A. Heavy metal adsorption onto agro-based waste materials: A review. J Hazard Mater 2008;157:220-9.
11. Tian Y, Gao B, Morales VL, Wu L, Wang Y, Muñoz-Carpena R, *et al*. Methods of using carbon nanotubes as filter media to remove aqueous heavy metals. Chem Eng J 2012;210:557-63.
12. Yu F, Wu Y, Ma J, Zhang C. Adsorption of lead on multi-walled carbon nanotubes with different outer diameters and oxygen contents: Kinetics, isotherms and thermodynamics. J Environ Sci (China) 2013;25:195-203.
13. Rao GP, Lu C, Su F. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. Sep Purif Technol 2007;58:224-31.
14. Ren X, Chen C, Nagatsu M, Wang X. Carbon nanotubes as adsorbents in environmental pollution management: A review. Chem Eng J 2011; 170:395-410.
15. Atieh MA, Bakather OY, Al-Tawbini B, Bukhari AA, Abuilaiwi FA, Fettouhi MB. Effect of carboxylic functional group functionalized on carbon nanotubes surface on the removal of lead from water. Bioinorg Chem Appl 2010;5:383-92.
16. Pyrzynska K. Carbon nanostructures for separation, preconcentration and speciation of metal ions. Trends Anal Chem 2010;29:718-27.

17. Sheng G, Li J, Shao D, Hu J, Chen C, Chen Y, *et al.* Adsorption of copper(II) on multiwalled carbon nanotubes in the absence and presence of humic or fulvic acids. J Hazard Mater 2010;178:333-40.
18. Wu CH. Studies of the equilibrium and thermodynamics of the adsorption of Cu(2) onto as-produced and modified carbon nanotubes. J Colloid Interface Sci 2007;311:338-46.
19. Pourzamani H, Bina B, Rashidi A, Amin MM. Performance of raw and regenerated multi-and single-walled carbon nanotubes in xylene removal from aqueous solutions. Int J Environ Health Eng 2012;1:4.
20. Ozcan SG, Satiroglu N, Soylak M. Column solid phase extraction of iron(III), copper(II), manganese(II) and lead(II) ions food and water samples on multi-walled carbon nanotubes. Food Chem Toxicol 2010;48:2401-6.
21. Li Y, Liu F, Xia B, Du Q, Zhang P, Wang D, *et al.* Removal of copper from aqueous solution by carbon nanotube/calcium alginate composites. J Hazard Mater 2010;177:876-80.
22. Shin KY, Hong JY, Jang J. Heavy metal ion adsorption behavior in nitrogen-doped magnetic carbon nanoparticles: Isotherms and kinetic study. J Hazard Mater 2011;190:36-44.
23. Mobasherpour I, Salahi E, Pazouki M. Comparative of the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} by nano crystallite hydroxyapatite from aqueous solutions: Adsorption isotherm study. Arabian J Chem 2010;4:339-446.

Source of Support: This article is the result of MSc thesis approved in the Isfahan University of Medical Sciences. The authors are grateful to them for financial support. **Conflicts of Interest:** None declared.