

Removal of High-Concentration Fe(III) by Oxidized Multiwall Carbon Nanotubes in a Fixed Bed Column

Abstract: The aim of this work was to study the use of modified multiwall carbon nanotubes (MWCNTs) for high concentration of ferric iron removal in acid mine drainage. Fourier transform infrared spectrum demonstrated that hydroxyl and carbonyl functional groups were introduced to the surface of MWCNTs after oxidation with nitric acid. Then, the adsorption behavior of modified MWCNTs was investigated in removing high concentration of Fe(III) through batch and continuous flow fixed bed experiments. Batch experiment results demonstrated that the Fe(III) adsorption capability of oxidized MWCNTs was better than pristine MWCNTs. Adsorption equilibrium was achieved during the first 90 min. Langmuir model can be successfully employed for the equilibrium of isotherms with $R^2=0.9878$ and $q_{\max}=89.05$ mg/g. In addition, effect of column bed depths and influent Fe(III) concentrations were studied through the continuous fixed-bed adsorption studies. Results indicated that Fe(III) uptake was particularly favoring higher bed depth and lower influent concentration. And the bed uptake capacity of Fe(III) was found to be 30.30-41.51 mg/g, which was much lower than in batch experiment.

Key word: Adsorption, Ferric Ions, Fixed-bed column system, Oxidized multiwall carbon nanotubes

1. Introduction

With development of industry and agriculture, heavy metal pollution of terrestrial and aquatic ecosystems becomes more serious [1]. Most of all, mining of ore deposits that contain large amounts of sulfide minerals and heavy metals pollutes the environment seriously [2]. The oxidation of pyritic mining waste is a self-perpetuating corrosive process which continuously generates acid mine drainage (AMD). AMD waters contain high concentrations of mineral acid, dissolved iron, and sulfates, as well as a variety of toxic chemicals such as cadmium, lead, copper, and arsenic [3]. It was known that ferric iron is predominant in the AMD waters, and the concentration can be as high as several hundred milligrams per liter [4,5]. However, the presence of total iron more than 0.3 mg/L may cause anorexia, oliguria and diphasic shock.

30 And, it can give a metallic taste and odor to water [6]. Therefore, a special attention should be
31 paid on the removal of high concentration of ferric iron from AMD waters.

32 Heavy metals in AMD waters are usually treated by adding alkaline materials such as
33 lime, fly ash and alkaline industrial wastes and form precipitate as hydroxides [7-9]. Major
34 disadvantages of this method are the need for continuous addition of the amendment, low
35 reaction rates, and the production of huge amounts of secondary wastes [10]. Recently,
36 adsorption onto solid adsorbent is reported to be the potential alternative technique to remove
37 heavy metals from water. Carbon nanotubes were first discovered by Iijima in 1991 [11]. Then
38 this novel and interesting graphitic carbon materials has been proven to possess excellent
39 adsorption capacity in the removal heavy metal ions and organic pollutants [12-14] from
40 aqueous solutions, as a result of high specific surface area and strong interactions between
41 carbon atoms and hydrogen molecules. In addition, the adsorption capacity of carbon
42 nanotubes can be improved by surface modifications, such as oxidization [15,16] and other
43 chemical or physical modifications [17,18]. For example, Rao et al. [19] have investigated the
44 adsorption efficiency of carbon nanotubes towards divalent heavy metal ions, such as Ni^{2+} ,
45 Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} , in which the adsorption capacity of carbon nanotubes was
46 significantly improved by the oxidation of carbon nanotubes with acid solutions. However,
47 the studies on the adsorption of high concentration of Fe(III) onto MWCNTs are still very
48 limited in the literature.

49 The efficiency of an adsorption process is usually controlled by the overall adsorption
50 rate, which depends on transport processes outside and inside the adsorbent particles and on
51 the kinetics of binding. Over the years, the batch experiment has become the most commonly
52 used configuration in wastewater treatment. However, the adsorption efficiency in a fixed-bed
53 adsorption column is a function of the liquid flow pattern (axial and radial mixing) through
54 the porous bed of particles and the liquid residence time. Furthermore, in practical wastewater
55 treatment process, continuous fixed-bed adsorption experiments are most likely preferable,
56 and the experimental data obtained from the studies are important for industrial applications
57 [20].

58 Broadly, the goal of this study is to evaluate the performance of oxidized MWCNTs in
59 removing Fe(III) from aqueous solution through batch and continuous fixed-bed system. The

specific objectives are to (1) prepare and characterize oxidized MWCNTs, (2) test the Fe(III) removal by oxidized MWCNTs in batch experiment and calculate the parameters of adsorption isotherms, (3) study the effect of bed depth and initial Fe(III) concentration on breakthrough curve in the fixed-bed system.

2. Experimental work

2.1 Materials and chemicals

The pristine MWCNTs were purchased from Beijing boyu gaoke new material technology Co., Ltd, China. All the chemicals and reagents used were analytical grade or higher. A stock solution of Fe(III) (1000 mg/L) was prepared by dissolving ferric chloride in deionized water. The solution was further diluted to the required concentrations and the pH of the solutions was adjusted by using 0.1 mol/L hydrochloric acid or sodium hydroxide solutions.

2.2 Oxidation of MWCNTs

The pristine MWCNTs were prepared using chemical vapor deposition method. The outer diameter was about 10-20 nm, inner diameter was 5-10 nm, and the length was 10-30 μm . Its special surface area was more than 200 m^2/g , and the purity was higher than 95%. The pristine MWCNTs were oxidized by using nitric acid to remove the hemispherical caps and particles of catalyst at the tips of nanotubes. 3 g of pristine MWCNTs were immersed in 50 mL concentrated nitric acid for 24 h, and then washed with deionized water until the solution pH reached 6.5, and dried in the oven at 105 $^{\circ}\text{C}$ for 4 h, and used in the following experiments.

2.3 Characterization of MWCNTs

For characterization of the functional groups on the surface of MWCNTs, Fourier transform infrared (FTIR, 560E.S.P, Nicolet, USA) spectra of samples were measured by the standard KBr disk method.

2.4 Batch experiments

Adsorption experiments were carried out in serum bottles at a temperature of 25 $^{\circ}\text{C}$. The pH of Fe(III) solution was adjusted to 3.5 prior to the experiment. Then, a certain amount of pristine and oxidized MWCNTs were added to 50 mL of Fe(III) solution respectively. All reactors were agitated on a shaker at a rate of 180 revolutions per minute during the

experiment. Samples were withdrawn at appropriate time intervals, filtered through a 0.22 μm membrane. The samples were analyzed for total iron concentrations using 1, 10-phenanthroline spectrophotometry [21]. Duplicate tests were conducted for all the experiments.

Isotherm models

In order to gain a better understanding of the mechanism and to quantify the sorption data, Langmuir [22] and Freundlich [23] isotherm models are conducted to simulate the sorption of Fe(III) on the oxidized MWCNTs. The equations of Langmuir isotherm model can be expressed by:

$$\frac{1}{q_e} = \frac{1}{K_L C_e q_m} + \frac{1}{q_m} \quad (1)$$

where “ q_e ” is Fe(III) amount adsorbed on oxidized MWCNTs surface at equilibrium (mg/g); “ C_e ” is equilibrium concentration or final concentration of Fe(III) ions in the aqueous solution (mg/L); “ q_m ” is the maximum sorption capacity (mg/g); “ K_L ” is the Langmuir sorption constant (L/mg) which is related to the energy of adsorption.

The equations of Freundlich isotherm model can be expressed by:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

where “ K_f ” and “ n ” are the Freundlich constants which are indicators of adsorption capacity and adsorption intensity. The slopes and intercepts of the linear Langmuir and Freundlich plots are used to calculate the Langmuir and Freundlich constants

2.5 Continuous fixed-bed adsorption study

The breakthrough curve of Fe(III) was determined through continuous fixed-bed adsorption studies. The studies were conducted in a column made of glass tube with an internal diameter of 2.0 and 50 cm in length. The tube was packed with quartz sand. A layer of glass wool with 1 cm thickness was placed at the bottom of the column to prevent the adsorbent from leaching out, as well as on the top of the column to provide a uniform flow of the solution through the column. After the oxidized MWCNTs were packed in the column at a known quantity (1, 2 and 3 g) to yield the desired bed depth of 10, 20 and 30 cm, each column was flushed with 150 mg/L of Fe(III) solution. At the bed depth of 20 cm (equivalent to 2 g

MWCNTs), known concentration of Fe(III) solutions (150, 200 and 300 mg/L) was pumped in a upward flow mode at a flow rate of 3 mL/min, respectively. The effluent samples at the outlet of the column were collected and analyzed for total iron concentrations at regular time intervals, and the column was operated until the concentration of Fe(III) exceeded 99.5 % of its initial concentration. The experiments were carried out at room temperature, and the solution pH was adjusted to 3.5.

3. Results and discussion

3.1 Characterization of pristine and oxidized MWCNTs

Figure 1 shows the FTIR spectra of pristine and oxidized MWCNTs. As shown in Figure 1, the spectrum of pristine MWCNTs displayed three main bands at 1380, 1620, and 3440 cm^{-1} . However, these peaks became sharper after oxidation with nitric acid especially at 1380 cm^{-1} . The peak at 3440 cm^{-1} can be assigned to the stretching vibration of O–H band. The signature of C=O functional groups was evident at 1620 cm^{-1} . The peak at 1380 cm^{-1} was associated with C–H deformation vibration from aliphatic $-\text{CH}_3$ and $-\text{CH}_2$. New bands at 830 cm^{-1} appeared in oxidized MWCNTs due to the bending of $-\text{C}=\text{O}$ in carboxylic acid [24]. These peaks implied that oxidation by nitric acid was an effective process to introduce a lot of oxygen containing functional groups on the surfaces of MWCNTs.

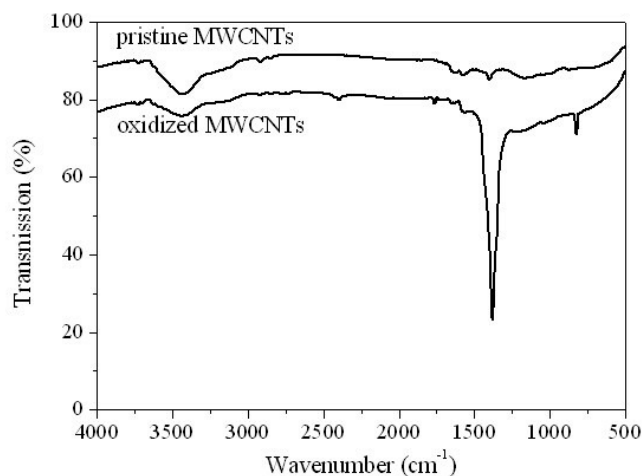


Fig. 1 FTIR spectra of pristine and oxidized MWCNTs

3.2 Comparison of Fe(III) adsorption on pristine and oxidized MWCNTs

The goal of adsorption experiments at this stage was to provide a preliminary understanding of the adsorption capacity of oxidized MWCNTs for Fe(III) ion. The

adsorption of Fe(III) on the pristine and oxidized MWCNTs as a function of contact time is shown in Figure 2. It can be seen that the adsorption ratio of Fe(III) onto MWCNTs was improved significantly after oxidation. The adsorption ratio of pristine Fe(III) was only 43% while the adsorption capacity increased to 75% for the oxidized MWCNTs at the same reaction condition. This significant adsorption improvement was due to the increasing of the oxygen-containing functional groups and total number of acid site on MWCNTs, which provided a large number of chemical adsorption sites [12]. Further, the hydrophilic properties of these functional groups can improve the dispersion of oxidized MWCNTs in aqueous solutions. The specific surface area, the pore volume and average pore diameter of MWCNTs increased after oxidation was also a factor [25].

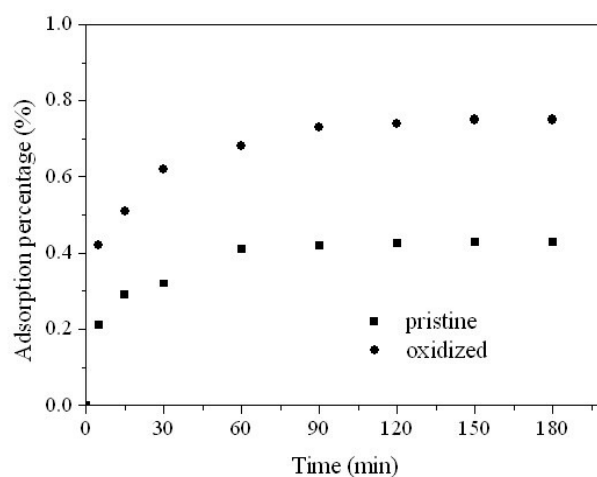


Fig. 2 Comparison of Fe(III) adsorption ratio on pristine and oxidized MWCNTs. Initial MWCNTs dose: 1 g/L, initial Fe(III) concentration: 50 mg/L.

The adsorption percentage of Fe(III) on MWCNTs increased rapidly in the first 1 h, and then slowed down as equilibrium was approached. The contact time to reach equilibrium was about 90 min. The high initial adsorption rate may be attributed to the existence of large number of adsorption sites on the surface of MWCNTs. As the sites filled up gradually, the adsorption became slow and the mechanism of kinetics became more dependent on the rate at which the adsorptive was transported from the bulk phase to the actual adsorption sites. The adsorption reached equilibrium very quickly, which also indicated that the chemical adsorption or surface complexation rather than physical adsorption was the main sorption mechanism of Fe(III) on MWCNTs.

3.3 Adsorption Isotherms

Figure 3 shows the removal of 50 mg/L Fe(III) ions using different dosages of oxidized MWCNTs. The removal percentage increased sharply while the adsorption capacity decreased with a rise in MWCNT mass. The maximum removal ratio can reach 96 % at the MWCNTs dosage of 1.6 g/L as a result of increasing number of the adsorption site in the MWCNTs adsorbent.

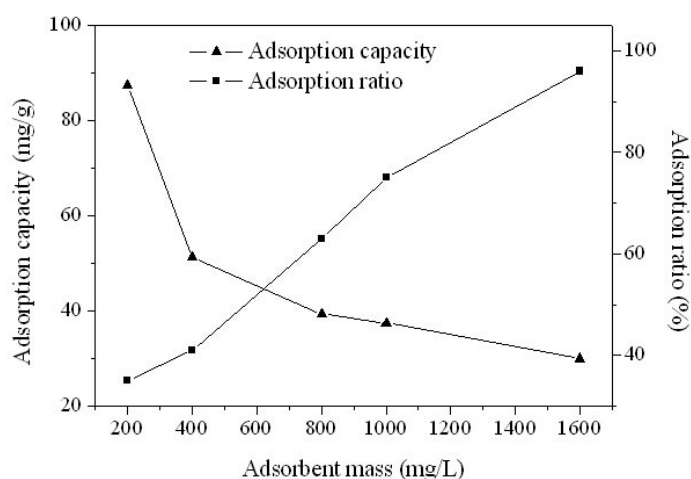


Fig. 3 Fe(III) adsorption to MWCNTs with increasing adsorbent dose. Initial Fe(III) concentration: 50 mg/L, adsorbent dose: 0.2, 0.4, 0.8, 1.0, 1.6 g/L.

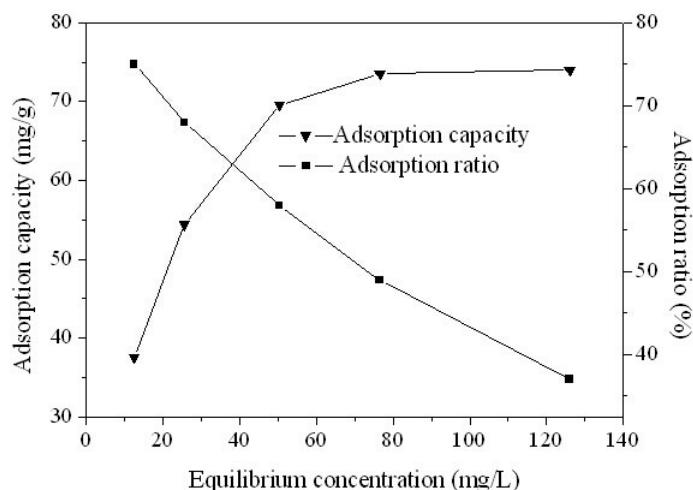


Fig. 4 Fe(III) adsorption to MWCNTs with increasing equilibrium aqueous Fe(III) concentration. Initial Fe(III) concentration: 50, 80, 120, 150, 200 mg/L, MWCNTs dose: 1 g/L.

Figure 4 shows the removal percentage of Fe(III) using oxidized MWCNTs under the influence of different initial Fe(III) concentrations (50, 80, 120, 150 and 200 mg/L). As shown in Figure 4, the Fe(III) equilibrium concentration and adsorption capacity increased by increasing initial Fe(III) concentration under the specific experiment conditions. However, the

adsorption percentage of Fe(III) decreased with the increase of the initial concentration at the same MWCNTs mass. For example, the removal percentage was 75 % at initial Fe(III) concentration of 50 mg/L, while it was 37 % at initial Fe(III) concentration of 200 mg/L. This phenomenon can be explained by the fact that, at the same MWCNT dosage, there was constant number of functional groups available on MWCNT surface. Therefore, the increase of Fe(III) concentration caused a decrease in the adsorption percentage of Fe(III).

The equilibrium adsorption data of Fe(III) for oxidized MWCNTs was approximated by Langmuir and Freundlich isotherm models. The Freundlich model assumed that different sites with several adsorption energies were involved, whereas the Langmuir model assumed that there was no interaction between the adsorbate molecules and the adsorption was localized in a monolayer [26]. The linear plot of $1/q_e$ versus $1/C_e$ is shown in Figure 5. From the slope and intercepts of Figure 5, the maximum adsorption capacity of Fe(III) and Langmuir adsorption constant of oxidized MWCNTs were calculated in Table 1. The linear plot of $\ln q_e$ versus $\ln C_e$ is shown in Figure 6. The calculated Freundlich parameters, K_F and $1/n$, from the slope and intercepts of Figure 6 were also tabulated in Table 1.

As can be seen in Table 1, the adsorption data of Fe(III) for oxidized MWCNTs were fitted to the Langmuir equation. The correlation coefficients of the linear regressions (R^2) were found to be 0.9878. Freundlich model showed not good agreement with the experimental data. In a word, it indicated that the Langmuir model fitted the adsorption equilibrium data better than the Freundlich model. At the same time, the Fe(III) adsorption to oxidized MWCNTs was based on chemical adsorption. The foregoing FTIR analysis also supported this deduction.

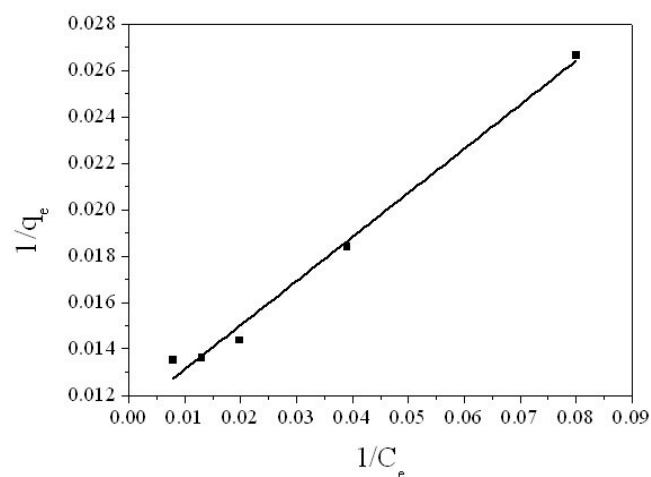


Fig. 5 Langmuir isotherm of Fe(III) adsorption to MWCNTs

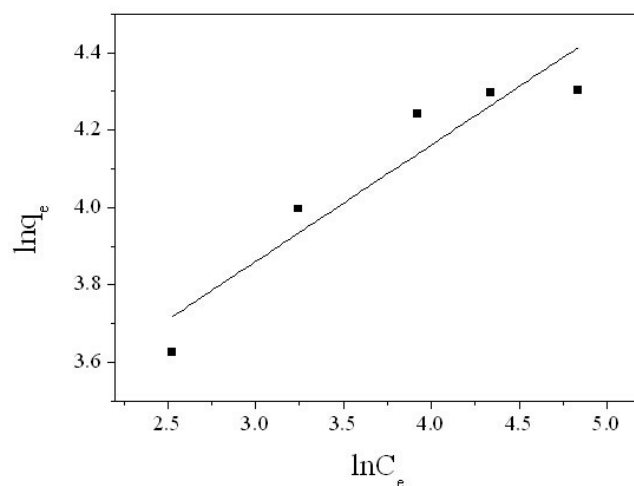


Fig. 6 Freundlich isotherm of Fe(III) adsorption to MWCNTs

Table 1 Langmuir and Freundlich isotherm parameters of Fe(III) adsorption to MWCNTs

Langmuir			Freundlich		
$Q_{\max}$	K_L	R^2	$1/n$	K_F	R^2
mg/g	L/mg				
89.05	0.059	0.9878	0.30	19.21	0.8545

3.4 Column Experiments

The breakthrough characteristics from column experiments gave important information about adsorption behavior and adsorbent capacity. The effluent Fe(III) concentration was a function of time and can be presented in the form of a breakthrough curve. Figure 7 shows the breakthrough curves obtained for 150 mg/L Fe(III) adsorption onto different column bed depths of 10 cm (1 g), 20 cm (2 g), and 30 cm (3 g) at a constant flow rate of 3 mL/min. C_t/C_0 is the ration of the outlet to the inlet Fe(III) concentration as a function of time. In this figure,

under three different operating conditions, breakthrough curves exhibited a characteristic S shape but with varying degrees of steepness. Also the position of the breakpoint was different. As shown that, the first few layers of fresh oxidized MWCNTs were able to adsorb the Fe(III) rapidly and effectively during the initial stages of operation. However, after 175 min of adsorption the removal rate of Fe(III) dropped to 0% in the 10 cm long fixed-bed column. As the bed depth increased to 30 cm, the exhaustion time increased to 350 min. Also the increase of MWCNTs mass at higher bed depth led to an increase in the volume of treated effluent. In general, Fe(III) ions adsorption in a fixed-bed column system was highly associated with the quantity of oxidized MWCNTs. Basically, the mass transfer zone in a column moved from the entrance of the bed and proceeded towards the exit at the top of the column. Therefore, an increase in bed depth would broaden the mass transfer zone and create a longer distance to reach the exit resulting an extended of breakthrough time [27, 28].

In addition, Fe(III) uptake capacity in column experiment was found to be 30.30-41.51 mg/g, which was much lower than in batch experiment. It was because that the MWCNTs dispersion was not good, that make effective area reduced. Moreover, the flow rate of water in the column experiment was much lower, therefore the mass transfer was reduced.

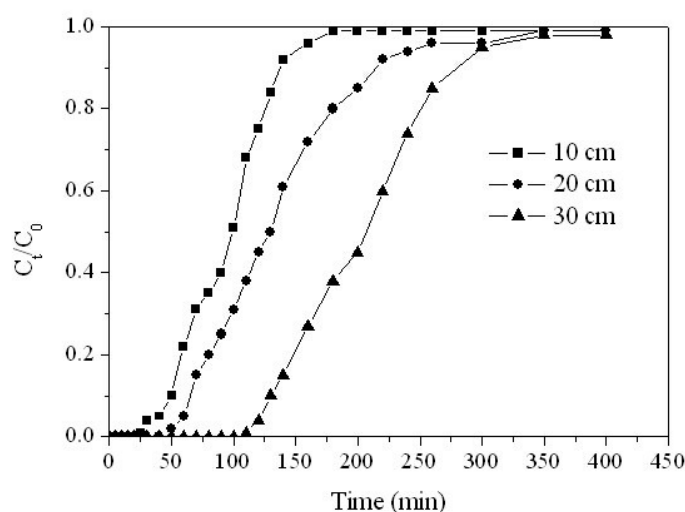


Fig. 7 Breakthrough curves for adsorption of Fe(III) onto oxidized MWCNTs at different bed depths.

Figure 8 shows the effect of Fe(III) influent concentrations on the breakthrough curves by varying the concentrations to 150, 200 and 300 mg/L and bed depth of 20 cm. In this study, high-range concentration of metal solution was employed to obtain a breakthrough curve as acid main drainage was found within this range [5]. As illustrated in Figure 8, the MWCNTs

beds reached faster saturation with the increasing influent Fe(III) concentration. The breakthrough curves were steeper as the influent concentration increased, indicating that higher influent concentrations led to higher driving force for mass transfer; hence, the adsorbent achieved saturation faster, which also resulted in a decreasing exhaust time [29]. Nevertheless, the adsorption capacity for Fe(III) increased with higher influent metal concentration. The highest bed capacities of oxidized MWCNTs for adsorption of Fe(III) were 35.3 mg/g, at influent metal concentration of 200 mg/L.

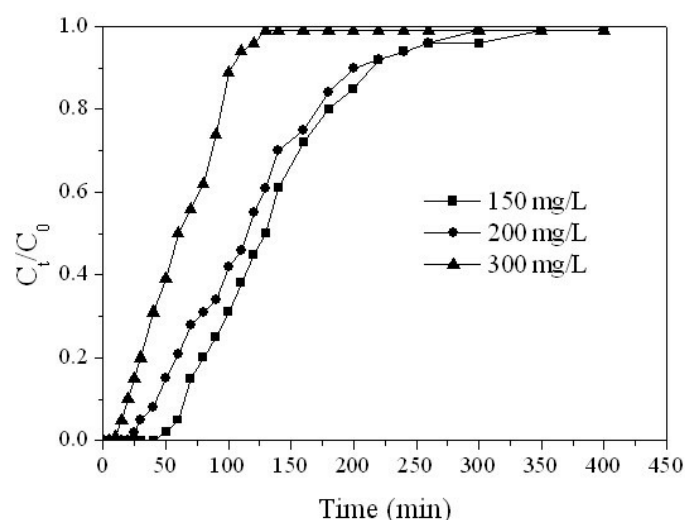


Fig. 8 Breakthrough curve for adsorption of Fe(III) onto the oxidized MWCNTs at different influent concentrations

3.5 Comparison of adsorption capacity for the removal of Fe(III) using various adsorbents

Table 2 Comparison of adsorption capacities of Fe(III) with other adsorbents

Type of adsorbent	pH	Temperature °C	$q_{\max}$ mg/g	Reference
Natural feldspar	1.15	30 °C	25	[30]
Chitosan	3.0	25 °C	90.09	[31]
Acid activated clays	3.0	30 °C	30.00	[32]
Eggshells	6.0	20 °C	5.99	[33]
Modified resin	2.5	20 °C	179	[34]
Oxidized MWCNTs	3.5	25 °C	89.05	This study

Research regarding the use of different adsorbents for removing heavy metals was conducted for a number of years. The adsorption capacities of different adsorbents used for the removal of Fe(III) ions are listed in Table 2. It was found that the oxidized MWCNTs undoubtedly contained high adsorption capacity indicating it's potential to be utilized as a natural adsorbent for heavy metal removal from wastewater effluent.

Conclusions

The oxidized MWCNTs were selected to investigate the uptake behavior of high concentration Fe(III). The modification of MWCNTs by nitric acid was verified by FTIR and it indicated that different functional groups such as carboxylic and hydroxyl were formed. In batch studies, the adsorption of Fe(III) was dependent on initial Fe(III) concentration, adsorbent dose. The Freundlich and Langmuir isotherm models were used to describe the Fe(III) adsorption by oxidized MWCNTs. The Langmuir model fitted the adsorption equilibrium data better than the Freundlich model. Fe(III) removal in a fixed bed column was investigated as a function of the bed depth and initial Fe(III) concentration. It confirmed a faster approach to saturation when the mass of the MWCNTs was low and initial concentrations of Fe(III) were high. This study demonstrated that the oxidized MWCNTs could be utilized as an effective adsorbent for the removal of high concentration Fe(III) from aqueous solution in batch experiment or a fixed-bed column system.

References

1. Alloway BJ, Ayres DC. Chemical principles of environmental pollution. Blackie academic & professional, London, 1997.
2. Banks D, Younger PL, Arnesen RT, Iversen ER, Banks SB, Mine-water chemistry: the good, the bad and the ugly. Environmental geology. 1997; 32: 157-174.
3. Lottermoser B. Mine wastes characterization, Treatment and environmental impacts, Springer: Berlin, 2003.
4. Wingenfelder U, Hansen C, Furrer G, Schulin R. Removal of heavy metals from mine waters by natural zeolites. Environmental Science & Technology. 2005; 39(12): 4606-4613.
5. Zheng YJ, Peng YL, Le HC, Li CH. Separation and recovery of Zn, Fe and Mn in acid mine drainage. Journal of Central South University (Science and Technology).2011; 42(7): 1858-1864.
6. Michalakos GD, Nieva JM, Vayenas DV, Lyberatos G. Removal of iron from potable water using a trickling filter. Water Research. 1997; 31(5): 991-996.
7. Madzivire G, Petrik LF, Gitari WM, Ojumu TV, Balfour G. Application of coal fly ash to circumneutral mine waters for the removal of sulphates as gypsum and ettringite. Minerals Engineering. 2010; 23: 252-257.

8. Alakangas L, Andersson E, Mueller S. Neutralization/prevention of acid rock drainage using mixtures of alkaline by-products and sulfidic mine wastes. *Environmental Science and Pollution Research*. 2013; 20(11): 7907-7916.
9. Khorasanipour M, Moore F, Naseh R. Lime treatment of mine drainage at the Sarcheshmeh porphyry copper mine, Iran. *Mine Water and the Environment*, 2011; 30(3): 216-230.
10. Ziemkiewicz PF, Skousen JG, Simmons J. Long-term performance of passive acid mine drainage treatment systems. *Mine Water and the Environment*. 2003; 22: 118-129.
11. Iijima S. Helical microtubules of graphitic carbon. *Nature*. 1991; 354: 56-58.
12. Yu JG, Zhao XH, Yu LY, Jiao FP, Jiang JH, Chen XQ. Removal, recovery and enrichment of metals from aqueous solutions using carbon nanotubes. *Journal of Radioanalytical and Nuclear Chemistry*. 2014; 299(3): 1155-1163.
13. Vadahanambi S, Lee SH, Kim WJ, and Oh II-Kwon. Arsenic removal from contaminated water using three-dimensional graphene-carbon nanotube-iron oxide nanostructures. *Environmental Science & Technology*. 2013; 47(18): 10510-10517.
14. Vecitis CD, Gao GD, Liu H. Electrochemical carbon nanotube filter for adsorption, desorption, and oxidation of aqueous dyes and anions. *The Journal of Chemical Physics*. 2011; 115(9): 3621-3629.
15. Ye YL, Tang YQ, Niu ZL, Su L, Guo ZJ, Wu WS. Experiment and modeling of the interaction of copper(II) and salicylic acid with oxidized multi-walled carbon nanotubes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2014; 451: 16-24.
16. Wang JP, Ma XX, Fang GZ, Pan MF, Ye XK, Wang S. Preparation of iminodiacetic acid functionalized multiwalled carbon nanotubes and its application as sorbent for separation and preconcentration of heavy metal ions. *Journal of Hazardous Materials*. 2011; 186: 1985-1992.
17. Alothman ZA, Habila M, Yilmaz E, Soylak M. Solid phase extraction of Cd(II), Pb(II), Zn(II) and Ni(II) from food samples using multiwalled carbon nanotubes impregnated with 4-(2-thiazolylazo) resorcinol. *Microchim Acta*. 2012; 177: 397-403.
18. Yoo DH, Rue GH, Seo JY, Hwang YH, Chan MHW, and Kim HK. Study of argon adsorbed on open-ended carbon nanotube bundles. *Journal of Physical Chemistry B*. 2002; 106(35): 9000-9003.
19. Rao GP, Lu C, Su F. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review. *Separation and Purification Technology*. 2007; 58: 224-231.
20. Baral SS, Das N, Ramulu TS, Sahoo SK, Das SN, Chaudhury G.R. Removal of Cr (VI) by thermally

- 311 activated weed *Salvinia cucullata* in a fixed-bed column. *Journal of Hazardous Materials*. 2009; 161:
312 1427-1435.
- 313 21. APHA-AWWA-WEF, Standard methods for examination of water and wastewater (20th ed)",
314 American Public Health Association, Washington DC, 1998.
- 315 22. Langmuir I. The constitution and fundamental properties of solids and liquids. *Journal of the American*
316 Chemical Society. 1916; 38: 2221–2295.
- 317 23. Freundlich HMF. Uber die adsorption in losungen. *Z Phys Chem (Leizig)*. 1906; 57A: 385–470.
- 318 24. Sun WL, Zhou K. Adsorption of 17 β -estradiol by multi-walled carbon nanotubes in natural waters with
319 or without aquatic colloids. *Chemical Engineering Journal*. 2014; 258: 185-193.
- 320 25. Perez-Aguilar NV, Muñoz-Sandoval E, Diaz-Flores PE, Rangel-Mendez JR. Adsorption of cadmium
321 and lead onto oxidized nitrogen-doped multiwall carbon nanotubes in aqueous solution: equilibrium
322 and kinetics. *Journal of Nanoparticle Research*. 2010; 12: 467-480.
- 323 26. Chen C, Li X, Zhao D, Tan X, Wang X. Adsorption kinetic, thermodynamic and desorption studies of
324 Th(IV) on oxidized multi-wall carbon nanotubes. *Colloids and Surfaces A*. 2007; 302: 449-454.
- 325 27. Ahmad AA, Hameed BH. Fixed-bed adsorption of reactive azo dye onto granular activated carbon
326 prepared from waste. *Journal of Hazardous Materials*. 2010; 175: 298-303.
- 327 28. Qaiser S, Saleemi AR, Umar M. Biosorption of lead from aqueous solution by *Ficus religiosa* leaves:
328 batch and column study. *Journal of Hazardous Materials*. 2009; 166: 998-1005.
- 329 29. Baral SS, Das N, Ramulu TS, Sahoo SK, Das SN, Chaudhury GR. Removal of Cr (VI) by thermally
330 activated weed *Salvinia cucullata* in a fixed-bed column. *Journal of Hazardous Materials*. 2009; 161:
331 1427-1435.
- 332 30. Al-Anber M. Adsorption of ferric ions onto natural feldspar: kinetic modeling and adsorption isotherm.
333 *International Journal of Environmental Science & Technology*. 2013; 12(1): 139-150.
- 334 31. Wan WS, Ghani SA, Kamari A. Adsorption behavior of Fe(II) and Fe(III) ions in aqueous solution on
335 chitosan and cross-linked chitosan beads. *Bioresource Technology*. 2005; 96: 443-450.
- 336 32. Bhattacharyya KG, Gupta SS. Adsorption of Fe(III) from water by natural and acid activated clays:
337 Studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Adsorption*. 2006;
338 12(3): 185-204.
- 339 33. Yeddou N, Bensmaili A. Equilibrium and kinetic of iron adsorption by eggshells in a batch system:
340 effect of temperature. *Desalination*. 2007; 206: 127-134.

- 341 34. Khalil MMH, Al-Wakeel KZ, Rehim SSAE, Monem HAE. Efficient removal of ferric ions from
342 aqueous medium by amine modified chitosan resins. Journal of Environmental Chemical Engineering.
343 2013; 15: 66-573.