

Response surface methodology, modeling to improve mercury removal from aqueous solutions using L-cysteine functionalized multi-walled carbon nanotubes

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Abstract

The aim of this study was to evaluate the mercury removal from aqueous solutions by using L-cysteine functionalized Multi-walled Carbon Nanotubes. The effect of pH, adsorbent dose, contact time and mercury concentration in removal efficiency was evaluated. Multi-walled carbon nanotubes were functionalized with L-cysteine. The Response Surface Methodology (RSM) was used to find the optimum process parameters. The results showed that an increase in contact time, pH and adsorbent dosage resulted in an increase of the adsorption rate. However, removal efficiency decreases by increasing mercury concentration. The highest and lowest removal efficiencies of mercury were 89% and 17%, respectively. The maximum adsorption rate was occurring at 120 min. It is concluded that L-cysteine functionalized multi-walled carbon nanotubes is an effective adsorbent for removal from aqueous solutions.

Keywords: Carbon nanotubes, L-cysteine, mercury, absorption.

1. Introduction

Contaminating of the water sources with heavy metal is one of the most challenging environmental issues. Heavy metals are normally found in small amounts in natural waters, soils and rocks with high concentrations in industrial wastewater (Boparai *et al.*, 2013). Industrial and agricultural activities are the major sources of the heavy metal which are releasing into the environment and consequently entering the human food chain (Zazouli *et al.*, 2014b; Chen *et al.*, 1999; Malakootian *et al.*, 2013). Meanwhile, mercury is known as a toxic and stable metal in the environment. Several epidemiological studies have demonstrated that mercury not only cause to irreversible neurological damages, but also can cause diseases such as Alzheimer, Mina Mata, tremors Paresthesia, and loss of vision, hearing, smell and taste, memory loss (Girginova *et al.*, 2010; Zhu *et al.*, 2009). Mercury with metallic odorless

and white silver color is the only metal that is liquid at room temperature. Mercury is widely used in various industries such as the paper industry, petrochemical industry, cosmetics, pharmaceutical and also agriculture (Zhu *et al.*, 2009). According World Health Organization (WHO) suggestion 0.001 mg L⁻¹ Maximum Concentration Level (MCL) mercury in drinking water. In addition, it was determined for natural mineral water, bottle drinking water and tap drinking water 0.001, 0.001 and 0.006 mg L⁻¹, respectively, by Institute of Standards and Industrial Research of Iran (Gibičar *et al.*, 2009). Also, maximum mercury concentration in wastewater effluent was stated 10 µg L⁻¹ by USEPA (Zazouli *et al.*, 2014b; Chen *et al.*, 1999). Existing used techniques remove mercury, such as chemical precipitation, oxidation and reduction process, electric flotation, ion exchange, reverse osmosis, evaporation, biological processes due to low efficiency are under question. Meanwhile, the use of adsorption process known as a cost-effective process (Maleki *et al.*, 2011; Zazouli *et al.*, 2013). The various substances have been studied as an adsorbent such as fruit shell of Terminalia Catappa (Inbaraj and Sulochana, 2006), sawdust (Šćiban *et al.*, 2006), biomass of the marine macroalga Cytoseira Baccata (Herrero *et al.*, 2005), mesocraps of orange and sour orange (Zazouli *et al.*, 2014a), activated carbon from furfural (Yardim *et al.*, 2003) and, biomass materials and waste tiers (Skodras *et al.*, 2007). Least amount of adsorbent and high removal efficiency are two important factors in selecting adsorbent so, carbon nanotubes are the most suitable material (Zazouli *et al.*, 2013). Carbon nanotubes (CNTs) are composed of different shapes and sizes graphite which are divided into single-walled (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) based on the number of layers of carbon atoms in their walls (Ren *et al.*, 2011). The chemical interaction between the metal ions and functional groups of CNTs level is the most important adsorption mechanism (Shamspur and Mostafavi, 2009). Modification surface properties of nanotubes can be

reduces emissions adsorption sites by adding functional groups (Ganjkhanelou *et al.*, 2014; Mansouri *et al.*, 2016). That is reported that adding functional groups help to improve metal ions adsorption and recovery of CNTs dispersion in water (Ren *et al.*, 2011). The aim of this study is to evaluate the mercury removal from aqueous solutions by using L-cysteine functionalized Multi-walled Carbon Nanotubes (L-MWCNTs) and, investigate the optimization of operation parameters such as pH, adsorbent dose, contact time and mercury concentration in removal efficiency using Response surface methodology (RSM).

2. Materials and methods

2.1. Chemical and reagent

Multi-walled carbon nanotubes (MWCNT, O.D. × L.D. 7-15 nm × 0.5-10 μm, ≤ 90% purity) and, L-cysteine were purchased from Sigma-Aldrich Co. Analytical standard of Mercury (HgCl₂) was purchased from Merck Co., Germany. Stock solutions (1000 mg/L) were prepared and serial dilutions of the stock solutions were obtained. Acid nitric (0.1 N) and NaOH (0.1 N) for adjusting pH of the solution was purchased from Merck Co.

2.2. Preparation of L-MWCNTs

MWCNT functionalization was performed by adding 5 g of carbon nanotube in 50 ml sulfuric (v/v 3:1). Then, nitric acid was dispersed in the solution and was suspended with *sonication* in an hour. The produced container was placed in a hot water bath at 50 °C and mixed with a magnetic stirrer for 8 hours and was cooled to room temperature. The oxidized nanotubes were isolated with 12,000 centrifuges and were rinsed repeatedly with Double-distilled water. Finally was dried under vacuum. Then oxidized nanotubes were dispersed in thionyl chloride at 60 °C degrees during 24 hours. In the next step, a solution of Triethylamine and Dimethylformamide solution was prepared from cysteine methyl ester salt. The nanotube prepared in the previous step was added to the environment. After 24 hours contact time at 55 °C, the nanotubes were separated and washed in three stages with deionized water. Finally, Modified nanotubes were put in the oven at 105 °C (Liu *et al.*, 2008). Surface morphology and surface functional groups of L-MWCNTs were determined by Scanning Electron Microscope (SEM, KYKY factory, China) and Fourier transform infrared spectroscopy (FTIR), respectively. Atomic adsorption spectrophotometer (WFX-210, RAYLEIGH model) instrument was used for determining Mercury.

2.3. Experimental design

Number of required experiments and also investigate the combined effect of the independent variables were estimated by using regression coefficients and Box-Behnken mode (Zazouli *et al.*, 2013). The four independent variables were pH, MWCNTs dose, initial Hg concentration, and contact time. The number of tests required for model was determined by $N = 2 K (K-1) + C_0$ equation that the N = number of samples (tests), K = number of factors (variables) and C₀ = the central

point number. A total of 27 experiments were introduced. Table 1 shows the ranges and levels of the independent variables. The low, middle, and high levels of each variable were designated as -1, 0, and +1 respectively (Zazouli *et al.*, 2013). A full quadratic model (FQM) was used to evaluate the obtained data. Optimizations were performed using Minitab 16 software. The experiments were conducted randomly to prevent systematic error. The coefficients of the full quadratic model were used to determine the Hg removal rate as an independent variable. The data were analyzed using the analysis of variance (ANOVA) and multiple regressions. The amount ($p \leq 0.05$) was set at the level of significance. The ability of the final model was evaluated by numerical and graphical analysis using the Minitab 16 software. This statistical model gives the final form of the equation.

Table 1. The studied independent variables and their coded levels and actual values

Variable	pH	Contact time	Hg concentration	L-MWCNTs dose
Unit	-	min	mg L ⁻¹	mg L ⁻¹
Symbol	X ₁	X ₂	X ₃	X ₄
+1	11	120	10	100
0	7.5	65	5.05	55
-1	4	10	0.1	10

2.4. Batch experiments

All the adsorption experimental setups was carried out according according Standard Methods for the Examination of Water and Wastewater guidelines (A.P.H. Association and A.W.W. Association, 1989). Removal efficiency of Hg was evaluated in different variables such as initial mercury concentration (10, 5.05 and 0.1 mg L⁻¹); pH (4, 7.5, 11); contact time (10, 65 and 120 min); and MWCNTs dosage (10, 55 and 100 g). At the end of each step, the supernatant liquids were filtered using 0.2 μm membrane filter to separate adsorbent. The purified samples were acidified by HNO₃ to pH less than 2. The acidify samples were stored in the 50 ml glass containers in the refrigerator before analysis by Atomic adsorption spectrophotometer.

3. Results and discussion

3.1. Characterization of L-MWCNTs

SEM images of the MWCNT_s (A) and, L-MWCNTs (B) was shown in following Figure 1. Figure 2 shows the FTIR image of MWCNTs and L-MWCNTs. Obtained result confirms presence of functional and connective groups on carbon nanotubes. FTIR spectrums of MWCNTs and L-MWCNTs show the stretching vibration band of hydrogen bonded alcohol, O-H, around 3435 cm⁻¹ that confirmed the presence of carbonyl on the surface of the nanotube. A vibration which is observed in the 3000 to 3200 is related to modify multi-walled carbon nanotubes in the form of the integration. In addition, CH₂- bond was correspond to vibrations in the 3435 cm⁻¹. L-MWCNTs has the characteristic stretching of amide carbonyl (C=O) and amide II ν (NH) stretching vibrations adsorption bands at 1637 and 1421 cm⁻¹, respectively.

The connection of a cysteine group to carbon nanotubes can be shown on the line appeared in the 1178 area which is related to the C-O stretching vibration.

3.2. Full quadratic model

The correlations between the Hg removal efficiency and parameters for the L-MWCNTs are described by:

$$Y = 41 + 17.25(X1) + 13.9167(X2) - 10(X3) + 9(X4) + 12.7083(X1)^2 \quad (1)$$

Where Y is the percentage removal of Hg (%) and X1, X2, X3, and X4 represent the coded values for pH, contact time, initial Hg concentration and L-MWCNTs dosage, respectively.

Table 2. Analysis of variance for the proposed model for Hg removal using L-MWCNTs

Source	DF	Sum of squares	Mean square	T	P-Value
Regression	14	9393.2	671.02	8.45	<0.00<
Linear	4	8066.8	2016.71	25.4	<0.001
Square	4	1157.4	289.34	3.64	0.036
Interaction	6	170	28.33	0.36	0.892
Residual error	12	952.8	79.4	-	-
Lack of fit	10	950.8	95.08	95.08	0.01
Pure Error	2	2	1	R-squared	90.79%
Total	26	10347	-	Adj R-squared	80.05%

DF: Degrees of freedom

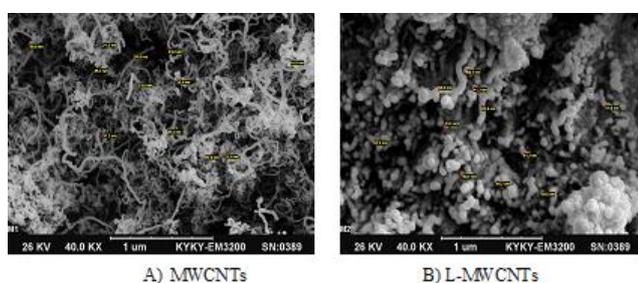


Figure 1. SEM images of Multi-Walled Carbon Nanotubes and MWCNTs (A) and, L-MWCNTs (B). Magnification: 40,000× and Accelerating Voltage: 30-26000 V

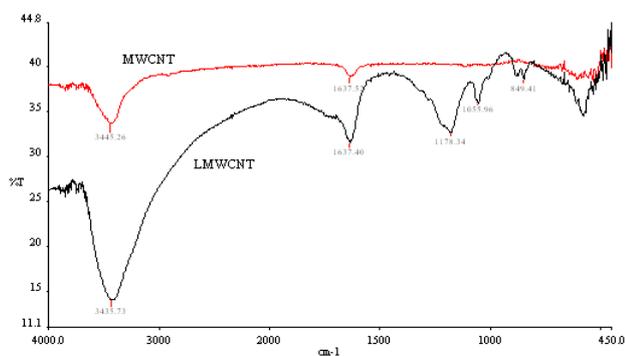


Figure 2. FTIR spectra of MWCNTs and L-MWCNTs

3.2.1. Model validation

To gain a suitable model, the results were summarized in a common ANOVA (Table 2). To confirm the goodness of fit between the model and the experimental results, regression coefficient (R-squared) analysis was applied. The adjusted R-squared values close to 1.0 indicate that the regression line fits the experimental data well (Asl *et al.*, 2012). This equation can be used to predict the results at specific points with accuracies of 80.05%. This model could also be used to predict the percentage of Hg removal at other adsorbents and times. The adjusted R-squared value is a modification of R-squared that adjusts for the number of explanatory terms in a

model. Unlike R-squared, the adjusted R-squared value increases only if the new term improves the model more than would be expected by chance. The adjusted R-squared value can be negative and will always be less than or equal to R-squared. The adjusted R-squared value is more suitable for comparing models with different numbers of parameters (Asl *et al.*, 2012). The adjusted R-squared value is 0.8005. Based on ANOVA analysis, experiment data in Table 2 show that the model statistically follows a linear pattern.

3.2.2. Verification of the response surface model

A scatter plot of results against predicted values from the model shows that the model is acceptable. The summary of variance analysis results for the L-MWCNTs are shown in Figure 3.

3.3. Effect of pH

Figures 4–6 shows the interactions between the independent variables and the dependent variable for the mercury removal by using L-MWCNTs. Figure 4 reveals that the removal efficiency increases with increasing adsorbent dosage and increasing pH. Also, Figure 6 shows that removal efficiency of mercury increases with increasing pH and contact time. In investigating of pH (4 to 11) with increasing contact time, the amount of mercury adsorption increased from 2.76 to 8.18 mg g⁻¹ and also, removal efficiency increased 30 % to 89 %. The maximum removal efficacy (89%) was observed at pH = 11 with 5.05 mg L⁻¹ initial mercury concentration, 120 minutes contact time and 55 mg adsorbent dosage. In addition, in this condition maximum adsorption capacity of MWCNTs was 32.9 mg g⁻¹. It will be demonstrated that even at low pH = 4 and 120 minutes contact time the removal efficiency can also be higher (70%). Several researchers have reported that the adsorption capacity of adsorbents rises with an increase in pH value (Tajar *et al.*, 2009; Wang *et al.*, 2010). Zazouli *et al.* reported that the adsorption rate of mercury from aqueous solutions in using a single-walled carbon nanotubes functionalized by L-cysteine increased by increasing the pH and the concentration of carbon

nanotubes (Anbia and Mohammadi, 2009). Also the result shows same result in investigating removal cadmium by single-walled and multi-walled carbon nanotubes functionalized by L-cysteine (Tajar *et al.*, 2009; Wang and Xing, 2004). Decrease adsorption efficiency at pH< 6.0 is due to electrostatic repulsion between the surface of L-MWCNTs, and the cationic mercury ions and the high concentration of H⁺ in the solution (Tajar *et al.*, 2009; Wang and Xing, 2004). On the other hand, number of the positively charged sites on the adsorbent surface decrease and the number of negatively charged sites increase by an increase in initial pH of the solution (Wang *et al.*, 2010). Vukovic *et al.* have reported that maximum adsorption rate for multi-walled carbon nanotubes oxidized occurred at pH = 6-10 (Anbia and Mohammadi, 2009).

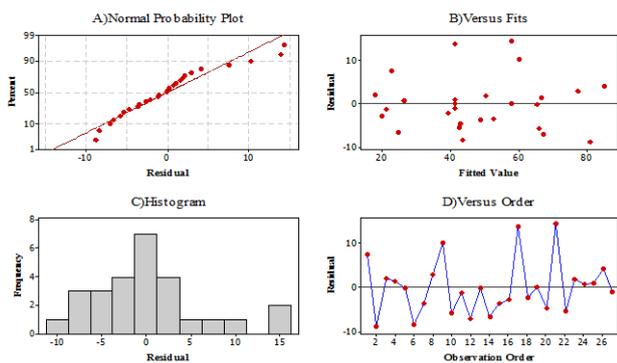


Figure 3. Residual plots for Hg removal via the L-MWCNTs

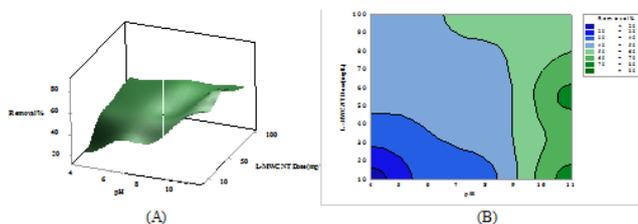


Figure 4. Response (A) surface plot and (B) contour plot of the mercury removal efficiency (%) as a function of pH and adsorbent dosage

3.4. Effect of L-MWCNT dosage

Mercury removal efficiency as a function of pH, adsorbent dosage and contact time, was illustrated in Figures 4 and 5. As obtained results mercury ions removal efficiency remarkably increased from 17 to 89% with an increase in L-MWCNTs dosage from 10 to 100 mg. Increase of adsorbent dosage resulted in greater availability of exchangeable sites for mercury ions (Al-Anber and Matouq, 2008). This result is same with the other researches results (Zazouli *et al.*, 2013, 2014b; Taghavi *et al.*, 2015). Maleki *et al.* achieved to 90% removal efficiency by increasing dosage until 5 g (Maleki *et al.*, 2011). The adsorbent structure can affect the behavior of adsorption. Also, by increasing the weight of adsorbent, the mercury percentage will increase and the amount of mercury ions adsorbed per unit weight of

adsorbent would be reduced (Puanggam and Unob, 2008). In addition, that is reported that by increasing the weight of granular activated carbon, the mercury removal rate increases and the ratio of absorbed mercury ions per unit mass will decrease (Zhang *et al.*, 2010). Kosa *et al.* have investigated heavy metal removal efficiency and have founded that by an increase in adsorbent mass from 0.05 to 0.25 g, the removal efficiency of Cd⁺², Zn⁺², Pb⁺² and Cu⁺² reached 0-39 %; 6.58-97.68%; 19.23-97.34% and 99.83-99.94 %, respectively (Kosa *et al.*, 2012).

3.5. Effect of contact time

The mercury removal efficiency as a function of contact time and adsorbent dosage. Shows at Figure 5. The mercury adsorption per unit mass of L-MWCNTs increases from 10.1 mg g⁻¹ at 10 min contact time to 24.8 mg g⁻¹ at 120 min contact time. Thus, the removal efficiency increases when contact time and the carbon nanotubes dosage increase. The maximum adsorption rate is 32.9 mg/g at 65 min contact time, which the removal efficiency of mercury is 68%. In the initial contact time, more active sites and more functional groups were available so, lead to more removal efficiency of heavy metal (Saif *et al.*, 2012). Available active sites and functional groups decreased with the passage the time so effect on the adsorption rate. Similar phenomena have been reported in the previous literature (White *et al.*, 2009; Xiong *et al.*, 2011). The optimum contact time for removal of mercury ions depend on the nanotubes dosage, pH and initial mercury concentration. Other research showed that mercury adsorption per unit mass of single-walled carbon nanotubes increases from 1.92 to 3.03 mg g⁻¹ and the removal efficiency increases from 38 to 60 percent (Zazouli *et al.*, 2014b). In the study which have done by at Iran on the removal of Biphenyl A by activated carbon and egg shell also reported same result (Zazouli *et al.*, 2013). Evaluation removal of Cd²⁺ by the monocarps of orange and sour orange also have same result (Zazouli *et al.*, 2014b). In the study which have done by Lu *et al.*, they reported that more time is needed to reach equilibrium adsorption and to increase adsorption efficiency by increasing the concentration of adsorbent, correspond to the present study (Liu *et al.*, 2008; Puanggam and Unob, 2008).

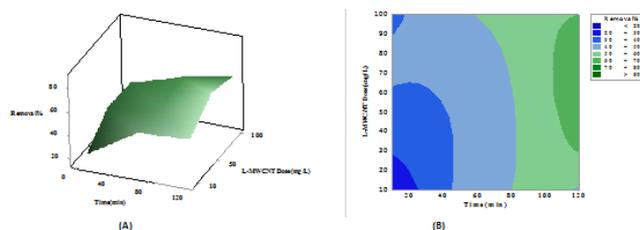


Figure 5. Response (a) surface plot and (b) contour plot of the mercury removal efficiency (%) as a function of contact time and adsorbent dosage

3.6. Effect of initial mercury concentration

The results show that initial mercury concentration has opposite effect on the removal efficiency. The removal

efficiency decreased from 72% at 0.1 mg/l of mercury concentration to 17% at 10 mg/l of mercury concentration (Figure 6). This phenomenon can be explained to saturation of active adsorption sites on L-MWCNT at the higher initial mercury concentration (Saif *et al.*, 2012). In other words, at lower mercury concentrations, the ratio of initial moles of mercury to the available adsorption sites is low, so, higher removal efficiency adsorption can be achieved (Boparai *et al.*, 2013). With the increase in mercury concentration from 1.0 to 10 mg L⁻¹ at the contact time of 10 minutes, pH = 7.5 and adsorbent dosage of 55 mg, removal efficiency decreased from 45 to 27 percent; and in a contact time of 120 minutes, pH = 7.5 and adsorbent dosage of 55 mg, the removal efficiency decreased from 60 to 57 percent. In the study which have applied carbon nanotubes to removal of chromium adsorption efficiency decreased with increasing its initial concentration in the solution. The results were consistent with the present study (Hu *et al.*, 2009). Other literature have also reported same result (Zazouli *et al.*, 2013, 2014b).

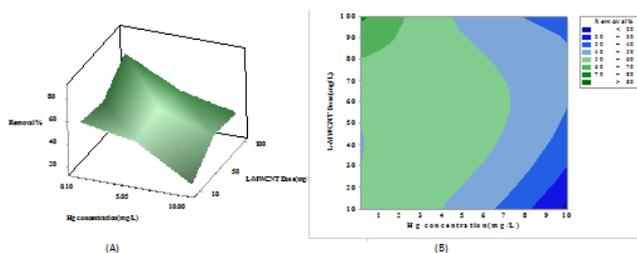


Figure 6. Response (A) surface plot and (B) contour plot of the mercury removal efficiency (%) as a function of mercury concentration and carbon nanotubes dose

In compression efficiency of single-walled and multi-walled carbon nanotubes functionalized by L-cysteine in Cd²⁺ results showed that single-walled carbon nanotubes have higher efficiency than multi-walled carbon nanotubes. Also by increasing the pH and the concentration of carbon nanotubes, the removal efficiency increases (Zazouli *et al.*, 2013). Also, another research reported that Hg²⁺ removal efficiency decreased by increasing of initial Hg concentration. In addition they mentioned that the adsorption rate increased by increasing of pH, contact time and mass CNTs dose. And the maximum and the minimum adsorption rate were reported 95 and 22 percent, respectively (Zazouli *et al.*, 2014b). However, the total amount of mercury adsorbed rapidly increased with an increase in the amount of initial mercury concentrations. High mercury concentration at the higher initial mercury concentrations, led a higher driving force for the mercury ions from the solution to the adsorbent (Gupta and Nayak, 2012; Tofighy and Mohammadi, 2011). Thus, more collisions occurred between mercury ions and active sites on the adsorbent. Therefore, the amount of adsorbed mercury ions on L-MWCNTs increased at higher initial cadmium concentration.

4. Conclusion

This research was performed to evaluate the efficiency of the multi-walled carbon nanotubes functionalized L-cysteine for mercury removal from aqueous solutions. The results reveal that the adsorption of mercury to L-MWCNTs is strongly dependent on initial pH, L-MWCNTs dosage, initial mercury concentration and contact time. With an increase in L-MWCNTs dosage, contact time and pH has a positive effect on the removal efficiency, which the removal efficiency of mercury ions increased. However, an increase in the initial concentration of mercury ions caused by an increase and decrease in the amount of mercury ions adsorbed per unit weight of the L-MWCNTs (q_e) and the removal efficiency of mercury ions, respectively. Finally, the multi-walled carbon nanotubes functionalized L-cysteine is an effective adsorbent for metal removal from aqueous solutions especially mercury ions.

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