

Original Article



Removal of mercury (II) from aqueous solutions by multi-walled carbon nanotubes coated with manganese oxide

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Abstract

Background and aims: Water pollution by heavy metals is one of the most important environmental problems. Among the heavy metals, mercury (Hg) is a very toxic metal and its high concentration can lead to impaired pulmonary and renal dysfunction. The aim of this study was to determine the amount of Hg removal by carbon nanotubes coated with manganese (Mn) oxide from aqueous solutions.

Methods: In this study, multi-walled carbon nanotubes coated with Mn oxide were prepared and used to remove Hg from aqueous environments. In addition, the physical and structural characteristics of the nanotubes were determined by the X-ray diffraction (XRD). The impact of diverse variables was further investigated, including the initial concentration of Hg, the initial pH of the solution, contact time, mixing rate, as well as the amount of nano-composite and the impacts of confounders (nitrate and chloride). Finally, optimum conditions for each of these parameters were obtained by the Taguchi statistical method.

Results: The XRD analysis showed that the nanotubes were properly coated with Mn oxide. Furthermore, the results demonstrated that under pH 7, the rate of mixing of 150 rpm, the contact time of 60 minutes, the amount of nano-composite of 60 mg, and the initial density of Hg 80 mg/L can be achieved by removing 95% Hg. Moreover, the confounder factors of nitrate and chloride reduced the amount of Hg removal by 4 and 5%, respectively.

Conclusion: Based on the results, the nanotubes coated with Mn oxide can be used as easy and strong absorbents for the rapid absorption of Hg from drinking water and industrial wastewater.

Keywords: Mercury, Multi-walled carbon nanotubes, Nano-manganese, Taguchi method

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Introduction

Nowadays, water pollution is undoubtedly one of the major problems facing the world (1). In addition, pollution by heavy metals is one of the most important environmental problems (2). Contrary to the organic pollutants of heavy metals, they cannot be decomposed but can accumulate in living tissues and thus constitute a major threat to human health and the environment (3). Among the heavy metals, mercury (Hg) is considered as a very toxic metal that even has a high toxicity in low doses (1). This metal may come from natural phenomena such as volcanic activity, erosion, mineral deposition, and extensive human activities such as mining, smelting, coal production, coal-fired power plants, paper pulp production, and residential heating systems, due to which disposal waste, waste incineration, and chemical synthesis enter the environment (4). Neuromuscular and renal disorders are the main causes of

Hg poisoning. This metal can also easily pass through the blood and brain barrier and affect the fetus's brain. A high concentration of Hg⁺² results in impaired pulmonary and renal dysfunction and causes pain in the chest (5).

According to the World Health Organization guidelines, the allowed amount of mineral Hg in drinking water is 0.06 mg/L and its total daily intake is 2 µg/kg of body weight (6). Given the high importance of Hg, many methods are used for its removal from aqueous solutions, some of which include precipitation, ion exchange, adsorption, and more advanced methods such as reverse osmosis, membrane processes, evaporation, and solvent extraction. These methods have often several disadvantages such as expensive equipment and operations, sludge production, or other toxic waste, as well as the need for high energy and vast space. Among these methods, adsorption, due to its easiness and low

cost, is an efficient and cost-effective method for removing heavy metal ions in low and medium densities, as well as for its lower sludge production compared to conventional methods for the removal of heavy metals such as chemical treatments that have attracted many researchers' attention. In recent years, different studies have used the absorption method to remove mixed and non-mixed carbon monoxide oxidized nanotubes in order to eliminate heavy metals such as Hg. For example, Saleh et al. examined the combination of multi-walled carbon nanotubes with manganese (Mn) dioxide to remove arsenate and obtained favorable results in this regard. Also, Wang et al used this combination to remove lead, which is extremely more than non-compound carbon nanotubes (7,8). The advantages of nanotubes can be eliminated from many conventional adsorbents and the conventional methods can be noted as follows.

Heavy metal removal is much more effective than active carbon (7). Heavy metals have high reactivity and create strong interactions between nanotubes and contaminating molecules (8,9). Further, nanotubes are easily refined and reused (10), and their surface area, high absorption capacity, and simple refining increase the absorption capacity (11). According to previous evidence, if carbon monoxide nanotubes are combined with Mn oxides, nano-composite is obtained, which has a specific absorption capacity and specific surface area that is much higher than that of non-oxidized carbon monoxide nanotubes (12).

The above-mentioned problems occur due to the presence of Hg in water and the lack of satisfactory efficiency in these methods. On the other hand, Mn oxide-coupled nanotubes have the most desirable performance in comparison with non-combinational carbon monoxide nanotubes. Therefore, the present study aimed to use multi-walled carbon nanotubes coated with nanotubes for Hg removal and to evaluate the impacts of effective factors such as pH, contact time, Hg concentration, mixing rate, and the interfering effect on Hg removal efficiency.

Materials and Methods

The present experimental study was performed on a laboratory scale. In this research, the required carbon nanotubes were supplied from Tehran Oil Industry Research Institute. Other chemicals such as potassium permanganate, Mn sulfate, mercuric chloride (HgCl_2), nitric acid, chloride, sodium hydroxide, ammonium hydroxide, and 99% pure ethanol were all prepared from Merck Company (Germany) (7,11).

Moreover, the Varian 240 atomic absorption device and the X-ray diffraction (XRD) were used to measure the amount of Hg and to determine the structural phases of XRD, respectively. All chemicals were purchased in analytical purity and used in the experiments directly without any further purification.

Preparation of Carbon Nanotubes

Nanotubes must be oxidized to increase the removal rate of carbon nanotubes. For this aim, carbon nanotubes were placed in concentrated nitric acid (65%) at 70°C for 12 hours. Then, they were separated by filtration, rinsed with distilled water, and placed in a continuous apparatus for six hours at 110°C. Next, the oxidized carbon nanotubes were again placed in nitric acid at 50% concentrated and at 120°C for 12 hours in order to obtain their purity. Finally, they were washed by filtration and distilled water for 24 hours at the oven machine until they were dried (11).

Stages of multi-walled carbon nanotubes coverage with Mn nano-oxide

About 5 g of oxidized nanotubes was added to 250 mL of 0.5 M potassium permanganate solution and the mixture was then stirred at 70 °C and rotated at about 500 rpm, followed by preparing 200 mL of Mn sulfate 0.125 M and 100 mL of sodium hydroxide 0.225 M. Then, the two solutions were added drop-wise to a potassium permanganate mixture and nanotubes until producing a tall brown solution of Mn oxide. The solution was then heated at a temperature of 70°C for an hour. After the end of the set time, the suspension was filtered off, washed with distilled water, and dried at 110°C by the oven (13). Finally, the XRD was used to determine the characteristics of the nano-composite structure.

Experimental Procedures

First, the parameters of pH, contact time, mixing rate, and the amount of nano-composite were given to the Mini-Tab software to design the test surfaces. Then, the experiments were carried out based on the information obtained from the Mini-Tab software. In this experiment, the Taguchi test method was used to determine the sample size, and the number of samples was 100 with three replicates to 300. In addition, the stock solution was daily prepared using HgCl_2 chloride (13). Then, the dilutions of 20, 40, 60, and 80 mg/L were prepared as well. Subsequently, the amounts of 10, 20, 40, 60, and 80 mg of the composite were separately added in Erlenmeyer flasks with a volume of 100 mL and mixed with 0, 50, 100, 150, and 200 rpm at the pH values of 3, 5, 7, 9, and 11 during the contact time of 10, 20, 40, 60, and 80 minutes, respectively. In most similar studies, after the 80-minute contact, the removal rate remained almost constant, thus the contact time was not considered to be higher than 80 minutes in this study (1,13-15). Finally, the nano-composite was measured using a separation filter and solvent to determine the residual Hg by atomic absorption. It should be noted that all experiments were repeated twice.

After the experiment, the Mini-Tab software and the Taguchi method were used to analyze the data and to determine the optimum conditions of the test, respectively. The criterion for selecting the parameter as the optimal

Table 1. Average mercury removal efficiency in optimal conditions

Initial Concentration of Mercury (mg/mL)	pH	Nano-composite (mg/mL)	Mixing Time (min)	Mixing Rate (rpm)	The Average Mercury Removal Efficiency ± SD
20	7	20	10	150	91.33 ± 5
40	7	20	20	150	92.8 ± 3.5
60	7	60	60	150	93.2 ± 6
80	7	60	60	150	94.8 ± 3

Note. SD: Standard deviation.

signal to noise ratio (S/N) is more in Taguchi analysis. This ratio was obtained from Equations (1) and (2). At least, the mean square deviations (MSDs) are calculated by the mini-Tab software and the software yields the S/N output (16). In the optimal conditions, the experiments were repeated three times and the effect of the anions (nitrate and chloride) on the absorption of Hg was investigated accordingly.

$$MSD = \frac{1}{n} \left(\frac{1}{y_1^2} + \frac{1}{y_2^2} + \dots + \frac{1}{y_n^2} \right) \quad \text{Eq. (1)}$$

$$S/N = -\log(MSD) \quad \text{Eq. (2)}$$

MSD = The minimum average square of standard deviations

N = The number of test repetitions

y_n = The measured response value for each test

Ethical considerations

This paper was derived from a research project that was approved (approval No. 1537) by the Assistance of Research and Technology with the collaboration of Shahrekord University of Medical Sciences under the ethics code of IR.SKUMS.REC.92-7-21.

Results

The effects of time variables, mixing speed, and pH, as well as the nano-composite values for concentrations of 20, 40, 60, and 80 mg/L were examined separately. Thus, the experiments were repeated twice for each concentration and then the results of the experiment were analyzed by the Taguchi method using Mini-Tab software. The results are shown in Figures 1-4

After obtaining the optimal conditions using the Taguchi analysis, the experiments were repeated three times, the results of which are presented in Table 1. Then, the effect of the interfering factors (nitrate and chloride) on the amount of Hg removal was examined with the optimal conditions in different concentrations of Hg. The related data are shown in Figure 5.

Characterization of nanotubes coated with manganese oxide

Carbonate nanotubes oxidized from the XRD were used to study the identification of crystalline phases of nano-composite (Figures 6 and 7). XRD was analyzed by X'Pert High Score software. Using the Sigma Plot software and the Scherer equation (3), the mean particle size of the nano-sized composite was 29 nm with the peaks in the XRD diagram and fitting peaks (16-20).

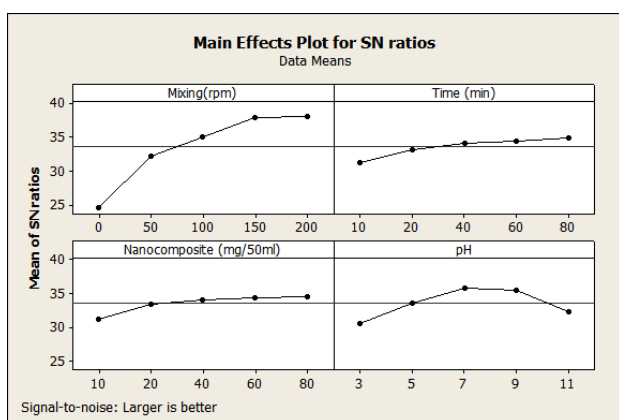


Figure 1. Determination of optimal conditions for mercury removal in the concentration of mercury input of 20 mg/L using the Taguchi test and selecting the signal/noise mode (S/N), the largest, and the best.

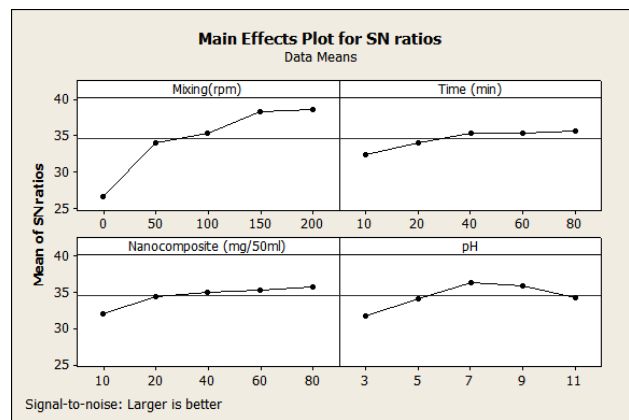


Figure 2. Determination of Optimal conditions for mercury removal in the concentration of mercury input of 40 mg/L using the Taguchi test and selecting the signal/noise mode (S/N), the largest, and the best.

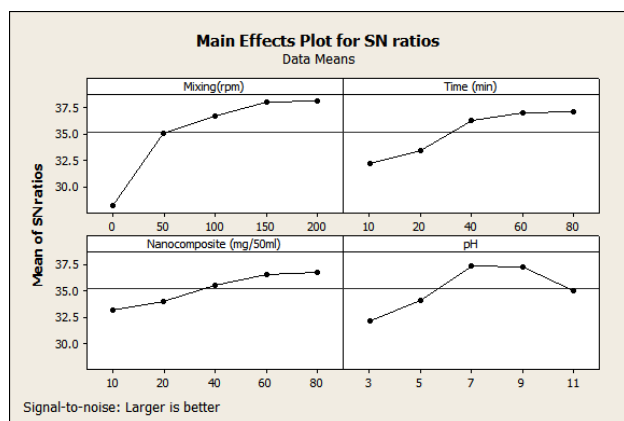


Figure 3. Determination of optimal conditions for mercury removal in the concentration of mercury input of 60 mg/L using the Taguchi test and selecting the signal/noise mode (S/N), the largest, and the best.

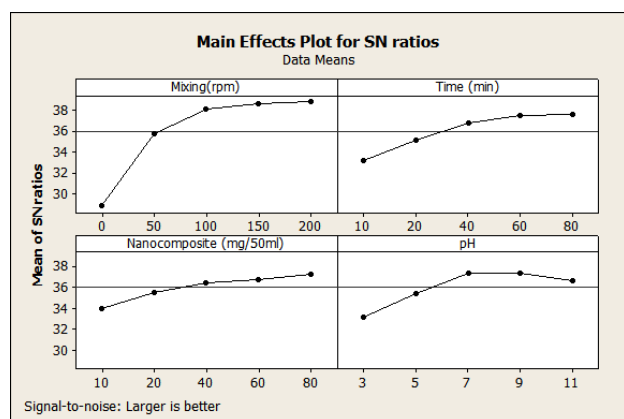


Figure 4. Determination of optimal conditions for mercury removal in the concentration of mercury input of 80 mg/L using the Taguchi test and selecting the signal/noise mode (S/N), the largest, and the best.

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{Eq. (3)}$$

In the above equation,

d = the particle size (nm)

λ = the wavelength of the X-rays (nm)

β = the peak width at half of its height (radian)

2θ = the angle of diffraction (degree)

Discussion

Effect of mixing speed

In all concentrations (20, 40, 60, and 80 mg/L) of Hg, there was a significant increase in the removal rate of Hg by increasing the mixing rate from zero to 150 rpm (Figures 1-4). In addition, increasing the mixing speed from 150 to 200 rpm resulted in a slight increase in the signal/noise mode (S/N). This mixing rate is not economical and thus the best mixing rate of 150 rpm was considered in this study. Generally, the amount of Hg absorption increases

by increasing the mixing rate from zero to 150 rpm, which is due to a change in the thickness of the boundary layer around the adsorbent particles. The thickness of this layer decreases as the mixing rate increases, leading to an increase in the absorption of Hg (11,20). Further, increasing the mixing speed improves the release of Hg ions on the surface of the nano-sized composite, thus increasing the absorption of Hg by nano-composites.

Consequently, as the shaking speed increases, a reduction occurs in the boundary layer surrounding the particle. The mass transfer effect became insignificant because the system was well-mixed under higher shaking speed (17-20). Studies by Gupta et al, Amin et al, and Tawabini et al (21) achieved similar results in this regard. In these studies, the removal of chromium and Hg increased by increasing the mixing rate from zero to 150 rpm (11,20,21) considering that the mixing speed was not more than 150 rpm.

The effect of contact time

According to Figure 1, the Hg input did not show a high increase in the ratio of S/N as well as the percentage of removal of Hg by increasing the contact time from 10 to 80 minutes for the concentration of 20 mg/L. Due to the fact that the concentration of Hg is low in adsorbent and adsorption sites, less time is needed to absorb Hg at this concentration (20 mg/L). Therefore, the best contact time for this concentration was considered 10 minutes. Considering that there was not much increase in Hg

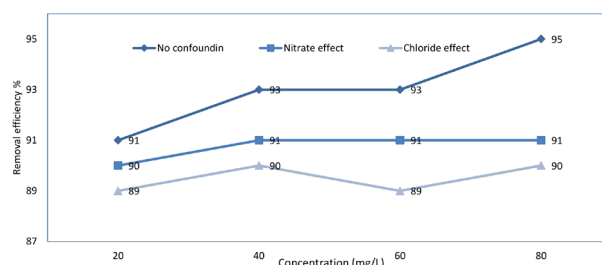


Figure 5. The effect of confounder factors (nitrate and chloride) on mercury removal efficiency.

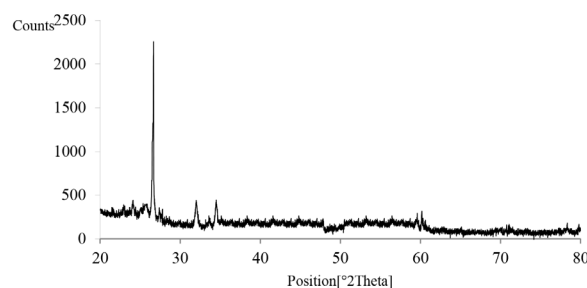


Figure 6. The x-ray diffraction of oxidized multi-walled carbon nanotubes.

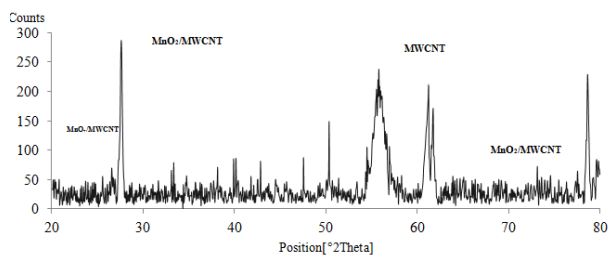


Figure 7. The x-ray diffraction of multi-walled carbon nanotubes coated with manganese oxide.

removal rates, as well as a concentration of 40 mg/L of Hg by increasing the contact time from 20 to 80 minutes, the proper contact time was considered 20 minutes. This contact time is also economical. In addition, the concentrations of 60 and 80 mg/L of Hg were considered suitable for 60 minutes. This phenomenon is due to the fact that the Hg molecules can be quickly absorbed on the adsorbent surface in the early stages of adsorption, but the velocity of the pollutant adsorption as the initial adsorption phenomenon is vigorous, which slows down as the process proceeds. Within the pores, the repulsive force between the negative charges absorbed on the adsorbent surface and the negative charges in the fluid mass decreased (22). Kosa et al obtained the same results. In this study, the contact time from 10 to 200 minutes was investigated, by which the contact time increased up to 60 minutes and then remained constant (14).

Effect of nano-composite dose

Based on Figures 1 and 2 of the nano-composite optimum value for 20 and 40 mg/L of Hg, 20 mg was obtained and 60 mg/L of Hg (Figures 3 and 4) was considered to be 60 mg/L. In general, the amount of Hg absorption increased significantly by increasing the amount of the nano-composite due to increasing the adsorption surface, as well as possible access to the adsorption sites with the results of the Kosa et al and Amin et al (14,20). The reason for such a phenomenon is the unsaturated active sites in the pollutant adsorption. In other words, some adsorption sites remain unsaturated during the adsorption process. These findings are in line with those of Zheng et al (23), Wang et al (24), and Khodabakhshi et al (25).

Effect of pH

The aqueous solution pH is an important controlling parameter in heavy metal adsorption processes. According to Figures 1-4, the initial pH values of 20, 40, 60, and 80 mg/L were considered the best values for the removal of Hg, which corroborates the results obtained by Jamshidi Shadbad et al (26). The reason for reducing the absorption

capacity of Hg at a pH of 3 or less is that the chloride in the solution produces highly stable compounds at low pH values. Compounds such as HgCl_2 , and reduce the amount of Hg uptake (27). Further, H^+ ions compete with Hg^{+2} on the surface of the nano-composite in acidic pH, which reduces the absorption of Hg^{+2} (28,29). At a pH greater than 4, almost all the Hg contained in the solution is $\text{Hg}(\text{OH})_2$ mercuric hydroxide (27) and the absorption of this compound on the nanoscale surface is high. However, the compounds of mercuric hydroxo complexes such as $\text{Hg}(\text{OH}_4^-)$ and $\text{Hg}(\text{OH}_3^-)$ are formed by increasing the pH at a level greater than seven. Furthermore, these compounds are soluble in water and do not react with nano-composite surfaces. Moreover, in alkaline pH values, competition begins between the Hg ions and this group by an increase in the OH^- group, and the OH^- sites occupy the absorbent material, which is why the absorption of Hg on the surface of the nano-sized composite decreases in the alkaline pH (1,30).

Effect of confounder (nitrate and chloride) on Hg removal rate

According to Figure 5, chloride and nitrate reduce the amount of Hg removal and ion chloride has a greater effect on nitrate removal than Hg removal. The maximum percentage of Hg removal without interfering agents is 95%, while this removal percentage decreased to 89.63 and 90.8%, respectively by the addition of chloride and nitrate. In the presence of chloride ion, this ion with Hg forms stable compounds such as HgOHCl , HgCl^+ , HgCl^+ , HgCl_2 , and. These compounds lead to a reduction in Hg absorption. At $\text{pH} = 7$ (the optimum pH), the effect of these compounds on Hg removal is lower than the acidic pH. However, according to Figure 5, chloride has a negative effect on the rate of Hg removal (31). The chloride anion is more inclined to correlate with the complex Hg, which is why chloride is quickly combined with Hg and forms stable compounds by adding the chloride. On the contrary, nitrate has fewer tendencies for complex formation with Hg due to less effective results on the amount of Hg removal by the nano-composite, which is in conformity with the results of Yu et al and Amin et al (19,20,32).

The XRD was used to determine the structural phases of oxidized carbon nanotubes and oxidized carbon nanotubes coated with Mn oxide, the results of which are shown in Figures 6 and 7, respectively. The XRD analysis of nanotubes demonstrated that the pattern phases are more than $2\theta = 27.5$ and 57.5 , indicating MWCNTs and $\text{MnO}_2/\text{MWCNTs}$, respectively. These peaks revealed that Mn oxide formed at the surface of MWCNTs was $\delta\text{-MnO}_2$ polymorph, which conforms with the results obtained by Abdel Salam et al and Ting et al (12,33)

Conclusion

The results of this study showed that carbon nanotubes coated with manganese oxide can be used as an easy and strong adsorption process to absorb Hg from drinking water and industrial wastewater. Therefore, this composition has good adsorption capability in high concentrations of Hg. Moreover, the results indicated that chloride and nitrate decrease the amount of Hg removal, and the ionic chloride has a greater effect on reducing the amount of Hg removal compared to nitrate. Eventually, the XRD results indicated that the size of the composite particles is nanoscale (29 nm).

Conflict of Interests

None.

Acknowledgment

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