



Removal of heavy metal ions from wastewater by carbon nanotubes (CNTs)

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HIGHLIGHTS

- Functionalized MWCNTs show better dispersibility in water.
- In addition to its far lower with decreasing of the initial concentration of the cadmium. The optimum pH values was 5.5, the dose of adsorbent was 1g functionalized Multi Wall carbon Nanotubes(f-MWCNTs) /100 ml of Cd+2.
- The Freundlich isotherms model is fitted for Cd(II).
- The exhaustion time and breakthrough are decreased as initial heavy metal ion molecules concentration increase.

ABSTRACT

This work is an attempt to remove cadmium (II) from wastewater by adsorption on multi-walled carbon nanotubes (MWCNTs) and functional group of carbon nanotubes (fMWCNTs) by using the batch process system and continuous reactor. In the batch reactor, the main variables that govern process efficiency such as the initial Cd (II) concentration, MWCNTs dose, contact time, stirring speed, and pH were studied. The experiments revealed that the amount of cadmium absorption (II) was higher on the increasing fMWCNTs dose and stirring speed. In addition, it decreased significantly with a decrease in the initial concentration of cadmium. The optimum values for the ratio of the acidic function in solution 5.5, the adsorbent dose (fMWCNTs) 1 g in 100 ml of Cd (II) solution, and the contact time was 30 minutes, in addition to C_0 of 125 mg per liter of the cadmium ion with mixing speed (stirring) 100 rpm, these are the optimum values by which the cadmium ion removal efficiency was obtained for no more than 99%. Equilibrium data were better explained by the Freundlich isotherm model which was converted inside what was achieved with 30 minutes of Cd⁺².

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1. Introduction

The wastewater containing heavy elements is the most important problem facing society because they are non-degradable and also because of the accumulation of organic tissues [1-2]. Cadmium is a Heavy metal present in multiple different forms such as Cd⁺². The essential sources of Cd are metallurgical, electroplating, certain defense equipment, and cosmetics manufacturing [3-4]. Several mechanisms possess been developed to eliminate profound metals from waste. These techniques are precipitated, electrochemical communication dissolvent extraction, ion commercialism, and adsorption. Sorption is an oblancoate mechanism [5]. The (CNTs) are Inherent in an element that is characteristic, a tube-like or hollow system [6]. CNTs can be Single-Walled sheets nanotubes (SWNT) and Multi-Walled sheets nanotubes (MWNT) As shown in Fig (1). CNTs possess saga Characteristics that are applied in widely Industries such as the electronics industry, wet remedy, and added doggy of Great science [7]. CNTs are somebody double circumstantial opencast region and teensy, sunken, and layered structures [8] CNTs are large peculiar articulator roof as shaft as the existence of a vast vision of rising useable set [9]. Sheets Nanotubes (CNTs) are open to hit extraordinary voltage which is a nice sorbent for the sorption of Cd (II) in water solution. The sorption factors, such as the value of MWCNTs, contact time, arousal quicken, and pH affect the elimination of Cd⁺² [10]. The outcome Separation between the of Cd⁺² is fundamentally referred to as the annuity of Cd+2 to the physiological and chemical features of the CNTs. Rao et al. [11] Have intended the separation of divalent mix ions (Cd+2) from solution statements using modified CNTs serene and cover change sheets nanotubes (CNTs) for adsorption.

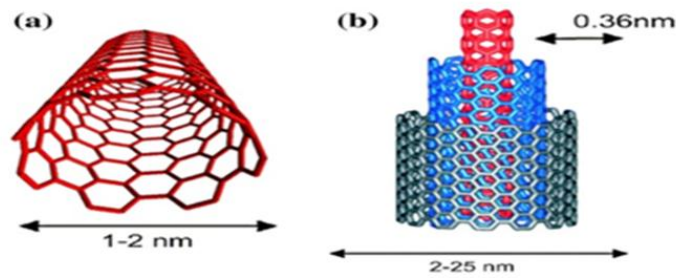


Figure 1: (a) Single-Walled sheets Nano. (SWNT), (b) Multi-Walled sheets Nano. (MWNT)

2. Chemicals and equipment's

Table 1: Chemicals and equipment's

Chemicals	Equipment's
Multi Walled carbon nanotubes. 99% purity and external D. (13-18) nm and have particles length 3-30 μm . (Sigma Aldrich, USA). cadmium nitrate tetrahydrate [Cd(NO ₃) ₂ .4H ₂ O]	Electronic balance - M-Power Gem gold. (Country of Origin: Korea) Meter of pH (5011A, Epode). (Country of Origin: Japan). Spectrophotometer, (7000 UV- Jenna Type). (Country of Origin: Germany) Sulfuric acid and nitric acid for functionalization of the MWCNTs. (Country of Origin: England) Hydrochloric acid (HCl) and Sodium hydroxide (NaOH) to control the pH. (Country of Origin: England) Microwave for airing the sample, (WZF, 2070). (Country of Origin: Korea) Sonication with 60 KHz. Italy. (Country of Origin: Korea) Magnetic stirrer. Germany. (Country of Origin: Sweden) Atomic absorption spectrophotometer type: (Shimadzu). (Country of Origin: Australia)

3. Materials and Methods

3.1 Materials

3.1.1 Multi-Walled carbon nanotubes (MCNTs)

MWCNTs, of 99% purity and external D. (13-18) nm and have particles length (3-30) μm , the internal diameter is 4.5 nm \pm 0.5 nm, roof area of 220 m²/g, was purchased from Sigma Aldrich, USA. It was selected as a sorbent for this work for its suitable sorption characteristics of heavy metal ions from solutions.

3.1.2 Cadmium ion (II)

Solution of Cd²⁺ containing 103 mg/L solutions were prepared by dissolving 2.758 g of cadmium nitrate tetrahydrate [Cd(NO₃)₂.4H₂O] in 1 L of deionized water with the aid of a magnetic stirrer.

3.2 MWCNTs Functionalization

One gram of MWCNTs was soaked within 100 ml (1:2) mixture by volume of concentrated HNO₃:H₂SO₄ at 25°C with sonication at 60 KHz for 30 min. The mixture was filtered and diluted, then washed with deionized water to remove the acid. The left solid was dried at 110°C in a microwave, grind, and shrieved to ash [12].

New methods and procedures should be described in detail while well-established methods can be briefly described and appropriately cited. A brief description of the characterization of the materials testing instruments or design and manufacturing of a test rig should be present. Present the name, version, and code of any software used in the research work. Page: 1940 In this section, the author should be state manufacturer, city, and country from where the equipment has been sourced.

3.3 Methods

Two types of experimental setup were carried out in this study, the batch process was used in the first one, and the continuous system in the second as shown in the following:

3.3.1 Batch system

To measure the equilibrium isotherm curves the batch process was used, and the equilibrium isotherm datum was measured.

The optimum pH was adjusted using by using 0.1 moles from both NaOH and H₂SO₄. The temperature for the workout was 25°C ±. The optimum mass values of multi-wall carbon nanotubes (MWCNTs) were 0.1, 0.15, 0.20, 0.25 g/100 ml. The best pH value substance equal was 5.5 was utilized for Cd⁺² in this work. The experiments were used to acquire the isotherm balance, equilibrium scheme for Cd + 2 by plotting the mass of the adsorbent material for each mass of adsorbents, Q_E, against the equilibrium concentration of the substance C_e, then to obtain the isotherm equilibrium constants. A solution of 100 ml cadmium (II) was applied at different initial concentrations of (25-125) mg/l in vials containing the stable mass of adsorbents. The vials were shaken at a constant speed of (100) rpm in the device from a jar test at 25 ± 1 ° C for 30 minutes. The adsorbent was detached after shaking by refinement through a filter sheet (0.2) μm in pore size. The remaining Cd (II) concentration was analyzed by atomic absorption spectrophotometer (AAS). Factors affecting adsorption such as pH, contact time, agitation (stirring) speed, amount of sorbent, initial concentration were studied, and all details are shown in Table (2).

3.3.2 Continuous system

A simple laboratory stager fixed-bed absorber was built in the Laboratory of Environmental Central, Ministry of Environment, Iraq. The media (MWCNTs) were filled in the vessel to the coveted depth and federal to the vessel as a slurry by blending the packed with deionized water in order to avert the consistency of air blister within the media. After that, the substance was placed in the entry vessel, and the flux was regulated by checking valves one and two. The polluted water of synthetic was equipped, and its pH was regulated to the coveted value and then put up in the entry vessel to flow with the vessel by gravity, these samples were collected every 15min from the outing and its Cd⁺² ion concentration was found by (AAA). Experiments were carried out at various flow rates (Q) and bed heights (H). Table (3) shows the experimental conditions.

3.3.3 Equilibrium Isotherms

The adsorbent area of the sorption of heavy metal ions at the time was calculated by mass balance equation [13]

$$q=V(C_0-C_e)/W \quad (1)$$

Table 2: Conditions of batch tests for Cd+2

Test type	Type of adsorbent	W g of (adsorbent / 100 ml)	pH	C _i (mg/L)	Time of stirring min	Speed of stirring rpm
Effect of PH	MWCNTs	0.1	(2, 3, 4, 5, 5.5, 6, 6.5, 7)	50	30	100
Effect of adsorbent amount	MWCNTs	0.1,0.15, 0.20,0.25	5.5	50	30	100
Effect of contact time	MWCNTs	0.1	5.5	50	(10, 20, 30, 40, 50, 60, 70)	100
Effect of initial Cd (II) concentration & biosorption isotherm (by changing C _i)	MWCNTs	0.1	5.5	(25,50, 75, 100,12 5)	30	100
Effect of stirring speed	MWCNTs	0.1	5.5	50	30	(0, 50, 100, 200)

Table 3: The experimental conditions for fixed-bed experiments

Sorbent	MWCNTs
Adsorbate	Cd(II)
Flow rate (Q), L/hr	1, 3, 5, 7
Bed height (H), cm	10, 20, 30
Temperature (T), °C	25 ± 1
pH	5.5
Concentration (C _i), mg/L	100

Where q (mg/g) is the adsorbed amount, V (L) is the volume of a total of adsorbate, C₀ and C_e are the initial and effluent concentration of an adsorbate substance at equilibrium in (mg/l) respect., W (g) is the adsorbent weight.

The efficiency of removal is given by [14]:

$$\% \text{ Adsorption} = (C_0 - C_e / C_0) * 100 \quad (2)$$

Where: C_0 is the initial concentration of adsorbate substance mg.l^{-1}
 C_e = Concentration of adsorbate substance at equilibrium mg.l^{-1} .

3.3.4 Freundlich Isotherm

Given by the following non-linear Equations [15-16]

$$q_e = K_f C_e^{1/n} \quad (3)$$

The logarithmic form of the equation becomes:

$$\text{Log } q_e = \text{log } K_f + 1/n \text{ log } C_e \quad (4)$$

3.3.5 The Langmuir ISOTHERM

Model of Langmuir is represented in Eq. (5) [17-18]:

$$q_L = q_e b C_e / 1 + b C_e \quad (5)$$

The above equation can be wording as:

$$1/q_e = 1/q_m + 1/q_m b * 1/ C_e \quad (6)$$

Where: C_e is the effluent concentration of adsorbate in the substance (mg.l^{-1}), q_e is the effluent adsorb at concentration (mg.l^{-1}) on the adsorbent, b ($1/\text{g}$) are constants, q_m ($\text{mg } 1/\text{g}$) the utmost the sorption ability.

4. Results and Discussion

4.1 Effect of pH solution on adsorption efficiency of MWCNTs

In general, it is noted from Figure (2) that the absorption of Cd (II) for fMWCNTs is very low at pH 2.0. Then, increasing the pH in solution 2 to 4 leads to a rapid increase in Cd^{+2} absorption. The optimum Cd^{+2} uptakes occur at pH 5.0 to 6.0 or around pH 5.5. The Cd^{+2} uptakes by fMWCNTs decrease due to the hydrolysis and precipitation of cadmium ions. [19] It was found that the removal percentage of Cd (II) grew from (25%) to (76%), where the pH increased from (1.0) to (6.0). This behavior is predictable for many metals, nickel, and cadmium.

The pH effect can be linked with the fact that in the acidic environment, competition has occurred between minerals and H ions, and metal retention in such a state is not significant, with increasing pH, electros. Discord lowering because of at discord for a density of the positive charge on the adsorption locations, and so on, producing an improved of metal ions sorption, As a result, according to the previous discussion, the optimum pH value adopted from the experiments is within the range of 5 to 6. The Cd +2 uptake ($\text{mg Cd } +2/\text{g}$ of Sorbents) by fMWCNTs at different pH for ($C_i = 50 \text{ mg/L}$, $\text{vol.} = 100 \text{ ml}$, $W = 0.1 \text{ g}/10+2 \text{ ml}$ of substance, agitation speed=100 rpm, contact. Time=30 m. is illustrated in fig. (3).

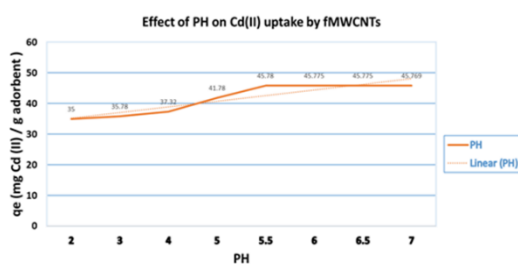


Figure 2: Influence of pH on Cd^{+2} uptake by fMWCNTs

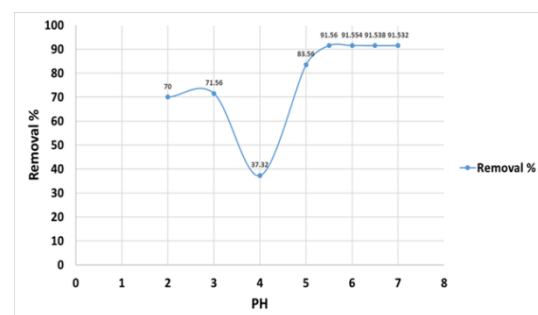


Figure 3: The removal efficiency of Cd^{+2} at concentration 50 mg/L, temp. = $25 \pm 1^\circ\text{C}$ and $S = 100 \text{ RPM}$ at different values for PH.

4.2 Effect of dosage adsorbent (MWCNTs)

The batch process was carried out with doses of (0.1 - 0.25) g of adsorbent/100 ml Cd substance of 50 mg/l and a contact time of 30 min. Fig 4 shows the removal efficiency with time at dosage 50 ppm at initial Cd(II) concentration 50 mg/L. The removal efficiency has been improved by increasing the absorbed dose from 100 ppm to 250 ppm, and the optimal adsorbent amount required for effective treatment can be observed. Whereat 50 ppm concentration of Cd (II) at a contact time of 30 min and temp. = 25°C , ($S = 100$) RPM, maximum of percent removal for Cd (II) was about (99.30 %).

Compare with Figure 4, the removal efficiency for (fMWCNTs) increases by approximately 9% after operating MWCNTs. At a 30-minute contact time and the absorbed dose of 250 mg/l, the clearance efficiency was (99.30%) for functionalization (fMWCNTs) and 90.30% for (MWCNTs).

4.3 The Influence of the contact time

The adsorption movement by adsorbent was relatively rapid within 5 minutes and during the first hour, it significantly changed over time. The equilibrium time was taken in 30 minutes, Figure (5) shows the percentage plot of the percentage of minerals against the contact time of Cd (II) ions by fMWCNTs at an optimal pH value.

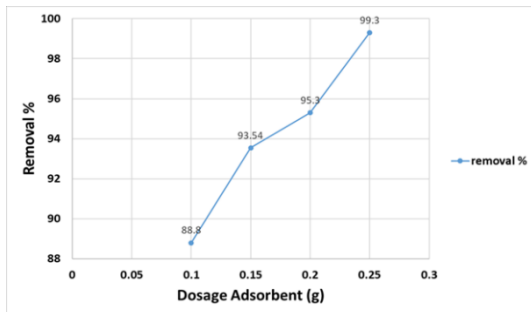


Figure 4: The efficiency of removal Cd (II) (concentration 50 Mg/L), temp. =25°C and S=100 RPM at a different adsorbent dosage of 100 mg/100L of fMWCNTs.

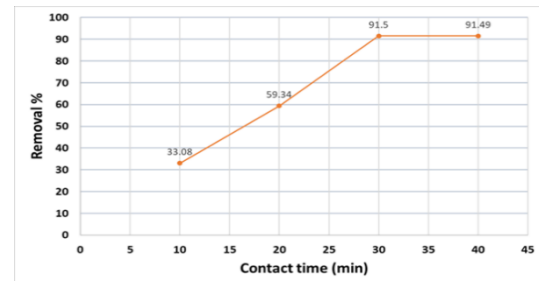


Figure 5: Effect of sorbent type on percent removal of Cd (II) at contact time= 30 min.

5. Conclusions

1. The MWCNTs were used to remove cadmium ions very efficiently.
2. The percentage of cadmium removal (II) was increased with increasing contact time, stirring speed, and the dose of MWCNTs, but it was decreasing with increasing initial Cd (II) concentrations.
3. The maximum absorption of Cd (II) on CNWs functional MWCNTs was increased with an increase in pH = 5.5.
4. The percentage of Cd (II) removal on fMWCNTs was decreased with increasing temperature to (15,25,35 and 45) C.
5. Exhaustion and the breakthrough time were reduced with an initial concentration of heavy metal ion particles increased

Author contribution

All authors contributed equally to this work.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

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