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# Microwave assisted multiwall carbon nanotubes enhancing Cd(II) adsorption capacity in aqueous media

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ABSTRACT

Novel multiwall carbon nanotubes (MWCNTs) have been successfully synthesized using tubular microwave chemical vapour deposition technique and proved to be an outstanding adsorbent for the removal of Cd(II) from aqueous solution. The effect of process parameters such as pH, MWCNTs dosage, agitation speed and time were investigated. The maximum adsorption capacities of Cd(II) were found to be 88.62 mg/g and a statistical analysis reveals that the optimum conditions for the highest removal (98%) of Cd(II) are at pH 5, MWCNTs dosage 0.1 g, agitation speed and time of 160 rpm and 50 min, respectively with the initial concentration of 10 mg/L. The Langmuir and Freundlich isotherm models match the experimental data very well and adsorption kinetic obeyed pseudo-second order. Our results proved that MWCNTs can be used as an effective Cd(II) adsorbent due to the high adsorption capacity as well as the short adsorption time needed to achieve equilibrium.


## Introduction

New era industries have immensely improved the living standard of human being. But however, these modern industries also pose serious adverse impacts on our living surrounding. One of the major environmental concerns is the water pollution by the heavy metals. Heavy metals in water are the main preoccupation for many years because of the toxicity towards aquatic-life, human beings and also the environment [1]. Even though trace amounts of heavy metals are vital for the human body, they are considered as harmful when they become excessive. Contrasting with organic pollutants, most of which are susceptible to biological degradation, heavy metal ions do not end product that is harmless to the environment. The contamination of crucial concern includes lead, cadmium, mercury, zinc, chromium, silver, Tin, and other mutagenic nature which also makes up the earth's surface [2–6]. Contamination of heavy metals exists in aqueous wastes of various industries, such as mining operations, tanneries, metal plating, alloy industries and smelting [7]. A process involving industries such as metal plating and battery manufacturing can be counted as the primary source for cadmium pollution in water [8]. Cadmium is heavy metal ion which is vastly known as one of the toxic material which can be exposed to mankind either in the environment or at work. Due to the low rate of excretion of body, cadmium has a long biological half-life [9]. This explains why, if it is absorbed in one's body, cadmium remains there and accumulates throughout life. Primarily, Cadmium affects the kidney, specifically to the proximal tubular cell, main site of accumulation. Moreover, prolonged exposures to cadmium cause toxicity due to accession over time in various body tissues, including liver, chronic disorders like 'itai-itai diseases, renal damages and emphysema [10,11]. The World Health Organization recommended the drinking water guideline value to be 0.005 mg Cd/L [12]. Cadmium and certain cadmium compounds are probable or suspected carcinogens, hence, it is compulsory to remove cadmium from drinking and waste waters.

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Various chemical removal methods have been utilized and also further developed over the decades to take charge of the heavy metal contaminations. Removal of heavy metal from aqueous solution consists of physical, chemical and biological techniques. Suggested conventional methods are electrochemical treatment, chemical precipitation, membrane technologies and adsorption on activated carbon [13]. Amongst all the methods, adsorption on activated carbon is considered to be very promising in terms of its efficiency of removal from aqueous solutions [14]. In addition, it is another good method to be taken into account from the aspect of handling methods and economics. Even though there are so many adsorbents available, researchers had to come up with a new adsorbent as the existing adsorbents were lacking in its efficiency to remove metal ions [15].

Carbon nanotubes (CNTs) are a new member in carbon family, essentially a new type of adsorbents that proves to retain great potential for removal of pollutants such as herbicides, chloro-benzenes, as well as lead and cadmium ions [11]. CNTs consist of a hollow and layered structure along with a large specific surface area [16] which leads to a remarkable application as an adsorbent with a high adsorption capacity for water treatment by utilizing the adsorption method. Hence, nanomaterial proves to be an essential adsorbent due to its high specific surface area along with efficient active sites for adsorption of Cd(II) from water. CNTs have a relatively larger specific are that provides a good opportunity for the removal of heavy metals [17–19]. Carbon based nanomaterial was opted to provide an alternative method for water treatment and few of these materials provided an astonishing outcome with a high rejection of contaminant from water Carbon nanotubes based technologies found its water-treatment applications in various fields, for instance, as sorbents, catalyst, filters, or membranes [17]. It is of common interest that the development of a new technique for an efficient and the selective synthesis of carbon nanotubes at the cheapest possible cost [20]. One of such possibility is the use of microwave radiation. The reason behind the choice of microwave used to produce carbon nanotubes is the novelty of this method [21]. Microwave-assisted modification of carbon nanotube is non-invasive, simple, fast, environmentally friendly and clean method as compared to traditional methods. Usually, the use of the microwave facilitates and accelerates reactions, often improving relative yields [22]. The use of microwave radiation in the synthesis and functionalization of carbon nanotubes or other nanostructures is advantageous because it provides a fast and uniform heating rate that can be selectively directed towards a targeted area compared to the conventional method used. In our innovation microwave-assisted synthesis, including fast multiwall carbon nanotube (MWCNTs) growth and ambient reaction condition, lowers the cost, and simplifies the procedure leading to a high yield synthesis of high-quality MWCNTs with minimal impurity. Unlike conventional heating, microwave heating has a higher heating rate, which results from the intrinsic transition of electromagnetic energy to thermal energy by a molecular interaction with the electromagnetic field, rather than heat transfer by conduction or convection.

In this research, a novel MWCNTs was synthesized using tubular microwave chemical vapour deposition. The developed MWCNTs tested for Cd(II) adsorption capacity in aqueous media, also a statistical optimization of process parameters such pH, MWCNTs dosage and agitation speed and time of removal of Cd(II) were investigated. The studies on the isotherm kinetic and isotherm model were developed and investigated as well. The thermodynamic parameters and desorption studies were investigated as well.

## Materials and methods

### *Experimental setup for MWCNTs production*

The schematic of tubular microwave chemical vapor deposition (TM-CVD) for MWCNTs production as described in my previous work [23]. The horizontal tubular microwave model Synotherm-T1500, China reactor for production of MWCNTs. It comprised a quartz tube of 55 mm OD, 50 mm ID and 615 mm length. Ferrocene catalyst was placed at the entrance of the chamber and quartz boat size was placed at middle of the reaction chamber. The system was initially flushed with Ar in order to ensure an oxygen free environment. The gas flow rate of $C_2H_2$ and $H_2$ was free mixed before entering into the tubular microwave chamber using gas mixture Model KM-20-2, Germany, after the gas mixture was sent to microwave chamber. The reaction was carried on for the desired time period and on completion, the total amount of MWCNTs produced in the quartz boats was collected and weighed. The optimized conditions for the high weight of MWCNTs production was at 900 W microwave power, 35 min radiation time and 0.6 gas ratio of $C_2H_2/H_2$. The optimized produced MWCNTs have high BET 206 $m^2/g$ surface area having a particle size of 450 $\mu$m that leads to high efficiency in removal of Cd(II) from aqueous solution.

### *Preparation of stock solutions*

Analytical grade Cd(II) standard solution which was obtained from Merck was used to prepare stock solutions containing 1000 mg/L of Cd(II) metal ions which were further diluted with distilled water to obtain the required concentrations. As for this research, the initial concentration of Cd(II) metal ions was set to 10 mg/L and the prepared solution were used for batch adsorption experiments.

### *Batch adsorption experiment*

A batch adsorption experiment was performed by using 100 mL of 10.0 mg/L of Cd(II), agitated with varying dosages of MWCNTs and other variable parameters according to the design obtained from the Design of Expert (DOE). The parameters used for this research is as shown in Table 1. The initial pH of the stock solution was adjusted by using 1.0 M of NaOH by adding in a few drops of the alkaline solution in the 100 mL of 10 mg/L of Cd(II) until the desired pH was obtained. The MWCNTs were then added into the 100 mL of 10 mg/L of Cd(II) solutions and it was agitated according to the parameters displayed in Table 1. At the end of each interval of the time, the suspensions were shaken and centrifuged at 4000 rpm for 10 min and the supernatant was withdrawn and filtered by using qualitative filter paper having a pore size of 3 $\mu$m. The filtrates were analyzed for contaminants by ICP-OES (PerkinElmer 7000 DV) in an air-argon flame using PerkinElmer multimetal standard solutions. By ICP-OES, the metals in water sample can be analysed. It detects the concentration of Cd(II) in ppm level in the solution and volume of sample required is only 1 mL for one analysis. The experimental errors of ICP-OES were within the range of $\pm$2.461% to $\pm$2.983%. The Cd(II) residual concentrations were measured from the standard calibration

**Table 1**
Experimental design for batch adsorption.

| Factor | Name | Units | Low | High | Low coded | High coded |
|---|---|---|---|---|---|---|
| 1 | pH | | 4 | 6 | −1 | 1 |
| 2 | CNTs dosage | g | 0.05 | 0.15 | −1 | 1 |
| 3 | Agitation Speed | rpm | 120 | 200 | −1 | 1 |
| 4 | Contact Time | min | 20 | 80 | −1 | 1 |