# Adsorption of Silver Nanoparticles from Aqueous Solution by Multiwalled Carbon Nanotubes

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## Abstract

Silver nanoparticles (AgNPs) are becoming an emerging pollutant of the environment. In this study, the efficacy of Multiwalled carbon nanotubes (MWCNTS) to remove AgNPs from aqueous solution at a concentration of 250 and 500 mg/100 ml MWCNTS was investigated. The results showed that the adsorption of AgNPs by 250 and 500 mg/100 ml MWCNTS after a contact time of 10 min., 30 min., 60 min., 120 min. and 240 min was 33.95%, 34.36%, 40.32%, 45.33%, 58.53% and 57.29%, 61.27%, 64.89%, 87.21%, 88.58%, respectively. The statistical analysis of data showed that, after adding 250 and 500 mg/100 ml MWCNTS, the total residues of AgNPs were significantly reduced in all MWCNTS exposed samples when compared to the control groups (P < 0.05). Moreover, at the two used concentrations, there were significant differences between 240 min. and all other contact times. The result concluded that the removal percent of AgNPs from aqueous solution was increased with the increase in contact time and concentrations of MWCNTS. Additionally, MWCNTS are expected to be potential adsorbent in the future due to their high removal capacity of nano-sized silver.

## 1. Introduction

Water scarcity in many regions of the world is exerting a great pressure on establishing more advanced technology to provide good quality water for human, animals and other uses. Recently, nanomaterials (materials less than 100 nm in at least one dimension) have attracted more attention due to the increase of their production, their wide applications [1], their unique physicochemical properties,

and their potential hazards to the natural environment [2]. Nowadays, nanoparticles are becoming more common emerging contaminants of water [3]. As one of the most promising metals nanoparticles of various antimicrobial and antiviral properties, silver nanoparticles (AgNPs) have been widely used in the daily life such as biomedical devices, air and water filters, packaging of food, cosmetics, clothing/textiles, electronic appliances, and cleaning agent [2] [4] [5] [6]. In a 2013 survey, from 622 companies in 32 countries, there are 1814 consumer nano products, and silver (Ag) is the most frequently used nanomaterial (435 products, or 24%) [7]. According to Blaser *et al.* [8], silver (Ag) residues from Asia, Europe, and North America reached 190 - 410 tonnes/year. Furthermore, between 11.5% to 31.7% of Ag residues passed through Waste Water Treatment Plants and were found in receiving natural water [9] [10].

The widespread uses of AgNPs can result in their leaching into natural water, where AgNPs can be toxic to bacteria [11], invertebrates [12], algae [13], and plants [14]. The behavior and toxicity of AgNPs vary according to sediment characteristics and water chemistry [15], while, in natural water, AgNPs could be transformed through oxidation, sulfidation, reduction, dissolution, aggregation, and adsorption [16]. These transformations have an influence on the mobility, persistence, and bioavailability of the AgNPs [16].

In order to assess the emerging threats from AgNPs, one should take into account their toxicity degree and exposure route [17]. After oral administration of silver in mammals, it can distribute to all organs. The following dose-dependent toxicity findings have been reported in animals: death, hypoactivity, weight loss, altered liver enzymes, altered neurotransmitter levels, enlarged hearts and immunological effects [18], in addition to argyria of the skin.

AgNPs consider a new class of emerging drinking water pollutants, and there is pressing need to remove them during drinking water treatment. Carbon nanotubes (CNTs) have drawn great attention since they were discovered in 1991 [19]. Carbon nanotubes (CNTs) include multiwalled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) depending on the number of layers comprising them. MWCNTs have cylindrical shape consisting of a multiple layers of graphene sheets rolled up in a tube-like structure [20]. CNTs have a great potential due to their unique properties such as remarkable chemical, mechanical stabilities, nano sizes, and their strong adsorption properties [21] that are mainly attributed to their pore structure and the existence of a wide surface functional group [25] [26]. MWCNTs have been used as adsorbent for many types of pollutants such as many heavy metals [22], pesticides [23], and sulfonamides [24].

Although there are numerous laboratory tests and experimental studies carried out in recent years concerning the adsorption of several contaminants by using MWCNTs, there is still a significant gap in the literature to investigate the adsorption capabilities of MWCNTS for the removal of AgNPs. For this reason, this work has been conducted as a novel study specifically aimed to determine the effects of different concentration of MWCNTs and different contact time on

the removal of AgNPs from aqueous solution.

## 2. Material and Methods

### 2.1. Synthesis of AgNPs Stock Solution

One typical step protocol was used to synthesize AgNPs according to Vignesh-waran *et al.* [27] where; 1.0 g of soluble starch was added to 100 mL of distilled water and heated till complete dissolution. Then, 1 mL of a 100 mM aq solution of silver nitrate ($AgNO_3$) crystal, (GAMMA laboratory chemicals, with minimum assay of 99.0%) was added and mixed well. This mixture was transferred into dark glass bottle and kept in an autoclave at 121˚C for 5 min. The use of soluble starch for the production of AgNPs is a simple and fast method and offers several benefits of compatibility for biomedical applications. After preparation of AgNPs, the stock solution was kept in dark bottle away from direct sunlight at room temperature; the concentration and size of the particles were measured before it's used in experiments.

### 2.2. Characterization of AgNPs

The size of AgNPs was measured by Transmission Electron Microscopy (TEM) Model JEOL-JEM-100CX II, in Electron Microscopy Unit, Assiut University, Egypt. The total concentration of AgNPs stock was analyzed by Atomic Absorption spectrophotometer (Graphite Furnace) Model 210VGP in heavy metals analysis lab, Faculty of Science, Assiut University, Egypt.

### 2.3. Adsorbent Properties

Multi-walled carbon nanotubes (MWCNTs) were purchased from Nano Tech Company (Al Giza, Egypt), and used as the adsorbent materials in the present study. According to the manufacture report sheet, the MWCNTs have been prepared by arc-discharge in solution. The arc discharge technique involves the use of two graphite electrodes of high purity as the anode and the cathode. The electrodes were vaporized by the passage of a 100A DC current through two graphites separated in 400 mbar of Helium atmosphere. After arc discharging for a period of time, a carbon rod is built up at the cathode. Size, diameters and shapes of MWCNTs were measured by the Transmission Electron Microscopy (HR-TEM) model JOEL JEM-2100 operating at 200 kV equipped with Gatan digital camera Erlangshen ES500.

According to data provided by the manufacturer, MWCNTs were Tubular-like shape, their length was >660 nm and the diameters were 20 ± 5 nm (Figure 1).

### 2.4. Adsorption Experiments

#### 2.4.1. Preparation of Test Solutions (Samples)

Preparation of test solutions was carried out in 2 conical flasks of 1 L capacity, each flask containing 240 ml of distilled water with neutral pH. In the next step, 10 ml of silver nanoparticles from a stock solution were added into each conical flask.
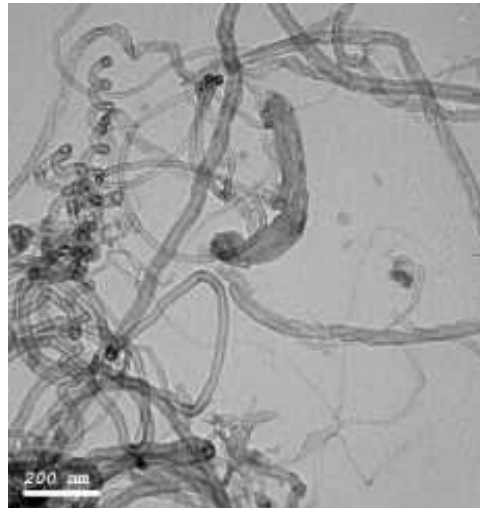
**Figure 1.** TEM micrographs showed that, the as-prepared CNT has multiwall structure and size of 20 ± 5 nm.

### 2.4.2. Effect of Adsorbent Amount and Contact Time

In this study, the amount of MWCNTS specified for each sample was weighed and added to test solutions to obtain a final concentration of 250 and 500 mg/100ml MWCNTS. After that, the conical flasks containing test solution and adsorbents were shaken at 150 rpm in a thermostatic horizontal shaker set at 30°C for several specified contact times namely; 10 min., 30 min., 60 min., 120 min. and 240 min. The experiments were carried in triplicate.

### 2.4.3. Analysis and Detection of AgNPs

At the end of each specified contact time, the conical flasks were removed from the shaker and the solution was passed through a filter paper (Whatman No. 43 and 15 cm diameter) to separate the MWCNTs from the solution, the filtrate was labelled and transferred to Heavy metals analysis lab. at Faculty of Science, Assiut University to analyze the residual amount of total silver by using Atomic absorption spectrophotometer (Model No: 210VGP).

### 2.4.4. Evaluation of Adsorption Efficacy of MWCNTs

The efficiency of MWCNTs to adsorb AgNPs was calculated by comparing the amount of AgNPs before *(The control)*, and after adding the MWCNTs at specified contact time to determine if there were significant differences between them. *Percent efficacy was calculated with the following equation*:

$$P = \left(C_0 - C\right)/C_0 \times 100$$

where *P is the percent of adsorption efficacy*; $C_0$ *is the initial amount of* AgNPs *(control)*; *C is the amount of AgNPs after a certain contact time with MWCNTS.*

### 2.5. Statistical Analysis of Data

Statistical analysis of data was carried by using SPSS software version 17.1. The data was subjected to analyses of variance using the ANOVA procedure of SPSS software. The results were presented as mean and standard errors for each varia-

ble. Differences between mean values were tested using Duncan's multiple range test. P-value consider statistically significant when $P < 0.05$.

## 3. Results and Discussion

### 3.1. Characterization of Synthesized AgNPs

After autoclaving, the resulting solution was yellow in color indicating the formation of AgNPs. The size of AgNPs was ranged from 3.76 to 10.9; they have spherical shapes as shown in **Figure 2**. The concentration of the stock solution of AgNPs was 132 mg/L. Prepared Nanoparticles were stable in solution over a period of 3 months at room temperature (25°C) and show no signs of aggregation.

### 3.2. Effect of MWCNTS on Adsorption of AgNPs

The increasing and wide application of silver nanoparticles (AgNPs) has resulted in their appearance in water specially, wastewater. In consideration of their potential toxicity and environmental impacts, it is urgently to find effective technology for their removal from water. In this study, the AgNPs contaminated Distilled Water (DW) with 132 mg/l was treated by using two different MWCNTS doses (250 and 500 mg/100 ml). The results showed that the mean values of AgNPs after adding 250 mg/100ml and 500 mg/100ml MWCNTS were
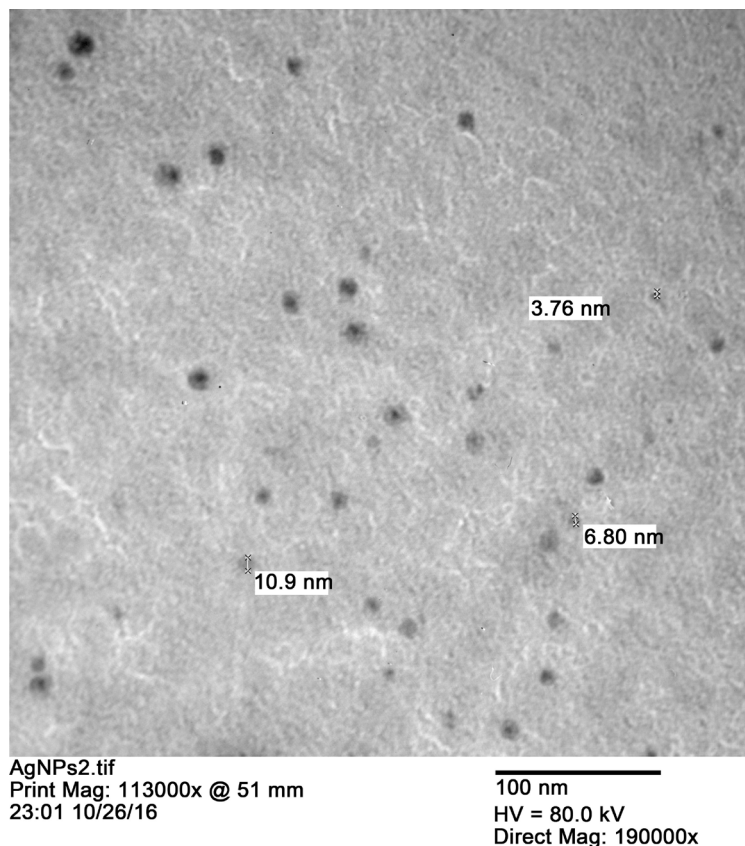


**Figure 2.** TEM image of AgNPs showing spherical shaped nanoparticles with size particles ranged from 3.76 to 10.9.

($17.18 \pm 0.41$, $17.07 \pm 0.67$, $15.52 \pm 0.55$, $14.22 \pm 0.32$, $10.78 \pm 0.07$, and $26.00 \pm 3.04$), and ($11.11 \pm 0.35$, $10.07 \pm 0.25$, $9.13 \pm 0.55$, $3.33 \pm 0.31$, $2.97 \pm 0.02$ and $26.00 \pm 3.038$) at contact time of 10 min., 30 min., 60 min., 120 min. and 240 min and control (before adding MWCNTS) samples, respectively Table 1 and Figure 3.

The statistical analysis of data showed that at the 1st (250 mg/100ml) and the 2nd (500 mg/100ml) MWCNTS concentrations, the total amount of AgNPs was significantly reduced in all MWCNTS exposed samples when compared with the control groups ($P < 0.05$). Moreover, at the 250 mg/100ml MWCNTS, there were significant differences between 240 min contact time and the other four contact times (120 min., 60 min, 30 min, and 10 min) ($P < 0.05$) (Table 1). However, there were no significant differences between 120 min., 60 min, 30 min, 10 min and their each other. At the 2nd used MWCNTS concentration (500 mg/100ml), the analysis of variance showed significant differences between each 240 min, 120 min and the other 3 contact times (60 min, 30 min, and 10 min) ($P < 0.05$). However there were no significant differences between 240 min and 120 min contact times and also no differences between 60 min, 30 min, 10 min and each other (Table 1). These findings indicate that both used concentrations of MWCNTS have efficiency on the removal of AgNPs from aqueous solution. Although many studies have been shown that MWCNTs have been used as adsorbent for many kinds of heavy metals such as zinc (Zn) [28], cadmium (Cd) [29], lead (Pb) [30], nickel (Ni) [31] and copper (Cu) [32], this is the first study showed an effective removal of AgNPs by MWCNTS. The mechanisms by which the metal ions are sorbed onto CNTs are very complicated, however, the most dominant mechanisms reported in the literature are physical adsorption, sorption-precipitation, electrostatic attraction, and chemical interaction between the metal ions and the surface functional groups of CNTs [33] [34] [35]. The surface functional groups and the chemical interaction between CNTs and the metal ions are the most obvious mechanism [36].
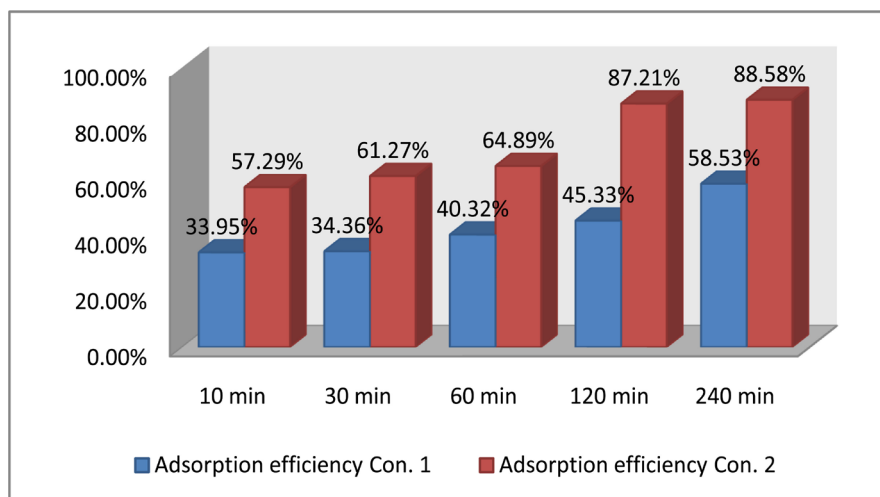


Figure 3. The effect of contact time on the adsorption of AgNPs onto MWCNTS. Con.1 was 250 mg/100ml MWCNTS and Con.2 was 500 mg/100 ml MWCNTS.

Various researchers have demonstrated that the acid modified CNTs have higher removal efficiency for heavy metals than raw CNTs [33] [35] [37] [38] [39]. However, our results indicate that raw CNTs have good adsorption for AgNPs and that finding agreed with the other group of researchers as [40] [41].

### 3.3. Effect of Different Concentration of MWCNTs on Adsorption of AgNPs

Table 1 showed the effect of 2 concentrations of MWCNTs (250 and 500 mg/100 ml) on removal efficiency of AgNPs. To compare between the two concentrations, the analysis of variances showed that there were significant differences between each contact time of the second concentration (500 mg/100ml) and the same contact time of first concentration (Table 1). The results also magnified the efficacy of 500 mg/100 ml MWCNTS on AgNPs removal, as seen in Table 1 and Figure 3, where the amount of AgNPs remaining in the solution shows a more decreasing trend when comparing by the 1st conc. Our findings showed that there were no significant differences between adsorption of AgNPs at 10 min. onto 500 mg/100 ml and the adsorption of AgNPs at 240 min. onto 250 mg/100 ml MWCNTS (Table 1). This means that the removal efficiency of AgNPs by 500 mg/100 ml MWCNTS for 10 min (57.29%) closely similar to the removal efficiency of AgNPs by 250 mg/100 ml MWCNTS for 240 min (58.53%) (Table 2 and Figure 3). The present data revealed that the removal efficiency of AgNPs increase by increasing the amounts of MWCNTS (Table 1). This result was agreed with [42] who use four synthetic and natural coagulants as attractive option for AgNPs removal at small-scale, the authors observed that the removal percent of AgNPs increases with the increase in coagulant doses, and also in agreement with [43] who used modified MWCNTS for the removal of Cu, Pb, Cd and Zn from aqueous solutions. The present results also agreed with [33] [34] [37] [44] [45] who concluded that, the sorption of heavy metals such as $Ni^{2+}$, $Cd^{2+}$, $Cu^{2+}$, and $Pb^{2+}$ is reported to increase with increase in the CNTs dosage. The increase of adsorption percent of AgNPs with the increase of CNTS dose may be attributed to the fact that, increasing the CNTS dose provided a greater surface area or more adsorption sites for the metal [33] [34] [45] [46].

### 3.4. Effect of Contact Times

Figure 3 and Table 2 showed the effect of different contact times on the adsorption of AgNPs onto MWCNTS. From the present findings, the positive effect of contact time on the AgNPs removal process was achieved by increasing the contact time between MWCNTS and AgNPs. Where, at contact times of 10, 30, 60, 120 and 240 min., the removal of AgNPs reached to 33.95%, 34.36%, 40.32%, 45.33%, 58.53% and 57.29%, 61.27%, 64.89%, 87.21%, 88.58% for 250 and 500 mg/100 ml MWCNTS, respectively Table 2 and Figure 3. Our results showed that the adsorption of AgNPs onto MWCNTS increased quickly with time, and this agreed with the finding of [28] [33] [34] [38] [43].

**Table 1.** Mean ± Std Error of AgNPs amount before (control) and after adding different concentrations of MWCNTS.

| Time | Con. | Mean values ± Std. Error | |
|---|---|---|---|
| | | MWCNTS (250 mg/100) | MWCNTS (500 mg/100) |
| 10 min. | | $17.18 \pm 0.41^b$ | $11.11 \pm 0.35^c$ |
| 30 min. | | $17.07 \pm 0.67^b$ | $10.07 \pm 0.25^c$ |
| 60 min. | | $15.52 \pm 0.55^b$ | $9.13 \pm 0.55^c$ |
| 120 min. | | $14.22 \pm 0.32^b$ | $3.33 \pm 0.31^d$ |
| 240 min. | | $10.78 \pm 0.07^c$ | $2.97 \pm 0.02^d$ |
| control | | $26.00 \pm 3.04^a$ | $26.00 \pm 3.04^a$ |

$^{a,b,c,d}$Values within columns with no common superscript differ significantly ($P < 0.05$).

**Table 2.** The percent removal of AgNPs by MWCNTS after 10, 30, 60, 120, and 240 min.

| Time | Con. | Adsorption efficiency | |
|---|---|---|---|
| | | MWCNTS (250 mg/100) | MWCNTS (500 mg/100) |
| 10 min. | | 33.95% | 57.29% |
| 30 min. | | 34.36% | 61.27% |
| 60 min. | | 40.32% | 64.89% |
| 120 min. | | 45.33% | 87.21% |
| 240 min. | | 58.53% | 88.58% |

## 4. Conclusion and Future Research

From this study, it can be concluded that the MWCNTS possesses a good adsorption performance so that material can be useful in removing nano-sized silver from aqueous solutions. The acceptance of the MWCNTS as an effective adsorbent is expected to remove AgNPs from environment as well as mitigate the toxic effect to both animal and human health. Furthermore, based on the information presented in this study we can make predictions that concentrations of AgNPs may be used in various applications such as water treatment with an increased amount than the permissible limit (0.1 mg/l), and their removal will be achieved by MWCNTS as additional filtration stage. Finally, further investigations may be needed for MWCNTS exact desorption mechanisms, their possible regeneration, and their application for real aqueous media. The feasibility of CNTs application in large scale treatment also still needs further studies.

## Conflict of Interest

The authors declare that they have no conflict of interest.

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