

Trace Metal Modified Engineered Carbon Nano Tubes for Arsenic Removal

A. Ashiq, B. Abussaud, M. Vithanage and B. C. L. Athapattu

Abstract: Carbon nanotubes were used to study the adsorption behavior of arsenic (As) found in aqueous media and its effect in the adsorption efficiency when they are modified with certain trace metals onto the multi-walled carbon nanotubes (MCNTs) as adsorbents. Iron, titanium, silver, gold, copper were made to be impregnated on the CNTs for this study. The effect on the surface functional group of the carbon nanotubes were further studied on the removal of As. Batch experiments were performed to study the effect of the As removal in the aqueous media, the independent variables considered are pH, contact time and agitation speed. The morphology of the CNTs were characterized by using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) which indicates the dimensions of the adsorbents and the impregnation were seen before and after the adsorbents were made. Results of the study showed that iron and titanium impregnated on the surface of the CNT has the highest As removal percentage compared to pure CNT and the functionalized CNT with carboxylic group. Almost 70% of the As was removed from the water that contained 1 mg/L initial arsenic contamination. The highest removal was at pH 3, contact time of 24 hours and agitation speed of 200 RPM. Part of the study is also dedicated to investigate the effect of dosage in the removal of arsenic from water.

Keywords: Modified Carbon nanotubes, functionalized CNTs, impregnation, water treatment

1.0 Introduction

Arsenic present in the water bodies originate from natural resources and human activity. They are released into the surface ground water by means of geological formation that happens in sedimentary rocks, geothermal water and from weathered volcanic rocks. Human activities like mining, manufacturing, metallurgy, wood preservation and as pesticides also introduce arsenic into the water bodies (Gorchev&Ozolins, 2011; Mandal & Suzuki, 2002). The maximum possible concentration that can be present in water that is set by the World Health Organization is 10 ug/L (Greenwood & Earnshaw, 1997; Smedley & Kinniburgh, 2002). The National Arsenic Occurrence Survey investigated that more than 5 ug/L arsenic are present in 21 percent of the ground water and 10 percent of the surface water (Black, Chinn, Rodriguez, Huckabee, & Frey, 1999; Charlet&Polya, 2006). The reason that put concerns with arsenic in drinking water was that the majority of the population who has been exposed to arsenic in drinking water reported cases of cancer- based health concerns. High levels of arsenic contaminant have been found in Taiwan, India and West Bengal where they have been exposed to much higher levels than the maximum possible concentration of 10 ug/L (Ahmed et al., 2004;

Anawar et al., 2003). Skin cancers; lung bladder and kidney cancers and other internal tumours; vascular diseases and diabetes are the diseases that are reported by population drinking arsenic contaminated water. There has been also reported case of infant mortality and weight loss of new born babies. These cases are only a correlation in the study as the main mechanism of the toxicology levels of arsenic have not been studied thoroughly but for sure both the individual and the population has been susceptible to the poisonous effects of arsenic contaminant water.

Other studies were carried out in the field to reduce arsenic levels in water cost- effectively

Eng. (Dr.) B.C.L Athapattu, BSc. Eng (Moratuwa), MEng.(Osaka), PhD(Osaka) CEng. MIE(Sri Lanka), Senior Lecturer,, Department of Civil Engineering, The Open University of Sri Lanka.

Dr. M Vithanage BSc(Sabaragamuwa), MSc.(Peradeniya), PhD(Copenhagen), Senior Lecturer, Faculty of Applied Sciences, University of Sri Jaywardenepura

Eng.A Ashiq. BEng (India), Post Graduate Institute of Science, University of Peradeniya

Eng.(Prof.)BasimAbussaud, BEng, PhD, King Fahd University of Petroleum & Minerals, Dharan , Saudi Arabia.

such as ion exchange, lime softening, coagulation, iron- manganese removal technique, using activated alumina and other specialized processes like reverse osmosis and ultrafiltration (Mandal & Suzuki, 2002; Vithanage, Dabrowska, Mukherjee, Sandhi, & Bhattacharya, 2012). Most of these technologies had their limitations which is why new methods need to be adopted to remove arsenic using nanotechnology.

Heavy research has been done on nanotechnology in this field of carbon nanotubes for making water pure for drinking. Nanotechnology basically deals with structures that are in the nanoscales ranging from 1 to 100 nano-meters. Our main focus is the carbon nanotubes (CNTs) where previous studies have shown significant results. Previously, studies have shown almost 100 percent removal of other trace metals like lead from water by using CNT as adsorbents but our focus is not only to use CNT as the only adsorbent but also we want to compare the percentile removal when silver, gold, iron, copper and titanium are each impregnated on the surface of CNT along with functionalized CNT with carboxylic group to remove arsenic from water (Jabeen, Kemp, & Chandra, 2013; Xu et al., 2018). As our study is very extensive and includes a wide range of adsorbents, this part of the paper will concentrate more on three basic parameters that influence the adsorbent rates of all these materials namely pH, contact time and the agitation speed. Part of our research is also dedicated to study the effect of dosage of the adsorbents and change in the concentration of the arsenic solution has on the removal percentage of the contaminant.

Carbon nanotubes are vital in water treatment because of its unique physical and chemical properties. It has been used as adsorbents for several heavy metals because of their highly porous and hollow structure with large specific surface area and light density. Also, CNT's have high Van Der Waals forces along its outside tube walls which makes it to aggregate easily in the aqueous solution. They can be modified into a wide spectrum of functional groups for optimal performance for distinct purposes (Brown, AtlyJefcoat, Parrish, Gill, & Graham, 2000; Diniz, Doyle, & Ciminelli, 2002). Despite all of the above studies on carbon nanotubes, limited work has been done on the function of impregnated CNTs for arsenic removal. Modifications were made to the surfaces of the CNTs with trace metals aluminium, silver, iron, copper, titanium and further changing the surface functional group

to study its effect and mechanism involved for the adsorption efficiency for As removal in aqueous environments.

2.0 Materials and Methods

2.1 Synthesis of Multi- walled carbon nanotubes (MCNTs)

The experimental procedure used to produce the carbon nanotubes is similar to that reported by Muataz et al (2006, 2009). But for this experiment the commercial carbon nanotubes of outer diameter 20- 30 nm and length 10- 30 nm of purity less than 95 weight percent is used throughout the experiment.

2.2 Oxidation of MWCNTs

The main purpose of oxidizing the large CNT surface is modifying the CNT to improve its surface area by adding carboxylic functional group on the surface thereby changing or maybe improving the properties of the CNT. The CNT used here was 97% pure with outside and inside diameters 10- 20 nm and 5- 10 nm respectively and their lengths 10- 30 nm. Concentrated nitric acids (300 mL) of AnalaR (69%) were added to the received CNT and the mixture is fluxed for 48 hours at 120°C followed by cooling at room temperature. The reaction mixture is then diluted with 500 mL of deionized water and then vacuum filtered through a 3 µm filter paper. This washing process continued until the pH reached that of the deionized water followed by drying in vacuum oven. A multi-walled nanotube fragments were obtained (Figure 1) with ends and side walls decorated with carboxylic groups (Abuilaiwi, Laoui, Al-harathi, & Atieh, 2010; Burghard, 2005; Zhang et al., 2003).

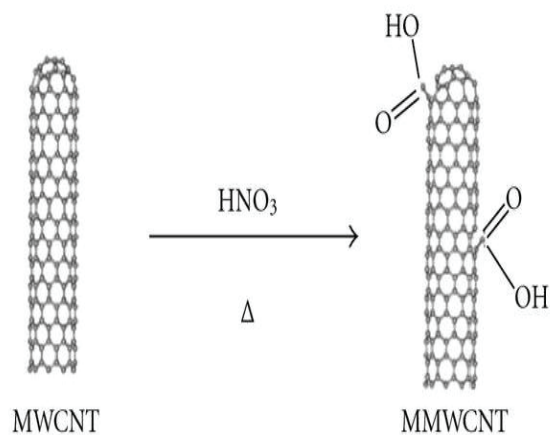


Figure 1: chemical modification of the carbon nanotubes through thermal oxidation

2.3 Preparation of the impregnated metals on the surface of CNTs

All the metals namely aluminium, silver, iron, titanium and copper are all impregnated separately on the surface of the carbon nanotubes separately by the same procedure. Aluminium is impregnated on the surface of the CNT by the following procedure. We required 5% of the total adsorbent containing aluminium. So out of 0.05 g of adsorbents used throughout the experiment contains 0.025 g aluminium and the rest CNT. The source of aluminium is not pure but from aluminium nitrate. The desired amount of aluminium nitrate and the received CNT are mixed and then dissolved in alcohol in a ratio of 200 mL to 5 grams minimum. The solution is sonicated for an hour at 40% amplitude. After sonification, the solution is filtered and the filtrate goes through calcination for removing the nitrate. Then, it rinsed with deionized water 5 times until the filtrate becomes colorless. Finally, the CNT is dried in the oven at 350 °C for 3 hours. The rest of the impregnation follows the same procedure except that the sources of the metals are different. The source for silver is silver nitrate where the nitrate is again later removed by calcination. The source for iron is iron nitrate; for titanium is titanium isopropoxide; for copper is copper nitrate.

2.4 Batch mode adsorption experiments

All the experiments were conducted at room temperature. Since there were many parameters to consider and seven different adsorbents, the experiments were done systematically as a batch varying one parameter at a time. The first batch was to analyse the effect of pH 3, 4, 5, 6 and pH 7 has on the removal. The second batch was to analyse the effect of agitation speed on the removal i.e. at 50, 100 and 200. Lastly, the final batch was to see the effect of contact time on the removal namely at 1, 4, 8 and 24 hours. In each experiment, 100 mL of the solution is taken for analyses and pre-weighed 50 mg of each adsorbent and mixed in 125 mL Erlenmeyer flask. The experiment throughout is performed in a manner that all of the samples used have uniformly the same time and amount of the adsorbents without any delay of the time. Filtrate was analysed by ICP- MS.

The amount of As removed from the solution was determined by calculating difference of the initial concentration (C_i) and the final concentration (C_f). The percentage removed from the solution of As ions was calculated

using the following relationship (Tawabini, Al-Khalidi, Khaled, &Atieh, 2011):

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100$$

The metal adsorption capacity (Q_e) was calculated by the following equation:

$$\text{Adsorption capacity } Q_e \left(\frac{\text{mg}}{\text{g}} \right) = \frac{C_i - C_f}{M_s} \times V$$

V = volume of the solution (L)

M_s = weight of adsorbent (g)

C_i = Initial concentration (ppm)

C_f = Final concentration (ppm)

3.0 Results and discussion

3.1 Characterization

For the whole experiment, the carbon nanotubes have been modified with six different materials, namely five metals which include- Iron, silver, Titanium, Aluminium, Copper and finally changing the functional group, in our case a carboxylic group.

Since we are dealing with nano- sized materials, structural analysis were studied through electron microscopy equipment's showing the presence of the fine fibres as well as the presence of the impregnated materials. The mechanisms of the adsorption could be depicted from the results of these images.

Before the experiment, the CNTs were characterized under Field emission scanning electron microscope (FE- SEM) in order to study the morphology of the nano structure. The SEM image of the CNT (Figure 2) shows the purity of the CNT used. The average diameter of the CNT produced is found to be 24 nm and the length reach up to few microns.

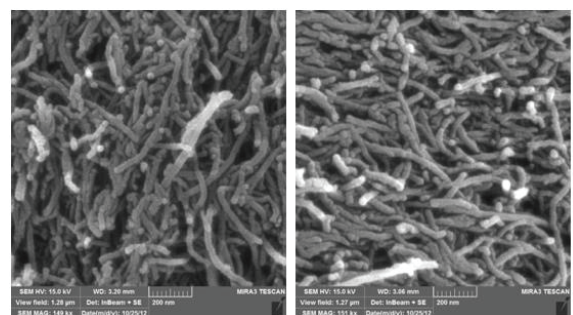


Figure 2. Scanning Electron Microscopic images (150K magnification) for (a) pure CNTs and (b) impregnated CNTs with 5% titanium oxide

SEM images shows (Figure 2) the modified carbon nano-tubes impregnated with titanium. From both the figures we could notice that the fibres in the pure are more straight chained and smooth enough whereas the impregnated shows some roughness on the surface which clearly shows the presence of the impregnations in them.

Transmission Electron Microscopy characterizes (Figure 3) the fine hollow tubular without any defilements which predicts the mechanism and adsorption of the trace metals on the surface of the fibres or in its interiors. EDX confirms the presence of the trace metals and the quantification can also be known as in the average percentages of each trace metal present on the different sides of the tubes.

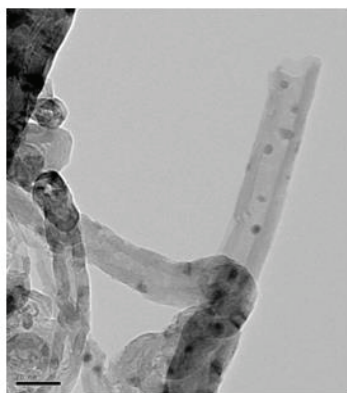


Figure 3. Transmission Electron Microscopic image for Fe impregnated MCNTs

3.2 Effect of pH on As Removal

The removal of arsenic is high for both the adsorbents at pH 3. It is seen that there is almost 74% removal for pure CNT and 73% for CNT- COOH. As the acidity decreases, the removal is very less and finally there is no removal at pH 7.

The lack of electrostatic force between arsenic ions and the CNTs has resulted in almost zero adsorption at neutral pH. While doing the experiments, another observation that was noted was that when the functionalized CNT where mixed in the solution, there were a sudden dispersion of the adsorbents within the solution compared to the other adsorbents in which they all were at the bottom of the flask.

We expected the functionalized CNT to have a greater removal because of this observation but it looks like as there has been not enough electrostatic force to pull out the arsenic ions from the solution.

3.3 Removal in Comparison with the Impregnated Adsorbents at Varying pH

The effect of various pH values has been studied and the results are depicted in Figure 4. The results show ample removal at pH 4 and pH 3, then a decrease as the pH decreases and finally almost no removal at neutral pH. The highest removal at pH 3 is CNT- silver which has 73% removal same as pure CNT. CNT- Fe and CNT- Ti seems to have a higher adsorption at neutral pH compared to the rest of the adsorbents. The reasons for all this could be resulted due to the electrostatic forces between the arsenic ions and the adsorbents. Higher the removal of arsenic from water, higher is the electrostatic forces of attraction between arsenic ions and the CNTs. While lower the removal of As, higher the electrostatic repulsion between the ions.

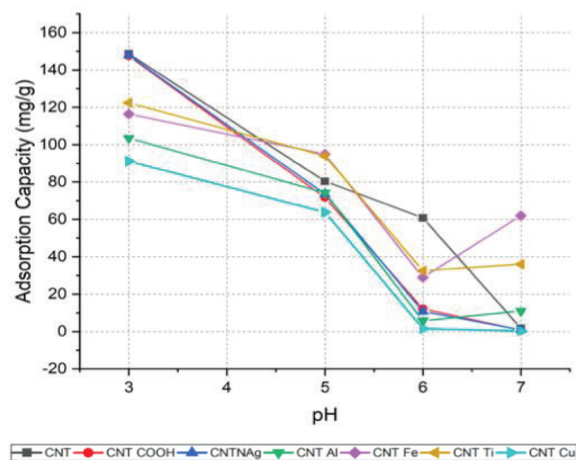


Figure 4. Removal of As in different MCNTs at different pHs

3.4 Effect of agitation speed on As Removal

The behaviour of the graph was not necessarily predictable. The removal of arsenic by functionalised CNT-COOH seems to be higher at 100 rpm and then desorption takes place as the time is extended for 24 hours (Figure 5). While compared to the non-modified CNT, the functionalised CNT-COOH is better for removal at 100 rpm.

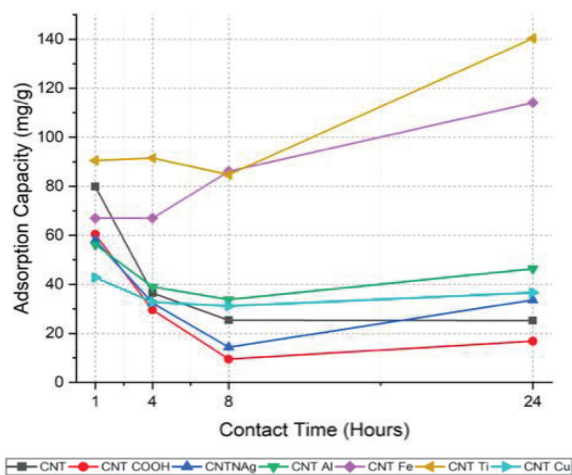


Figure 5. Removal of As in different MCNTs at different contact times

The effect of varying agitation speed has been studied for all the adsorbents (Figure 5). The influences of three agitation speeds (50, 100, 200 rpm) were considered keeping the contact time for 120 minutes at pH 6. The percentage of arsenic removed increased with increasing the mixing rate. The result from the graph shows that the removal of arsenic by CNT- iron and CNT- titanium seems to be high compared to rest of the adsorbents at 200 rpm. However, there is no much removal in 50 rpm except for CNT- silver which showed 23% removal. This behaviour in the speed range evaluated can be due to the fact that at high speed the mixing increases the contact between the metal ions in the arsenic solution and the CNTs thus, promoting effective transfer of arsenic ions to the adsorbents.

3.5 Effect of Contact Time on As Removal

The removal of arsenic by varying the contact time in 1 hour, 4 hours, 8 hours and 24 hours is studied for both non- modified CNT and functionalised CNT-COOH. For CNT pure, the adsorption in 1 hour is 40% but it drops significantly to 18% in 4 hours before it drops even more to 12% for both 8 and 24 hours. For CNT-COOH, the adsorption at 1 hour is 30% which then drops to 15% at 8 hours contact time. The removal remains constant as the time increases further.

3.6 Removal in Comparison with the Rest of the MCNTs

The effect of contact time on the adsorption behaviour of arsenic by the seven different adsorbents was studied by varying the contact time from 1 - 24 hours. For CNT-Ti, the graph

shows constant 45% removal in 1 and 4 hours. The adsorption percentage then drops to 41% at 8 hours of contact time before it increases dramatically to 70% at 24 hours. As for CNT-Fe, the graph shows adsorption of 32% at 1 and 4 hours. Adsorption hits 43% at 8 hours and 57% at 24 hours. However, the best removal of arsenic from water is delivered by CNT-Ti giving a 70.26% As removal at 24 hours of contact time along with CNT- Fe which also gave a much higher removal compared to the other adsorbents as the time increases. The reason of these results is again mainly accounted to the electrostatic forces between the arsenic contaminant and the adsorbents.

4.0 Conclusions

This study aimed to study the efficiency involved in having the CNTs modified with different trace metals with a certain amount and the mechanism for the removal of As (III) from aqueous media using these differently engineered adsorbents. Iron, titanium, silver, gold, copper; their salts were made to disperse at a significant amount on the surfaces of the CNTs and analyzed to compare the efficiency removal of each. Results of the study indicated 70% of the arsenic removal was shown the highest at pH 3, contact time of 24 hours and agitation speed of 200 RPM for CNT impregnated iron and titanium showing the optimum adsorption efficiency at 80 mg/g and equilibrium not achieved for both iron and titanium impregnated CNTs indicating high capacity.

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