Clean Production of Carbon Nanomaterials to Remove Arsenic from Drinking Water

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***Abstract*:**Novel carbon nanomaterials (CNM) were synthesized through a chemical vapour deposition (CVD) process to adsorb arsenic (As) from water. Iron (Fe) and Nickel (Ni) catalysts were used to produce two different types of CNM, namely carbon nanotubes (CNT) and carbon nanofibres (CNF). Powdered activated carbon (PAC) was used as a substrate, which played the key role for a less hazardous and clean production of CNM. Various concentrations of As (0.5, 5.0 and 10.0 mg/L) were used to prepare synthetically polluted drinking water, which was used for batch mode adsorption experiments in shake flasks. Adsorption capacities for CNF at respective concentrations were 1.46, 13.78, 27.97 mg/g and 1.86, 18.44 and 19.68 mg/g for CNT. Results showed that the CNT was suitable for low concentration of arsenic while CNF was good for high concentration. Two isotherms were studied for arsenic removal. It was observed that the CNT fitted better for Langmuir model with the correlation coefficient of 0.967, while Freundlich worked better for the CNF exhibiting correlation coefficient of 0.999.

***Keywords*:**Adsorption**,** CNM, Health Hazard, Toxic Metals.

I. INTRODUCTION

Presence of toxic arsenic (As) in groundwater is increasing in many parts of the world [1]. Development of an efficient and renewable adsorbent is necessary to reduce the concentration of As from drinking water to a safe level. Arsenic is a semi-metal element in the periodic table. It is odorless and tasteless. It enters drinking water supplies from natural deposits in the earth or activities such as from agricultural and industrial practices [2]. Arsenic is a poisonous element which can lead to health effects of the living beings at high concentrations. The presence of arsenic in the drinking water can be considered dangerous because of the large quantity of water consumed by the human beings in the long run. Therefore, an increasing awareness has been focused on the removal of arsenic from water due to its detrimental effects on human health.

There are different approaches to remove arsenic from aqueous solution, which includes chemical precipitation [3], ion exchange [4], coagulation [5], oxidation [4], cementation [3] and adsorption [4]. Adsorption method is reported to be the most common method used to remove arsenic from water and wastewater treatment due to its simplicity and cost effectiveness [6]. Various adsorbents have been used to remove arsenic from aqueous solution such as activated carbon [4], ferric hydroxide gel [6], aluminum substituted ferrihydrite [7], Zeolite [4], *Lessonia nigrescens* [8], and activated carbon [9]. Recently, potential adsorption property is found in carbon nanomaterials (CNM) too.

It was reported that CNM have high adsorption capacity and can be used as an adsorbent for removal of arsenic from aqueous solution [10]. Therefore, this study aimed at removal of arsenic from aqueous solution using CNM grown on Powdered Activated Carbon (PAC).

Carbon nanotubes (CNT) and carbon nanofibers (CNF) are the main forms of CNM. Both of them are well known as good adsorbents in removing heavy metals from wastewater [11], [12]. Previous study also demonstrated that CNT and CNF enhanced the adsorption rate. Thus, in this project, the adsorption

capacities of CNT and CNF grown on powdered activate carbon (PAC) were studied in removing arsenic ions from synthetic water. The effects of initial concentration of arsenic and contact time for adsorption process are studied too. Langmuir and Freundlich adsorption isotherms are also determined for the new composite adsorbents.

II. MATERIAL AND METHODS

A. Preparation of Substrate

The palm kernel shell granular activated carbon (obtained from Effigen Carbon Sdn. Bhd. Malaysia) was grinded by using commercial grinder and the PAC of size between 100-250 μm was collected by sieving, for the production of CNFs.

B. Batch Mode Adsorption Tests

The synthetic arsenic contaminated water was prepared by adding the arsenic into Ultrapure water to produce required initial concentration of As. HCl and NaOH were used to adjust the pH to 7. Then, 50 mL of solution were poured into 100 mL shake flask before 10 mg of adsorbent was added. The shake flasks were agitated inside incubator shaker at room temperature ($\pm 25°C$) at constant agitation speed of 150 rpm. The batch adsorption tests were done at various contact times and the adsorbents were filtered from water by using filter paper. Then the filtrates were analyzed using flame Atomic Absorption Spectrometer (AAS). The outcome from the AAS was the residual concentration of arsenic after the adsorption.

C. Isotherms

Adsorption isotherm is a mathematical expression that relates the concentration of the adsorbate in the interface to its equilibrium concentration in the liquid phase [1]. Before calculating the isotherm, equilibrium sorption capacity, q_e, was determined the using following equation:

$$q_e\,(mg/g) = \frac{(C_i - C_e)}{M_s} \times V \qquad (i)$$

where C_i and C_e are the initial and equilibrium concentration of metal element the solution (mg/L) respectively, V is volume of the solution (in Liter) and M_s is the weight of adsorbent (mg). The results from this computation were used in calculating the isotherm.

In this research, two types of isotherm were studied, namely Langmuir isotherm and Freundlich isotherm. For Langmuir isotherm, the equation is stated below (ii):

$$q_e = \frac{bK_{eq}C_e}{1 + K_{eq}C_e} \qquad (ii)$$

where b is the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent) and K_{eq} is the Langmuir constant related to energy of adsorption (l of adsorbent per mg of adsorbate). The linear form can be used for linearization of experimental data by plotting C_e/q_e against C_e. The Langmuir constants b and K can be evaluated from the slope and intercept of linear equation.

The Freundlich equation as stated in equation (iii):

$$Q_e = KC_e^{1/n} \qquad (iii)$$

where K and n are Freundlich constant. A plot of log C_e against log Q_e yields a straight line which indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept.

III. RESULTS AND DISCUSSIONS

A. Effects of initial concentrations

Figure 1 to Figure 3 display the percentage removal of arsenic using both CNT and CNF at different concentrations. Initial concentrations of arsenic influence the adsorption process. Percentage removal of arsenic decreased with the increase in initial concentration of arsenic. For initial concentration of 0.5 mg/L, percentage removal was 75%, followed by 5 mg/L (73%) and finally initial concentration of 10 mg/L with 40% removal. However, for CNF, removal of arsenic at those concentrations were within a narrow band varying from 56%-59%. The theory behind this is, since the amount of adsorbent added is fixed, the adsorption sites are constant to absorb the arsenic ions. When the concentration increases, more ions present and need to be removed. With the inadequate surface area, the quantity of ions to be absorb limited and left over some of the arsenic ions. That shows from the result that the remaining arsenic ions in 0.5 mg/L was less than the initial concentration of 10 mg/L.
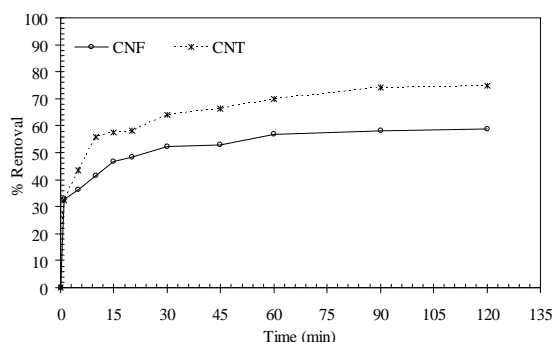
Figure 1: Percentage removal of CNT and CNF at initial concentration 0.5 mg/L (T=298°K, adsorbent dose=200 mg/L, pH=7)
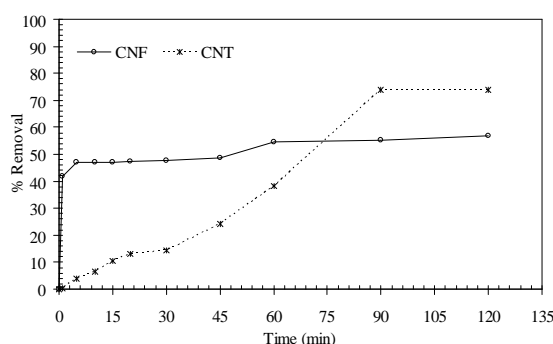

Figure 2: Percentage removal of CNT and CNF at initial concentration 5 mg/L (T=298°K, adsorbent dose=200 mg/L, pH=7)
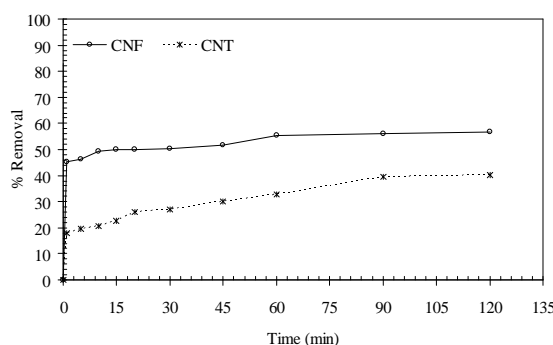

Figure 3: Percentage removal of CNT and CNF at initial concentration 10 mg/L (T=298°K, adsorbent dose=200 mg/L, pH=7)

B. Effects of contact time

The effects of contact times were studied too. It was observed that increasing the contact time has increased the adsorption of arsenic ions until it reached equilibrium. At equilibrium time, all adsorbent sites were occupied by the arsenic ions.

C. Equilibrium conditions

The times for adsorption to reach equilibrium for two adsorbents are shown in Table 1. It was observed

that both adsorbents reached equilibrium at the same time of 90 minutes.

D. Adsorption capacity

Table 1 also shows the adsorption capacity of both andosrbents at equilibrium at different initial concentrations. For low concentration, the adsorption capacity of CNT was better than that of CNF. However at 10 mg/L, CNF had higher adsortion capacity (27.97 mg/g), while the capacity of CNT was less (19.68 mg/g).

TABLE 1
TIME, CONCENTRATION AND CAPACITY AT EQUILIBRIUM

	C_i (mg/L)	Time (min)	C_e. (mg/L)	q_e (mg/g)
CNF	0.5	90	0.209	1.46
	5	90	2.245	13.78
	10	90	4.407	27.97
CNT	0.5	90	0.129	1.855
	5	90	1.312	18.44
	10	90	6.064	19.68

E. Adsorption Isotherm

Isotherm is a basic requirement for adsorption study to know the relationship between adsorbates and adsorbents. Such information is also required to design any adsorption system. Discussion on the isotherm studies are given below.

Langmuir isotherm

The linear Langmuir equation expressed in equation (iv):

$$\frac{C_e}{q_e} = \frac{1}{bK_{eq}} + \frac{C_e}{b} \qquad (iv)$$

The linear form can be used for linearization of experimental data by plotting C_e/q_e against C_e. The linearized plot of Langmuir isotherm for CNF and CNT are given in Figure 4 and Figure 5, respectively.
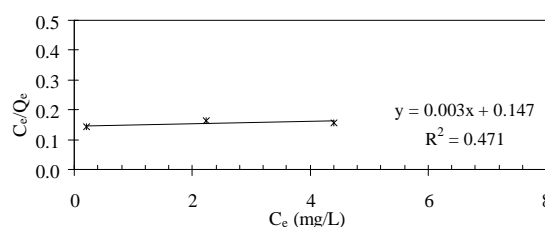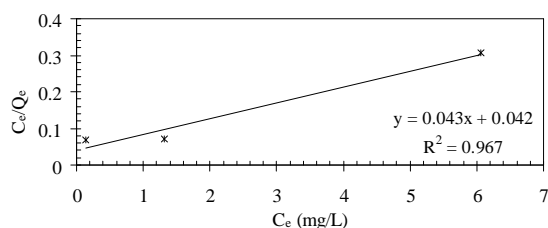

Figure 4: Langmuir plot for CNF

Figure 5: Langmuir plot for CNT

The slope and the intercepts were used to calculate the Langmuir adsorption constants stated in Table 2. Correlation coefficient (R^2) of the CNT was higher (0.967) than that of CNF indicating better fit of Langmuir model by CNT. As for CNF, the correlation coefficient was only 0.471, which was far less than the desired value of 1, indicating that CNF is not suitable for Langmuir model to represent the adsorption process for As removal. Maximum arsenic sorption capacity for CNT and CNF are 23.26 mg/g and 333.33 mg/g, respectively.

The Langmuir adsorption model is the most common model used to quantify the amount of adsorbate adsorbed on an adsorbent as a function of partial pressure or concentration at a given temperature. It considers adsorption of an ideal gas onto an idealized surface.

Inherent within this model, the following assumptions are valid specifically for the simplest case: the adsorption of a single adsorbate onto a series of equivalent sites on the surface of the solid.

- The surface containing the adsorbing sites is perfectly flat plane with no corrugations.
- The adsorbing gas adsorbs into an immobile state.
- All sites are equivalent.
- Each site can hold at most one molecule.
- There are no interactions between adsorbate molecules on adjacent sites.

When there are two distinct adsorbates present in the system (e.g. in this study PAC and CNT or CNF), the following assumptions can be applied:

- All the sites are equivalent.
- Each site can hold at most one molecule.
- There is no interaction between adsorbate molecules on adjacent sites.

Freundlich Isotherm

Linear equation for freundlich stated in equation (v):

$$log q_e = log K + 1/n log C_e \qquad (v)$$

Freundlich plot for CNF and CNT are shows in Figure 6 and Figure 7. The slope and intercepts from the plot were used to determine the n and K values. Unlike Langmuir isotherm, correlation coefficient for CNF was near 1 (0.999) which indicated that this adsorbent fits better for Freundlich model. The n charge determines the adsorption intensity. The favorable n value for Freundlich isotherm design must be between 1 and 10. The n value of CNF was 1.038 and that of CNT was 1.553; indicating that both of the materials fit the Freundlich model satisfactorily. Table 3 compared the adsorption capacity of other adsorbent material with those of CNT and CNF. It can be observed that the capacity of the CNF is relatively high.
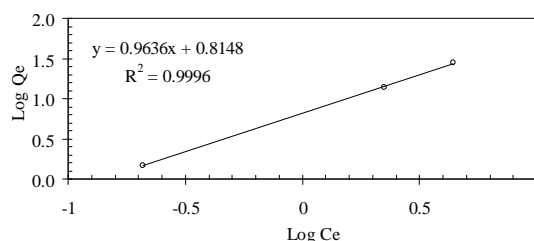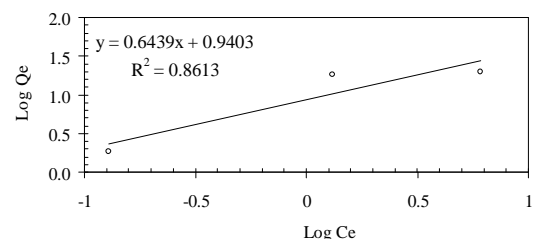

Figure 6: Freundlich plot for CNF

Figure 7: Freundlich plot for CNT

TABLE 3
COMPARISON OF MAXIMUM SORPTION CAPACITY FOR ARSENIC BY DIFFERENT ADSORBENT MATERIALS

Adsorbent	Maximum Capacity (mg/g)	Reference
CNT	23.26	This work
CNF	333.33	This work
Lessonia nigrescens	28.2	[7]
Activated Carbon	0.82-1.02	[13]
Activated alumina	15.56	[14]
Iron (III) oxide / silica	11.3	[15]
Penicillium purpurogenum	35.6	[16]
Hematite	0.4	[17]

TABLE 2
LANGMUIR AND FREUNDLICH CONSTANTS

Adsorbent	Langmuir			Freundlich		
	b (mg/g)	K_{eq}	R^2	K	n	R^2
CNF	333.33	0.020	0.471	6.528	1.038	0.999
CNT	23.26	1.023	0.974	8.716	1.553	0.861

Isotherm

IV. CONCLUSION

A new composite was produced with the use of PAC as a cheap substrate. The idea of growing CNM on substrate gave the advantage of clean production of CNM. The method was less hazardous compared to the floating catalyst CVD reactor. Adsorption tests showed that the CNT was suitable for low concentration while CNF was better adsorbent when deals with high concentration of As. Equilibrium capacity for CNT were 1.855 mg/g (Ci=0.5 mg/L), 18.44 mg/g (5 mg/L) and 19.68 mg/g (10 mg/L), while for CNF were 1.46 mg/g (0.5 mg/L), 13.78 mg/g (5 mg/L) and 27.97 mg/g (10 mg/L). Increasing of contact time increased the adsorption capacity until it reaches equilibrium. The adsorption process of CNT was a better fit for Langmuir isotherm model with the correlation coeficinte of 0.967, while Freundlich fit better for CNF ($R^2 = 0.999$).

V. ACKNOWLEDGMENT

REFERENCES

[1] M. R. Valk. Arsenic in Groundwater – A World Problem. Symposium organized by IAH's Dutch Chapter and the Netherlands' Hydrological Society. 2006. Netherlands. Article retrieved from http://webworld.unesco.org/water/ihp/pdf/arsenic _groundwater06.pdf

[2] D.N. Mazumder. Arsenic in drinking water and the prevalence of respiratory effects in West Bengal, India. *International Journal of Epidemology (29),* 2000. 1047-1052.

[3] R. G Robins, T. Nishimura & P. Singh (n.d.). *Removal of Arsenic from Drinking Water by Precipitation, Adsorption*

[4] *or Cementation.* Article retrieved from www.unu.edu/env/arsenic/ Robins.pdf

[5] J. Camerata. *Arsenic: Continuing Education Professional Development Course.* 2009. US: Technical Learning College. Article retrieved from www.tlch2o.com/courses/Arsenic.PDF.

[6] D. Lakshmanan, D. A. Clifford & G. Samanta. *Arsenic Coagulation with Iron, Aluminum, Titanium, and Zirconium Salts.* Houston: AWWA. 2008. Article retrieved from www.arsenicpartners.org/ 3078 Final Report.pdf

[7] B. Nayak, M. A. Hossain, M. K. Sengupta, S. Ahamed, B. Das, A. Pal & A. Mukherjee *Adsorption Studies with Arsenic onto Ferric Hydroxide Gel in a Non-oxidizing Environment: the Effect of Co-occurring Solutes and Speciation.* 2006. Article retrieved from http://www.cawq.ca/journal/temp/article/319.pdf

[8] Y. Masue. *Adsorption, Desorption, and Stabilization of Arsenic on Aluminum Substituted Ferrihydrite.* 2004. Article retrieved from http://repository.tamu.edu/bitstream/handle/1969. 1/3343/etd-tamu-2004C-2-SOSC-Masue.pdf?sequence=1

[9] H. K. Hansen, A. Rojo, O. Carla, M. O. Lisbeth, R Alexandra. & M. Eduardo. *Biosorption of Arsenic by Lessonia nigrescens in Wastewater from Copper Smelting.* (n.d). Article retrieved from http://www.cepis.opsoms.org/bvsacd/arsenico/Ar senic2004/theme3/paper3.6.pdf

[10] G. Ghanizadeh, M.H. Ehrampoush & M.T. Ghaneian. *Application of iron impregnated activated carbon for removal of arsenic from water.* 2010. Article retrieved from http://journals.tums.ac.ir/upload_files/aip/pdf/16 4.pdf

[11] A. Chatterjee & B.L. Deopura. Carbon Nanotubes and Carbon Nanofibre: an overview. *Journal for Fibers and Polymers, (3),* 2002. 134-139.

[12] P. M. Ajayan & O. Z Zhou. *Applications of Carbon Nanotubes.* 2001. Article retrieved from http://www.rpi.edu/locker/38/001238/pdfs/ applications%20of%20nanotubes.pdf

[13] M. A. Murphy, G. D. Wilcox & F. Marken. *Deposition and Application of Carbon Nanofiber Composite Electrodes.* 2003. Article retrieved from http://www.nuigalway.ie/eseac2004/P_14.pdf

[14] M. J. Rosen. Surfactant and Interfacial Phenomena.John Willy & Sons. 2005. 45.

[15] P. Bunnaul, R. Saejen, S. Arrykul & K. Kooptarnond. *Proceedings of FEISEAP'99 Inter-Regional Symposium on Sustainable Development (ISSD) Felix Kanchanaburi-Swissotel-River Kwai, Thailand, May 18-20, 1999.*

[16] T.S. Singh & K.K. Pant, *Proceedings of 9th APCCHE conference (paper #285), 2002.*

[17] L. Zeng, Water Quality Research Journal of Canada. 39(3), 2004. 269-277.

[18] R. Say, N. Yilmaz, A. Denizli. Separation Science and Technology, 38(9), 2003. 2039 – 2053.

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