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The Optimum Condition for the Synthesis of Carbon Nanofibers on Activated Carbon to Remove Lead from Aqueous Solution

Abdullah Al Mamun[1*], Yehya M. Ahmed[2], Ma'an Fahmi R. Al Khatib[1], Ahmad T. Jameel[1] and Mohammed A. Al Saadi[3]

[1]*Nanoscience and Nanotechnology Research Group (NANORG), Faculty of Engineering International Islamic University Malaysia (IIUM), Jalan Gombak, 53100 Kuala Lumpur, Malaysia.*
[2]*Department of Pathological Analysis, Al-Manara College of Medical Sciences, Amara Iraqf.*
[3]*National Chair of Materials Sciences and Metallurgy, University of Nizwa, Oman.*

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ABSTRACT

Optimum process condition for the production of Carbon Nanofibers (CNFs) to remove lead ion (Pb) from aqueous solution is reported here. The CNFs were produced on the catalyst (Ni^{2+}) impregnated palm oil-based cheap Powder Activated Carbon (PAC). Locally fabricated Chemical Vapour Deposition (CVD) system was used while acetylene (C_2H_2) was the carbon source. The porous nano-composite product is named "PAC-CNFs", which was synthesized through a process using impregnated oil palm shell based PAC as a solid substrate. Design Expert 6.0.8 software was used to design the experimental plan and to determine the optimized process parameters for the growth of CNFs by using sorption capacity for Pb^{2+} by the PAC-CNFs adsorbent, as a response. The effect of different factors on the growth of CNFs including the temperature of CNFs growth (550 to 750 °C), time of growth (30 to 60 min), and the ratio of input C_2H_2/H_2 gases (0.25 to 1.0) was evaluated. The predicted values for the sorption capacity of Pb^{2+} by the PAC-CNFs were in close agreement with the experimental data (R^2 = 0.99). The optimal process condition: temperature for the growth of CNFs, time, and C_2H_2/H_2 ratio was determined as 637 °C, 30 min, and 1.0, respectively. The CNFs grown under the optimized condition exhibited sorption capacity of 77 mg/g in removing Pb^{2+} from synthetic wastewater containing lead (Pb^{2+}) ion.

Keywords: Carbon Nanofibers, Powder Activated Carbon, Sorption, Water Remediation.

1. INTRODUCTION

Toxic elements such as copper (Shetty and Rajikumar, 2009), lead (Abdel-Ghani *et al*., 2009; Arunlertaree *et al*., 2007; Okoro and Ejike, 2007), cadmium (Rao *et al*., 2007), and chromium or compounds of them (Resmi *et al*., 2010) have been widely used by various metal-finishing, mining and other industries. This led to increasing cases of water pollution and toxicity. In general, aqueous bodies are the main targets of heavy metal deposition due to streams and rivers flow through agricultural sites that are rich in pesticides and fungicides, or rivers flow through industrial areas become a dumping place of metal waste (Malakootian *et al*., 2009; Okoye, 2010).

Due to their toxicity, high concentrations of these metals in water will render the usefulness of water for the living beings (Abdel-Ghani and Elchaghaby, 2007). Discharging lead into aqueous environment becomes a particular concern, as this metal is fixed to be bio-accumulated and

* Corresponding Author: *mamun@iium.edu.my*

exposure to these high metal concentrations are harmful to the living cells (Issabayeva *et al*., 2006). Various methods have been applied for the treatment of toxic metal-tainted wastewaters; e.g. chemical precipitation, adsorption, electrodialysis, ultra-filtration, reverse osmosis, ion exchange, and, phytoremediation (Yehya *et al*., 2015 and Muataz *et al*., 2009). These methods have limitations due to incomplete elimination of the metals, use of other chemicals, high energy consumption, and ultimate safe disposal of the toxic sludge produced from the treatment process (Gueu *et al*., 2007; Ahalya *et al*., 2003). However, due to more strict legislative enforcement around the world, the development of efficient metal removal methods has become necessary for the protection of the aquatic environment.

Among those approaches, using activated carbon and carbon nanomaterials to adsorb heavy metals showed an acceptable performance (Ayala *et al*., 1998; Faur-Brasquet *et al*., 2002; Imamoglu and Tekir, 2006; Goyal *et al*., 2008; Acharya *et al*., 2009; Onundi *et al*., 2010; Coq *et al*., 1998, Nhut *et al*., 2003, Mohammed *et al*., 2011; Figueiredo and Pereira, 2010).

Traditional ways for metal removal are expensive, time-consuming, does not consider the interaction effects of various parameters, and cannot decide the optimum conditions practically. Due to that, statistical data would be an effective tool for optimization. Design of Experiment (DOE) approach is one of these methods. Rene *et al*. (2007) used such method where the experiments were conducted according to the $2^{k/l}$ fractional factorial design for the identification of the prime factors and interactions among them. The Response Surface Methodology (RSM) was used to model various phenomena and to optimize the experimental results as a function of different parameters.

In this research work, the Central Composite Design (CCD) was used for the progression of CNFs growth on nickel impregnated PAC by obtaining the relation between synthesis variables to the adsorption of lead ions on the CNFs surface for the removal of Pb^{2+} ions. Several parameters were varied simultaneously with a minimum number of laboratory experiments. Later on, a mathematical model was developed by solving the regression equation used to predict the percentage removal of lead ion under various adsorption process conditions.

2. MATERIAL AND METHODS

2.1 Synthesis of PAC-CNFs

The preparation method and characterization of the PAC-CNFs were reported by Mamun *et al*. (2013). However, the details methodology on the process optimization conditions used for the synthesis of CNFs on PAC is provided in the following sections.

2.2 Design of Experiment (DOE) for CNFs Synthesis on PAC

Design Expert 6.0.8 software was used to design the experimental plan and determine the optimized process parameters for the growth of CNFs, using sorption capacity (mg/g) for Pb^{2+} by the PAC-CNFs adsorbent, as a response. Response Surface Method (RSM) is among the new ways that are separated into several categories. However, Box-Behnken and Faced Centred Central Composite Design (FCCCD) are commonly used (Kalali *et al*., 2011). The latter approach was utilized here for the determination of the CNFs production conditions in order to achieve the highest sorption capacity of the adsorbent. Three factors were used namely, reaction temperature (ºC), growth time (minute), and the gas ratio of C_2H_2/H_2as carbon source for CNFs. The range of the important parameters that play a significant role in the synthesis of CNFs is given in Table 1 below.

Table 1 CNFs growth variables with their levels used in the design expert software

Factor	Name	Unit	Low	Center Point	High
A	Temperature	ºC	550	650	750
B	Growth Time	min	30	45	60
C	C_2H_2/H_2 Ratio	-	0.25	0.63	1

The highest and lowest values of each parameter (reaction time, reaction temperature and gas flow ratio C_2H_2/H_2) were chosen depending on a study on the production of CNFs (Pham-Huu *et al*., 2006; Romero *et al*., 2007; Kalali *et al*., 2011).

2.3 Batch Adsorption Tests

A certain amount of PAC-CNFs (250 mg/L) was put into a flask containing 20 mL synthetic lead aqueous solution. The pH of the solution was 5.5 while it contained 20 mg of lead ions per litre. The pH value of 5.5 was determined from another screening exercise (Mamun *et al*., 2015), where pH of various ranges was tested to determine the optimum pH for the removal of lead ions using PAC-CNFs composites. After adding the PAC-CNFs adsorbents into the flasks, the samples were shaken at 200 rpm at room temperature (25±1°C). Filtration for each sample was done after the end of each test using membrane filters of 0.45 µm; the filtrate was stored in plastic bottles and the concentration of the residual lead ions was measured using atomic absorption spectrophotometer (AAS).

2.4 Statistical Analysis

Design Expert 6.0.8 software was used to determine the regression model for the adsorption of lead by PAC-CNFs. The ANOVA data was used to select the best model for the synthesis of PAC-CNFs for the specific objective of removing lead ions from aqueous solutions.

3. RESULTS AND DISCUSSION

3.1 Analyses of DOE Data

The experimental values of adsorption capacities for each condition (as given in Table 1) were calculated depending on the laboratory experiments. Interaction among the variables was studied using on the Face Centre Central Composite Design (FCCCD) as shown in Table 2. The experimental and values predicted by the model of the sorption capacity of PAC-CNFs in removing Pb^{2+} from synthetic wastewater is available in Table 2. The design was based on taking a centre point (temperature, time, and C_2H_2/H_2 gas ratio) of 650°C, 45 min and 0.63, respectively.

Table 2 Synthesis condition of PAC-CNFs production by CCD and corresponding adsorption capacity in removing Pb^{2+} from synthetic wastewater

Run	A: Temp. (°C)	B: Time (min)	C: C_2H_2/H_2 Ratio	Adsorption Capacity (mg/g)	
				Experimental	Predicted by Model
1	750	45	0.63	50.1	50.9
2	750	30	1.00	53.3	53.3
3	650	60	0.63	67.3	67.3
4	550	45	0.63	69.2	69.9
5	650	30	0.63	65.2	64.2

6	550	30	0.25	60.3	60.3
7	650	45	0.25	57.7	56.7
8	550	60	1.00	64.5	64.5
9	750	60	0.25	62.6	62.6
10	650	45	1.00	65.1	65.1
11	650	45	0.63	60.1	60.4

The response in this study was the sorption capacity of PAC-CNFs for Pb^{2+}. Each sample was used as an adsorbent and the results of the capacity were entered in the software as given in Table 2. The sorption capacity of PAC-CNFs given by ANOVA is presented in Table 3.

Table 3 Analysis of variance (ANOVA) for quadratic model

Source	Sum of Squares	DF	Mean Square	F-Value	Prob> F	Status
Model	342.86	8	42.86	25.15	0.0388	significant
A	181.83	1	181.83	106.70	0.0092	significant
B	2.4	1	2.4	1.41	0.3673	insignificant
C	28.73	1	28.73	16.86	0.545	insignificant
B^2	47.71	1	47.71	28.00	0.0339	significant
AB	34.41	1	34.41	20.19	0.0461	significant
AC	7.05	1	7.05	4.14	0.1789	insignificant
BC	71.05	1	71.05	41.69	0.0232	significant
ABC	48.88	1	48.88	28.69	0.0331	significant
Residual	3.41	2	1.7			
Cor Total	346.27	10				

Std. Dev.	1.31	R-Squared	0.9902
Mean	61.41	Adj R-Squared	0.9508
CV	2.13	Pred R-Squared	N/A
PRESS	N/A	Adeq Precision	16.150

A: Growth temperature (^oC), B: Growth time (min), C:Gas ratio C_2H_2/H_2

For sorption capacity of PAC-CNFs, the F-value Model of 25.15 shows the significance of the model. It means that 3.88% possibility that a "Model F-Value" this big could happen because of noise. The data in Table 3 also reveals that A, B^2, AB, BC and ABC are significant model terms (as the values of "Prob> F" less than 0.05); while the other terms are not significant as the values of "Prob> F" are higher than 0.1. A high value of 16.15 of "Adeq Precision" (higher than 4) indicates an adequate and satisfactory signal of the data and analysis.

3.2 Statistical Model

The response surface analysis by the Design Expert software revealed that the adsorption process can be represented by multivariate statistical quadratic model (Equation 1):

$$\text{Adsorption (mg/g)} = 5.7 + 0.09A + 0.74B + 0.03B^2 - 0.003AB - 8.29BC + 0.01ABC \quad (1)$$

Where, A, B and C are the temperature of growth (^oC), time (min) and the gas ratio (C_2H_2/H_2), respectively.

The assessment of the reliability of the regression model was done based on the value of the correlation coefficient. The model (Equation 1) showed a high R^2 value of 0.9902 indicating that 99.02% of the data in the adsorption of Pb^{+2} can be explained by the growth temperature and time. The value of the correlation coefficient obtained was relatively high, indicating that the relation between the theoretical (model data) and experimental data was good. It's also been shown from the model that R^2 is acceptable with the adjusted R^2 value of 0.9518. A very good fit of the model and experimental data (as shown in Figure 1 below) indicates good quality and reliable results.

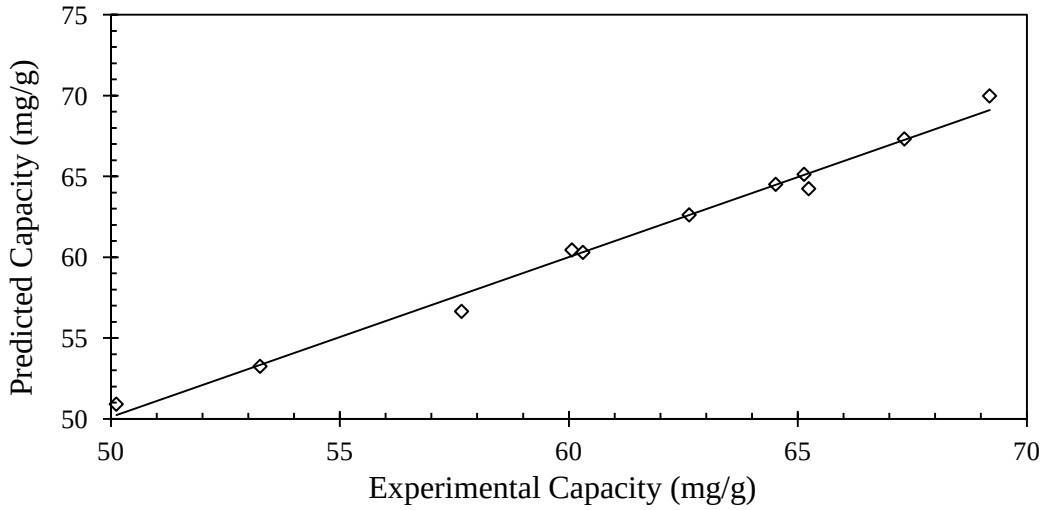

Figure 1. Actual and predicted sorption capacity for Pb^{2+}.

The statistical analysis of the Design-Expert software provides 10 solutions that are comparable for the production of CNFs that depends on best sorption properties of Pb^{+2}. A comparison between results obtained from the model and the experimental is shown in Table 4 below.

Condition 6 in Table 4 was chosen for the optimum growth condition of CNFs synthesis, where the temperature, reaction time, and C_2H_2/H_2 gas ratio is 637°C, 30 min, and 1.0, respectively. Additional experiments were conducted to validate the optimal condition for CNFs production. The condition agrees with the theoretical result and it will be used for future production since it is able to provide the highest sorption capacity value with shorter production time. Table 5 below shows the optimal conditions for the production of CNFs done by other researchers using the same CVD technique. The relation between contact times (minute) versus adsorption capacity of lead by the two adsorbents (mg/g) was plotted as in Figure 2.

Table 4 Process conditions suggested by the DOE for the optimum production conditions

Number	Temp. (°C)	Time (min)	C_2H_2/H_2 Ratio	Experimental Capacity (mg/g)	Calculated Capacity (mg/g)	Error (%)
1	556	37	0.7	74	73	1.35
2	562	54	0.5	66	69	4.35
3	556	50	0.7	68	69	1.47
4	559	38	0.7	73	73	0
5	592	31	0.6	71	71	0
6	637	30	1.0	77	77	0
7	575	43	0.4	71	73	2.18
8	554	57	0.6	69	71	2.98
9	558	54	0.5	73	70	4.11
10	591	60	0.5	71	72	1.41

Table 5 Comparison of optimum conditions for the production of CNFs

Catalyst	Time (minute)	Temperature (°C)	C/H_2 Ratio (carbon source)	Reference
Fe	45	1100-1200	0.5 (C_2H_6/H_2)	Fan *et al*., 2000
Ni-Fe/Al_2O_3	60	750	0.4 (C_2H_6/H_2)	Kvande *et al*., 2006
Ni	-	680	0.2 (C_2H_6/H_2)	Pham-Huu *et al*., 2006
Na/Y-zeolite	60	550-650	0.5 (C_2H_4/H_2)	Romero *et al*., 2007
Ni-Cu alloy	180	600	1.0 (C_2H_4/H_2)	Diaz *et al*., 2008
Ni	30	637	1.0 (C_2H_2/H_2)	This study

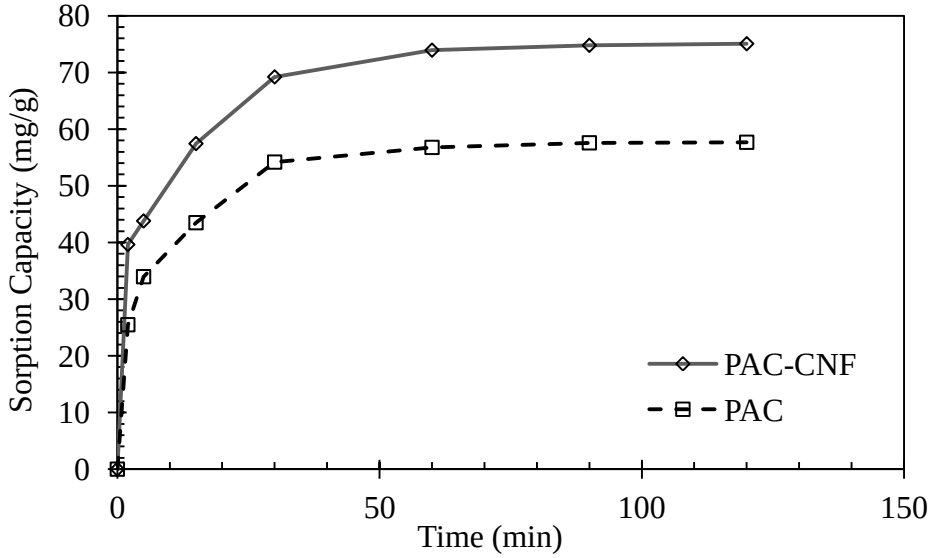

Figure 2. Adsorption of Pb^{2+} by the selected PAC-CNFs sample and PAC.

It was observed that the sorption capacity of Pb^{2+} by PAC and PAC-CNFs increased gradually with time and reached the optimum condition at an initial time of 60 minutes. The performance after that increased slightly and became almost constant. The results indicate that after 15 minutes, 53% and 76% of Pb^{2+} removal occurred when using PAC and PAC-CNFs adsorbents, respectively. Moreover, the highest removals of around 75% were recorded after 90 minutes contact time for PAC and around 91% for PAC-CNFs samples after 30 minutes, respectively.

Those results are consistent with the increase in the surface area of the PAC due to the growth of CNFs on the PAC surfaces. Similar findings were reported by Horsfall and Spiff (2004), Hepinstall *et al*. (2005), and Lin *et al*. (2010). The comparison study has confirmed the successful modification of the PAC surface through the growth of the CNFs and the improvement of the sorption capacity allowing a new adsorbent to be used for the adsorption of lead ions.

4. CONCLUSIONS

The CNFs growth parameters were optimized by using Central Composite Design (CCD). The statistical analysis provides ten comparative solutions for the production of PAC-CNFs based on the best sorption properties. The best process condition for the production of CNFs to remove maximum lead ion was achieved at a temperature of 637°C, the reaction time of 30 min, and C_2H_2/H_2 gas ratio of 1.0; this condition gave the highest value of the response (sorption capacity). At these conditions, the sorption capacity of PAC-CNFs for removal of lead ions from aqueous solutions was 77 mg/L. According to the ANOVA analysis, the sorption capacity was highly affected by the growth temperature and the interactions between the time of the growth and other factors (temperature and C_2H_2/H_2 ratio). The polynomial adsorption model was acceptable as the R^2_{adj} (0.95) and the adequate precision ratio (16.15) values were higher than the minimum values. Finally, the results reported in this article explain the possibility of using PAC-CNFs as an adsorbent for the removal of lead ions from wastewater and other aqueous solutions.

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