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Removal of Chromium (VI) from polluted water using carbon nanotubes supported with activated carbon

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Abstract

The environmental application of carbon nanotubes supported by activated carbon to remove chromium (VI) ions from polluted water was investigated. The experimental conditions that enhance the adsorption of Cr (VI) by carbon nanotubes have been studied. These conditions include the initial concentration of Cr (VI), the pH, the dosage of adsorbent, the contact time and the agitation speed. The activated carbon either alone or being coated with carbon nanotubes has be characterized by field emission scanning electron microscopy. A fractional factorial design was used to obtain a complete randomize experiment statistically. Adsorption isotherms have been applied to study the kinetics of the adsorption behavior and to determine the adsorption capacity of the absorbents. Regression analysis was used to study the empirical statistics of the experiment and to identify the significance of the parameters used to enhance the adsorption capacity. It was found that the activated carbon coated with carbon nanotubes is considered as an excellent adsorbent to Cr (VI) ions with an adsorption capacity of 9.0 mg/g.

Keyword: Carbon Nanotubes, Activated Carbon, chromium (VI) removal

1. Introduction

The pollution of water resources due to the disposal of heavy metals was causing worldwide concern. The main sources of these metals are mining, metallurgical, chemical manufacturing ,tannery, battery manufacturing industries, fossil fuel, the modern chemical industry is based largely on catalysts, many of which are metals or metal compounds, production of plastics, such as polyvinyl chloride, involves the use of metal compounds, particularly as heat stabilizers etc . The effects of heavy metals such as copper, lead, zinc, mercury, chromium(VI) and cadmium on human health have been investigated extensively. Lead is ubiquitous in the environment and is hazardous at high levels. Long-term drinking water containing high level of lead will cause the nervous system damage, renal kidney disease, mental retardation, cancer and anaemia [1]. Lead is non-biodegradable and, therefore, must be removed from water [2]. Many methods have been developed and used to remove metal ions from wastewater such as granulated activated Carbon [3,4], fly ash [5], peat [6], recycled alum sludge [7], peanut hulls [8], resins [9], kaolinite [10], manganese oxides [11], zeolite [12], biomaterials [13,14] .However, the removal efficiencies of metal ions of these adsorbents were low . Therefore, researchers have carried out various investigations to develop new

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promising adsorbents [15]. Carbon nanotubes (CNTs), a member in carbon family, have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics, water treatment and other fields of materials science. Since their discovery in 1991[16], carbon nanotubes (CNTs) have attracted the attention of many researchers, due their exceptional mechanical electrical properties, highly chemical stability and large specific areas [17]. Multi-walled carbon nanotubes (MWCNT) were previously used for removal of metal ions, such as lead, copper, cadmium, silver, nickel [18]. Li et al. reported that carbon nanotubes have high adsorption efficiency for lead removal from water and the adsorption of lead is higher than copper and cadmium and significantly influenced by the pH of the solution. Hsieh and Horng reported that the adsorption capacity of CNTs grown on aluminum oxide, for the removal of Pb2+, Cu2+ and Cd2+ from solutions is superior to that of active carbon powders, commercial CNTs, and aluminum oxide [20]. Kandah and Meunier found that the adsorption of Ni2+ by oxidized CNTs is 1.24 times greater than commercial activated carbon called MINOTAUR [21-26]. Xu et al. reported that removal of Pb (II) is strongly dependent on pH, ionic strength and the type of foreign ions [21].

In this work, activated carbon either alone or coated with CNTs were used to study the effect of these nanomaterials on the removal the chromium (VI) from water. The effective parameters such as pH, dosage of MWCNTs, agitation speed and contact time were optimized in order to maximize the removal of Cr (VI).

2. Materials and methods

2.1. Catalyst impregnation

The activated carbon (AC) was derived from palm kernel shell obtained from NanoC sdn bhd. Malaysia. The AC was previously treated with concentrated HNO_3 (70%, Sigma Aldrich) to eliminate inorganic impurities, such as Fe, that would lead to heterogeneity of the produced CNFs. Later in the text, AC is referred as the HNO_3-treated support. The AC samples were ground and sieved to particle size of < 50 micrometer before impregnated via the wet-impregnation method with Ni $(NO_3)_2$ in an acetone solution to achieve Ni weight loading of 1%. The samples were further dried overnight at 40 ^oC in static air [24].

2.2. Characterization of carbon nanotubes supported by activated carbon

The morphology of filamentous carbon (long carbon nanotubes) was observed by field emission scanning microscopy, FESEM (JEOL JSM-6700F). Platinum coating was used prior to the FESEM observation. The diameter of the carbon nanotubes was obtained and the surface of the adsorbents was observed.

2.3. Batch mode adsorption experiments

Batch mode adsorption studies were carried out by preparing solutions of 0.2-0.5 mg/l Cr (VI) by dissolving the required quantity of Potassium dichromate in a specific volume of deionized water. The working solutions were prepared by proper dilution. A volume of 50 ml of each of these solutions was placed in a 100 ml conical flask and the required weight of the activated carbon was added to each flask. Then, the conical flasks were agitated at desired speeds using a mechanical shaker. The pH was adjusted by using solutions of 0.1 N sulphuric acid or 0.1 N sodium hydroxide.

After the desired equilibrate time, the adsorbent and adsorbate were separated by vacuum filtration and the filtered solution was analysed by HACH-DR/2400 spectrophotometer with 1,5 diphenyl carbazide at 543 nm. Then, the effects of dosage of activated carbon (AC), the initial concentration of chromium (VI), pH, time contact and the agitation speed have been studied. All of the experiments were carried out in duplicate and mean values were calculated.

2.4. Experimental design

Table 1 shows the experimental parameters and their variations which were used in the batch mode adsorption experiments. The run orders for complete randomized experiments were determined by using MINITAB fractional factorial design software. Fractional factorial designs are useful in factor screening because they reduce the number of runs to a manageable size. The runs that were performed were a selected subset or fraction of the full factorial design.

Table 1: Experiment parameters and its variation

No.	Parameter	Variation		
		Low	**Medium**	**High**
1.	Concentration of Chromium(VI) (mg/L)	0.2	0.35	0.5
2.	Adsorbent Dosage (mg/50 mL)			
	• Normal Activated Carbon	2	11	20
	• Activated Carbon coated with Carbon Nanotubes (Type I)	2	11	20
	• Activated Carbon coated with Carbon Nanotubes (Type II)	2	11	20
3.	pH	2	3	4
4.	Time Contact (min)	60	150	240
5.	Agitation Speed (rpm)	100	150	200

2.5. Adsorption kinetics

As stated earlier, the influence of several operational parameters including the dose of adsorbent, agitation speed, initial pH, initial chromium (VI) concentration and contact time was investigated. The results were expressed as the adsorption capacity, (mg/g) of the adsorbent on chromium(VI) removal which was defined as

$$q_t = \frac{(C_o - C_t)V}{m_s} \quad (1)$$

Where;

C_o, and C_t are the Cr(VI) concentrations in mg/L initially and at a given time t, respectively
V is the volume of the Cr (VI) solution in ml
m_s is the weight of activated carbon in g.

The removal efficiency (E) of the adsorbent on Cr (VI) ions in solution was calculated using Equation (2):

$$E(\%) = \left[\frac{(C_O - C_t)}{C_o}\right] \times 100 \quad (2)$$

The differences in the concentration before and after removal of chromium give indication that the adsorption was taking place on the surface of the AC/CNTs.

The Langmuir equations were used to describe the data derived from the adsorption of Cr by each adsorbent over the entire operational parameters range studied. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions.

Therefore, from the batch mode experimental data obtained and by using Langmuir equation, the plot of *Ce/Qe* versus *Ce* for each adsorbent was developed.

$$\frac{C_e}{Q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \quad (3)$$

Where:
Q_e = the adsorption density (mg of adsorbate per g of adsorbent)
Ce = the concentration of adsorbate in solution (mg/l)
K is empirical constant dependent on several environmental factors.

3. Results and discussion

3.1. Characterization of adsorbents

The surface area of the activated carbon and the activated carbon coated with carbon nanotubes were measured on the basis of the N_2 isotherm performed at 77 K with a Quantachrome instrument as shown in table 2. Images of the activated carbon before undertaking adsorption experiments were characterized by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F) (Figure 1 & Figure 2). The activated carbon coated with carbon nanotubes samples were platinum coated prior to FESEM observation. Figure 1 (a) & (b) shows the normal activated carbon at different magnification. Figure 1 (b) shows the high magnification of the normal activated carbon. Furthermore, impurities have been observed over the surface of the activated carbon. Figure 2 (a) to (f) show the carbon nanotubes (CNTs) supported by AC at different magnifications. From figure 2 we noted that most of the surface of the activated carbon was completely covered with carbon nanotubes with diameters range of 16 - 19 nm. Figure 2 (f) shows the diameters of the three different carbon nanotubes which are 16.1, 16.2 and 19.2 nm approximately were identified. The carbon nanotubes which were observed are clumped to each other and not aligned with each other as well.

Table 2: Textural properties of sample AC-CNT.

Sample	Surface area m^2/g	Micropore volume cc/g	Total pore volume cc/g
AC	1233	0.438	0.455
AC/CNT	755.8	0.269	0.354

3.2. Removal of Chromium (VI) by using activated carbon and carbon nanotubes coated on activated carbon

The batch adsorption experiments which have been done were completely randomized by MINITAB fractional factorial design. The results obtained from the randomized experiments are shown in the Table 3 , 4 and 5. The optimum conditions were determined from the tabulated results of adsorption capacity. During the adsorption process, two types of adsorbents which are normal activated carbon and activated carbon coated with carbon nanotubes were used. The predictive values of the adsorption capacity have been determined from the regression equation obtained. From this tabulated results, the optimum conditions for each parameter were identified and highlighted. The optimum conditions are determined from the highest value of adsorption capacity, (mg/g) of the chromium(VI) concentration. The required parameters which contribute to the optimum adsorption capacity for

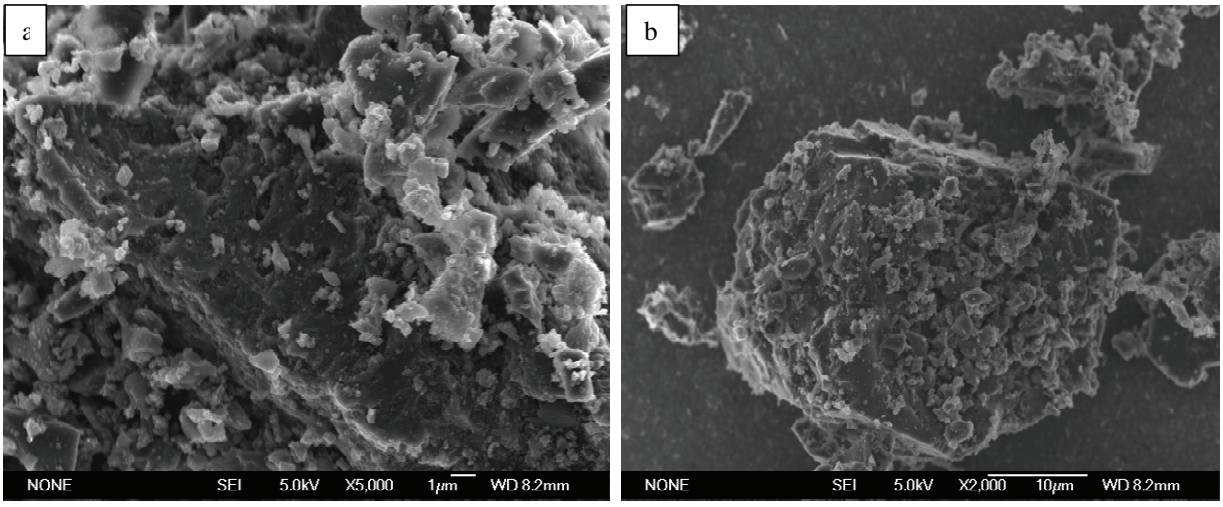


Figure 1: (a) & (b) FESEM images of normal activated carbon (AC) before the experiment with different magnifications.

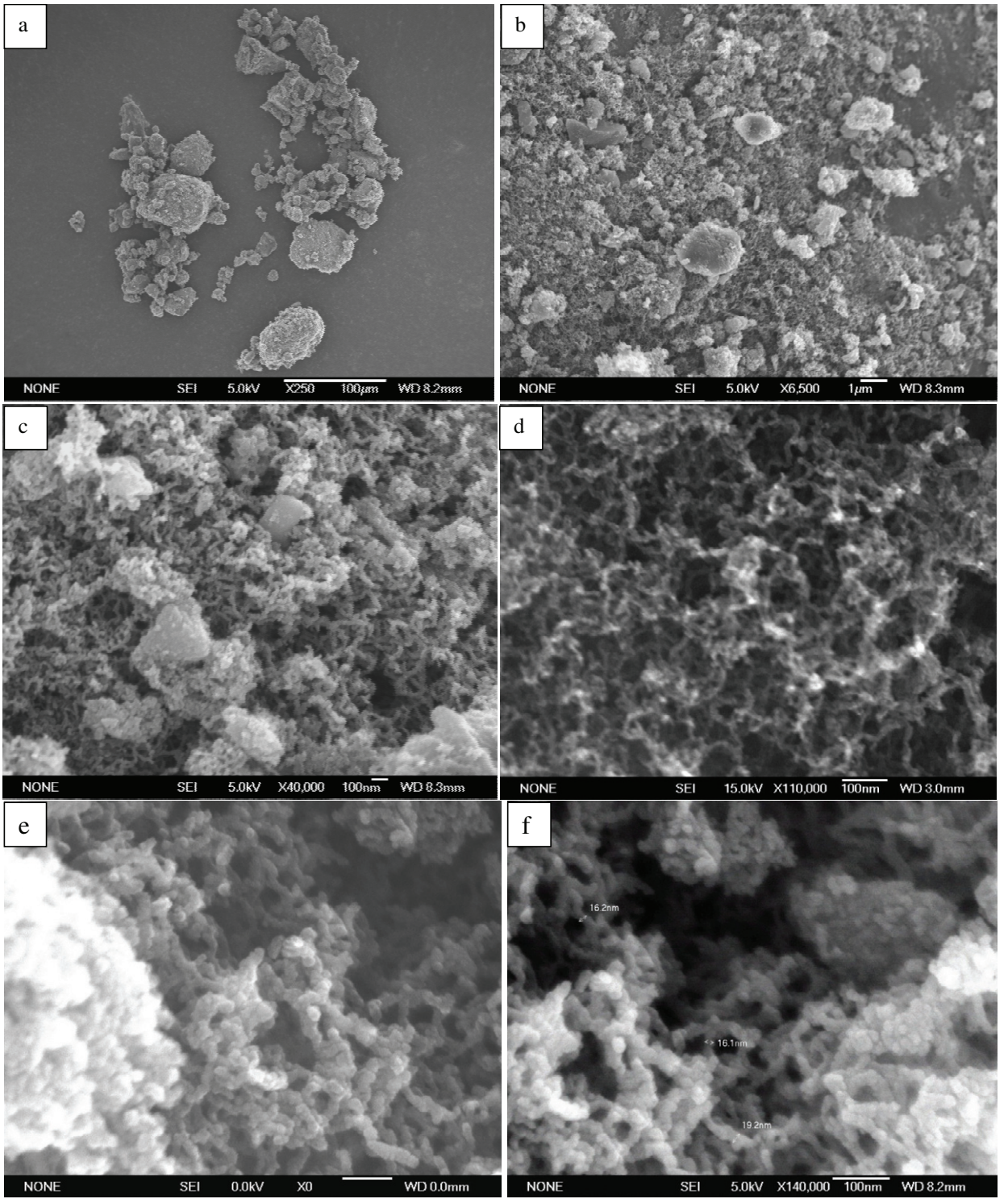


Figure 2: (a) to (f) FESEM images of carbon nanotubes (CNTs) supported by AC before the experiment with different magnifications

each adsorbents used are shown in Table 3. It is obvious from the results obtained, that the optimum parameters for each adsorbent are mainly dependent on the adsorbent characteristics. The values for each parameter used might be similar and it might vary in order to obtain a maximum adsorption capacity. As can be seen from Table 3, an

Table 3: The Parameters Condition for Optimum Adsorption Capacity (mg/gm) obtained from each Adsorbent used

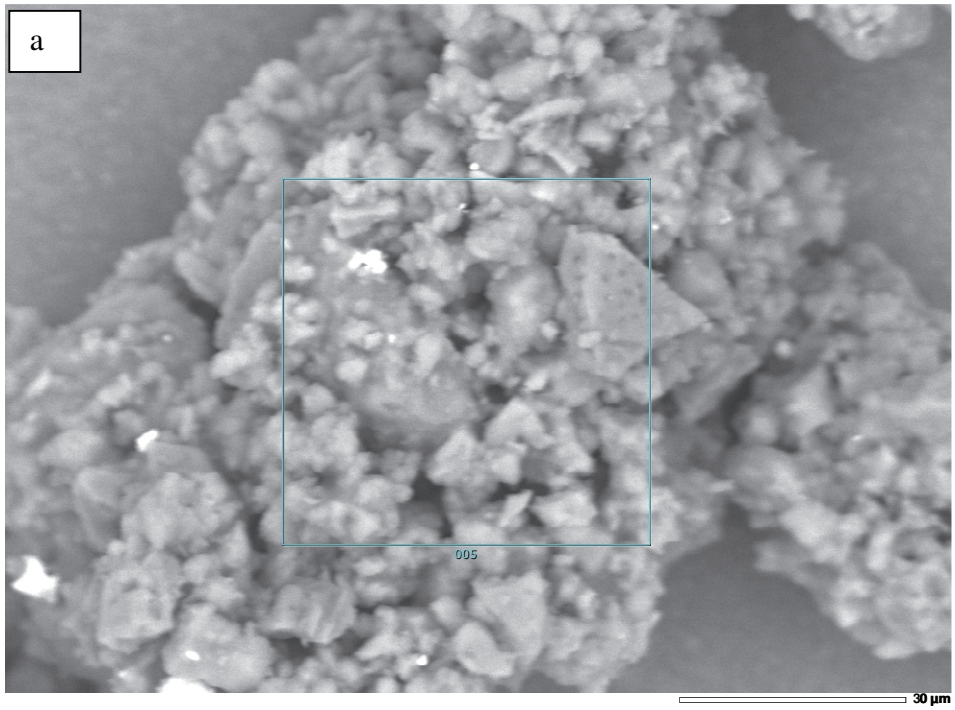
Adsorbent Type	Chromium Conc. (mg/l)	Adsorbent Dosage, m (mg/50ml)	Adsorbent Dosage, m (mg/L)	pH	Time Contact (min)	Agitation Speed (rpm)	Cr remaining, c (mg/L)	Cr Removed, x (mg/l)	% Cr removed	Predictive Adsorption Capacity, (mg/g)	Experimental Adsorption Capacity, x/m (mg/mg)
Normal Activated Carbon	0.5	2	40	4	60	200	0.17	0.33	66.0	7.49	**8.250**
Activated Carbon coated with Carbon Nanotubes	0.5	2	40	2	60	100	0.14	0.36	72.0	8.551	**9.000**

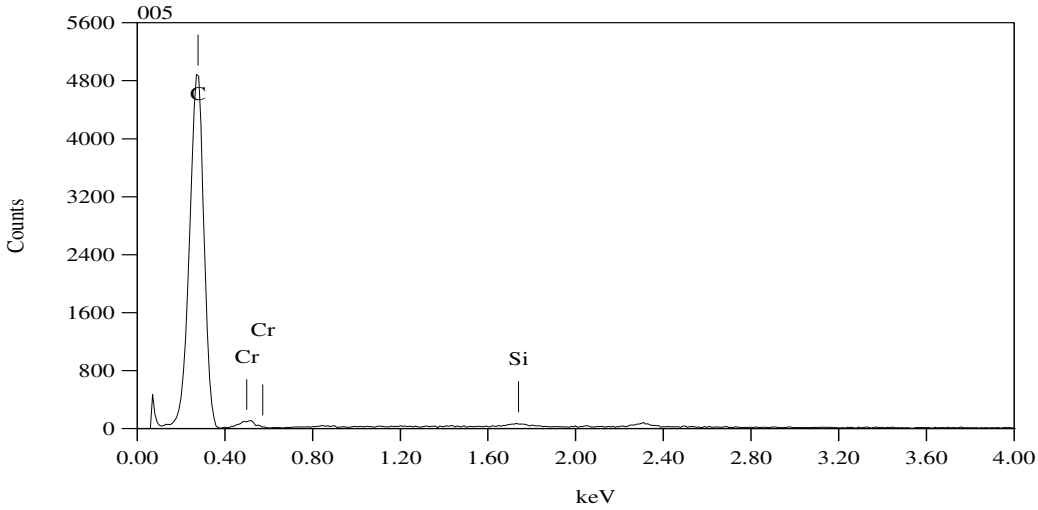
Table 4: Adsorption Capacity for Chromium Removal using Normal Activated Carbon

Run Order	Chromium Conc. (mg/l)	Adsorbent Dosage, m (mg/50ml)	Adsorbent Dosage, m (mg/L)	pH	Time Contact (min)	Agitation Speed (rpm)	Cr remaining, c (mg/L)	Cr Removed, x (mg/l)	% Cr removed	Predictive Adsorption Capacity, (mg/g)	Experimental Adsorption Capacity, x/m (mg/mg)
1	0.2	20	400	2	60	200	0.00	0.20	100.0	0.51	0.500
2	0.5	20	400	2	240	100	0.00	0.50	100.0	1.253	1.250
3	0.5	20	400	4	240	200	0.01	0.49	98.0	1.176	1.225
4	0.5	2	40	4	60	200	0.23	0.27	54.0	7.49	6.750
5	0.2	2	40	2	240	200	0.02	0.18	90.0	4.621	4.500
6	0.5	2	40	4	60	200	0.17	0.33	66.0	7.49	8.250
7	0.35	11	220	3	150	150	0.01	0.34	97.1	3.245	1.545
8	0.2	2	40	4	240	100	0.08	0.12	60.0	2.869	3.000
9	0.35	11	220	3	150	150	0.03	0.32	91.4	3.245	1.455
10	0.5	2	40	2	60	100	0.18	0.32	64.0	7.74	8.000
11	0.5	2	40	2	60	100	0.20	0.30	60.0	7.74	7.500
12	0.2	2	40	2	240	200	0.01	0.19	95.0	4.621	4.750
13	0.5	20	400	2	240	100	0.01	0.49	98.0	1.253	1.225
14	0.2	20	400	4	60	100	0.08	0.12	60.0	0.299	0.300
15	0.5	20	400	4	240	200	0.07	0.43	86.0	1.176	1.075

Table 5: Adsorption Capacity for Chromium Removal using Activated Carbon coated with Carbon Nanotube

Run Order	Chromium Conc. (mg/l)	Adsorbent Dosage, m (mg/50ml)	Adsorbent Dosage, m (mg/l)	pH	Time Contact (min)	Agitation Speed (rpm)	Cr remaining, c (mg/l)	Cr Removed, x (mg/l)	% Cr removed	Predictive Adsorption Capacity, (mg/g)	Experimental Adsorption Capacity, x/m (mg/g)
1	0.35	11	220	3	150	150	0.01	0.34	97.1	1.613	1.545
2	0.2	20	400	4	60	100	0.05	0.15	75.0	0.406	0.375
3	0.35	11	220	3	150	150	0.01	0.34	97.1	1.613	1.545
4	0.2	20	400	4	60	100	0.05	0.15	75.0	0.406	0.375
5	0.5	20	400	4	240	200	0.01	0.49	98.0	1.120	1.225
6	0.2	2	40	2	240	200	0.01	0.19	95.0	711	750
7	0.5	2	40	4	60	200	0.21	0.29	58.0	7.427	7.250
8	0.2	2	40	4	240	100	0.09	0.11	55.0	3.086	2.750
9	0.5	2	40	4	60	200	0.2	0.3	60.0	7.427	7.500
10	0.5	20	400	2	240	100	0	0.5	100.0	1.351	1.250
11	0.5	20	400	2	240	100	0	0.5	100.0	1.351	1.250
12	0.5	2	40	2	60	100	0.14	0.36	72.0	8.551	9.000
13	0.2	20	400	2	60	200	0	0.2	100.0	0.522	0.500
14	0.5	20	400	4	240	200	0.18	0.32	60	1.120	0.800
15	0.2	2	40	2	240	200	0.02	0.18	90.0	711	500

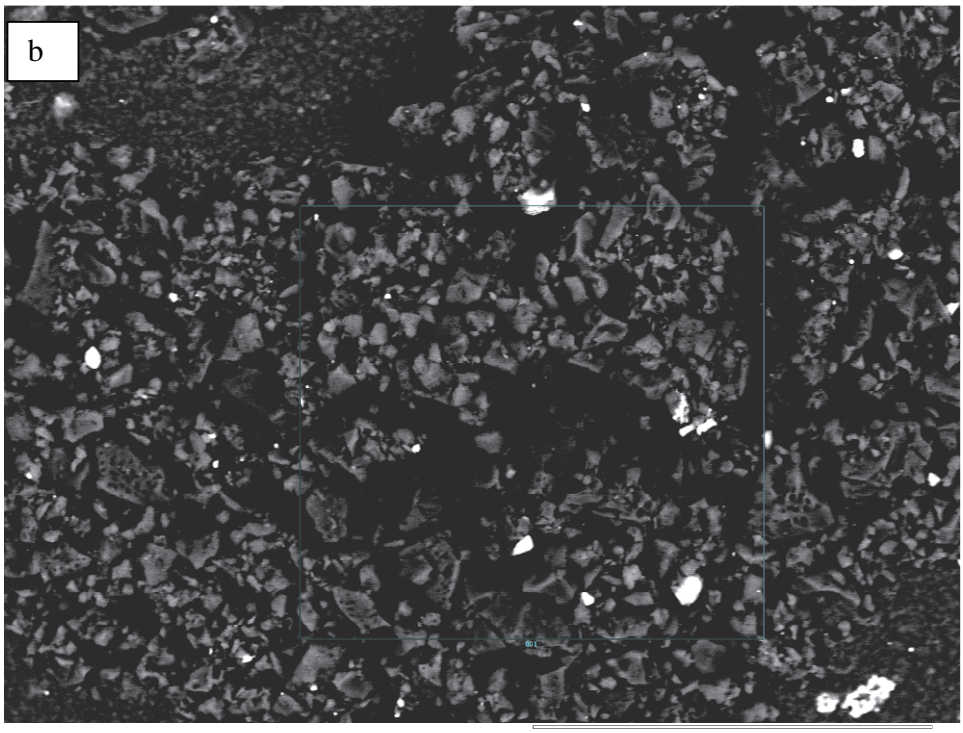


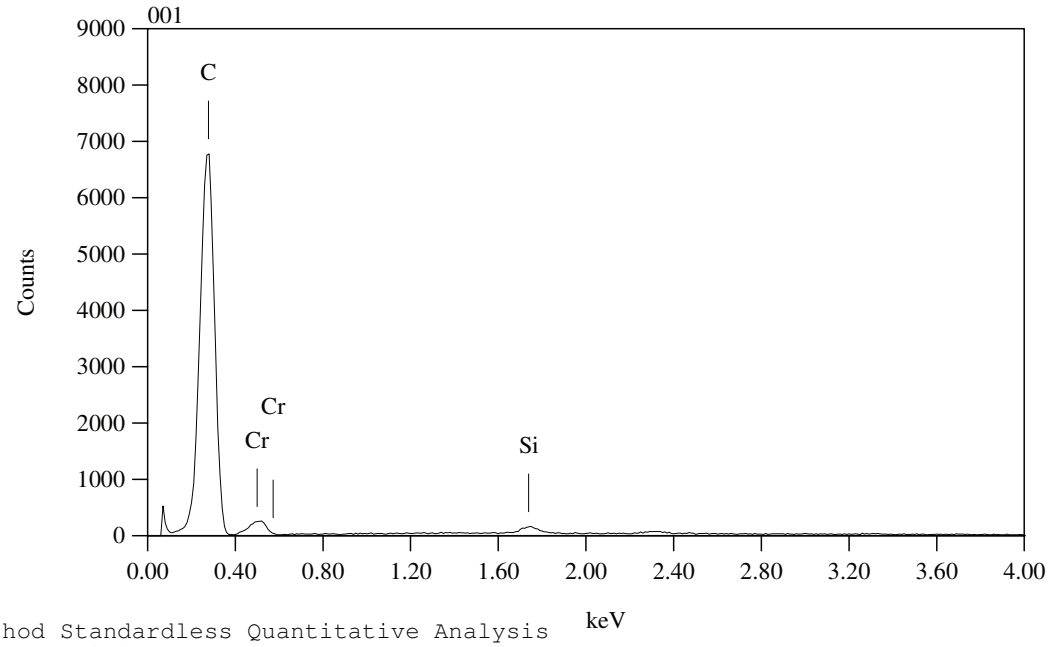


ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2020

Element	(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
C K	0.277	99.75	0.05	99.90				99.7489
Si K	1.739	0.23	0.12	0.10				0.2270
Cr K	5.411	0.03	0.53	0.01				0.0241
Total		100.00		100.00				

Figure 3: FE-SEM images with EDS analysis for (a) Normal activated carbon and (b) activated carbon coated with carbon nanotubes





ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2016

Element	(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
C K	0.277	99.29	0.05	99.72				99.2809
Si K	1.739	0.60	0.12	0.26				0.6183
Cr K	5.411	0.11	0.53	0.03				0.1008
Total		100.00		100.00				

Figure 3: continued

optimum value of an adsorption capacity can be achieved if the initial chromium(VI) concentration is 0.5 mg/L with an adsorbent dosage of 2 mg in a volume of 50 ml solution and a contact time of 60 minutes. The optimum pH for the normal activated carbon was found to be pH 4 while that for the CNTs supported by activated carbon was pH 2. Regarding the agitation speed it was 100 rpm for activated carbon coated with carbon nanotubes and 200 rpm in case of the normal activated carbon. From the tabulated results, the activated carbon coated with carbon nanotubes gives a higher value of adsorption capacity which is 9.0 mg/g compared to the normal activated carbon which gives an adsorption capacity of 8.25 mg/g. The required conditions which contribute to the optimum adsorption capacity for each adsorbent used are shown in Table 4. From the experimental results obtained, the optimum parameters for each adsorbent are dependent on the adsorbent characteristics. The values for each parameter used might be similar and it might vary in order to obtain a maximum adsorption capacity. From Table 4, it was noted that to obtain an optimum value of adsorption capacity, the optimized value for the initial chromium (VI) concentration should be 0.5 mg/L with an adsorbent dosage of 2 mg in 50 ml solution and a contact time of 60 minutes. However, the optimized pH for the normal activated carbon was at pH 4 while that of the activated carbon coated with carbon nanotubes was at pH 2 as shown in table 5. Furthermore, the agitation speed for activated carbon coated with carbon nanotubes is 100 rpm which is also different from the normal activated carbon and activated carbon coated with carbon nanotubes which was at 200 rpm. From the tabulated result, the activated carbon coated with carbon nanotubes gives an adsorption capacity of 9.0 mg/g which is higher than that obtained by the normal activated carbon 8.25 mg/g.

3.3. Characterization of Chromium adsorption by using field emission electron microscopy (FE-SEM)

FE-SEM was used to identify the existence of chromium (VI) on the adsorbents along with EDS analysis. Figures 3 and 4 show the results obtained and the mass percentage of Cr (VI) on AC coated with CNTs is 0.11. However in case of normal AC the mass percent of Cr was 0.03. It is evident that the tendency of AC coated with CNTs to remove Cr(VI) is much higher than that of normal AC.

4. Conclusion

The application of carbon nanotubes for the removal of chromium (VI) from wastewater is one of the pioneer studies which have been done in environmental field [22-23]. The characteristics of the carbon nanotubes make it possible to produce high quality and good results on the experimental outcomes. It also provides high expectations on the development of wastewater treatment and environmental contamination reduction.

In this study the application of both the activated carbon and the carbon nanotubes attached to the activated carbon have been investigated as potential adsorbents to Cr (VI) from waste water. The efficiencies of these two adsorbents have been determined by finding the adsorption capacity of each. Five parameters were found to contribute to the adsorption capacity, hence they were optimized. These parameters include: the initial concentration of Cr (VI), the adsorbent dose, the pH of the solution, the time contact and the agitation speed. The values for each parameter were completely randomized throughout the designed experiment as discussed earlier. All of the parameters used in the adsorption experiment were significant and have direct impacts on the adsorption capacity which was identified from the regression analysis. From the characterization of the adsorbents, it was found that, the surface area of the activated carbon coated with carbon nanotubes is higher compared to normal activated carbon.

This is due to the fact that the carbon nanotube attached to the surface of the activated carbon each has a size of 10 to 20 nm in diameter which provides more surface area to the adsorbents. It was also noted that the size of the adsorbent particles plays an important role in the adsorption capacity efficiency. By comparing the two types of the adsorbents, the results and analysis showed that the activated carbon coated with carbon nanotubes which is in the powder form gives higher adsorption capacity compared to the normal activated carbon which is in granular form.

The optimum conditions to achieve the maximum adsorption capacity for each type of the adsorbents were obtained. The highest adsorption capacity by using activated carbon coated with carbon nanotubes adsorbent obtained from the batch adsorption experiment was 9.0 mg/g. Therefore, it can be concluded that

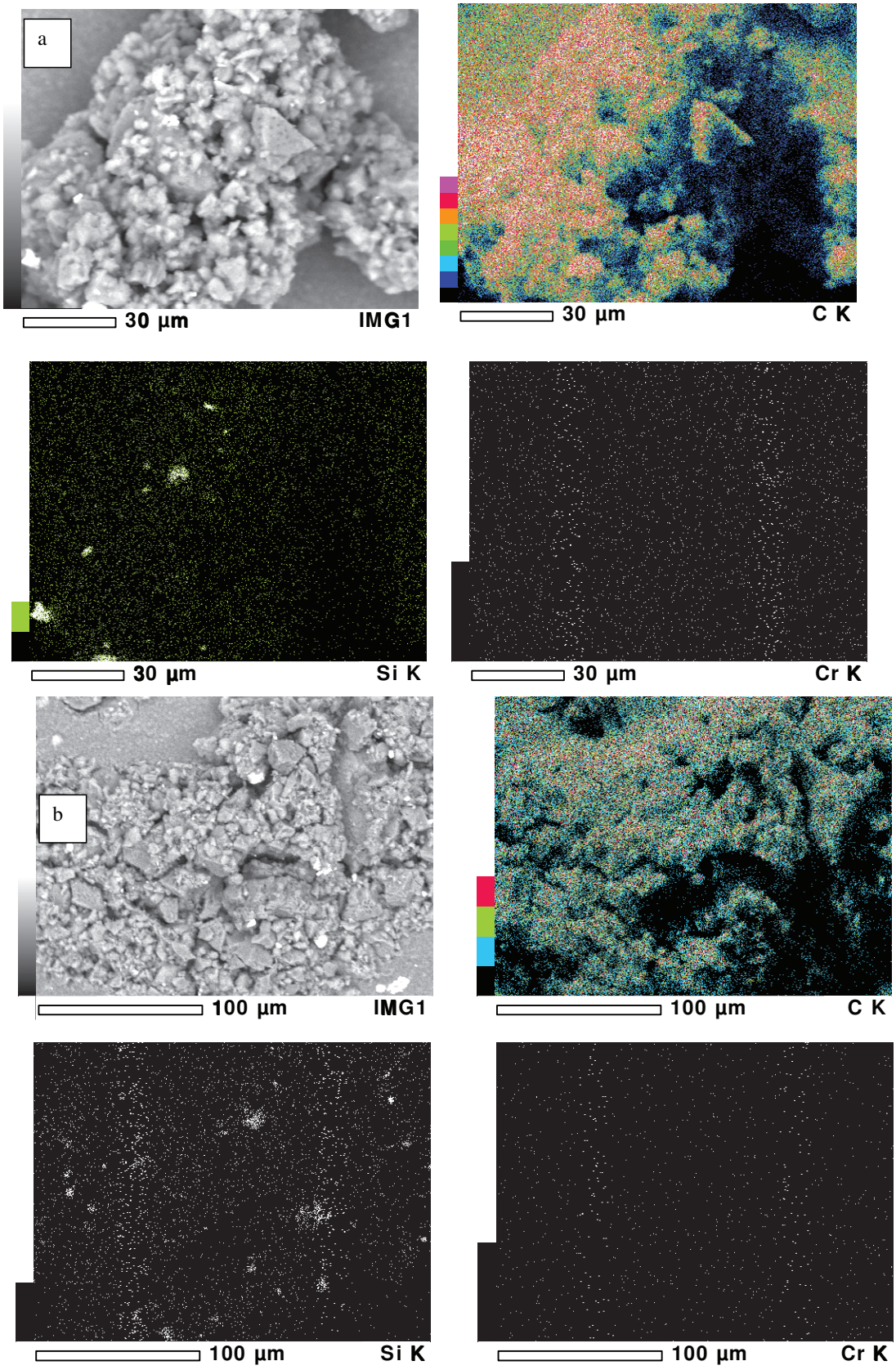


Figure 4: Back scattering FE-SEM images for (a) Normal activated carbon and (b) activated carbon coated with carbon nanotubes

the activated carbon coated with carbon nanotubes is most effective for the removal of chromium ions.

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