Adsorption of chromium (VI) on functionalized and non-functionalized carbon nanotubes

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Abstract−We did a comparative study on the adsorption capacity of Cr (VI) between functionalized carbon nanotubes (CNTs) and non-functionalized CNTs. The statistical analysis reveals that the optimum conditions for the highest removal of Cr (VI) are at pH 9, with dosage 0.1 gram, agitation speed and time of 120 rpm and 120 minutes, respectively. For the initial concentration of 1.0 mg/l, the removal efficiency of Cr (VI) using functionalized CNTs was 87.6% and 83% of non-functionalized CNTs. The maximum adsorption capacities of functionalized and non–functionalized CNTs were 2.517 and 2.49 mg/g, respectively. Langmuir and Freundlich models were adopted to study the adsorption isotherm, which provided a K_L and K_F value of 1.217 L/mg and 18.14 mg^{1-n}L^n/g functionalized CNT, while 2.365 L/mg and 2.307 mg^{1-n}L^n/g for non-functionalized CNTs. This result proves that functionalized CNTs are a better adsorbent with a higher adsorption capacity compared with the non-functionalized CNTs.

Keywords: CNT, Chromium, Heavy Metal, Adsorption, Separation, Functionalization

INTRODUCTION

Environmental issues and their consequences affect all living creatures and flora on earth, further creating a serious problem in the past few decades. Water pollution has been highlighted as one of the most crucial issues which needs an immediate solution to avoid further impact on the environment. One of the main contributions to water pollution is the emission of heavy metal ions from extensive industries such as mining, cement ceramics, glass industries fossil fuel, battery manufacturing industries and production of plastics, involving the use of metal compounds [1]. The indirect consumption of these heavy metals could lead to several disease problems such as kidney disease, anaemia, cancers of the digestive tract and lungs, nervous system failure [2-4] and eventually to death as well. Hence, to avoid further impact on the environment, these heavy metals have to be eradicated from the wastewater before they are discharged into any type of water source. Many methods and techniques have been investigated and applied to remove these heavy metals from the water such as ion exchange, membrane separation, reverse osmosis, electrolysis and adsorption [5,6]. All of these methods have been employed and have flourished in removing an impressive percentage of heavy metal ions from the wastewater, but the adsorption method stands out to be one of the most versatile

methods due to its flexibility and simplicity. Adsorbents are known to be the foundation of this adsorption technology. A variety of adsorbents such as zeolite, activated carbon, egg shell, silica gel and slag [7-11] have already been engaged with the removal of heavy metal applications, but it is more desirable to explore a higher adsorption capability of adsorbent to remove heavy metals from any aqueous solutions. Carbon nanotubes (CNTs) as a new member in the adsorbent family, which was first reported in 1991 [12], have been proven for their higher efficiency of the removal of heavy metal ions from aqueous solutions due to remarkable mechanical [13], electrical [14], and chemical properties [15]. On the same note, CNTs have large specific surface area, high thermal and chemical stabilities and provision for large scale synthesis, making them a good candidate for adsorption kinetics [16], and their light mass density [17] have made them one of the successful adsorbents to be integrated with the removal of heavy metal ions from aqueous solutions [18, 19]. Further research has also been carried out to prove that the adsorption capacity of CNTs can be increased by altering their chemical and physical properties by functionalizing them with acids or alkaline solutions such as nitric acid, sulfuric acid and potassium permanganate [20,21].

In this research, we performed statistical optimization and a comparative study on the removal of Cr (VI) from aqueous solution by the usage of and non-functionalized (NFCNTs) and functionalized CNTs (FCNTs). The effect of each process parameter pH, dosage and agitation time on the removal of Cr (VI) was investigated using FCNTs and NFCNTs. The equilibrium kinetic and isotherm model

equation for the removal of Cr (VI) was also investigated.

MATERIAL AND METHODS

1. Functionalization of CNTs

The experimental setup used to synthesize the multiwall carbon nanotubes (MWCNTs) is similar to that reported by Mubarak et al. [22]. There was 95% purity with an average diameter of 30 to 40 nanometers and 1.5 microns of average length. The FCNTs were carried out by immersing 9 grams of CNTs into a flask containing 0.4 M of nitric acid, HNO_3 and $KMnO_4$ solutions at a volume ratio of 3 : 1. This solution was then water bath sonicated (JAC-2010P) for 3 hours at $^{\circ}$C to modify the surface of 40 CNTs. The mixture was then filtered using a 0.45 mm polytetrafluoroethylene (PTFE) membrane filter. The residual acid from the mixture was removed by having it washed with the 1 M NaOH solution and finally with distilled water until the pH was 7.0. The residue was dried in a vacuum oven maintained at 80 $^{\circ}$C for 48 h and characterized by using the FESEM and FTIR.

2. Preparation of Stock Solutions

Analytical grade Cr (VI) standard solution obtained from Merck was used to prepare stock solutions containing 1,000 mg/L of Cr (VI) metal ions which were further diluted with distilled water to obtain the required concentrations. The initial concentration of Cr (VI) metal ions was set to 1.0 mg/L and the prepared solution was used for batch adsorption experiments.

3. Batch Adsorption Experiment

A batch adsorption experiment was performed by using 100 ml of 1.0 mg/L of Cr (VI), agitated with varying dosages of CNTs and other variable parameters according to the design obtained from the Design of Expert (DOE). The parameter used for this research is shown in Table 1. The temperature of the agitation process was kept constant at 50 $^{\circ}$C throughout the study by utilizing the water bath to avoid any additional effect on the adsorption process. If the temperature is too high, there are possibilities of the solution evaporating after a certain period of time. The initial pH of the stock solution was adjusted by using 1.0 M of NaOH by adding in a few drops of the alkaline solution in the 100 ml of 1.0 mg/L of Cr (VI) until the desired pH was obtained. The CNTs were then added into the 100 ml of 1.0 mg/L of Cr (VI) solution and it was agitated according to the parameters displayed in Table 1. The adsorption isotherm experiment was carried out by agitating 0.1 gram of adsorbent in three different pHs of 1.0 mg/L stock solution such as pH 5, pH 7 and pH 9 for 3 hours. The 3 hour time period was chosen based on the time the adsorption capacity attained an almost equilibrium level during the kinetic study.

The adsorption capacity of non-functionalized and functionalized CNTs at time t was determined by using Eq. (1) while the adsorp-

tion equilibrium of Cr (VI) was computed based on Eq. (2)

$$q_t \text{ (mg/g)}=[(C_o-C_t)V]/m \tag{1}$$

$$q_e \text{ (mg/g)}=[(C_o-C_e)V]/m \tag{2}$$

where C_o represents the initial concentration of Cr (VI) solution (mg/L), q_t represents the concentration of Cr (VI) at time t (mg/g), C_e represents the equilibrium concentration of Cr (VI) (mg/L) respectively; V represents the volume of Cr (VI) stock solution (L) and m indicates the weight of the adsorbent used (g).

As for the desorption study, the functionalized and non-functionalized CNTs were recovered after the adsorption experiments where 0.10 gram of these recovered adsorbents containing the adsorbed metal ions was stirred in 100 ml of deionized water at different acidic pH values, such as pH 1 to pH 5 at 50 $^{\circ}$C for a constant 3 hour time period. The final concentration was then measured to determine the desorption percentage value.

The novelty of this work over the other work studied would be the process of functionalization of CNTs. As for this research, the functionalization of CNTs was carried out by a volume ratio of 3 : 1 of 0.4 M of nitric acid, HNO_3 and potassium permanganate, $KMnO_4$ solution. The combination of nitric acid and potassium permanganate in this volume ratio is considered new in this type of research.

4. Characterization of CNTs

The physical structure and morphology of the CNTs were examined by the field emission scanning electron microscope (FESEM) (Brand: Zeiss Model: Auriga) technique. The Fourier transform infrared (FTIR) spectroscope ((Brand: Bruker, Model: IFS66v/S) was used to study the surface chemistry of CNTs before and after functionalization. FCNT was carried out using water bath sonication (JAC-2010P). All pH measurements were done by using Mettler Toledo type (MP220 model, USA).

RESULTS AND DISCUSSION

1. Characterization of the Functionalized and Non-functionalized CNTs

The functionalized and non-functionalized CNTs were examined by FESEM (Zeiss, Auriga) as shown in Figs. 1(a), (d). Figs. 1(a) and (b) indicate the functionalized CNTs at different magnifications of 1,000 and 1,000,000 nm. The vertical alignments of the CNTs can be clearly observed. On the other hand, Figs. 1(c) and (d) indicate the non-functionalized CNTs at different magnifications of 1,000 and 1,000,000 nm in which the vertical alignments of the CNTs can be clearly seen with the diameter of the CNTs falling in the range of 30 to 33 nm. Besides that, the surface of the non-functionalized CNTs is found to be much smoother than the functionalized CNTs due to the agglomeration of the CNTs' surface during the functionalization process. Generally, atomic force microscopy and Auger elemental surface analysis can be used to study the characteristics of the surface of the CNTs. The functionalization process would create an open end to the CNT tube where additional functional groups such as carboxylic group would attach to it or any available defect sites [23]. According to Oye et al. [24], the variation in the nature of the CNT growth is directly dependent on the surface roughness, which can eventually affect the surface growth chemistry of CNTs. Auger elemental analysis determines

Table 1. Experimental design for batch adsorption

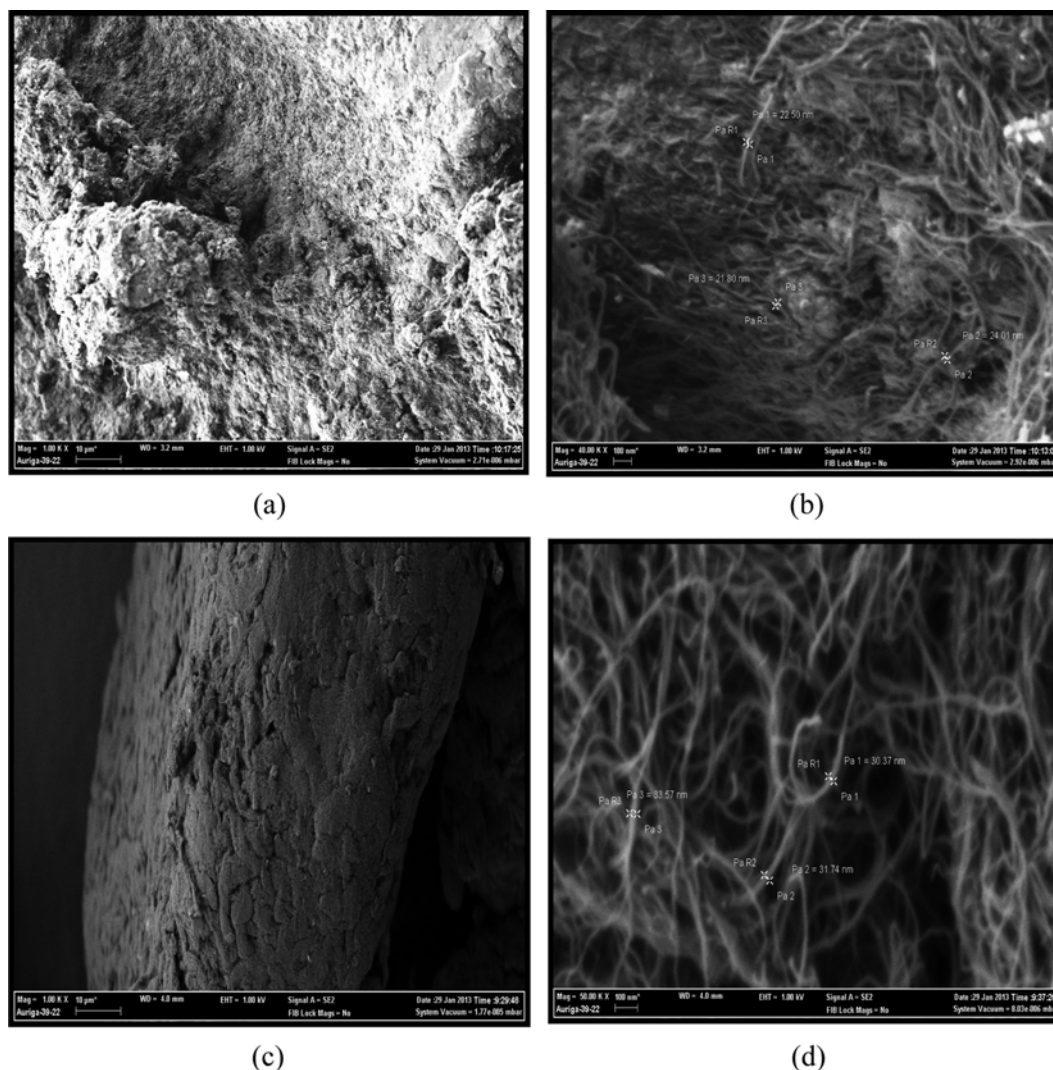| No	Parameter	Variations' range
1	pH of stock solution	pH 5, pH 7 and pH 9
2	Dosage of CNTs	0.04 g, 0.07 g and 0.10 g
3	Agitation speed	30 rpm, 75 rpm, 120 rpm
4	Contact time	30 minutes, 75 minutes, 120 minutes

Fig. 1. FESEM images (a), (b) functionalized CNTs, (c), (d), non-functionalized CNTs.

that carbon was observed all over the surface of the CNTs, but it was strongest over the smooth regions of high density growth of CNTs while less carbon was detected over the poor CNT growth. Hence, functionalized CNTs refer to the poor CNT growth which eventually leads to a poor surface roughness while non-functionalized CNTs refer to the high density growth of CNTs, which eventually leads to a smoother surface [24].

2. FTIR Analysis of CNTs

Generally, FTIR can be used to study the adsorption behavior of any adsorbent by the chemical reactivity of the surface, especially when chemically bonded oxygen exists on it in various forms of functional groups [25]. The rule of surface functionalities increases significantly relative to the pore size distribution or the BET surface area [26]. The surface chemistry in terms of functional groups attached on the surface of the CNTs can be identified by FTIR spectroscopy (Bruker, IFS66v/S). In this research, the FTIR was used to analyze the surface characteristics in terms of the functional group attached on the functionalized and non-functionalized CNTs. Fig. 2(a) denotes the peaks for non-functionalized CNTs where the absence of the functional group on the surface of CNTs was observed while Fig. 2(b) denotes the peaks for functionalized CNTS where
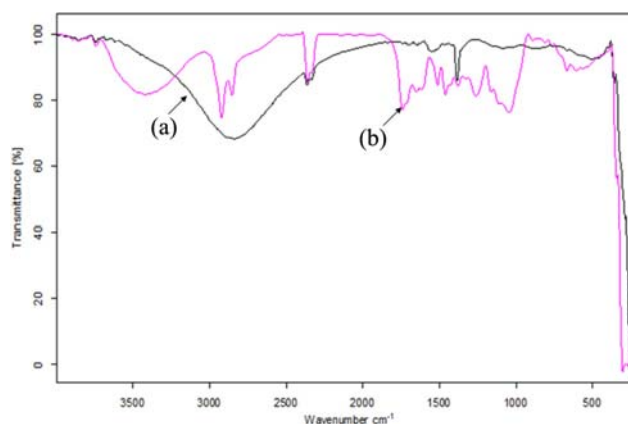

Fig. 2. FTIR adsorption spectra (a) non functionalized CNTs (b) functionalized CNTs.

the absorption peak by the carboxylic group can be observed at the range of 1,700 to 1,900 cm^{-1}, aromatic C=C groups at 1,450-1,600 cm^{-1} and O-H groups 2,800-3,000 cm^{-1}. Functionalized CNTs offer a more hydrophilic surface structure and introduce oxygen-contain-

ing functional groups to the surface of nanotubes as the carboxylic and hydroxyl groups. These functional groups are more hydrophilic, and hence functionalized CNTs will be more easily dispersed in the water. Hence, functionalized CNTs provide a higher adsorption capacity of Cr (VI) from the solution compared with non-functionalized CNTs. A similar result has been recorded by other researchers [27].

3. Statistical Analysis of Functionalized and Non-functionalized CNTs for Removal of Cr (VI)

To determine the most suitable adsorbent with the highest adsorption capacity of Cr (VI) from aqueous solutions, the first crucial step would be to determine the optimized condition of both the adsorbents, functionalized and non-functionalized CNTs. The specific runs for the optimized condition were conducted based on the design obtained from the DOE. The results obtained from this particular experiment were analyzed by analysis of variance (ANOVA) obtained from the DOE and the optimized variables attainable from Table 1. The analysis obtained by the application of ANOVA for the removal of Cr (VI) using functionalized and non-functionalized CNTs is indicated in Tables 2 and 3, respectively. From the values obtained in Tables 2 and 3, the fisher F-test value can be related to the mean square of the regressed model, which leads to the comparative mean square of the residuals (errors). The F value proves the efficiency of the model as its value increases. On the other hand, low probability, P value indicates higher significance for the regression model. Hence, from Tables 2 and 3, the F-test values for functionalized and non-functionalized CNTs were 125.7097 and 135.375,

respectively, which indicates that both models are significant. Besides that, the values of the correlation coefficient, R-Squared and Adj R-Squared for functionalized CNTs were 0.9899 and 0.9820, respectively, while for the non-functionalized CNTs 0.9906 and 0.9833, respectively. This value implies that both models of adsorbent are very close to each other, which indicates the high efficiency and significance of both models. The model equations evolved for the removal of Cr (VI) from aqueous solutions for functionalized CNTs (3) and non-functionalized CNTs (4) are as follows:

$$\text{Removal \% of Cr (VI)} = 85.41 + 1.08A + 1.94B + 0.14C - 0.069D \\ - 0.58AB + 0.094AC + 0.72AD \qquad (3)$$

$$\text{Removal \% of Cr (VI)} = 80.34 + 1.02A + 1.88B + 0.081C - 0.13D \\ - 0.64AB + 0.031AC - 0.78AD \qquad (4)$$

where A indicates the coded value of the pH of the stock solution, B indicates the coded value of the dosage of adsorbent, C indicates the coded value of contact time, and D indicates the coded value of the agitation speed. The coefficients of single factors represent the effect on that respective particular factor, while the coefficients of double factors represent the effect and interaction between those two respective factors. On that note, a positive sign in Eqs. (3) and (4) denotes a synergistic effect, while a negative sign denotes an antagonistic effect.

The 3-dimensional plot for the removal of Cr (VI) from aqueous solution using functionalized CNTs is demonstrated in Figs. 3(a)-(c), whereas for the non-functionalized CNTs it is demonstrated in

Table 2. Analysis of variance (ANOVA) for the removal of Cr (VI) using functionalized CNTs

Source	Sum of squares	DF	Mean square	F value	Prob>F	Status
Model	93.374375	7	13.33919643	125.7097	<0.0001	Significant
A	18.705625	1	18.705625	176.2834	<0.0001	
B	60.450625	1	60.450625	569.6918	<0.0001	
C	0.330625	1	0.330625	3.115838	0.1114	
D	0.075625	1	0.075625	0.712696	0.4204	
AB	5.405625	1	5.405625	50.94306	<0.0001	
AC	0.140625	1	0.140625	1.325262	0.2793	
AD	8.265625	1	8.265625	77.89594	<0.0001	
Curvature	2.975625	1	2.975625	28.04254	0.0005	Significant
Pure error	0.955	9	0.106111111			
Cor total	97.305	17				

Table 3. Analysis of variance (ANOVA) for the removal of Cr (VI) using non-functionalized CNTs

| Source	Sum of squares	DF	Mean square	F value	Prob>F	Status
Model	90.024375	7	12.860625	135.375	<0.0001	Significant
A	16.605625	1	16.605625	174.7961	<0.0001	
B	56.625625	1	56.625625	596.0592	<0.0001	
C	0.105625	1	0.105625	1.111842	0.3192	
D	0.275625	1	0.275625	2.901316	0.1227	
AB	6.630625	1	6.630625	69.79605	<0.0001	
AC	0.015625	1	0.015625	0.164474	0.6945	
AD	9.765625	1	9.765625	102.7961	<0.0001	
Curvature	3.270069444	1	3.270069444	34.42178	0.0002	Significant
Pure error	0.855	9	0.095			

(a)

(b)

(c)
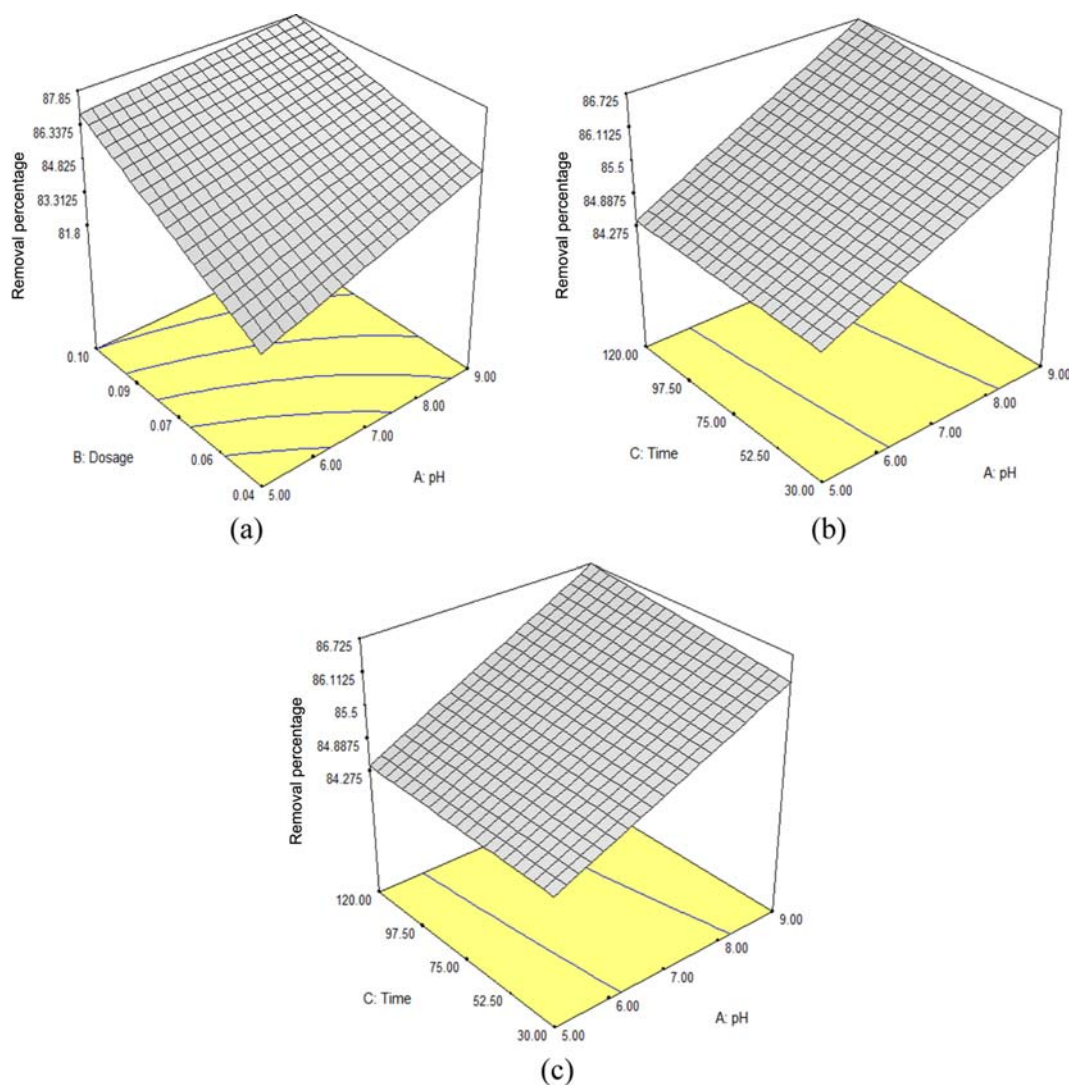
Fig. 3. A 3-D interaction plot of the removal of Cr (VI) using functionalized CNTs, (a) interaction of adsorbent dosage and pH of stock solution, (b) interaction of contact time and pH of stock solution, (c) interaction between agitation speed and pH of stock solution.

Figs. 4(a)-(c), respectively. The Cr (VI) ions are removed from the stock solution by utilizing the adsorption mechanism by available functionalized and non-functionalized CNTs. The difference between the surface charge of CNTs and the ions present in the different pHs of the stock solution leads to the varying removal percentages of Cr (VI) under different conditions of the manipulated parameters. The adsorption mechanism optimized in this research is based on chemisorption due to its attachment of ions on the surface of the CNTs. As can be seen from Fig. 3(a) and 4(a), as the adsorbent dosage of functionalized and non-functionalized CNTs, the pH of the stock solution of Cr (VI) increases, and the removal of Cr (VI) concerned increases as well. This is because there is more surface of adsorbent available for the adsorption process to take place. Hence, from Figs. 3(a) and 4(a), it can be concluded that the removal of Cr (VI) from the aqueous solution by using functionalized and non-functionalized CNTs can be maximized by capitalizing the dosage of adsorbent and pH of the stock solution. As for the Figs. 3(b) and 4(b), the 3-demonstration graphs demonstrate that as the contact time and pH of the stock solution increase, the removal percentage

of Cr (VI) from the aqueous solution increases as well. This happens due to the higher interaction time between the adsorbent surface ions and the heavy metal ions. On the same note, Figs. 3(c) and 4(c) illustrate that as the agitation speed and pH of the stock solution increase, the removal percentage of Cr (VI) increases as well. By way of explanation, as the speed increases, there is a higher frequency of collision and interactions between surface functional groups on the adsorbent and the heavy metal ions. Hence, as the frequency increases, more molecules interact with each other and lead to a higher adsorption capacity, and eventually the removal percentage of Cr (VI) increases. All the figures indicate that the removal percentage of Cr (VI) increases as the pH of the stock solution increases. As for the acidic pH, Cr (VI) metal ions are present as Cr (VI) while for the alkaline pH, Cr (VI) metal ions are present as the Cr (OH)$_3$. Hence, at lower pH, due to the competition between Cr (VI) and H$^+$ ions, the Cr (VI) metal ions could not adsorb well on the surface of CNTs. As the pH increases, the adsorption competition between the Cr (VI) and H$^+$ ions becomes lower due to the increase in the OH$^-$ ions. Hence, the Cr (VI) metal ion is more easily
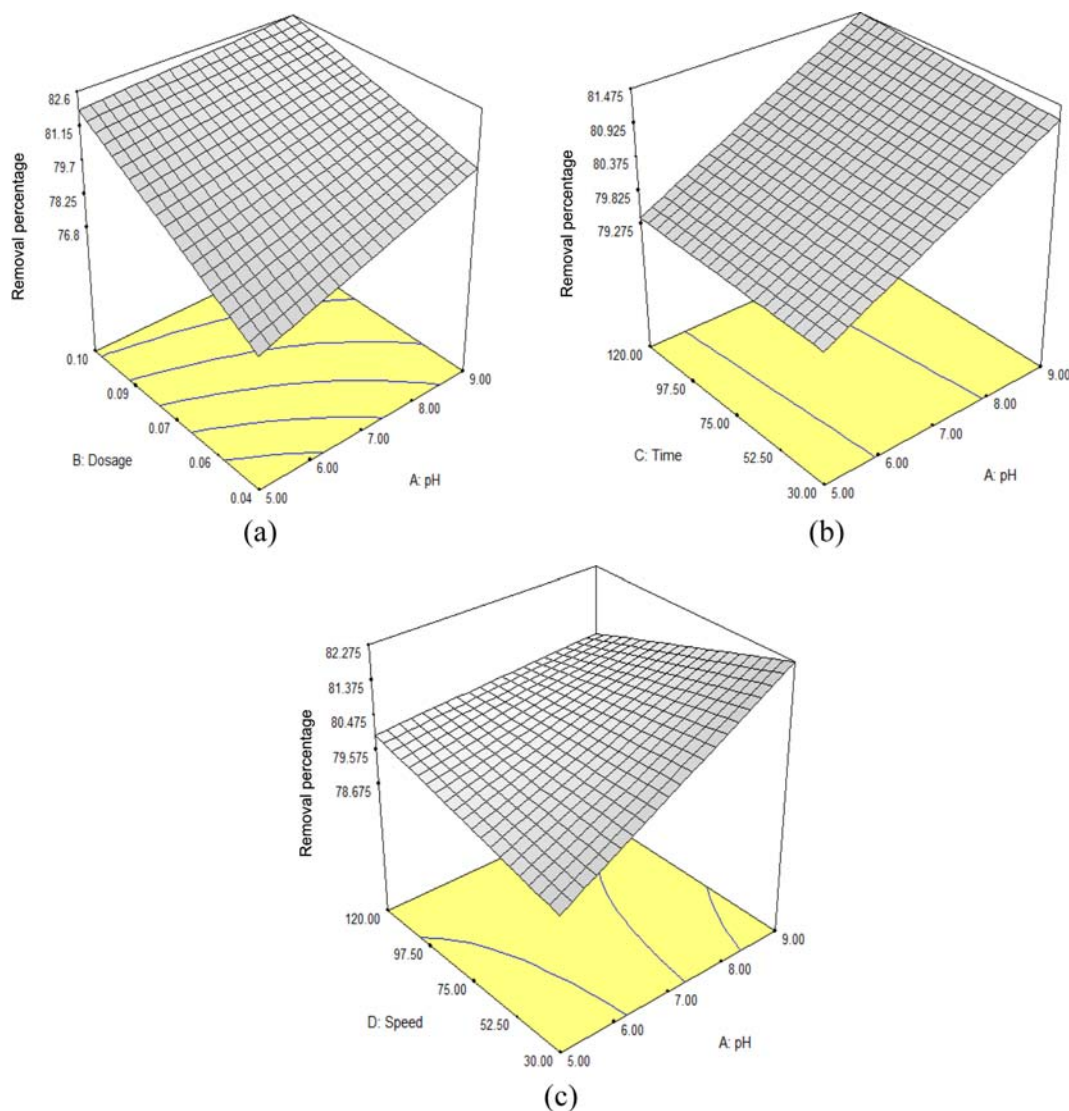
Fig. 4. A 3-D interaction plot of the removal of Cr (VI) using non-functionalized CNTs, (a) interaction of adsorbent dosage and pH of stock solution, (b) interaction of contact time and pH of stock solution, (c) interaction between agitation speed and pH of stock solution.

adsorbed on the surface of the CNTs. Besides, all the figures indicate that the functionalized CNTs possess a better Cr (VI) adsorption compared to the non-functionalized CNTs due to its higher and stronger interaction between the negatively charged adsorbent's surface group and the positively charged metal ions.

The 3-demonstration surface plot indicates that the maximized removal percentage of Cr (VI) using functionalized and non-functionalized CNTs can be obtained by utilizing the interactions between the high level of pH, dosage of adsorbent and contact time. Hence, by means of comparison between the functionalized and non-functionalized CNTs as the adsorbent, it is proven that functionalized CNTs provide a higher removal percentage of Cr (VI) from the aqueous solution by a numerical value of 88.4%, while non-functionalized CNTs only managed to provide a removal percentage with a numerical value of 83.4%.

The optimum process conditions obtained from the statistical results for the removal of Cr (VI) for functionalized and non-functionalized CNTs are evident when the contact time was 120 minutes,

the pH of the stock solution was 9, and the adsorbent's dosage was 0.10 gram while the agitation speed was 120 rpm.

4. Adsorption Kinetic Studies and Adsorption Isotherm

Fig. 5 represents the adsorption kinetic studies for a time interval 20 minutes on the adsorption of Cr (VI) metal ions on functionalized and non-functionalized CNTs, respectively, for an initial concentration, C_o value of 1.0 mg/L. As for the kinetics adsorption experiment, a duration of 5 hours was chosen to obtain a more precise removal percentage for every 20 minutes. The removal percentage did not reach its highest value for the first 20 minutes, but it did increase gradually for every 20 minutes during that 5-hour time period.

From the graph, the adsorption of Cr (VI) onto the adsorbent increased quickly with time and attained the equilibrium level quickly too. The adsorption capacities of Cr (VI) for functionalized and non-functionalized CNTs as per the kinetic study were 2.48 and 2.47 mg/g.

The adsorption isotherm and kinetic studies can be determined by important isotherm models such as Langmuir and Freundlich.
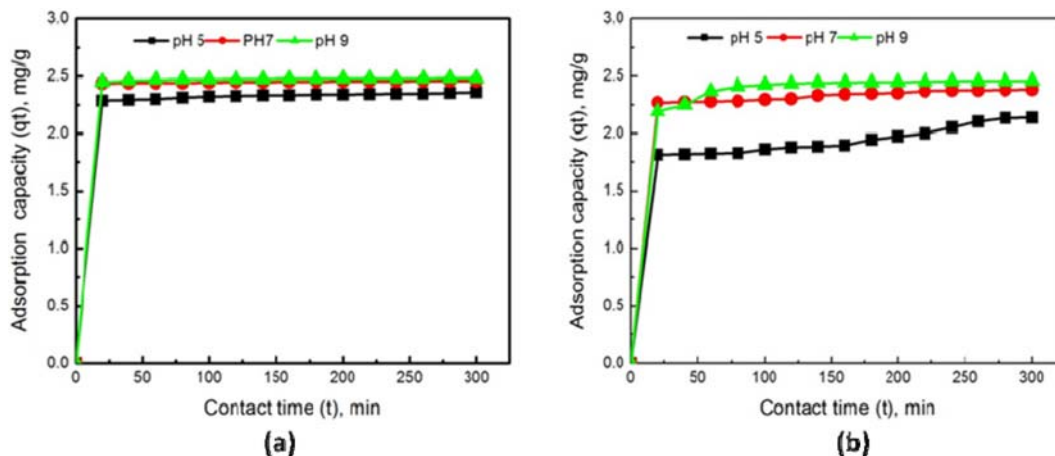
Fig. 5. Effect of pH on (a) functionalized (b) non-functionalized CNTs.

As for this research study, both models were employed to determine the optimum model for the Cr (VI) adsorption onto the functionalized and non-functionalized CNTs. The Langmuir model is able to relate the solid phase adsorbate concentration, q_e and the uptakes to the equilibrium liquid concentration, C_e as shown in the equation below:

$$(C_e/q_e)=(1/K_L q_m)+(C_e/q_m) \tag{5}$$

where q_e (mg/g) represents the amount of adsorbed Cr (VI) concentration per unit weight while the C_e (mg/L) represents an adsorbed Cr (VI) concentration in solution at an equilibrium. The Langmuir constant, which relates to the affinity of the binding sites in the above

equation, is represented by K_L (L/mg), while the maximum adsorption capacity of adsorbent is represented by q_m. A graph of C_e/q_e

Table 4. Calculated data for C_e and q_e for functionalized and non-functionalized CNTs

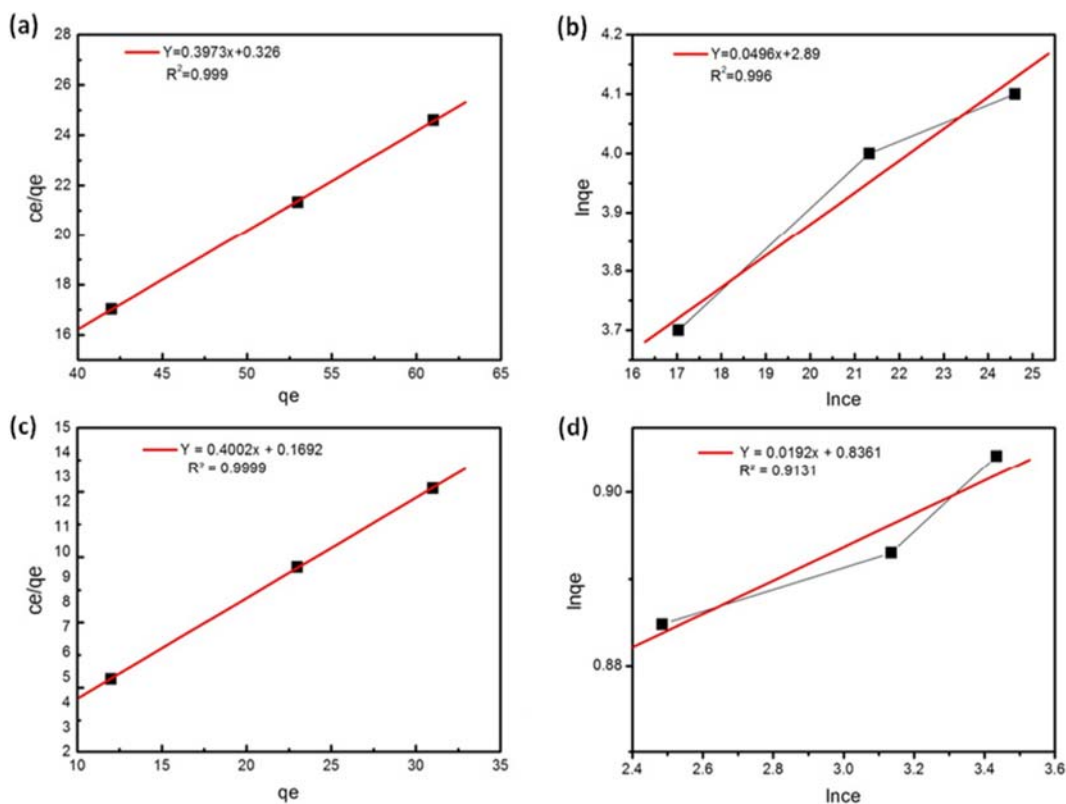| Functionalized CNTs		Non-functionalized CNTs	
C_e (mg/L)	q_e (mg/g)	C_e (mg/L)	q_e (mg/g)
42	2.465	12	2.4225
53	2.485	23	2.4425
61	2.48	31	2.47

Fig. 6. Langmuir and Freundlich isotherms of Cr (VI) using (a) functionalized (a)-(b), (b) non-functionalized (c)-(d), CNTs.

against C_e was plotted and the q_m and K_L values were calculated from the slope and the intercept of the graph. Table 4 below shows the calculated details of q_e and C_e for functionalized and non-functionalized CNTs.

Figs. 6(a)-(c) indicate the adsorption isotherm for the linearized Langmuir model for functionalized and non-functionalized CNTs as an adsorbent, respectively. From the graph, both the isotherm data fit well in the Langmuir equation, with an R^2 value of 0.998 for functionalized CNTs and an R^2 value of 0.999 for non-functionalized CNTs. The values of q_m and K_L were determined from the plot and were found to be 2.517 mg/g and 1.217 L/mg for functionalized CNTs, while 2.49 mg/g and 2.365 L/mg for non-functionalized CNTs.

Chromium (VI) adsorption isotherm was then plotted with the Freundlich model as shown in Figs. 6(b)-(d) in which the relationship between the Cr (VI) uptake capacities, q_e (mg/g) of adsorbent and the residual Cr (VI) equilibrium concentration, C_e in mg/L is provided by the following equation:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{6}$$

where K_F is the Freundlich constant, which indicates the adsorption capacity of the adsorbent, while n is a constant, which proves the greatness of the relationship between the adsorbate and adsorbent [28]. Both the n and K_F value can be determined from the slope and intercept of the linear plot of $\ln q_e$ against $\ln C_e$. The n and K_F determined for functionalized CNTs were 20.16 and 18.14 L/mg, whereas for non-functionalized CNTs they were 52.08 and 2.307 L/mg.

From the graph plotted, the isotherm data of both adsorbents fit the Freundlich equation, with an R^2 value of 0.996 for functionalized CNTs and an R^2 value of 0.9131 for non-functionalized CNTs. The calculated values for both Langmuir and Freundlich models are shown in Table 5.

The data obtained from Table 5 were then developed into a Langmuir and Freundlich equation to identify the Cr (VI) uptake capacity of q_e of adsorbent to the equilibrium liquid concentration, C_e as given below:

For functionalized CNTs:
Developed Langmuir Equation: $q_e = [2.517C_e/(0.8217+C_e)]$ (7)

Developed Freundlich Equation: $q_e = 18.14C_e^{0.05}$ (8)

For non-functionalized CNTs:
Developed Langmuir Equation: $q_e = [2.490C_e/(0.423+C_e)]$ (9)

Developed Freundlich Equation: $q_e = 2.307C_e^{0.019}$ (10)

From Table 5, both R^2 values of the Langmuir and Freundlich isotherm model prove that both models can be used to indicate the adsorption of Cr (VI) from aqueous solutions. Also, the q_m value also indicates that functionalized CNTs tend to have a higher adsorp-

tion capacity than the non-functionalized CNTs.

Based on the removal percentage obtained from the experiment, it proves that the functionalized CNTs have a higher adsorption capacity towards the Cr (VI). This is due to the additional negatively charged functional group present on the surface of CNTs as illustrated in the FTIR image. The overall interaction between the Cr (VI) and CNTs is known as adsorption since the process only occurs at the surface of CNTs. The Cr (VI) is adsorbed on the surface of CNTs due to the difference in the surface charge of CNTs and Cr (VI).

5. Thermodynamic Study

Generally, thermodynamic parameters are able to provide more information regarding the energetic change involved during the adsorption process. The adsorption isotherm of Cr (VI) onto functionalized and non-functionalized CNTs was measured at 293, 303 and 323 K; and the change in the thermodynamics parameters of the free energy of sorption (G), enthalpy (H), and entropy (S) were calculated from the variation of the thermodynamic equilibrium constant, K_o with a change in temperature. The constant K_o can be determined by the intercept of the plot of log K_o versus C_e as in Fig. 7(a)-(b), respective of functionalized and non-CNTs.

Free energy change (G) can be calculated using Eq. (11) below, where R is the universal gas constant while T is the temperature in kelvin.

$$(\Delta G) = -RT \ln K_o \tag{11}$$

By the rearrangement and substitution in Eq. (11), Eq. (12) is obtained which predicts a linear plot of $\ln K_o$ versus $1/T$ for the adsorption of Cr (VI) onto functionalized and non-functionalized CNTs. The slope of Eq. (12) provides the value of $-\Delta H/R$, while the intercept is $\Delta S/R$ as in Fig. 7(c)-(d), respectively, of functionalized and non-functionalized CNTs. The values of ΔG (kJ/mol), ΔH (kJ/mol), and ΔS (J/molK) are given in Table 6.

The negative ΔG value for both the adsorption of Cr (VI) on functionalized and non-functionalized CNTs at all temperatures proves that the sorption was spontaneous and thermodynamically favorable. In the same vein, the entropy change value, ΔS, of functionalized CNTs is higher compared to the non-functionalized CNTs, which implies different adsorptive mechanisms. The negative value of the enthalpy change value, H, proves that this adsorption experiment was an exothermic process. On that note, the enthalpy change value of functionalized CNTs is lower compared with non-functionalized CNTs. This observation can be supported by the fact that the adsorptive capacity of Cr (VI) is increasing on functionalized CNTs as the temperature increases. Nitric acid can oxidize the ends and sidewalls of CNTs and increase the amounts of oxygen-containing groups, which have been proven by previous work [29]. This functional group plays a vital role in the adsorption of Cr (VI) on to CNTs.

6. Desorption Study

An established adsorbent should be able to be recycled, regener-

Table 5. Isotherm model for functionalized and non-functionalized CNTs

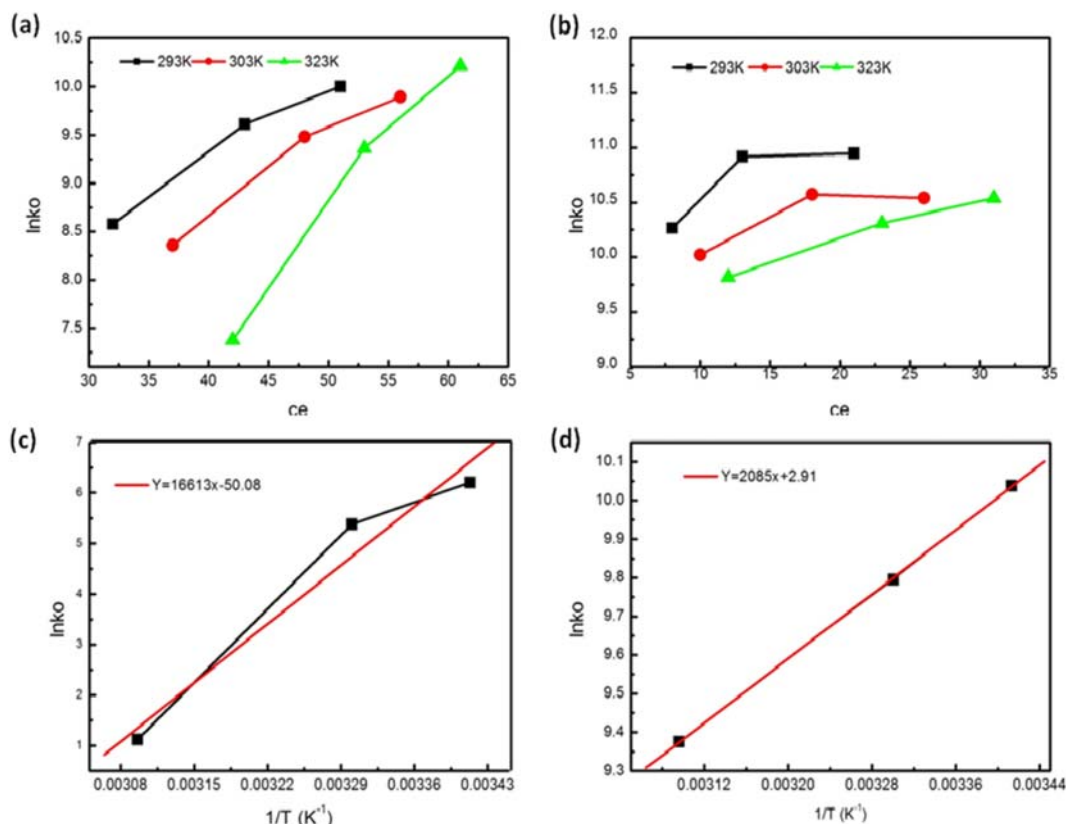| Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	K_L (L/mg)	R^2	n	K_F (mg^{1-n}L^n/g)	R^2
Functionalized CNTs	2.517	1.217	0.998	20.16	18.14	0.9960
Non-functionalized CNTs	2.490	2.365	0.999	52.08	2.307	0.9131

Fig. 7. A plot of ln K$_o$ versus ce for (a) functionlized (b) non functionlaized CNTs, and lnK$_o$ versus and 1/T for (c) functionalized, (d) non-functionalized CNTs.

Table 6. Thermodynamic parameters of Cr (VI) adsorbed on functionalized and non-functionalized CNTs

Temperature (K)	Functionalized CNTs			Non-functionalized CNTs		
	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/molK)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/molK)
323	−3015.46	−138120.5	−416.42	−25176.91	−17340.51	24.25
303	−13548.95			−24674.74		
293	−15116.61			−24452.59		

ated and repeated. These adsorbents display a good adsorption capabilities along with a good desorption properties as well. Although recent research has proven that CNTs can be produced in a large scale factor with different methods to mitigate the production cost [30], a better desorption capability reduces the overall costs associated with adsorbate removal. The fraction of metal ion desorbed from the functionalized and non-functionalized CNTs was calculated by using Eq. (12) below:

$$\% \text{ Desorption} = \frac{\text{Amount released to solution (mg/L)}}{\text{Total adsorbed (mg/L)}} \times 100\% \quad (12)$$

Fig. 8 shows the Cr (VI) recovered from functionalized and non-functionalized CNTs at pH values ranging from 1.0 to 5.0. A desorption experiment was conducted for 3.0 hour to ensure a full desorption equilibrium. Table 7 indicates that the percentage desorption increases with a decrease in the solution's pH ranging from pH 1 to pH 5.

Functionalized CNTs carry a lower desorption percentage value due to their strong binding of Cr (VI) to its surface compared with
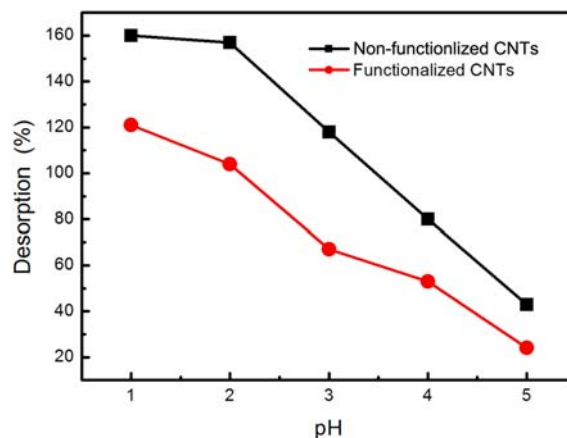

Fig. 8. Desorption of Cr (VI) from CNTs by adjusting the pH values of the solution.

the non-functionalized CNTs. Hence, these results demonstrate that the heavy metal ions adsorbed by CNTs could be easily desorbed.

Table 7. Desorption percentage value for variable pH

pH	Desorption (%)	
	Non-functionalized CNTs	Functionalized CNTs
1	160	121
2	157	104
3	118	67
4	80	53
5	43	24

Therefore, it is possible to employ CNTs repeatedly in heavy metal wastewater management, which also indicates that ion exchanges tend to occur in this adsorption mechanism. A similar result has been recorded by other researchers [31].

CONCLUSION

We conducted an optimization and kinetic study on the removal of Cr (VI) using functionalized and non-functionalized CNTs. Statistical analysis revealed that the optimum conditions for the highest removal of Cr (VI) were recorded to have pH 9, dosage 0.1 gram, contact time 120 minutes and agitation speed of 120 rpm. Functionalized CNTs emerge as a better promising adsorbent in the removal of Cr (VI) as the removal percentage is more than 88%, whereas the highest removal using the non-functionalized counterparts is only 83.4% based on the same variables. Maximum adsorption capacities (qm) for Cr (VI) ions were obtained as 2.517 and 2.49 mg/g for functionalized and non-functionalized CNTs, respectively. Langmuir and Freundlich models for functionalized CNTs show 1.217 L/mg and $18.14 \, mg^{1-n}L^n/g$, respectively, while it was 2.365 and $2.307 \, mg^{1-n}L^n/g$ for non-functionalized CNTs. Both Langmuir and Freundlich models exhibit a well-fitted linear for both functionalized CNT and non-functionalized CNTs.

ACKNOWLEDGEMENT

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