C Journal of Carbon Research

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Comparative Kinetic Study of Removal of Pb^{2+} Ions and Cr^{3+} Ions from Waste Water using Carbon Nanotubes Produced using Microwave Heating

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Academic Editors: Craig E. Banks and Vijay Kumar Thakur
Received: 20 November 2015; Accepted: 19 February 2016; Published: 26 February 2016

Abstract: A comparative study of the removal of Pb^{2+} ions and Cr^{3+} ions was conducted to determine the efficiency of carbon nanotubes (CNTs) produced using microwave heating as an adsorbent in removing heavy metal ions from waste water. Optimization of parameters such as adsorbent dosage, pH value, agitation speed, and agitation time was done using the Design Expert software version 6.0. The statistical analysis revealed that optimized conditions for the highest removal for Pb^{2+} are at pH 4.0, CNTs dosage of 0.09 g, agitation time and speed of 50 min and 150 rpm respectively. Meanwhile, the highest removal Cr^{3+} ions was observed at pH 8.0, CNTs dosage of 0.09 g, agitation time and speed of 60 min and 150 rpm respectively. For the initial concentration of 2 mg/L, the removal efficiency of Pb^{2+} ions and Cr^{3+} ions were 99.9% and 95.5% respectively. The maximum adsorption capacities of both Pb^{2+} ions and Cr^{3+} ions onto the CNT were 15.34 mg/g for Pb^{2+} ions and 24.45 mg/g for Cr^{3+} ions. Besides that, the Langmuir and Freundlich constants for the removal of Pb^{2+} ions were 0.073 and 1.438 L/mg while 0.071 and 1.317 L/mg for Cr^{3+} ions. The statistical analysis proved that the removal of Pb^{2+} ions and Cr^{3+} ions fits the Langmuir and Freundlich isotherm models, and both models obeyed the pseudo-second-order.

Keywords: CNTs; lead; chromium; microwave heating

1. Introduction

New era industries have immensely improved the living standard of human beings. However, modern industries also caused serious adverse impacts on our surroundings. One of the major environmental concerns is water pollution by heavy metals. Heavy metals in water have been the main preoccupation for many years because of the toxicity towards aquatic-life, human beings and the environment [1]. The United States Environment Protection Agency (USEPA) prepared a list called the Priority Pollutants List that identifies the organic and inorganic pollutants found in waste water which contribute the most to health hazards. The list includes antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc [2–6]. Even

though some of the trace elements are essential in biological systems [7], heavy metal ions at high concentration are considered to be harmful and toxic to mankind, aquatic lives, and other living creatures of earth [8], because unlike organic pollutants, the majority is susceptible to biological degradation and heavy metal ions do not degrade into harmless end products. These heavy metal ions enter the water stream as waste water, discharged by various industries such as mining, alloy manufacturing, metal plating, galvanizing, smelting and paints. The main industries that contributes to heavy metal ion contaminations as a form of water pollution in Malaysia are the electroplating and fabrication industries [9]. Lead has been known for its harmful impacts on the surrounding by accumulating readily into living systems. Its poison in human may cause serious illness like anaemia, kidney failure and nervous system damage, even fatal, as it accumulates mainly in bones, kidney, brain and muscles [10]. In addition, the contamination of low lead level in children could result in behavior and learning problems, hyperactivity, low IQ, slow growth and also hearing problems [11]. The cancer rate has also been increasing in the recent few years because of lead's presence in drinking and natural water [12]. Meanwhile, Chromium is one of the extremely toxic heavy metals found in various industrial waste waters [13]. The physiological effects of the ingestion of Cr^{3+} ions on human health have also been studied intensively. Public health consideration of chromium is mostly related to Cr^{3+} compounds that are irritants due to their high solubility and diffusivity in tissue, allowing them to cross biological membranes easily. It is documented that certain Cr^{3+} compounds are carcinogenic and mutagenic. The toxic effects of Cr^{3+} ions on humans include liver damage, internal hemorrhage, respiratory disorders, dermatitis, skin ulceration and chromosome aberrations [14]. Various chemical removal methods have been utilized and further developed over decades to take charge of the heavy metal contaminations. The removal of heavy metal from aqueous solution consists of physical, chemical and biological techniques. Suggested conventional methods are electrochemical treatment, chemical precipitation, membrane technologies and adsorption on activated carbon [15–17]. Among all the methods, adsorption on activated carbon is considered to be one of the method for removal heavy metals from aqueous solutions have been reported earlier [18]. In addition, it is another good method to be taken into account from the aspect of handling methods and economics. Even though there are so many adsorbents available, researchers had to come up with a new adsorbent as the existing adsorbents were lacking in its efficiency to remove metal ions [19].

Since discovery of carbon nanotubes (CNTs) is a new member in the carbon family, found by Iijama [20]. It is essentially a new type of adsorbents that proves to retain great potential for removal of pollutants such as herbicides and chloro-benzenes, as well as lead and chromium ions [21–25]. Researchers have found that CNTs have a relatively larger surface area, extraordinary surface morphology and good chemical and mechanical properties [26,27] that provide a good opportunity for the removal of heavy metals, [28–30]. CNTs based technologies found its water-treatment applications in various fields, for instance as sorbents, catalyst, filters, or membranes [31]. It is of common interest that the development of new technique for an efficient and selective synthesis of CNTs is at the cheapest possible cost. One of such possibilities is the use of microwave radiation. The reason behind the choice of microwave usage to produce CNTs is the novelty of this method [32]. Microwave-assisted modification of carbon nanotube is non-invasive, simple, fast, environmental friendly and clean method as compared to traditional methods. Usually, the use of microwave facilitates and accelerates reactions, often improving relative yields [33,34]. The use of microwave radiation in the synthesis and functionalization of CNTs or other nanostructures is advantageous because it provides a fast and uniform heating rate that can be selectively directed towards a targeted area compared to the conventional method usage.

The aim of this study, statistical optimization and comparative study on the removal of Pb^{2+} metal ions and Cr^{3+} metal ions from aqueous solution using CNTs produced using microwave heating was investigated. The operating parameters such as adsorbent dosage, pH value, agitation speed and time were exerted to study the effect of each parameter in the removal of heavy metal ions which are Pb^{2+} metal ions and Cr^{3+} metal ions in this case, using CNTs produced using microwave heating. Besides

that, the kinetic and isotherm model equation for the removal of both Pb^{2+} metal ions and Cr^{3+} metal ions were also investigated to determine the optimum condition to obtain the maximum adsorption capacity of CNTs used in this study.

2. Results and Discussion

2.1. Characterization of Carbon Nanotubes (CNTs)

The CNTs were examined by the Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM) as represented in Figure 1a–c respectively. As seen from the image, the diameter of the CNTs ranged from 10 to 20 nm with an average diameter of 15 nm, while the length was measured up to few microns. On the other hand, for the characterization on the structure of CNTs, the TEM was done. As observed from the images, the CNTs are tubular shaped with a hollow in it. Figure 1c is evident for the visibility of the catalyst particle inside the tubes. These CNTs are uniform in diameter distribution, have no deformation and are of high purity [35,36].

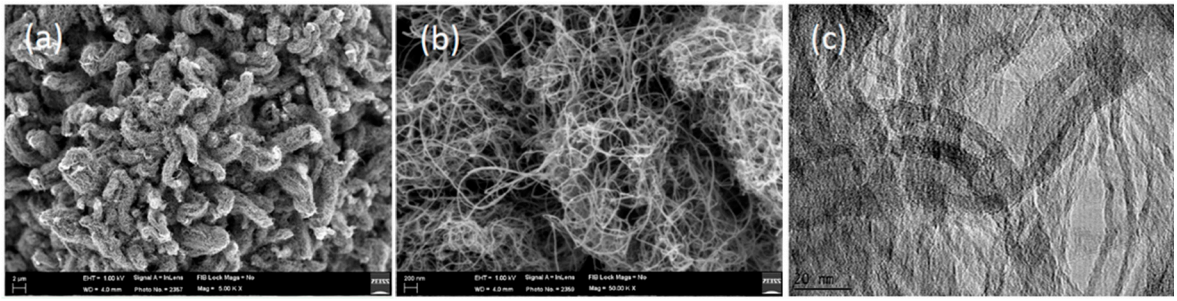

Figure 1. (**a**–**c**) FESEM and TEM images of carbon nanotubes (CNTs).

Figure 2a–c shows the Fourier Transform spectra of the raw CNTs and the Pb^{2+} and Cr^{3+} heavy metal adsorption respectively. From the figure, it can be seen that the raw CNTs (a) demonstrates the insignificant lower peaks compared to the CNTs after the adsorption process as shown in Figure 2b,c. The CNTs after the adsorption process has three major peaks near 1200, 2400, 3450 cm^{-1} which are associated with groups (O–H), carbonyl groups (>C & O) and hydroxyl groups (–OH). This result acknowledges the results obtained in previous study [37–41].

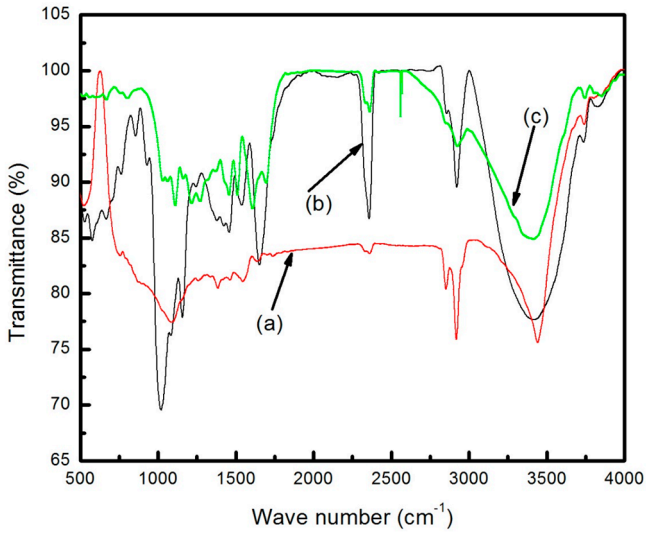

Figure 2. (**a**) Raw CNTs, (**b**) Pb^{2+} adsorption and (**c**) Cr^{3+} adsorption of heavy metals.

2.2. Statistical Analysis of Adsorption of Pb^{2+} and Cr^{3+} onto CNTs

The Design Expert software version 6.0.8 was used to further investigate the statistical analysis of the adsorption of both Pb^{2+} and Cr^{3+} from the stock solutions prepared onto the CNTs. The most significant step in this study is the design of experiment which was obtained from the Design Expert. The design of experiment for the heavy metal adsorption of Pb^{2+} and Cr^{3+} done using the Design Expert is shown in Tables 1 and 2 together with its effective removal percentage of Pb^{2+} and Cr^{3+} from the prepared stock solutions. The results obtained were utilized to further analyze the removal percentage of Pb^{2+} and Cr^{3+} from the prepared stock solutions with the usage of Design Expert that induces the optimum conditions for removal of both Pb^{2+} and Cr^{3+} from the prepared stock solutions. Attained optimized parameters and the successful removal percentage from Tables 1 and 2 were studied by the application of "Analysis of Variance" (ANOVA) from the Design Expert Software. Results from the ANOVA for the removal percentage of Pb^{2+} and Cr^{3+} from the prepared stock solutions are listed in Tables 3 and 4. Based on the results obtained from the ANOVA, the Fischer *F*-test value can be correlated to the mean square of the regressed model that leads to the comparison of the mean square of the residuals (errors). Efficiency of the model is validated as the *F* value increases. In contrast, the *p* value or lower probability indicates higher significance for the regression model. As seen from Table 3 for the adsorption Pb^{2+} onto the CNTs, the value of 48.81 for *F*-test value indicates that the model is significant. On the other hand, the *F*-test value of 60.03 from Table 4 for the adsorption of Cr^{3+} also proves that the model is significant.

Table 1. Design of Experiment and removal percentage of Pb^{2+} by CNTs.

No.	pH	Adsorbent Dosage(mg)	Agitation Time(min)	Agitation Speed(rpm)	Removal Percentage of Pb (%)
1	6	90	50	100	97.5
2	5	60	10	125	94.5
3	5	60	30	100	94.2
4	5	60	30	125	96.5
5	6	60	30	125	95.6
6	5	60	30	125	96.5
7	5	30	30	125	95.5
8	5	60	30	150	94.9
9	6	90	10	100	95.5
10	4	30	10	100	91
11	4	30	50	100	99
12	6	90	50	150	96.5
13	6	30	10	100	89.9
14	4	90	50	100	99.5
15	6	30	50	150	98.5
16	4	30	10	150	94.5
17	6	90	10	150	95.8
18	4	90	50	150	99.9
19	4	90	10	100	98.5
20	4	30	50	150	99.5
21	4	90	10	150	99.5
22	6	30	10	150	93
23	5	90	30	125	97.65
24	5	60	50	125	97.9
25	4	60	30	125	99.3
26	6	30	50	100	97.5

Table 2. Design of experiment and removal percentage of Cr^{3+}.

No.	pH	Adsorbent Dosage(mg)	Agitation Time(min)	Agitation Speed(rpm)	Removal Percentage of Cr (%)
1	6	30	35	125	65.55
2	6	60	35	150	63.05
3	4	30	60	150	72.05
4	8	90	10	100	88.35
5	4	90	10	150	73.6
6	8	60	35	125	91.8
7	8	30	60	100	92.05
8	4	30	10	150	70.1
9	6	60	35	125	68.05
10	8	90	10	150	92.35
11	8	90	60	100	85.55
12	6	90	35	125	69.25
13	6	60	10	125	70.1
14	4	30	10	100	73.05
15	4	30	60	100	74.5
16	8	90	60	150	95.3
17	4	90	60	100	75.55
18	4	60	35	125	76.5
19	6	60	60	125	72.8
20	8	30	60	150	95.5
21	4	90	10	100	74.1
22	6	60	35	125	68.35
23	4	90	60	150	76.65
24	6	60	35	100	67.9
25	8	30	10	150	94.5
26	8	30	10	100	94.05

Table 3. Analysis of variance (ANOVA) for the removal percentage of Pb^{2+} by CNTs.

Source	Sum of Squares	DF	Mean Square	*F* Value	Probability > *F*	Status
Model	168.4039	14	12.02884674	48.81014	<0.0001	significant
A	24.26722	1	24.26722222	98.47049	<0.0001	-
B	26.76681	1	26.76680556	108.6132	<0.0001	-
C	62.72	1	62.72	254.5025	<0.0001	-
D	5.013889	1	5.013888889	20.34514	0.0009	-
A2	4.693757	1	4.693756678	19.04612	0.0011	-
B2	0.587126	1	0.587125581	2.382413	0.1510	-
C2	0.027598	1	0.027598142	0.111987	0.7442	-
D2	6.122537	1	6.122537166	24.84377	0.0004	-
AB	3.0625	1	3.0625	12.42688	0.0048	-
AC	0.1225	1	0.1225	0.497075	0.4954	-
AD	0.25	1	0.25	1.014439	0.3355	-
BC	30.25	1	30.25	122.7472	<0.0001	-
BD	3.4225	1	3.4225	13.88767	0.0033	-
CD	3.0625	1	3.0625	12.42688	0.0048	-
Residual	2.710857	11	0.246441558	-	-	-
Lack of Fit	2.710857	10	0.271085714	-	0.234	Insignificant
Pure Error	0	1	0	-	-	-
Cor Total	171.1147	25	-	-	-	-

Table 4. Analysis of variance (ANOVA) for the removal percentage of Cr^{3+} by CNTs.

Source	Sum of Squares	DF	Mean Square	*F* Value	Probability > *F*	Status
Model	2867.508216	14	204.8220154	60.03209	<0.0001	significant
A	1482.40125	1	1482.40125	434.4828	<0.0001	-
B	0.023472222	1	0.023472222	0.00688	0.9354	-
C	5.28125	1	5.28125	1.547902	0.2393	-
D	3.555555556	1	3.555555556	1.042112	0.3293	-
A2	628.7683072	1	628.7683072	184.2882	<0.0001	-
B2	2.992392567	1	2.992392567	0.877052	0.3691	-
C2	22.57562427	1	22.57562427	6.616779	0.0259	-
D2	23.14033464	1	23.14033464	6.782292	0.0245	-
AB	38.28515625	1	38.28515625	11.22115	0.0065	-
AC	4.78515625	1	4.78515625	1.4025	0.2613	-
AD	31.50015625	1	31.50015625	9.232505	0.0113	-
BC	0.31640625	1	0.31640625	0.092737	0.7664	-
BD	15.70140625	1	15.70140625	4.601987	0.0551	-
CD	7.35765625	1	7.35765625	2.156484	0.1700	-
Residual	37.53062996	11	3.411875451	-	-	-
Lack of Fit	37.48562996	10	3.748562996	83.3014	0.0851	Insignificant
Pure Error	0.045	1	0.045	-	-	-
Cor Total	2905.038846	25	-	-	-	-

Meanwhile, the R-Squared and Adj R-Squared also hold an important function in determining the significance of the model. According to Tables 1 and 2 the values of R-Squared and Adj R-Squared for the adsorption Pb^{2+} onto the CNTs are 0.9842 and 0.9640 respectively, while for the adsorption of Cr^{3+} the values of R-Squared and Adj R-Squared are 0.9871 and 0.9706, respectively. This clearly shows that both values are quite close to each other, hence, indicating high significance and efficiency of the model. Evolved model equation for the removal of Pb^{2+} (1) and Cr^{3+} (2) from the prepared stock solutions is stated below;

$$\text{Removal \% of } Pb^{2+} = 96.20 - 1.16A + 1.22B + 1.87C + 0.53D - 0.44AB + 0.088AC - 0.12AD - 1.37BC - 0.46BD - 0.44\,CD \quad (1)$$

$$\text{Removal \% of } Cr^{3+} = 68.41071429 + 9.075A - 0.0361B + 0.5416C + 0.44D - 1.547AB - 0.5461AC + 1.403AD + 0.14BC + 0.99BD + 0.68CD \quad (2)$$

where, A represents the coded value of the pH of the prepared stock solution, B represents the coded value of the amount of adsorbent dosage, C represents the coded value of the agitation time or the contact time, and D represents the coded value of the agitation speed. In addition, the coefficient of single factor in the equation represents equation of the effect of that respective particular factor while the coefficients of double factors in the equation represent the effect and interaction between those two respective factors.

Three-dimensional diagrams were plotted to observe the relationship between optimizing conditions and the Pb^{2+} (Figure 3) and Cr^{3+} (Figure 4) heavy metal ions removal percentage. As shown in Figures 3a and 4a, the correlation between adsorbent dosage and pH in the removal of Pb^{2+} and Cr^{3+} heavy metal ions indicates that both the removal percentages of the heavy metal ion increase when the adsorbent dosage is increased. This is because the increment of the adsorbent increases the availability of the surface area for the adsorption process, in which more of the heavy metal ions uptake onto the surface of the CNTs could occur [42–44]. Based on Figures 3b and 4b which show the interaction between agitation time and the pH value in the removal of Pb^{2+} and Cr^{3+} heavy metal ions, they indicate the same pattern for both the heavy metal ions in which the removal percentage increases along with the agitation time allowed for the batch adsorption process. This is because longer contact time provides longer interaction duration between the heavy metal ions and adsorbent surfaces [45–48]. Meanwhile, referring to Figures 3c and 4c which identify the interaction between agitation speed and pH value, they reflect different effects on both heavy metal ions. As in for Pb^{2+} metal ions, the agitation speed does not have a significant effect on the removal percentage of Pb^{2+} metal ions because the suspension may not become homogenous due to the rapid agitation, increasing

the boundary layer between solid and liquid phase, hence lowering the removal percentage [49–51]. On the other hand, for the Cr^{3+} metal ions, as the agitation speed increases, the removal percentage increases owing to higher kinetic energy in which more molecules collide with each other increasing the adsorption capacity into the CNT binding sites, leading to higher removal percentages of Cr^{3+} metal ions [52]. Figure 5 shows the relationship between pH values and the removal percentages of both of the Pb^{2+} and Cr^{3+} heavy metal ions. As evident from the figure, the removal of Pb^{2+} metal ions was favorable at lower pH because the alkaline state enhances metal precipitation, hence lowering the removal percentage. At the same time, removal of Cr^{3+} metal ion was favorable at higher pH value because the acidic state increases the competition between Cr^{3+} and H^{+} in regards to the adsorption into the CNT. By increasing the pH value, the competition extinguishes as the OH^{-} ions increases. This proves that the removal of Cr^{3+} metal ions works well in high pH value as it is more easily adsorbed into the CNTs surface [53,54].

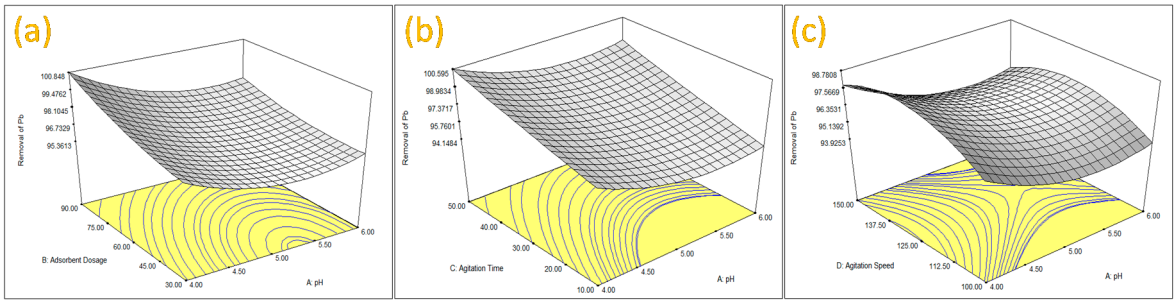

Figure 3. A 3D interaction plot of the removal of Cr^{3+} using CNTs (**a**) interaction of adsorbent dosage and pH, (**b**) interaction of agitation time and pH and (**c**) interaction of agitation speed and pH.

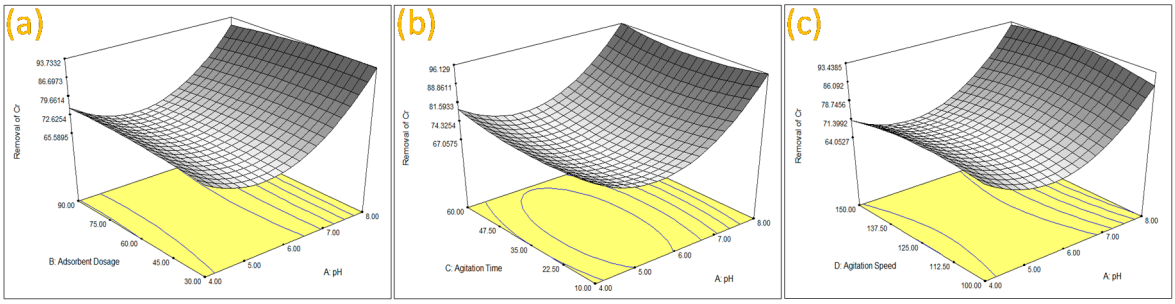

Figure 4. A 3D interaction plot of the removal of Cr^{3+} using CNTs (**a**) interaction of adsorbent dosage and pH, (**b**) interaction of agitation time and pH and (**c**) interaction of agitation speed and pH.

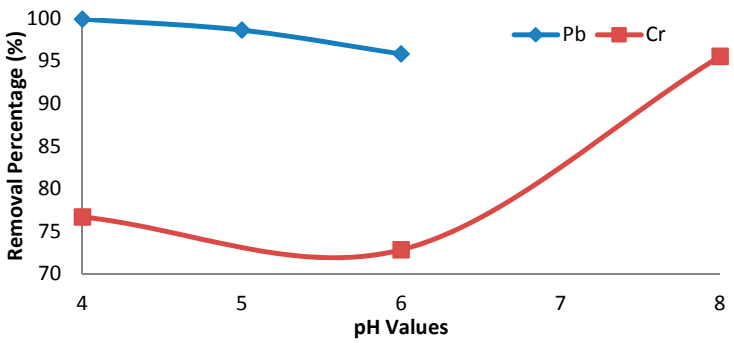

Figure 5. Effect of pH value on removal percentage of: (**a**) Pb^{2}+ metal ions (**b**) Cr^{3+} metal ions.

The correlation of four parameters used in this research study for the removal of both Pb^{2+} and Cr^{3+} heavy metal ions are based on the analysis; it was found that the optimized conditions of parameter for the maximum removal of Pb^{2+} as much as 99.9% could be attained with pH 4.0, agitation speed 150 rpm and the agitation time of 50, adsorbent dosage 0.09 g. As for Cr^{3+} ion, the optimized conditions for a maximum removal of 95.5% were found to be pH of alkaline state of 8.0, agitation speed 150 rpm and the agitation time of 60 with the maximum amount of dosage used which was 0.09 g.

2.3. Adsorption Kinetics and Adsorption Isotherm Studies

The kinetic study in this paper was conducted to identify the optimum time required for maximum adsorption of Pb^{2+} metal ions and Cr^{3+} metal ions into CNTs by altering the initial concentration of the solution at four different ranges of values. Based on the analysis done in Section 2.2, the best optimum conditions were determined to investigate the best contact time to denote the removal percentage. The amount of Pb^{2+} and Cr^{3+} metal ions adsorbed by both adsorbents, q_t were obtained as shown is Figure 6a,b. The samples were collected at every 10 min time interval with a total contact time of 1 h for both heavy metal ions. The removal percentage of both Pb^{2+} and Cr^{3+} metal ion gradually increased and attained an almost perfect equilibrium level within the 1 h of agitation time. The pH value set for Pb^{2+} metal ions stock solution was pH 4 while, the Cr^{3+} metal ions stock solution was set to pH 8.

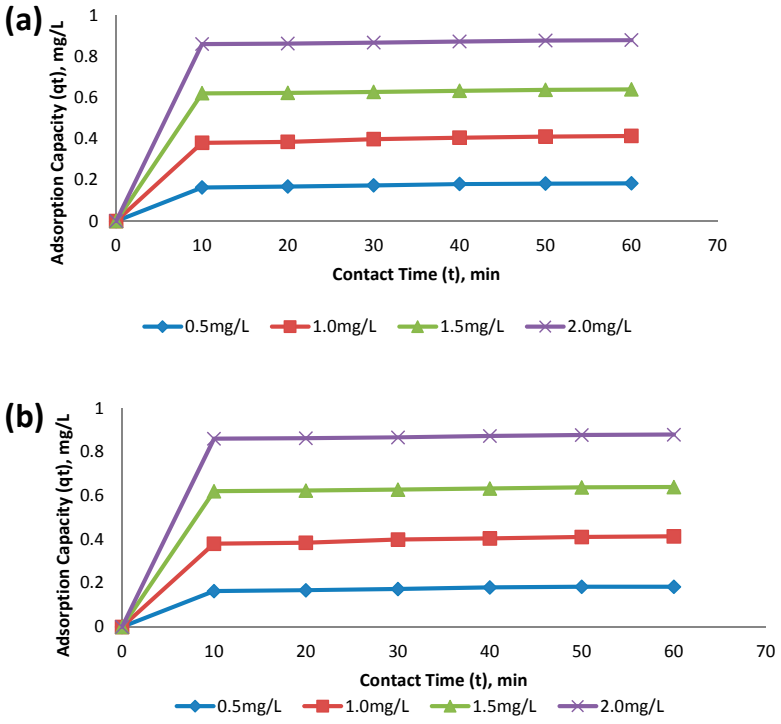

Figure 6. Adsorption capacity (q_t) *versus* contact time (t) with different initial concentrations (**a**) Pb^{2+} metal ions and (**b**) $Cr3^{+}$ metal ions.

In order to determine the adsorption isotherm and kinetic studies for this research, well known important isotherm models for instance Langmuir and Freundlich were employed. Both the isotherm models were tested to resolve the optimum model to determine the best model fit for the Pb^{2+} metal ions and Cr^{3+} metal ions adsorption into the Langmuir isotherm model which is capable of correlating the solid phase adsorbate concentration (q_e) and the uptakes to the equilibrium liquid concentration (C_e) is as follows:

$$q_e = \frac{q_m K_{LC_e}}{1 + K_L q_m} \quad (3)$$

Linearly,

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

where, C_e (mg/L) represents the unadsorbed heavy metal ions concentration at equilibrium, q_e (mg/g) represents the amount of adsorbed heavy metal ions concentration per unit weigh of the adsorbent. Meanwhile, the affinity of binding sites established in the equation above is denoted as K_L, and at the same time, q_m is known as the maximum adsorption capacity, in which it indicates the limiting adsorption capacity of a particle when the active sites are fully occupied. Equation (4), which is the linearized form of the Langmuir Isotherm equation, was used to plot a graph of C_e/q_e against C_e and the values of q_m and K_L were obtained respectively from the slope and interception of the graph. The adsorption isotherm for Langmuir model done for this study is represented in Figure 7a and it can be observed that the data retrieved satisfactorily fits the linearized equation for both heavy metal ions. The R^2 value obtained from the plot was 0.9941, and the values of q_m and K_L were calculated to be 15.34 and 0.078 mg/L. respectively for the Pb^{2+} metal ions. Meanwhile for the Cr^{3+} metal ions, the R^2 value obtained was 0.9846, calculated q_m and K_L were equals to 24.45 (mg/g) and 0.071 (L/mg) respectively.

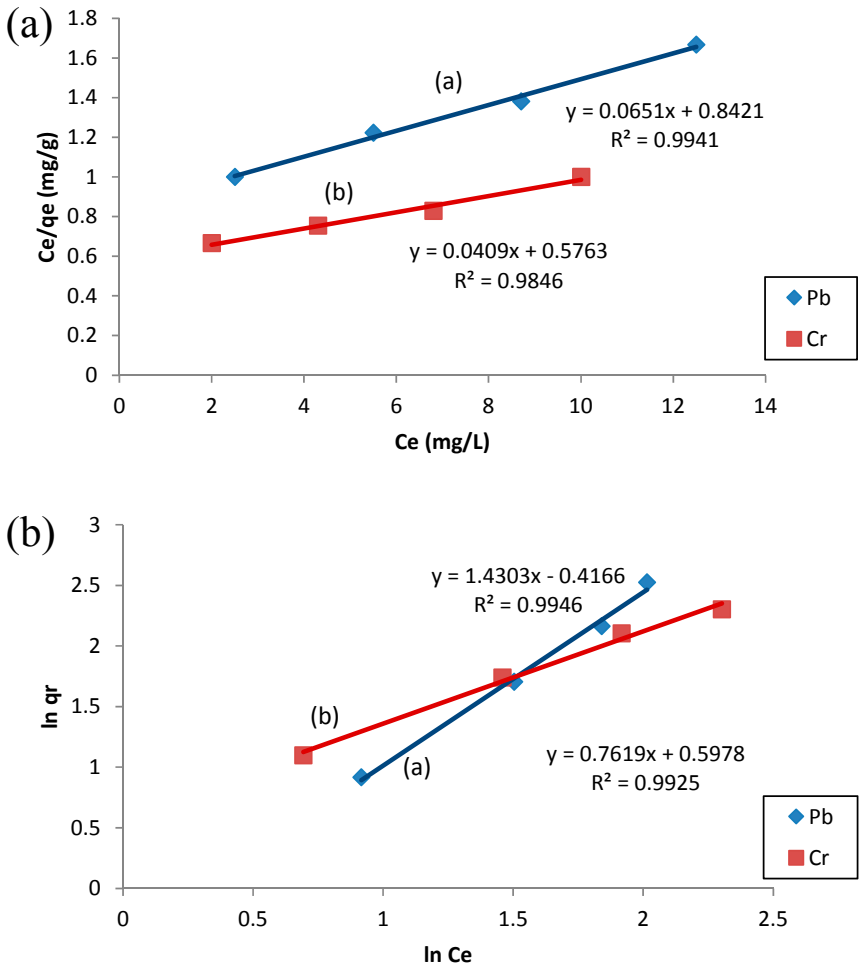

Figure 7. (**a**) Langmuir adsorption, and (**b**) Freundlich adsorption isotherm of both Pb^{2+} and Cr^{3+} metal ions CNTs.

Similarly, the adsorption isotherm for Pb^{2+} metal ions and Cr^{3+} metal ion were then plotted for another model which is the Freundlich model. The Freundlich model defines the interrelation between residual heavy metal ions equilibrium concentrations, C_e in mg/L with the heavy metal ions uptake

capacities, q_e (mg/g) of adsorbent. Equation (5) below indicates the Freundlich isotherm model that was used to plot the graph shown in Figure 7b.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where, K_F is a Freundlich constant that represents the adsorption capacity of adsorbent and on the other hand, n is a constant that validates the intensity of relationship between the adsorbate and adsorbent. K_F and n were both determined from the slope and interception of the linear plot of ln *qe versus* ln *Ce*. Based on the graph plotted, the values of n and K_F were determined to be 1.438 and 1.34 L/mg respectively for the adsorption of Pb^{2+} metal ions, whereby for the adsorption of Cr^{3+} metal ions, n was figured to be 1.818 and the K_F was evaluated to be 1.312 L/mg. In addition, by obtaining the R^2 value of 0.9946 for adsorption of Pb^{2+} metal ions and 0.9925 for adsorption of Cr^{3+} metal ions for the Freundlich plot, it indicates that the isotherm data fits well for the model. Table 5 shows the value determined for both Langmuir and Freundlich models. Review on removal of Pb^{2+} and Cr^{3+} as shown in Tables 6 and 7 respectively.

Table 5. Isotherm model for adsorption of Pb^{2+} and Cr^{3+} metal ions.

Adsorbate	Langmuir Isotherm			Freundlich Isotherm		
	q_m (mg/g)	K_L (L/mg)	R^2	n	K_F ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	R^2
Pb^{2+} metal ions	15.34	0.078	0.9941	1.438	1.34	0.9946
Cr^{3+} metal ions	24.45	0.071	0.9846	1.818	1.312	0.9925

Table 6. Review on Langmuir and Freundlich isotherm parameter for Pb^{2+} adsorption.

Adsorbent	q_m (mg/g)	K_L (L/mg)	R^2	K_F ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	n	R^2	References
CNTs	15.34	0.073	0.9941	1.438	1.34	0.9946	This Study
CNTs-soaked in HNO3	2	-	-	0.175	0.944	0.99	[1]
CNT reflexed in HNO3	-	-	-	0.183	0.944	0.99	[1]
CNTs	11.23	0.04	0.993	0.68	1.52	0.97	[24]
CNT/Al203	67.11	0.04	0.989	3.22	1.39	0.979	[24]
CNTs	17.44	0.586	0.995	5.99	1.91	0.987	[39]
MWCNT Oxidized	49.71	1.73	0.996	3.29	5.01	0.855	[40]
MWCNTs	6.71	3.71	0.96	4.76	7	0.98	[25]
MWCNTs-coxidized	27.8	1.33	0.93	12.8	3.42	0.899	[25]
MWCNT-TAA	71	0.13	0.945	8.34	1.43	0.99	[25]
MWCNT-oxidized	9.92	1.78	0.97	7.57	0.518	0.99	[29]
CNTs –oxidized	28	-	-	15.56	4.48	0.965	[29]

Table 7. Review on Langmuir and Freundlich isotherm parameter for Cr3+ adsorption.

Adsorbent	q_m (mg/g)	K_L (L/mg)	R^2	K_F ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	n	R^2	References
CNTs	24.45	0.071	0.9846	1.312	1.818	0.9925	This study
Raw CNTs	0.3853	0.0741	0.9089	2.4802	0.0642	0.9494	[16]
PAC	46.9	1.022	0.998	13.3	1.583	0.971	[17]
Chitosan	35.6	1.149	0.635	0.999	8.25	2.050	
SWNTs	20.3	1.831	0.522	0.997	5.90	1.285	
MWNTs	2.48	0.838	0.705	0.956	0.98	2.212	
dried red alga	12.85	0.015	0.998	0.688	0.752	0.913	[43]
Activated Carbon	66.75	0.06	0.994	0.401	10.32	0.996	
CeO_2/ACNTs	26.81	0.7064	0.9264	4.01	12.5021	0.9685	[44]

The Langmuir and Freundlich equations were developed to fit both the Pb^{2+} and Cr^{3+} metal ions equilibrium adsorption capacity, q_e and the concentration of unadsorbed metal ions and below equations were derived. The equations 6 and 7 represent the Langmuir and Freundlich equations for adsorption of Pb^{2+} metal ions, while equations 8 and 9 represent the Langmuir and Freundlich equations for adsorption of Cr^{3+} metal ions as shown below:

$$\text{Developed Langmuir Equation: } q_e = \frac{1.121 C_e}{1 + 0.073\ C_e} \quad (6)$$

$$\text{Developed Freundlich Equation}: \; q_e = 1.34{C_e}^{\circ.6954} \tag{7}$$

$$\text{Developed Langmuir Equation}: q_e = \frac{1.7359C_e}{1 + 0.071\ C_e} \tag{8}$$

$$\text{Developed Freundlich Equation}: \; q_e = 1.818{C_e}^{\circ.762} \tag{9}$$

The pseudo-first-order kinetics and pseudo-second-order kinetics of Pb^{2+} metal ions and Cr^{3+} metal ions adsorption using CNTs were also investigated and the calculated kinetic adsorption values were further analyzed to estimate the sorption rates as well as to determine the suitable rate expressions characteristic of possible reaction mechanism. The pseudo-first-order and pseudo-second-order models employed for the data analysis are as shown below;

$$\ln (q_e - \ q_t) = lnq_e - \ k_1 t \tag{10}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{11}$$

where, q_t represents the amount of heavy metal ions removed at time , while q_e represents the adsorption capacity at equilibrium. The pseudo-first-order rate constant (L/min) is denoted as K_1 and t indicates the contact time (min). k_2 represents the rate constant of the pseudo second order adsorption (g/mg/min). The plotting of the graph log $(q_e - q_t)$ *versus* time (t) for pseudo-first-order kinetic model did not yield in good convergence while in the pseudo-second-order adsorption, the equation 14 was applied to plot graph t/q_t (min.g/mg) *versus* time (min) where all data converged well into a straight line with a high correlation coefficient R^2. The values of slopes and intercepts obtained from the graph were tabulated in Table 8. As seen from Table 8, coefficients gained from the both the pseudo-first-order and pseudo-second-order models, it is evident that the pseudo-second-order-model fits the best. From Table 8, it is obvious that the R^2 values of the pseudo-second-order kinetic model are much higher than that of pseudo-first-order-kinetic-model and it experienced a consistent increase with the concentration compared to the values of the pseudo-first-order kinetic model [55].

Table 8. Pseudo-first-order and pseudo-second-order kinetics for adsorption of Pb^{2+} and Cr^{3+} metal ions.

Heavy Metal Ions	Pseudo-First-Order			Pseudo-Second-Order			
	C_0 (mg/L)	K_1 (1/min)	R^2	C_0 (mg/L)	q_e	K_2 (g/mg/min)	R^2
Pb^{2+} metal ions	5	0.0004	0.9856	5	0.337	1.1724	0.999
	10	0.0005	0.9567	10	0.8328	0.6379	0.9567
	15	0.0003	0.9619	15	1.2675	0.7424	0.9619
	20	0.0001	0.9783	20	1.7277	1.2495	0.9783
Cr^{3+} metal ions	5	−0.0002	0.9611	5	0.1899	2.2940	0.9994
	10	−0.0001	0.9542	10	0.4228	1.4640	0.9997
	15	−0.00005	0.9848	15	0.6442	2.5560	0.9999
	20	−0.00004	0.9782	20	0.8835	2.5862	1.0000

3. Materials and Method

3.1. Raw Material

Microwave assisted single stage production of Multiwall carbon nanotubes (MWCNTs) with a 16–23 nm outer diameter) and (98%) purity obtained from our previous work [32].

3.2. Preparation of Stock Solution

Analytical grade Pb^{2+} and Cr^{3+} standards which were obtained from Merck were used to prepare stock solutions containing 1000 mg/L of Pb^{2+} and Cr^{3+} metal ions which were further diluted using distilled water to attain the desired concentrations. In this research, the initial concentration of both

Pb^{2+} and Cr^{3+} metal ions were both set to 2 mg/L and prepared stock solution was used to batch adsorption experiments.

3.3. Batch Adsorption

The batch adsorption experiment was conducted by treating the prepared stock solutions with different ranges of CNTs dosage from 0.03 to 0.09g, agitation speed from 100 to 150 rpm, pH of adsorption process from 4–6 for Pb^{2+} and from 4–8 for Cr^{3+} with varying agitation time from 10 to 50 min and from 10 to 60 min, respectively for Pb^{2+} and Cr^{3+} metal ions based on the design obtained from the Design of Expert software V6.0.8 arrangement (Perkin–Elmer, Waltham, MA, USA). The desired pH value of the stock solution was adjusted using 0.5 M of the NaOH solution. The Atomic Spectrometer (PerkinElmer Analyst 400, Perkin–Elmer) was employed to determine the initial and final concentrations of the Pb^{2+} and Cr^{3+} metal ions in order to calculate the amount of metal ion adsorbed by the CNTs. The detailed experiment design obtained from the Design Expert V6.0.8 for the removal of both the Pb^{2+} and Cr^{3+} metal ions were tabulated in Table 9a,b.

Table 9. Optimizing conditions for batch adsorption of removal of (**a**) Pb^{2+} and (**b**) Cr^{3+}.

(a) Pb^{2+}			(b) Cr^{3+}		
No.	**Parameters**	**Variations**	**No.**	**Parameters**	**Variations**
1	Pb^{2+} stock solution	2 mg/L	1	Cr^{3+} stock solution	2 mg/L
2	Adsorbent Dosage (g)	0.03, 0.06, 0.09	2	Adsorbent Dosage (g)	0.03, 0.06, 0.09
3	pH values	4, 5, 6	3	pH values	4, 6, 8
4	Agitation Time (min)	10, 30, 50	4	Agitation Time (min)	10, 35, 60
5	Agitation Speed (rpm)	100, 125, 150	5	Agitation Speed (rpm)	100, 125, 150
6	Volume (mL)	10	6	Volume (mL)	10

Equations 12 and 13 below were used to calculate the metal ion adsorption capacities using the CNTs produced by microwave heating at a certain time designed, t and also to calculate the adsorption equilibrium of the metal ions.

$$q_t = \frac{(C_o - C_t)\,V}{m} \tag{12}$$

$$q_e = \frac{(C_o - C_e)\,V}{m} \tag{13}$$

where q_t denotes the amount of metal ions adsorbed (mg/g) at given time, t and the q_e indicates equilibrium concentration. C_0, and C_t denote the initial concentration of the metal solution, concentration metal ions at time t respectively, while Ce represents the equilibrium concentration of metal ions (mg/L) .V is the volume of metal ions stock solutions used (L) and m is the weight of the adsorbent dosage in grams (g).

3.4. Kinetic Study

The adsorption kinetics of Pb^{2+} and Cr^{3+} metal ions were carried out using four different concentrations for both Pb^{2+} and Cr^{3+} metal ions stock solution with the best optimizing parameters such as agitation speed and agitation time, and the adsorbent dosage of CNTs to be used was decided by the batch adsorption process and those conditions were employed for the adsorption kinetics study. The adsorption kinetic study for this research was done for an hour with 4 different concentrations of 30 mL of Pb^{2+} and Cr^{3+} metal ions stock solution whereby for every 10 min interval, a small amount, about 5 mL of the metal ions solution was withdrawn, filtered and checked for its concentration by using the Atomic Adsorption Spectrometer (AAS, Perkin–Elmer). The optimized parameters used to carry out the adsorption of Pb^{2+} on the CNTs were adsorbent dosage of 0.06 g and agitation speed of 150 rpm, while for the adsorption of Cr^{3+} were adsorbent dosage of 0.03 g and agitation speed of

125 rpm, gained from the Design Expert. The final concentrations of the stock solutions were again measured using the AAS.

3.5. Adsorption Isotherm

The adsorption Isotherm study for Pb^{2+} and Cr^{3+} metal ions were done by preparing four different concentrations of 5, 10, 15 and 20 mg/L of 30 mL of Pb^{2+} and Cr^{3+} metal ions stock solution. The best optimizing conditions were used to conduct this experiment in which the solutions were agitated for an hour with the agitation speed and adsorbent dosage of CNTs of 150 rpm and 30 mg respectively for both the Pb^{2+} and Cr^{3+} metal ions stock solutions prepared. The Atomic Adsorption Spectrometer was used to measure the final concentration of the solutions. Langmuir (14) and Freundlich Isotherm (15) models were applied to get the best model.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{14}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{15}$$

where q_e: the adsorption density at the equilibrium solute concentration C_e: (mg of adsorbate per g of adsorbent), C_e: the equilibrium adsorbate concentration in solution (mg/L), q_m: the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent), and K_L: the Langmuir constant related to energy of adsorption (of adsorbent per mg of adsorbate), while K_F and n are the empirical constants dependent on several environmental factors and is greater than one.

4. Conclusions

Based on all the analysis carried out for the obtained results, it is found that the Pb^{2+} metal ions and Cr^{3+} metal ions could be successfully removed from aqueous solution by using the CNTs. This proves that the CNTs serves as a good adsorbent in the removal of heavy metal ions, and it can be considered as a very convenient adsorbent to be used. The CNTs uses were characterized by using the Field Emission Scanning Electron Microscopy, Transmission Electron Microscopy and FT-IR. The effect of adsorption parameters such as the adsorbent dosage (CNTs) used, pH of stock solution, agitation speed, and agitation time for the heavy metal ion removal process were studied and optimized. The adsorption isotherm study was done by using the Langmuir and Freundlich Isotherm models while the kinetics studies on optimized conditions were done by employing the pseudo-first-order kinetics and pseudo-second-order kinetic modeling. Experimental results on the adsorption conditions showed that Pb^{2+} have the highest adsorption capacity at a pH value of acidic state of 4.0, agitation speed 150 rpm and the agitation time of 50 with the maximum amount of dosage used which was 0.09 g. Meanwhile, the Cr^{3+} has the highest adsorption capacity at a pH of alkaline state of 8.0, agitation speed 150 rpm and the agitation time of 60 with the maximum amount of dosage used which was 0.09 g. The Langmuir and Freundlich isotherm studies for Pb^{2+} were calculated to be 0.9941 and 0.9948 respectively. On the other hand, the adsorption isotherm study for Cr^{3+} results in R^2 of 0.9846 for the Langmuir model and 0.9925 for the Freundlich. The Langmuir and Freundlich constants for adsorptions of Pb^{2+} metal ions show 0.078 and 1.38 L/mg respectively, and 24.45 and 1.312 L/mg for adsorption of Cr^{3+} metal ions.

These values prove that both the isotherm models describe the adsorption process well. In addition, kinetics data obtained for both the Pb^{2+} metal ions and Cr^{3+} metal ions were best fitted by the pseudo-second-order model. Hence, the isotherm equilibrium on optimized condition was studied and the model equations were developed.

Acknowledgments: The authors are grateful to the UCSI University for funding environmental & sustainable engineering cluster project code Proj-In-FETBE-015. The authors are thankful to the authorities of the University of Malaya for FESEM analysis under the Ministry of Higher Education High Impact Research (UM.C/HIR/MOHE/ENG/20).

Author Contributions: Nabisab M. Mubarak initiate the project and design experiments. Manimaran Thobashinni performed experiments and collect data from the experimental study. Nabisab M. Mubarak and Manimaran Thobashinni analyzed the data. Nabisab M. Mubarak wrote paper with a help of Manimaran Thobashinni. Ezzat C. Abdullah, Jaya N. Sahu helping in correcting the paper with scientific and technical input provided.

Conflicts of Interest: The authors declare no conflict of interest.

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