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Multiwall carbon nanotube promising route for removal of chromium from wastewater via batch column mechanism

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Abstract. Water pollution regarding heavy metals issue keep lingering our days from time to time, and some problems even left unattended. The most crucial cause of this pollution is the industrial waste, especially waste water that had been released into the drainage system without being treated first. This activity had been done illegally and left a huge impact towards the environment also human. In this study multiwall carbon nanotubes (MWCNTs) are promising route for removal of chromium was investigated. Results revealed that the optimum conditions for highest removal (99.97%) of chromium are pH7,0.04g of MWCNTs dosage, and flowrate of 20.83 mL/s. Based on adsorption isotherm for this experiment, the amount of chromium adsorbed, q_m calculated was 50.51 mg of chromium/gram of MWCNTs. From the results obtained, it had been proved that MWCNTs can be used as an effective adsorbent in chromium removal from aqueous solution due to high adsorption capacity.

1. Introduction

Water is the most essential element for living things on this Earth, which are human, animal and plant. Nowadays, the most popular worldwide issues involving basic need is to provide a clean and affordable water[1-3].Currently, natural water resources had faced few problems due to the contaminated environment and also global climate change[4]. Contamination of heavy metals had become worsen from days to days and this can affect the environmental performance especially water. The nature of heavy metals is it is not biodegradable thus it can be accumulated in water bodies and

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aquatic life[5]. In addition, this can cause hazards towards human and its surrounding, for example kidney damage if exposed to cadmium and increase in blood pressure due to barium exposure. Even though, we have technologies for treating the wastewater but those treatment process have their own limitation in term of infrastructure and also the technologies itself[6]. Thus, CNTs had been introduced as another advanced solution in wastewater treatment in order to ensure the quality of water will be in good condition for next generation. The great properties of CNTs can provide a high performance and affordable water and wastewater treatment systems[7]. Thus, CNTs had been introduced as a solution provider for water and waste water treatment [8, 9].

In this research, the main objective was to optimize the removal of Cr from aqueous solution using MWCNTs by batch column study. Lastly, the adsorptions isotherm kinetic and isotherm model was developed.

2. Materials and Methods

2.1. Materials

The MWCNTs had been obtained from previous work [10]. 1000 mg/L Chromium and 1.0 M NaOH had been obtained from Company Merck

2.2. Preparation of stock solution

Analytical grade chromium standard solution obtained from Merck was used to prepare stock solutions containing 1,000 mg/L of chromium metal ions which were further diluted with distilled water to obtain the required concentrations. The initial concentration of chromium metal ions was set to 10.0 mg/L and the prepared solution was used for batch column adsorption experiments. This step will be repeated by using lead standard solution 1,000 mg/L in order to test for Chromium removal.

2.3. Batch column study

A batch column adsorption experiment was performed by using 100 ml of 1.0 mg/L of chromium standard solution pour into the batch column system that had been custom made. The process parameter was pH, CNTs dosage, and flow rate. The initial pH of the stock solution was adjusted by using 1.0M of NaOH by adding in a few drops of the alkaline solution in the 100 ml of 1.0 mg/L of chromium standard solution until the desired pH was obtained. The CNTs were then packed in the batch column system with varying amount of dosage. After few minutes being adsorb, the concentration of final solution will be measured by using Atomic Absorption Spectroscopy (AAS) machine. The adsorption capacity of CNTs at flowrate f was determined by using Eq-1.

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

where C_o represents the initial concentration of chromium solution (mg/L), q_t represents the concentration of chromium at a flowrate f (mg/g), C_e represents the equilibrium concentration of chromium (mg/L) respectively represents the volume of chromium stock solution (L) and m indicates the weight of the adsorbent used (g). The Langmuir model demonstrates a relationship between the concentration adsorbate in solid phase, q_e and the Cr liquid concentration from uptakes to the equilibrium, C_e as represented in the equation below Eq-2.

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \left(\frac{1}{q_m}\right) C_e \qquad \text{Eq-2}$$

Where, q_e (mg/g) – The amount of adsorbed Cr concentration per unit weight. C_e (mg/L) – The adsorbed Cr concentration of solution in equilibrium. K_L (L/mg) – Langmuir constant relates to affinity of the binding sites. q_m - Maximum adsorption capacity of the adsorbent. While for the Freundlich isotherm, it demonstrates the relationship of the Cr uptake capacities of adsorbent, q_e and the Cr concentration at equilibrium, C_e. This relationship had been expressed by the equation below Eq-3.

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad \text{Eq-3}$$

Where, q_e (mg/g) – The amount of adsorbed Cr concentration per unit weight. C_e (mg/L) – The adsorbed Cr concentration of solution in equilibrium, K_F (L/g) – Freundlich constant relates to adsorption capacity of the adsorbent – a constant that shows the greatness relationship between the adsorbate and adsorbent.

3. Result and Discussion

3.1. Effect of CNTs dosage

Based on Figure 1 , the optimum condition for CNTs dosage is 0.04 g. From the result obtained, we can see that the percentage of chromium removal still high since the percentage is more than 95%. Thus, in can be concluded that the amount of CNTs dosage do not affect much on the chromium removal in aqueous solution since the difference in percentage removal is not that big. From previous research in removing chromium, the most effective in achieving highest percentage of removal is by using minimum amount of adsorbent [11].

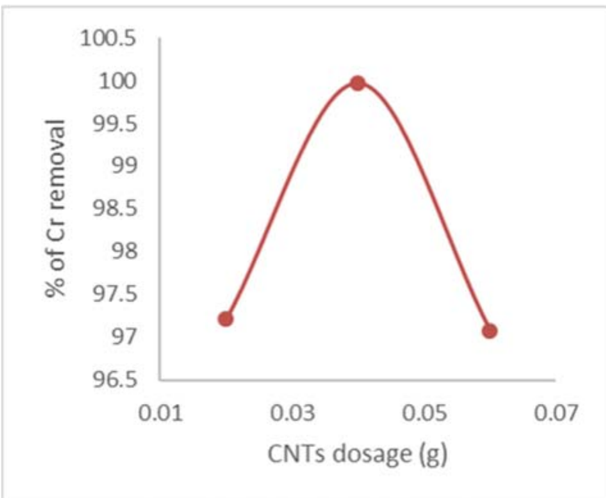

Figure 1. The effect of CNTs dosage on Chromium removal.

3.2. *Effect of pH*

The effect of pH on removal of Cr as shown in figure 2. the optimum condition for pH parameter is pH 7. From the result obtained, we can see that the percentage of chromium removal reducing a lot when the pH is lower or higher than pH 7. This shown that initial pH of the stock solution gives big impact on chromium removal from aqueous solution where we can see from the percentage of removal the differences in between lower and higher pH of pH 7 is about 35%[12].

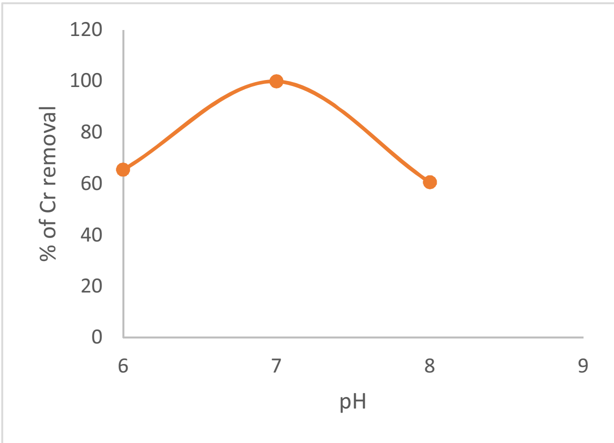

Figure 2. The effect of pH on removal of Chromium

3.3. *Analysis on percentage of chromium removal using Central Composite Design (CCD)*

Figure 3(a-c) shown 3-D interaction plot of percentage of chromium removal with the parameters involve which are pH of stock solution, CNTs dosage and the flowrate. Since the model is 2FI which mean two factor interactions, thus all the interaction plots are having linear relationship. Referring to Figure 3(a), the line plot of percentage of chromium removal is linearly increasing as there is values increment in pH while for CNTs dosage the line almost straight. This shown that parameter pH is influential compare to CNTs dosage. Meanwhile for Figure 3(b), both parameters which are flowrate and CNTs dosage shown almost straight plot with the percentage of chromium removal. Thus, these parameters left less impact on the percentage of chromium removal. Lastly, for Figure 3(c), the line plot almost the same as Figure 3(a), since pH is the most dominant parameter compare to flowrate in achieving highest percentage of chromium removal as we can see the adsorption of chromium is minimum at pH 5 which is in acidic condition while the maximum adsorption of chromium is maximum at pH 7 which is in neutral conditions. In this study, the effect of flowrate towards the removal of chromium from aqueous solution is not so important because the system that had been custom made was using the plastic stopcock that act as the valve for the system. Thus, sometimes the flowrate is not even uniform due to ensure the CNTs in the filter paper will not fly away from the set up. The pH that affect the removal of chromium in this figure is pH 9 and it is proof that neutral to alkaline condition is

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the optimum condition to remove chromium from aqueous solution. These findings agree with previous researchers [13-15].

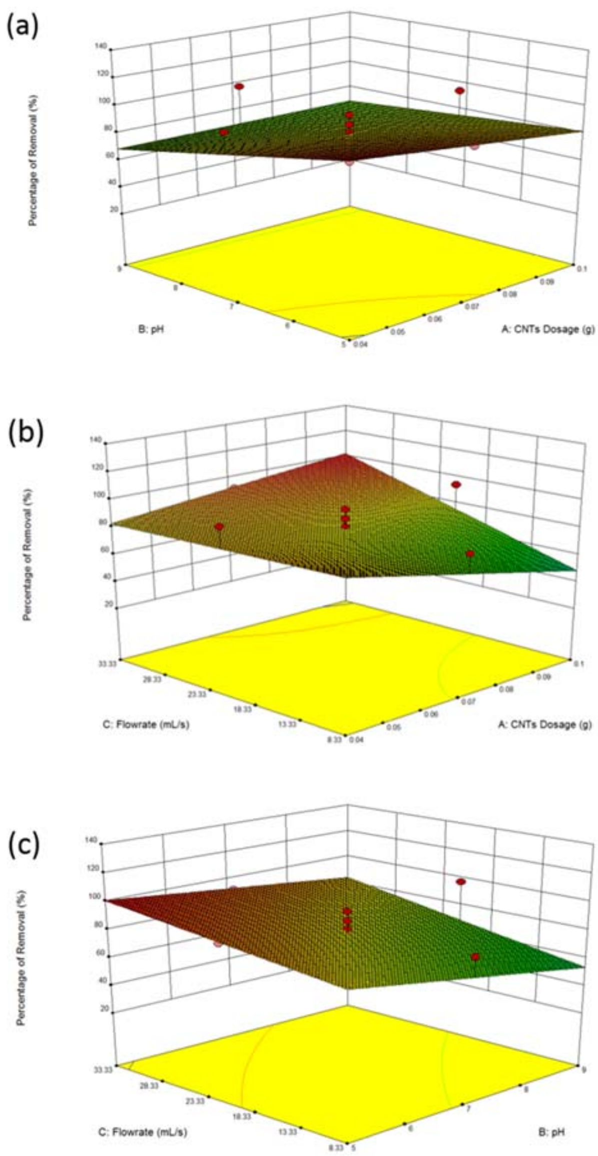

Figure 3. Response surfaces for percentage of chromium removal on a) effect of pH and CNTs dosage. b) effect of flowrate and CNTs dosage. c) flowrate and pH.

3.4. Adsorption Isotherm

Adsorption isotherm is the correlation created in between amount of chromium adsorbed at constant pH and CNTs dosage, in addition the initial concentration of chromium solutions had been varied in order to study the response towards the adsorption process. This is to ensure that the applicability of the adsorption process to be measured. As shown in Figure 4, a graph of adsorption capacity versus flowrate for different Cr initial concentration had been plotted in order to observe the relationship. Based on the plot pattern, the adsorption capacity is increasing as the initial Cr concentration is increasing and this is due to the increment in mass transfer driving force that lead into a higher adsorption rate. The rate of adsorption capacity rapidly increasing as the flowrate reaches 20.83mL/s and start to decrease after that. The reason behind the rapid increment of adsorption capacity is due to the high availability of adsorbent sites that result in a high adsorption rate. As the flowrate pass 20.83mL/s, the adsorption rate reducing due to the sites of the adsorbent reduced, hence the adsorption of Cr decreasing. As at lower concentration, the adsorption capacity is less because of difficulties for less-polar adsorbents which is CNTs to adsorb Cr from a more polar solvent.

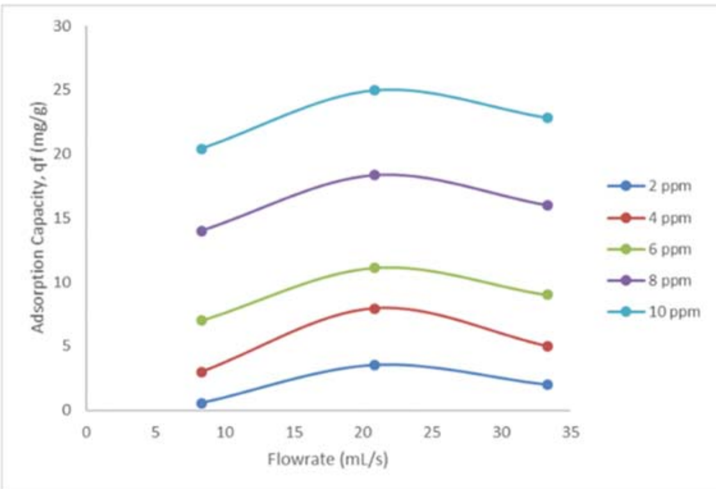

Figure 4: Adsorption capacity (qt) versus flowrate (f) with different initial concentration of Cr.

3.5. Kinetic study

Kinetic studies on the removal of chromium had been carried out by varying the initial concentration of stock solution. Based on the result obtained, the percentage of chromium removal keep increasing as the stock solution concentration increasing except for 6 ppm stock solution. Kinetic models such as Langmuir and Freundlich was examined. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2 values close or equal 1). A relatively high R^2 values indicate that the model successfully describes the kinetics of Cr adsorption. As shown in Figure 5(a-b), the adsorption process can be enhanced by concentrating the stock solution with condition all the parameters involve are the same. These results are good agreement with previous researchers [2]

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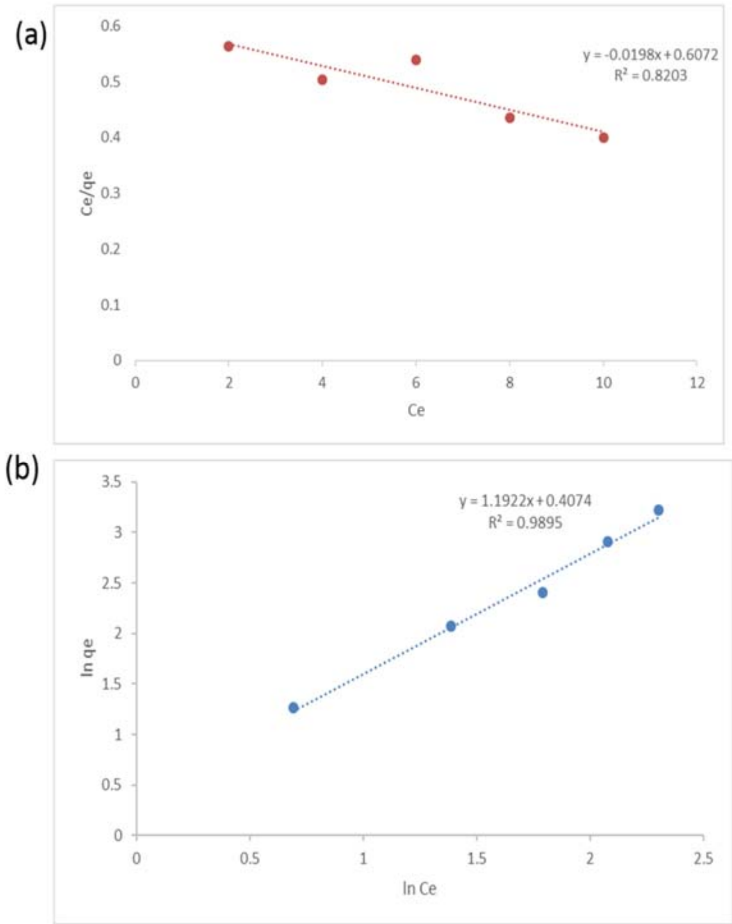

Figure 5.a) Langmuir isotherm b) Freundlich isotherm

TABLE I. LANGMUIR AND FREUNDLINCH ISOTHERM

Langmuir Isotherm		Freundlich Isotherm	
q_m (mg/g)	50.51	K_F (L/g)	1.503
K_L (L/mg)	0.033	n	0.839
R^2	0.8203	R^2	0.9895

3.6. SEM analysis before and after adsorption of Cr

SEM was used to study the surface physical morphology of CNTs before and after adsorption of Cr as shown in figure 5(a-b). It is observed that Small thread-fibrils like structures are observed in the pure CNTs as shown in Figure 6(a). These structures look interconnected between them and they made up in the inter spaces between the connections. Besides that, there are no signs of clumped solid structure presence in the pure CNTs probably due to the existence of CNTs in long tube forms. On the hand figure 6 (b) shows that after adsorption of Cr it was observed that CNTs structure becomes agglomerated this is due to absorption of Cr on the surface of CNTs. Similar findings were observed in the previous study [16].

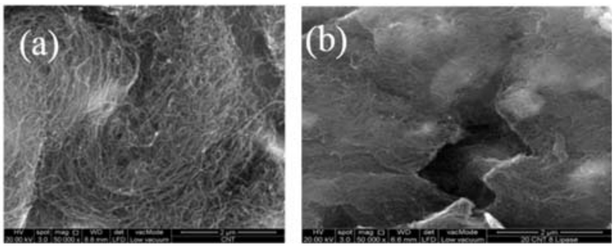

Figure 6. a) CNTs before b) CNTs after Cr adsorption

3.7. FTIR analysis before and after adsorption of Cr

FTIR analysis in order to identify the specific presence of particular bands which relates to certain functional groups. Figure 7(a-b) show FTIR analysis of CNTs before (a) and after adsorption of Cr (b). The Figure 7 (a) the peaks observed on before CNTs adsorption at a range of 1700 to 1900 cm-1 defines the carboxylic group, followed by aromatic C=C groups at 1450-1600 cm-1 and O-H groups at 2800-3000 cm- 1 as well. This observation was observed CNTs, a very small amount of oxygen group present on the surface of CNTs due to synthesis condition to enhance high quality and high purity of MWCNT. Fig.7 (b) shows after adsorption of Cr, it was observed several peaks were observed. The C= O and C–O are stretching frequencies shifted from 1705 and 1200 cm−1. Peaks at 1600 cm−1 of amino-functionalized MWCNTs are due to the N–H stretching of amine groups. Peaks at 2930 and 2860 cm−1 are greatly enhanced because of the attachment of additional methyl groups. Peaks between 950 and 700 cm−1 are due to the stretching mode of aromatic amine groups, and peaks at 2370 cm−1 may be because of the existence of ammonium ions[17, 18]

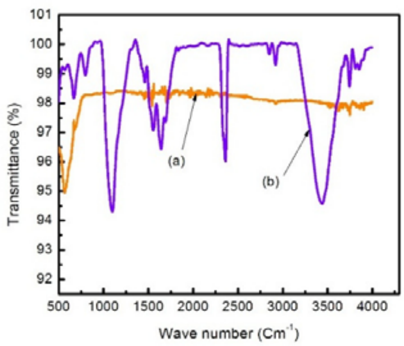

Figure 7.a) CNTs before b) CNTs after Cr adsorption

4. Conclusion

As a conclusion, microwave assisted MWCNTs had good adsorption properties where it is better in quality than common CNTs that had been produced by others method such as arc-discharge or laser ablation. In this study Chromium re that had been conducted, optimum condition of removal of chromium from aqueous solution had been obtained. With the percentage removal of 99.97% and adsorption capacity of 24.993 mg of chromium/ g of CNTs, the optimum conditions are pH 7, 0.04 g of CNTs dosage and 20.83 mL/s for the flow rate. Adsorption kinetics had been demonstrated by Langmuir and Freundlich model, the qm calculated was 50.51 mg/g, KL is 0.033 L/mg, KF is 1.503 L/g and n is 0.839. Thus, multi-walled carbon nanotubes proved as a promising adsorbent in removing heavy metals from aqueous solutions.

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