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POTENTIAL OF LOW CARBON NANOTUBES DOSAGE ON CHROMIUM REMOVAL FROM WATER

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ABSTRACT: This paper was involved by a method of eliminating a hexavalent chromium (Cr (VI)), from the synthetic water via low dosage of carbon nanotubes (CNT). The ability of CNT to remove Cr (VI) from synthetic water through the adsorption process was studied in batch experimentation. The findings revealed up to 100% elimination of Cr (VI) in the 0.07mg/L Cr (VI) concentration. These excessive elimination proficiencies were expected credited to the powerful adsorption of chromium ions to the physical properties of the CNT. The pattern layout has been created in these experimental runs in order to locate the ideal situation of the Cr (VI) deletion from synthetic water. To accomplish the purposes of the experiment, there are 4 independent variables with several points influenced which are the CNT dosage, the pH of the water, the agitation speed and the contact time. The StatGraphics Centurion XV software has been used to create the adsorption equivalence and to discover the major impacts that caused to the elimination of Cr (VI). The results shown that, the adsorption capability of the carbon nanotubes was considerably reliant on the pH of the Cr (VI) solution, supported by the CNT dosage the contact time, and the agitation speed. The optimization expected using the adsorption equation shows that 1 mg CNT dosage, pH=2 is being the optimal, 120 minutes contact times, and moderate agitating rate at 150 rpm.

ABSTRAK: Kertas kajian ini melibatkan kaedah untuk menyingkirkan kromium (VI) dari air sintetik menggunakan karbon tiub nano berdos rendah. Eksperimen kelompok dilakukan untuk menentukan keupayaaan karbon tiub nano untuk menyingkirkan kromium (VI) dari air sintetik melalui proses penjerapan. Hasil penemuan menunjukkan kromium (VI) telah disingkirkan sebanyak 100% dari kepekatan 0.07 mg/L kromium (VI). Kecekapan penyingkiran ini adalah disebabkan penjerapan ion-ion kromium yang kuat terhadap sifat fizikal karbon tiub nano tersebut. Rekabentuk eksperimen telah dibina untuk menentukan kondisi optima bagi penyingkiran kromium (VI) dari air sintetik. Untuk mencapai matlamat kajian, empat faktor yang terdiri daripada dos karbon nano tiub, pH air, kelajuan goncangan dan masa sentuhan. Perisian StatGraphics Centurion XV telah digunakan untuk mendapatkan nilai setara proses penjerapan dan kesan utama yang menyebabkan tersingkirnya kromium (VI). Hasil kajian menunjukkan keupayaan penjerapan oleh karbon tiub nano sangat bergantung kepada pH larutan kromium (VI), disusuli dengan dos karbon tiub nano, masa sentuhan dan kelajuan goncangan. Penjerapan optimum kromium (VI) dapat dicapai pada kondisi 1 mg dos karbon tiub nano, larutan pada pH 2, masa sentuhan selama 120 minit dengan kelajuan goncangan sebanyak 150 rpm.

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KEY WORDS: *STatGraphics; low CNT dosage; polluted water; Chromium*

1. INTRODUCTION

Carbon nanotubes (CNTs) are a newly found. They take the shape of cylinder-shaped carbon fragments and have various schemes that make them hypothetically beneficial in a wide range of functions in medicines, engineering, biotechnology and other areas of materials science [1]. They demonstrate extraordinary strength and exceptional electrical properties. The characteristics of nanotubes are defined by their thickness and chiral angle, both of which depend on *n* and *m* [2]. The thickness, d_t, is simply the length of the chiral. vector divided by ¼, and it was found that $d_t = (\text{Ö}3/p)\ a_{c\text{-}c}\ (m^2 + mn + n^2)^{1/2}$, (1)

where $a_{c\text{-}c}$ is the space among neighbouring carbon atoms in the flat sheet. In turn, the chiral angle is given by $\tan^{-1}(\text{Ö}3n/(2m + n))$ (2)

The existence of heavy metals in the environment is of most important worry because of their harmfulness to many life methods. Various manufacturing practices produce aqueous wastes that have heavy metal toxins. Since the bulk of heavy metals do not destroy into nontoxic end products, their concentrations must be decreased to appropriate amounts before release of industrial effluents [3]. Else, they could create warnings to public health and disturb the visual quality of potable water. Agreeing to the World Health Organization (WHO), the metals of highest immediate alarm are chromium, aluminum, iron, manganese, nickel, cobalt, zinc, copper, mercury, cadmium, and lead. The highly conventional methods for elimination of metals from industrial effluents involve solvent extraction, chemical precipitation, electrolytic extraction, dialysis, reverse osmosis, cementation, ion exchange, membrane filtration, adsorption and co-precipitation [4,5]. Traditional chemical and physical treatment of low concentration, large volume wastes be likely very costly [6]. Consumptive processes, such as chemical precipitation, entail large capital and operating costs. Awareness has therefore centered on non-consumptive techniques that involve ion-exchange and other sorption processes. The concept of using low-cost carbons and agricultural products and by-products for the removal of toxic metals from water has been examined by number of sources [7]. Findings to evaluate the capability of scrap rubber to adsorb dissolved metal ions from water noticed it to be a reasonably effective adsorbent [8].

Chromium removal in water treatment is a big challenge since the maximum limit concentration allowed in drinking water is only 0.1 ppm. Cr can be found in many oxidation forms; Cr (VI) being the most toxic and soluble, and Cr (III), the least toxic form of chromium [9]. Conventionally, heavy metals are removed by techniques that produce hazardous chemical wastes and require post-treatment [10]. Therefore, a wider interest has been shown in finding alternative methods to remove Cr species from water to ensure sustainable and consumable water supply. In this premise low carbon nanotube dosage will be used to remove Chromium from water. The elimination of chromium from wastewater can be valuable in the environmental research as the carbon nanotubes have comparatively low growth temperature, high yields, high purities that can be attained and low cost [11]. In another study by El-Shafey [12], he reported that Chromium sorption was highly dependent on the initial pH value with reduction taking place in solution with pH up to 7 showing sorption maxima in the pH range 1.8–2.8 for concentration range 100–500 mg/l with an increase in the equilibrium pH. Carbon dioxide evolved from the sorption media was determined.

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2. Methods for removal of Cr (VI)

A quantity of treatment techniques for the elimination of metal ions from water have been described, mostly ion exchange, reduction, electrochemical precipitation, electrodialysis, solvent extraction, evaporation, chemical precipitation, reverse osmosis and adsorption [13,14].The physical and chemical estates of Cr (VI) is displayed in Table 1.

Table 1. Physical and chemical properties of Cr (VI)

Elements	**Properties**
Physical State	liquid
Appearance	orange
Odour	none reported
pH	~7
Vapor Pressure	14 mm Hg @20C
Vapor Density	0.7
Evaporation Rate	>1 (ether=1)
Viscosity	Not available
Boiling Point	212 ° F
Freezing/Melting Point	32 ° F
Decomposition Temperature	Not available
Solubility	Soluble in water
Specific Gravity/Density	1.0
Molecular Formula	Solution
Molecular Weight	Not available.

(Source: M.A. Atieh, 2020)

The Cr (VI) intensity is essential to be eliminated as it offers side effect to the wellbeing and described to be carcinogenic [15]. Table 2 below indicates numerous possible health impacts of the Cr (VI) to human being.

Table 2. Impact of Cr (VI) to the wellbeing

Where it can affect	**Effect**
Ingestion	May affect kidney and cause harm. May affect serious gastrointestinal tract irritation with nausea, vomiting and possible burns
Eye	Produces eye irritation and likely burns
Skin	May affect skin sensitization, an allergic reaction, which becomes obvious upon re-exposure to this material. Contact may cause irritation and likely burns. Lengthy skin contact may produce injury especially if the skin is abraded
Chronic	Long-time contact or repeated skin contact may affect sensitization dermatitis and likely destruction and/or ulceration. May affect respiratory tract cancer. May affect liver and kidney damage. Chronic inhalation may affect nasal septum ulceration and perforation
Inhalation	May affect liver and kidney harm. May affect ulceration and perforation of the nasal septum if inhaled in excessive amounts. Affects respiratory tract irritation with likely burns

(Source: S.M. Nomanbhay, 2005)

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2.1 Formulation of the Chromium stock solution

The stock solution of 1000mg/L of Cr (VI) ions was prepared using 2.829g $K_2Cr_2O_7$ salt or solids. New dilutions were applied for each study of the Cr (VI) elimination which is 0.07mg/l. The pH of the solutions was modified using 0.1M HCl and 0.1M NaOH and buffer was employed for keeping the pH of the solutions matching to the pH needed [2].

2.2 The adsorption findings

The adsorption capability of carbon nanotubes was established by the matrix design by setting the Cr (VI) concentrations (0.1mg/L) of 50mL Cr solution in 100mL shake flasks, with several carbon nanotubes dosage (10mg, 5mg, 1mg and 0.1mg). The combination was stirred in a rotary shaker at different speed (200 rpm, 150 rpm, 100 rpm and 50 rpm) supported by filtration make use of the syringe filter. The filtrate comprising the remaining concentration of Cr (VI) was verified spectrophotometrically at 540 nm after complexation with 1,5 diphenylcarbazide [16]. For the purpose of rate of metal adsorption by carbon nanotubes, the supernatant was studied for remaining Cr (VI) after the contact period of 10, 20, 30, 40, 60, 120 and 1440 minutes. The impact of pH on Cr adsorption by carbon nanotubes was revealed at pH values of 2, 4 and 6. The impact of various dosages of carbon nanotubes were 0.1, 1mg at 0.1mg/L Cr (VI) carbon nanotubes was decided. All the variable quantity is shown in the table 3 below whereas figure 1 confirms the overall summary of the Cr (VI) elimination using carbon nanotubes.

Table 3. Experimental system layout

No.	Independent Variables	No. of Levels	Descriptions
1	Cr (VI) concentration (mg/l)	1	0.07
2	pH	3	6
			4
			2
3	CNT Dosage (mg)	4	1
			0.1
4	Contact Time (min)	7	20
			10
			30
			40
			60
			120
			1440
5	Agitation Speed (rpm)	4	200
			150
			100
			50

3. OUTCOMES AND ANALYSIS

3.1 Consequences of Variables on the Cr (VI) elimination

From the results obtained, showed that the chromium exhibits different types of pH dependent equilibria in aqueous solution, Cr (VI) is a highly toxic compound causing severe human health effects. For smaller pH (pH=2.0) values, $Cr_3O_{10}^{-}$ and $Cr_4O_{13}^{2-}$ varieties are created. The best possible original pH for the adsorption of hexavalent chromium on to carbon nanotubes was detected at pH=2. This implies the creation of more polymerized chromium oxide varieties with reduced pH.

Nearly 100% of Cr (VI) ions were adsorbed from a solution of 0.07 mg/l [Cr (VI)], at pH=2.0, while the adsorption was reduced by the altered of the pH from 2 to 4 and 6 (as in figure 1). The results showed that alcoholic groups are converted to carboxylic groups while reducing Cr (VI) to Cr (IV). The adsorption of metal ions varies on solution pH, which affects electrostatic attachment of ions to related metal groups.

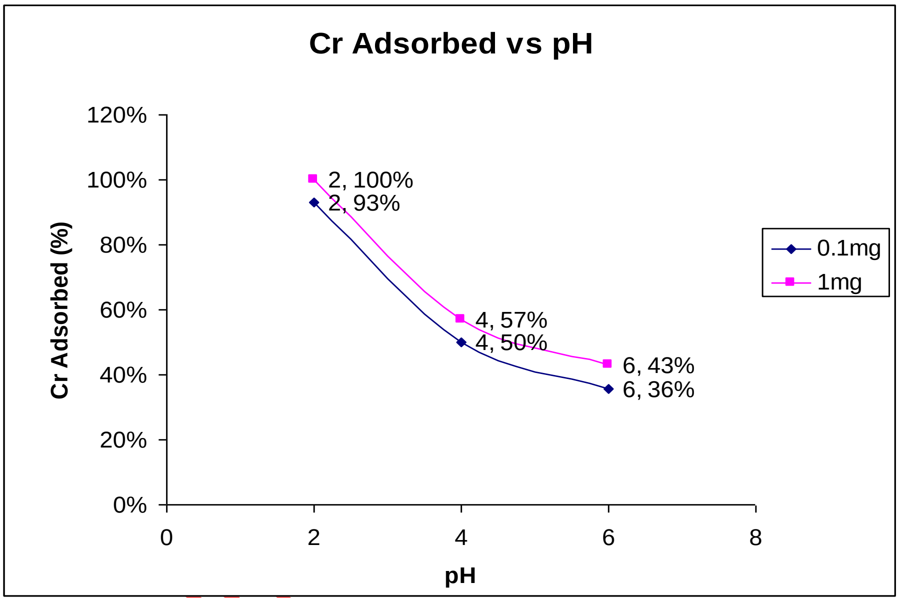

Figure 1. Impact of pH on the adsorption of Cr (VI) at 0.07mg/L Cr (VI) concentration

3.2 Impact of Carbon Nanotubes amount on chromium application

The intensity of mutually the metal ions and the carbon nanotubes is a substantial component to be studied for efficient adsorption. The amount of adsorption is a purpose of the original intensity of ions. The carbon nanotubes were different from 10mg, 5mg, 1mg and 0.1mg and created interaction with the Cr (VI) solutions of 0.07 mg/L intensities. The intensity of the carbon nanotubes in the 50mL solution is 2mg/L for 0.1mg and 20mg/L for 1mg CNT. For 1 mg CNT, the elimination of chromium is successful and accomplished 100% elimination with pH=2, agitation speed of 150 rpm and 120 minutes as displayed in figure 2.

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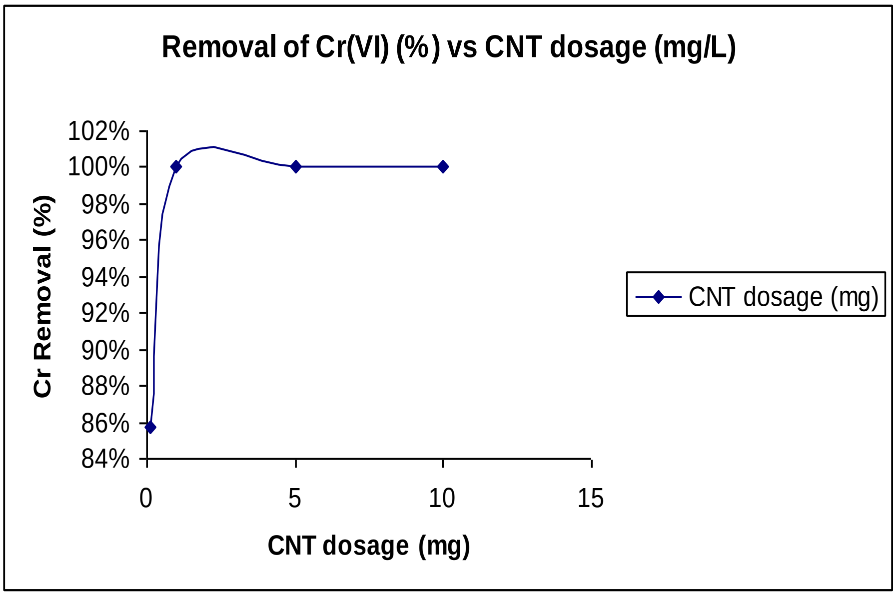

Figure 2. Impact of CNT amount on Cr (VI) adsorption from solutions at 0.07mg/L Cr (VI)

3.3 Impact of agitation speed

The result of the agitation of the adsorption system in Cr adsorption was observed at 200 rpm, 150 rpm, 100 rpm and 50 rpm of agitation. All agitation speeds were discovered to have positive impact to the adsorption process as shown in figure 3.

Agitation enables appropriate interaction among the metal ions in solution and the CNT binding sites and by this means supports efficient move of chromium ions to the carbon nanotubes sites. At 100 rpm and 50 rpm, the adsorption speeds observed were discovered to be marginally smaller than that at 200 rpm and 150 rpm. These findings reveal that the interaction between solids and liquid is more efficient at 200 rpm and 150 rpm but medium speed at 150 rpm is the safest. This remark as in Figure 3 concurs with the earlier told biosorptive elimination of Cr (VI) by the *husk of Bengal gram (Cicer arientinum)* [17].

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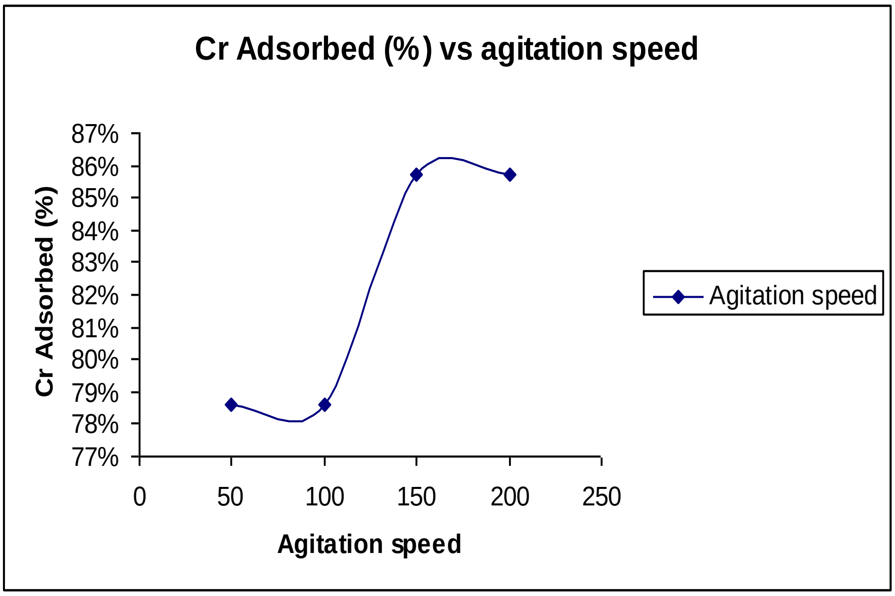

Figure 3. Impact of agitation speed on Cr (VI) adsorption, Cr (VI) concentration=0.1mg/L

3.4 Impact of contact time

A deviation of contact times was studied to explore its impact on the elimination of Cr (VI). Figure 4 indicates that the reduction ratio improved with rising contact time. At 120 minutes contact time, the elimination efficacy was almost 100 %. This might be clarified by the rise of contact time causing in continuing reduction of Cr (VI) till it achieved its stability. This outcome is coherent with the findings of Gupta *et al.* [18], and Junyapoon *et al.* [19] and Binqiao Ren *et al.* [20].

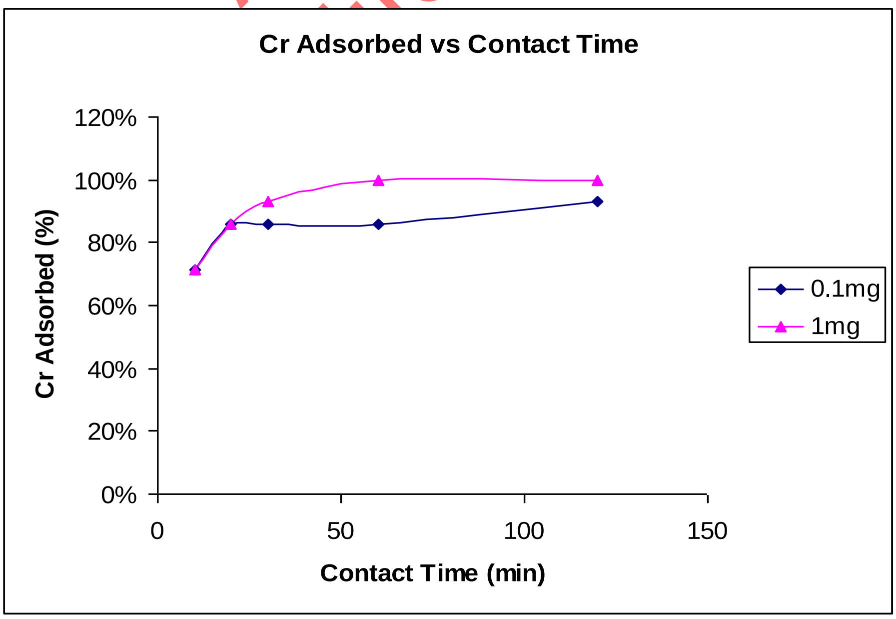

Figure 4. Impact of contact time on the adsorption of Cr (VI) with [Cr (VI)] = 0.07mg/L.

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3.5 Modelling of data using StatGraphic Centurion XV Software

The Pareto chart below (figure 5) indicates each of the expected consequences in declining order of significance. The amount of each bar is proportionate to the standardized result, which is the expected outcome divided by its standard error. This is comparable to computing a t-statistic for each impact. The perpendicular line can be manipulated to decide which impacts are statistically significant. Any bars which expand away from the line relate to impacts which are statistically significant at the 95.0% trust level. Therefore, 5 consequences are significant. The largest effect is the pH, supported by time, dosage, speed and correlation among speed and pH.

The R-Squared statistic suggests that the model as equipped supports 51.8007% of the flexibility in percentage elimination. The adjusted R-squared statistic, which is more appropriate for assessing models with diverse numbers of independent variables, is 49.6985%. The standard error of the assessment reveals the standard deviation of the residuals to be 22.8074. The mean absolute error (MAE) of 17.5874 is the average value of the remainders. The Durbin-Watson (DW) statistic tests the residuals to ascertain if there is any significant correlation established on the order in which they appear in the data file. Since the P-value is greater than 5.0%, there is no hint of serial autocorrelation in the residuals at the 5.0% significance level.

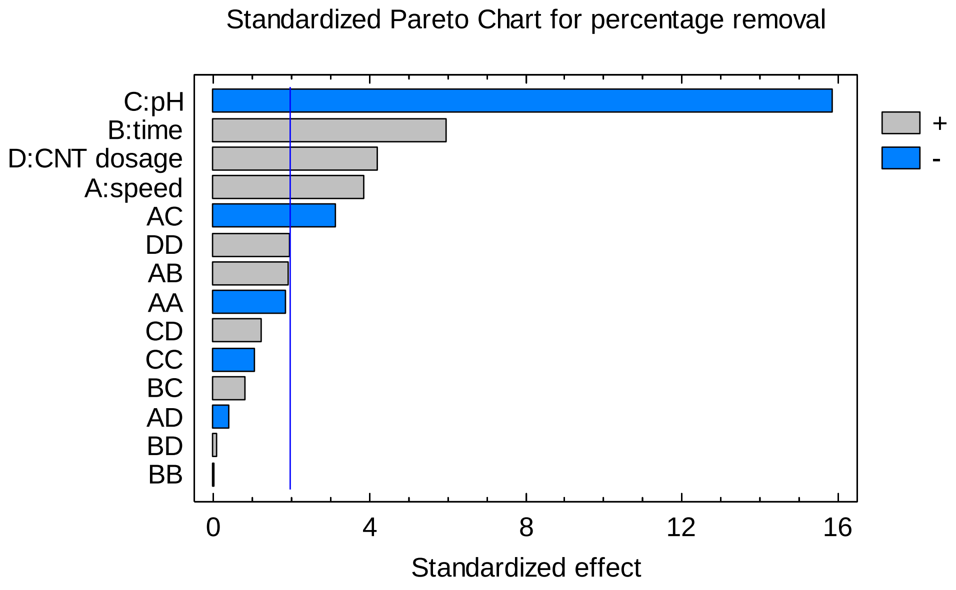

Figure 5. Pareto chart analysis

The edges in figure 6 signify the expected alter in percentage elimination of Cr (VI) as each factor is shifted from its low level to its high level, with all additional factors kept constant at a value halfway between their lows and their highs. Note that all the factors with significant main impacts have a better effect on the response which is the percentage elimination. From the Pareto chart above, the *adsorption equation model* can be created as shown below:

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$$CrAdsorbed(\%) = 85.80 - 12.06 * pH + 0.14 * Speed + 0.013 * Time$$
$$- 0.0135 * Speed * pH + 1.89 * CNTDosage$$

Note that the underlying model uses the form of a multiple linear regression model. Each maintained main impact is incorporated in the model by itself, while the two-factor interface is represented by a cross product of *speed* and *pH*. The equation was outlined as illustrated below in figure 6.

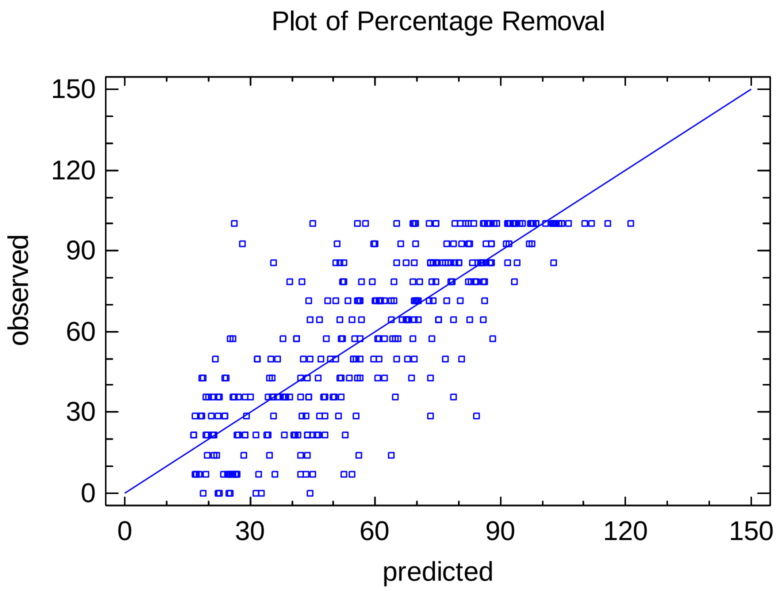

Figure 6. Multiple Linear Regression results.

R-squared = 64.1761 percent

R-squared (adjusted for d.f.) = 63.6333 percent

Standard Error of Est. = 18.7668

Mean absolute error = 14.2147

Durbin-Watson statistic = 0.950296 (P=0.0000)

4. CONCLUSIONS

The observations of the adsorption study on the capability of carbon nanotubes to eliminate Cr (VI) reveals its possibility of usage to separate heavy metals from low concentration water. With 99.99% carbon nanotubes concentration, incredible properties and structure, the elimination of Cr (VI) was good and could accomplished until 100% elimination. Hence, the application of the carbon nanotubes to eliminate Cr (VI) has been analysed in this experiment with four factors contributing which is the CNT dosage, the pH of the water, the agitation speed and the contact time for the Cr (VI) to be adsorbed with the carbon nanotubes.

The experimental design that has been applied is the pattern designs which or the multilevel factorial. This experiment deals with one level of Cr (VI) concentration, four levels

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of CNT dosage, three levels of pH, seven levels of contact time and four levels of agitation speed. There are 336 experimental runs that have been done with 2 replicates, the optimum conditions for Cr removal have been reached by 1 mg CNT dosage, pH=2, 120 minutes contact times, and moderate agitating rate at 150 rpm.

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