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POTENTIAL OF LOW CARBON NANOTUBES DOSAGE ON CHROMIUM REMOVAL FROM WATER

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ABSTRACT: This paper involves a method of eliminating hexavalent chromium (Cr (VI)) from the synthetic water via a 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 0.07 mg/L Cr(VI) concentration. These excessive elimination proficiencies were credited to the powerful adsorption of chromium ions to the physical properties of the CNT. A pattern layout was 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 were 4 independent variables influencing several points, namely 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 to the elimination of Cr(VI). The results show 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 expected optimization, using the adsorption equation, shows that a 1 mg CNT dosage with a pH=2, 120 minutes contact time, and moderate agitation rate at 150 rpm is the most optimal.

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

1 mg dos nano tiub karbon, larutan pada pH 2, masa sentuhan selama 120 minit dengan kelajuan goncangan sebanyak 150 rpm.

KEYWORDS: *STatGraphics; low CNT dosage; polluted water; chromium*

1. INTRODUCTION

Carbon nanotubes (CNTs) are new technology. They consist 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 4, and it has been found that

$$d_t = (\text{Ö}3/\text{p})\, a_{c\text{-}c}\, (m^2 + mn + n^2)^{1/2}, \tag{1}$$

where $a_{c\text{-}c}$ is the space among neighboring carbon atoms in the flat sheet. In turn, the chiral angle is given by

$$\tan^{-1}(\text{Ö}3n/(2m + n)) \tag{2}$$

The existence of heavy metals in the environment is of prime concern because of their harmfulness to many life forms. Various manufacturing practices produce aqueous wastes that contain heavy metal toxins. Since the bulk of heavy metals do not break down into nontoxic end products, their concentrations must be decreased to appropriate amounts before the release of industrial effluents [3]. Without extraction, the presence of these heavy metals could create threats to public health and disturb the visual quality of potable water. According 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. 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 can 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 found 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. Chromium can be found in many oxidation forms; Cr(VI) being the most toxic and soluble, and Cr(III) being 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 environmental research as the carbon nanotubes have comparatively low growth temperature, high yields, and 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 solutions with pH up to 7, showing sorption maxima in the pH range of 1.8–2.8 for the concentration range of 100–500 mg/L with an increase in the equilibrium pH. Carbon dioxide evolved from the sorption media was determined.

2. METHODS FOR REMOVAL OF Cr(VI)

A number of treatment techniques for the elimination of metal ions from water have been described here, with emphasis on ion exchange, reduction, electrochemical precipitation, electrodialysis, solvent extraction, evaporation, chemical precipitation, reverse osmosis and adsorption [13,14].The physical and chemical properties of Cr(VI) are displayed in Table 1. The Cr(VI) concentration must be eliminated as it comes with deleterious effects to human health and is described as carcinogenic [15]. Table 2 indicates numerous possible health impacts from human exposure to Cr(VI).

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

Parameter	Properties
Physical State	liquid
Appearance	orange
Odor	none reported
pH	~7
Vapor Pressure	14 mm Hg @20 ºC
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: Atieh, 2010)

Table 2: Impact of Cr(VI) to human health

Type of Exposure	Effect
Ingestion	May affect kidneys and cause harm. May cause 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 cause respiratory tract cancer. May cause liver and kidney damage. Chronic inhalation may cause nasal septum ulceration and perforation.
Inhalation	May cause liver and kidney damage. May cause ulceration and perforation of the nasal septum if inhaled in excessive amounts. Causes respiratory tract irritation with likely burns.

(Source: Nomanbhay, 2005)

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, CNT dosage is from 0.1 to 1 mg, contact time is shown in Table 2 as well as agitation speed. 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 (0.07 mg/L) of 50 mL Cr solution in 100 mL shake flasks, with several carbon nanotubes dosage (1 mg and 0.1 mg). The combination was stirred in a rotary shaker at different speeds (200 rpm, 150 rpm, 100 rpm and 50 rpm) supported by filtration making use of a 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, 1 mg at 0.07 mg/L Cr(VI) carbon nanotubes was selected. All the variable quantity is shown in Table 3 below whereas Fig. 1 confirms the overall summary of the Cr(VI) elimination using carbon nanotubes.

Table 3: Experimental system layout

No.	Independent Variables	No. of Levels	Description
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	10, 20, 30, 40, 60, 120, 1440
5	Agitation Speed (rpm)	4	50, 100, 150, 200

3. OUTCOMES AND ANALYSIS

3.1 Consequences of Variables on the Cr (VI) Elimination

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) values, $Cr_3O_{10}^-$ and $Cr_4O_{13}^{2-}$ varieties are created. The best possible original pH for the adsorption of hexavalent chromium onto 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, while the adsorption was reduced by the alteration of the pH from 2 to 4 and 6 (as in Fig. 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.

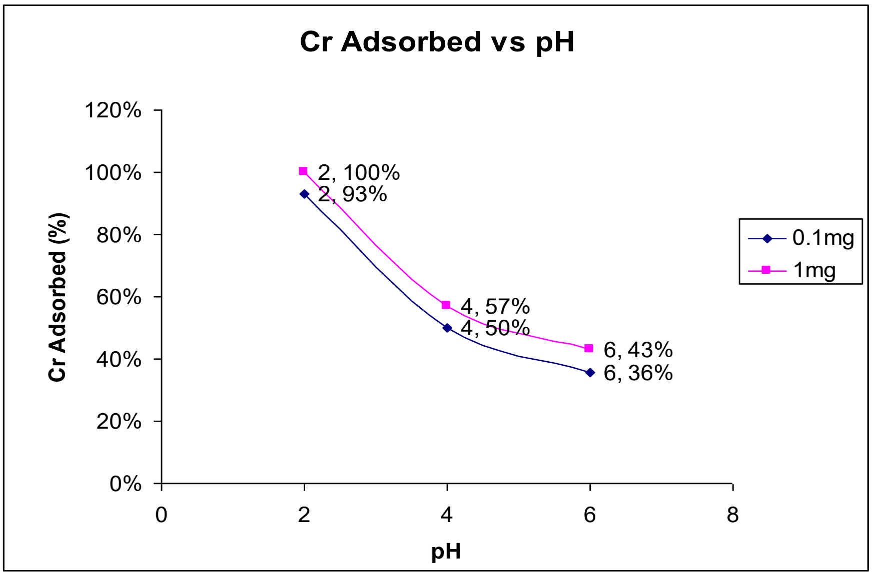

Fig. 1: Impact of pH on the adsorption of Cr(VI) at 0.07 mg/L Cr(VI) concentration.

3.2 Impact of Carbon Nanotubes Amount on Chromium Application

The concentration of both the metal ions and the carbon nanotubes is a substantial component to be studied for efficient adsorption. The amount of adsorption is a function of the original intensity of ions. The carbon nanotubes were different from 10 mg, 5 mg, 1 mg and 0.1 mg and caused interaction with the Cr(VI) solutions of 0.07 mg/L intensities. The concentration of the carbon nanotubes in the 50 mL solution is 2 mg/L for 0.1mg and 20 mg/L for 1 mg 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 Fig. 2.

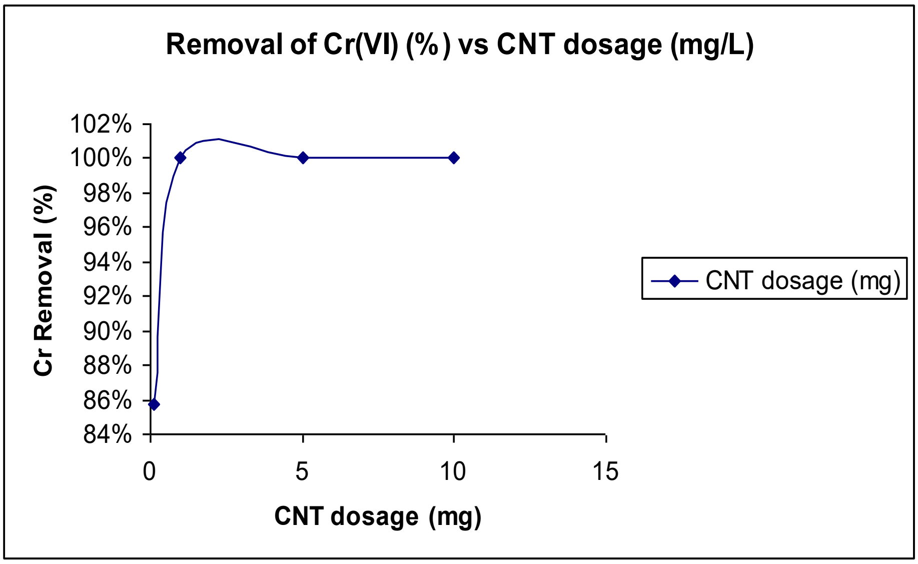

Fig. 2: Impact of CNT amount on Cr(VI) adsorption from solutions at 0.07 mg/L Cr(VI).

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 Fig. 3.

Agitation enables appropriate interaction among the metal ions in solution and the CNT binding sites and, by this means, supports efficient moving 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 of 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 a medium speed at 150 rpm is the safest. This remark, as in Fig. 3, concurs with the earlier described biosorptive elimination of Cr(VI) by the husk of Bengal gram *(Cicer arientinum)* [17].

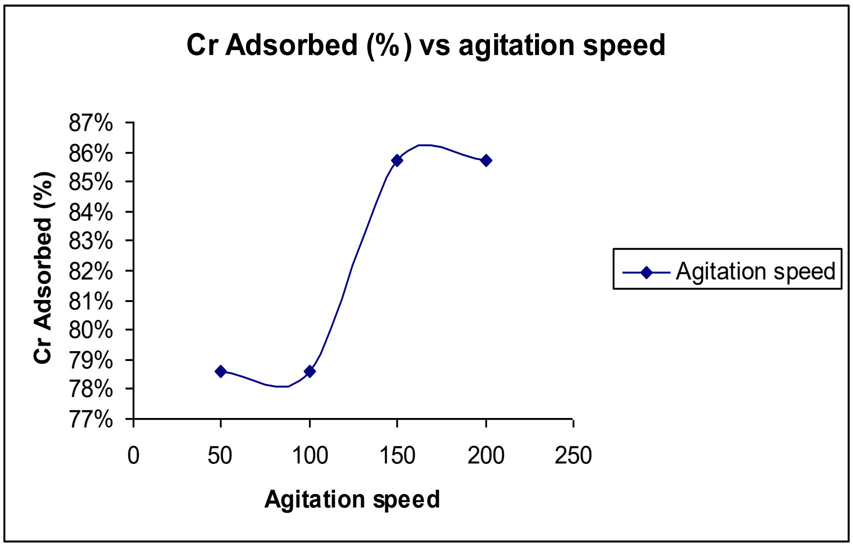

Fig. 3: Impact of agitation speed (rpm) on Cr(VI) adsorption, Cr(VI) concentration=0.1 mg/L.

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 of contact time, the elimination efficacy was almost 100%. This might be clarified by the rise of contact time causing a continuing reduction of Cr (VI) until it achieved its stability. This outcome is coherent with the findings of Gupta et al. [18], and Junyapoon. [19] and Binqiao Ren et al. [20].

3.5 Modelling of Data using StatGraphic Centurion XV Software

The Pareto chart below (Fig. 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.

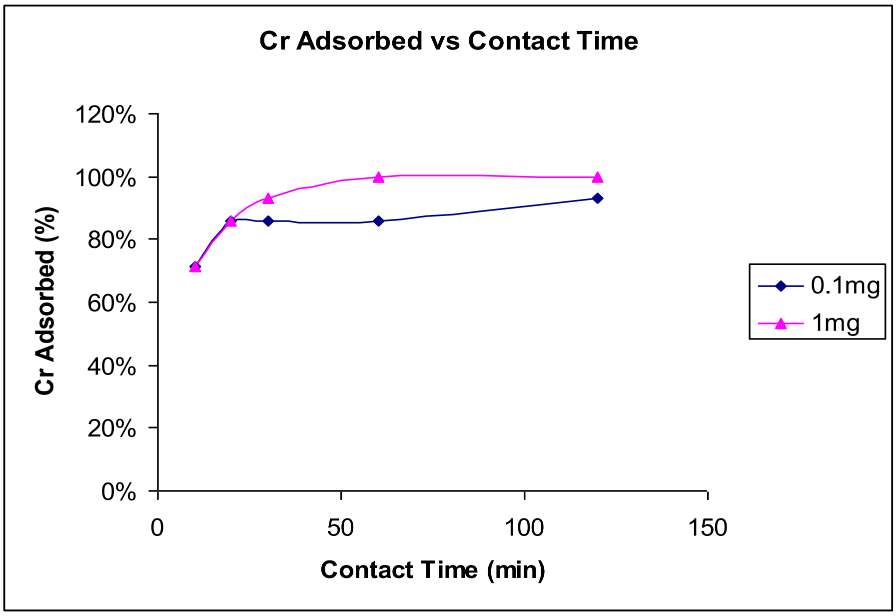

Fig. 4: Impact of contact time on the adsorption of Cr(VI) with [Cr(VI)] = 0.07 mg/L.

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.

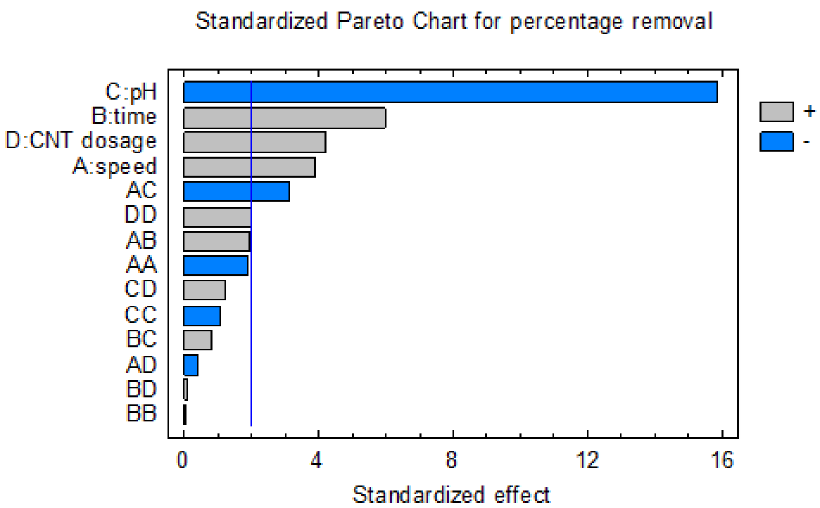

Fig. 5: Pareto chart analysis.

The edges in Fig. 6 signify the expected change 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:

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

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 in Fig. 6.

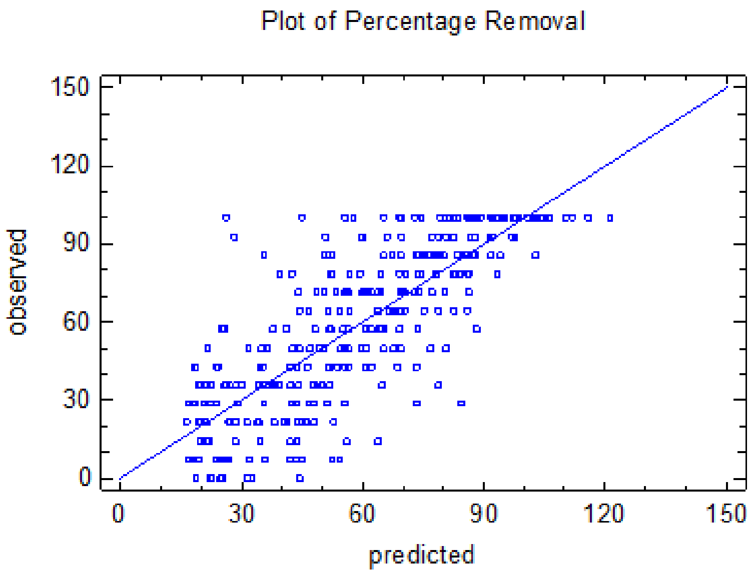

Fig. 6: Multiple linear regression results.

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. CONCLUSION

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 accomplish up to 100% elimination. Hence, the application of the carbon nanotubes to eliminate Cr(VI) has been analysed in this experiment with four factors contributing namely 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 design or the multilevel factorial. This experiment deals with one level of Cr(VI) concentration, four levels of CNT dosage, three levels of pH, seven levels of contact time and four levels of agitation speed. There were 336 experimental runs that were done with 2 replicates, the optimum conditions for Cr removal were reached by 1 mg CNT dosage, pH=2, 120 minutes of contact time, and a moderate agitation rate of 150 rpm.

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