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Removal Performance Assessment of Chromium (*VI*) in Solution using Grape Leaves Powder and Carbon as Adsorbent

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Abstract: *Batch removal of hexavalent chromium from aqueous solutions via grape leaf powder (GLP) and carbon (GLC) as adsorbent, was investigated in this paper. Some experiments were conducted in order to study the adsorption of metal species and effect of different pH values, contact time, metal concentration, adsorbent weight and temperature on Cr (VI) removal. Freundlich, Langmuir and Temkin isotherm models have been utilized to describe the adsorption behavior, so that the experimental results implied that they all followed Langmuir model perfectly (R^2 = 0.99). The results indicated that the absorption of chromium significantly depends on the pH values of the solution that is, the most proper pH value which may optimize the adsorbent, was found to be pH= 1.5. The optimal time for grape leaves powdered (GLP) was about 60 minutes while it was 90 minutes for carbon (GLC) at the same circumstances. The optimum concentration of grape leaves powder (GLP) was measured about 25 milligrams per liter; however it was 50 grams per liter for carbon (GLC). The adsorbent weight of grape leaves powdered (GLP) and carbon (GLC) were 0.3 g and 0.5g respectively. It should be mentioned that the temperature of carbon (GLC) was 40 C^0. Consequently, the results implied that Grape leaf powder (GLP) is stronger adsorbent in comparison with carbon (GLC) to remove hexavalent chromium from wastewater.*

Keywords: *natural absorbent grape leaves, hexavalent chromium, carbon, isotherm, contaminated wastewater.*

1. INTRODUCTION

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades [1]. Among the different heavy metals, hexavalent chromium Cr(*VI*) is a common and very toxic pollutant [2], which based to the maximum concentration limit for Cr(*VI*) for discharge into inland surface waters is 0.1 mg/l and in potable water is 0.05 mg/l [3; 4]. Cr(*VI*)can by variety of industries such as electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation discharged into the environment [5]. In the environment chromium occurs mainly in the oxidation states(*III*) and (*VI*) whereas Cr (*III*) is essential in human nutrition (especially in glucose metabolism) as well as for plants and animals at trace concentrations [6]. Acute exposure to Cr (*VI*) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhaging, and respiratory problems. Inhalation may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma) and may also increase cancer risk. Also skin contact with chromium may cause allergy, dermatitis, skin necrosis and skin corrosion [7; 8]. It is therefore essential to remove Cr (*VI*) from wastewater before disposal into the environment. In wastewater treatment, various methods applied to remove chromium include chemical precipitation, ion exchange, electrochemical precipitation, reduction, adsorption, Solvent extractions, membrane separation, concentration, evaporation, reverse osmosis and biosorption [9]. The conventional process used for removal of Cr (*VI*) from wastewater is reduction and its precipitation as chromium (*III*) hydroxide. But this procedure is not completely satisfactory and has several disadvantages like generation of a large amount of secondary waste products due to various reagents used in a series of treatments such as reduction of Cr (*VI*), neutralization of acid solution and precipitation. The various researches have shown that the adsorption process can be a substantial method for the removal of chromium species from aqueous solutions. For these purpose, a variety of natural and synthetic materials have been tested as chromium adsorbents [10]. The various adsorbents tested include activated carbon and char [11; 12] the modified clay [13], rice husk ash, activated alumina, coal fly ash [14] and modified corn stalk [15], etc. Therefore, there is a need for the development of low cost, easily available materials that could allow to remove and recover Cr (*VI*) economically [10]. The objectives in this work were to study ‘i’ the modification of properties of Carbon and powdered Grape leaves in order to increase the power of heavy metal removal from aqueous solutions and wastewater ‘ii’ study the removal efficiency of heavy metals by low cost sorbents comparing with commercial active carbon and resin.

2. MATERIALS AND METHODS

2.1. Preparation of Adsorbent

Grape leaves used in this study were obtained from South Khorasan province (Birjand city), dried grape leaves in oven at 70°C for 24 h. the dried leasves were pulverized and sieved using standard sieve. The product was stored in plastic bottles for biosorption and further use. In addition to providing carbon grape leaves, we burned the samples in the ovenat 450°C for1hour [16].

2.2. Preparation of Stock Solution

The stock solutions (1000 mg/L) were prepared in distilled water using $K_2Cr_2O_7$ salt (Merck). All working solutions were prepared by diluting the stock solution with distilled water. HCl and NaOH were used for changing of solution pH.

2.3. Batch Adsorption Experiments

Adsorption experiments were performed using standard batch method. In this method, 0.1 g of adsorbent was added to 100 ml of metal ion solution of varying concentrations placed in a set of 100 ml glass Erlenmeyer flasks with stoppers and the experiment conditions were optimized at different concentrations (25–200 mg/L), temperature (22– 50 °C), pH (1.5–9), and contact time (10–120 min). The effect of pH was examined with metal ion solution (50 mg/L) for 10 min in the pH range from 1.5 to9. The pH of the sample was adjusted by adding HNO_3 or NaOH solution. In each case, the mixture was agitated in a Shaker at a speed of 200 rpm for a given time at 22 °C. The suspensions were centrifuged at 200 rpm for 10 min and filtered. Three replicates per sample were done and the average results are taken for calculation.

2.4. Metal Analysis and Adsorbent Characterization

Final residual metal (Cr (*VI*)) concentration after adsorption was directly measured by atomic absorption (Buck scientific 21OVGP). All experiments were performed in duplicate. The quantity of metal adsorbed at equilibrium was calculated by the following expression: To estimate the percentage removal of Cr (*VI*) from aqueous solution the following equation (1) was used:

$$\%\ Adsorption = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}$$

Metal uptake (q_e) at equilibrium time was calculated by mass balance expression:

$$W(q_e - q_0) = v(C_0 - C_e) \tag{2}$$

When $q_o = 0$ Eq. (2) becomes equivalent to

$$q_e = \frac{(Co - Ce)v}{1000W} \tag{3}$$

Where *q*e (mg/g) is the amount of Cr (*VI*) adsorbed, *C*o is the initial metal concentration (mg/l), *C*f and *C*e are the final residual concentrations of chromium (mg/l) after adsorption at time ‘*t*’ and at equilibrium time, respectively, *v* is the volume of aqueous solution (ml) and w is the adsorbent weight (g).

3. RESULTS AND DISCUSSION

3.1. Effect of pH

pH Solution is one of the most important variables affecting the adsorption characteristics. Cr (*VI*) adsorption was studied as a function of pH over a pH range of 1.5–9 on grape leaf powder (GLP) and grape leaf carbon (GLC) at the initial concentrations of 50 mg/l as shown in Fig. 1. It is clear from Fig. 1 that there was a sharp decrease in the sorption capacity when pH was raised from 1.5 to 9 by both adsorbents. As seen in Fig. 1, the amount of Cr (*VI*) adsorbed onto GLC decreases from 89.5 (pH 1.5) to 43 mg/g (pH 9). Also, the mount of Cr (*VI*) adsorbed on to GLC decreases from 77.5 (pH 1.5) to 40.5 mg/g (pH 9). This could be explained that the Cr (*VI*) exists in different ionic forms such as H_2CrO_4, $HCrO_4^-$, $CrO_4^{2-}$and $Cr_2O_7^{2-}$in aqueous solutions and the stability of these forms in aqueous systems is mainly pH dependent. The active form of Cr (*VI*) adsorbed on the adsorbent is $OHCrO_4^-$. This form is stable at only lower pH range which leads to high adsorption of Cr (VI) [17]. But the proportion of this form in solution decreases when there is an increase in pH. Therefore, Cr (*VI*) adsorption at higher pH decreases [17]. The study results carried out by [9] showed that maximum adsorption of Cr (VI) on to rice husk carbon and saw dust carbon was observed at pH 2 and increase in pH lead to the decrease of chromium adsorption by both adsorbents. Also study undertaken by [18] on Adsorption of chromium by maple saw dust indicated that Increase in pH resulted in the increase of chromium adsorption. It can due to active ions on surface of adsorbent at different pH. Also, the significant difference between adsorption capacity of GLP and GLC is visible. The reason for difference the high adsorption of Cr (*VI*) between GLP and GLC may due to increase ratio of surface to volume after powdering of GLC that it shown by FTIR analyses. On the other hand, regarding to FTIR analyses it was found that by powdering GLC, action of functional groups in reaction between adsorbent and existing chromium compounds in solution increased. So the difference of efficiency in GLP and GLC is significant.

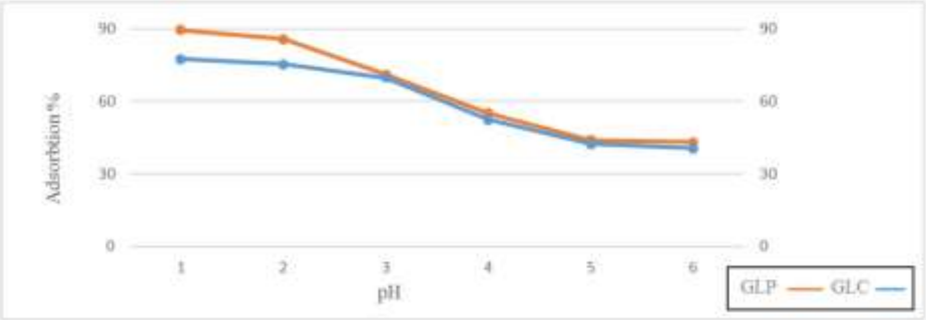

Fig1. *Effect of pH on Cr (VI) removal efficiency (RE%) using GLP and GLC*

3.2. Effect of Contact Time

Fig. 2 shows the effect of contact time on the removal efficiency. Contact the optimal time for powdered grape leaves 60 minutes, and 90 minutes for its carbon was obtained. it is clear that absorption was rapid and steep in the first minutes of physical adsorption is shown in Fig.2 the diagrams [19].

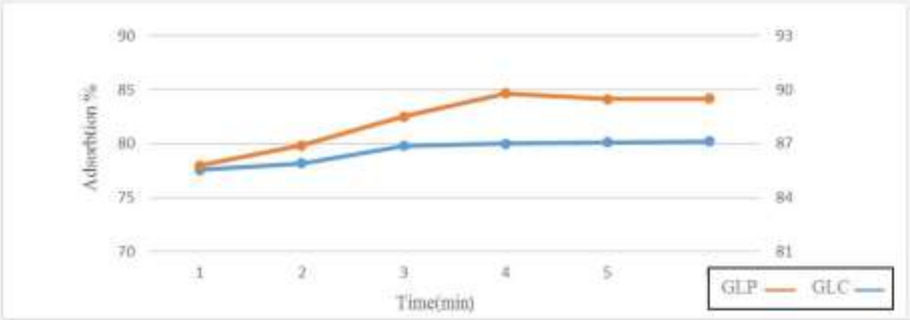

Fig2. *The effect of contact time on the adsorption of Cr (VI) using an absorbent GLP and GLC*

3.3. Effect of Adsorbent Weight

The effect of adsorbent dosage on the adsorption of Cr (*VI*) process is shown in Fig. 3. As can be seen, removal of Cr (VI) decreases with an increase in the adsorbent dosage for both GLP and GLC. The percentage removal by GLP decreases from 85.5% to 82% by increasing the adsorbent dosage from 0.3 to 2 g. this trend for GLC is also visible, as the percentage removal decreases from 91.6% to 91% by increasing the adsorbent dosage from 0.3 to 2 g. This can be explained due to the fact that higher the dose of adsorbent in the solution, greater the availability of exchangeable sites for metal ions and greater the surface area. Although the of GLP in comparison with increase the dose of GLC has more effect in the removal of Cr (*VI*) under the same codition. That is, by increasing the adsorbent dose, the volume of produced sludge increases as well which is important regarding the economical and environmental problems. Therefore by a small amount of GLC comparing to GLP, can achieve to excess amount of removal. [3] study results showed that the removal efficiency of Cr by Silver impregnated groundnut husk carbon and groundnut husk carbon increases by increasing the adsorbent dosage. Also [1] reported that the removal efficiency of Cr using walnut, hazelnut and almond shell increases when adsorbent dosage increased.

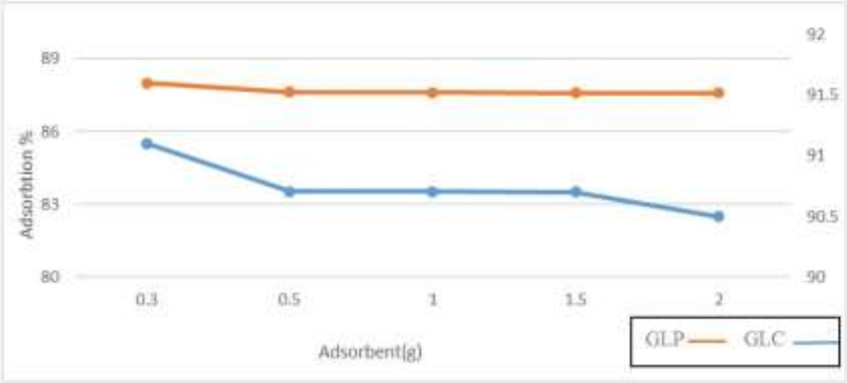

Fig3. *Effect of adsorbent weight on there moval of Cr (VI) using GLP and GLC*

3.4. Effect of Initial Metal Concentration

With regard to the fig. 4 View correlated with increasing the initial concentration of 25 to 200 milligrams per liter for both catchy removal efficiency decreases. The optimum concentration of 25 milligrams per liter for grape leaves powder and carbon were obtained from 50 grams per liter.The reason was that adsorbents have a limited number of active sites saturated at high concentrations occur [20]. In the study on removal Cr (*VI*) from aqueous solution using soil Saw used as an adsorbent to the conclusion that increasing Concentrations of Cr (*VI*) removal efficiency decreases [21]. By increasing the concentration of absorbent, the number of sites available to bind Cr (*VI*) absorption increases with increasing concentration of the Grape leaf powder absorption of Cr increases [22].

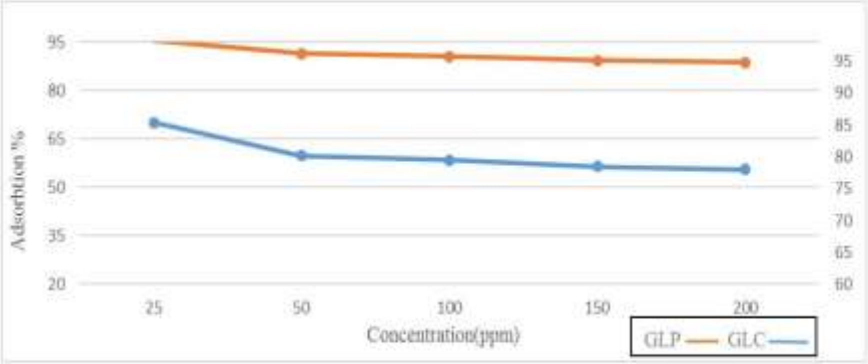

Fig4. *Effect of initial concentration of Cr (VI) using GLP and GLC*

3.5. Effect of Temperature

The adsorption of metal ions were carried out at six different temperatures 22, 25, 35, 40, 45 and 50 C^0. The experimental results showed that Fot the both GLP and GLC adsorbents capacity decreases with increase of temperature. Fig. 5 shows the effect of temperature on the removal efficiency. According to the fig. 5, it is shown that with increasing temperature from 22 ° C to 50 ° C, the removal efficiency increased for the both adsorbents. The optimum temperature of 25 ° C for absorbent powder, grape leaves, and the carbon from the 40 ° C, respectively. The increase in sorption capacity of the biosorbent is attributed to the enlargement of pore size and activation of the sorbent surface with rise in temperature. A further rise in temperature increases the mobility of the metal ions and reduces the swelling effect in biosorbent, thus, enabling the metal ions to penetrate further [23; 24].

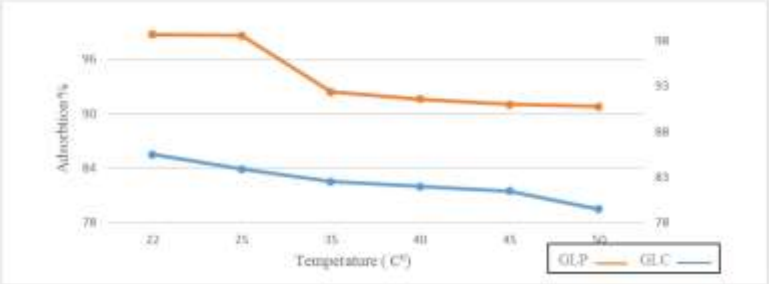

Fig5. *Effect of temperature on adsorption of Cr (VI)) using GLP and GLC*

3.6. Adsorption Isotherm Studies

Equilibrium studies were undertaken to understand the behavior of the adsorbent of Cr (*VI*) onto Grap leaf powder and carbon at equilibrium conditions. Three adsorption isotherm models, Langmuir, Freund-lich and Temkin were used to describe the equilibrium between adsorbed Cr on the adsorbent and Cr (*VI)* in solution at constant temperature. The Langmuir equation is valid for monolayer sorption onto a surface with a finite number of identical sites [25].The linear Langmuir equation may be written as:

$$q_e = \left(\frac{Q_0 b C_e}{1 + bC_e}\right) \tag{4}$$

$$\frac{Ce}{qe} = \left(\frac{1}{qob}\right) + \left(\frac{Ce}{qo}\right) \text{ (Linear form)} \tag{5}$$

By plotting $\frac{C_e}{q_e}$on the Y axis relative to the equilibrium concentration of C_e on the X axis, will yield astraight line with aslope of$\frac{1}{q_0}a$ and y-intercept $\frac{1}{q_e b}$, Dimension less parameters (R_l) are used to evaluate the Langmuir equation can be expressed as follows [19].

$$R_l = \frac{1}{1+bC0} \tag{6}$$

The initial concentrations C_0 and b is the Langmuir constant. If the path is drawn from the line, the mechanism of adsorption on Langmuir model is otherwise pursuing does not. As indicated in Fig. 6 and Fig.7, the linear trend (R^2 vs. 0.99), which follows the Langmuir model well. The higher the R^2-value closer to one indicates that the mechanism of adsorption of the model follows.

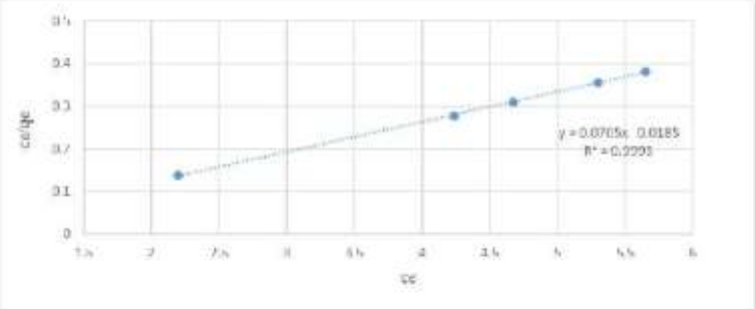

Fig6. *Langmuir isotherm for the adsorption of Cr (VI) using GLP*

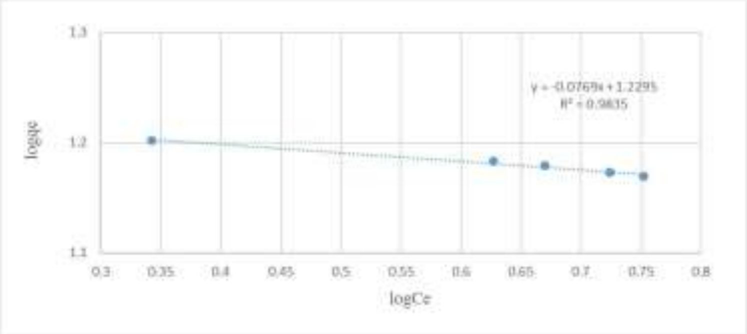

Fig7. *Langmuir isotherm for the adsorption of Cr (VI) using GLC*

Freundlich model on the basis of the assessment of the Adsorption sites on solid, heterogeneous (non-uniform) and they are absorbed differently. He is no limit to the absorption $q_e = KCe^{1/n}$ not discriminate, therefore our model by the relationship stated that it is logarithmic form as follows.

The empirical Freundlich equation is based on sorption onto a heterogeneous surface [26]. The linear form of the Freundlich equation is given as:

$$\mathrm{Log}\,q_e = \mathrm{Log}\,K_f + \left(\frac{1}{n}\right) Log Ce \qquad (7)$$

Straight line is obtained Log q(on the Y)than the values log Cf (on the X)The resulting straight line will The gradient 1/n and intercept log kf. n and Kf Freundlich constants are. Which respectively represent the adsorption capacity and adsorption intensity of the adsorbent are [27]. As indicated in Fig. 8 and Fig.9:

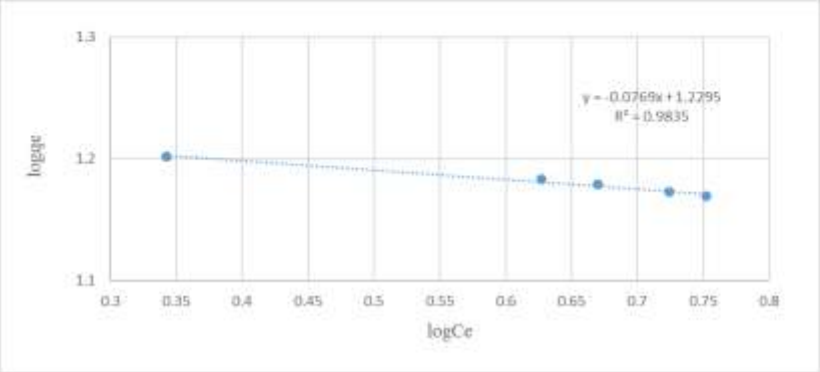

Fig8. *Fraundlich isotherm for the adsorption of Cr (VI) using GLP*

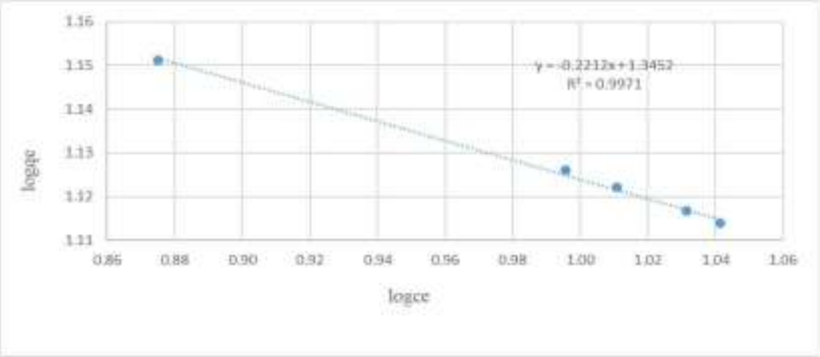

Fig9. *Fraundlich isotherm for the adsorption of Cr (VI) using GLC*

The Temkin isotherm model contains a factor that takes care of the adsorbent interactions. Temkin considered the effects of some indirect adsorbate interactions on adsorption isotherms [28]. The linear form of Temkin equation is given by Eq.(8).

$$q_e = \mathrm{B}\ln \mathrm{A} + \mathrm{B}\ln C_e \qquad (8)$$

Here A and B are Temkin isotherm constants, and B ln A indicates the maximum binding energy that illustrates the bond between adsorbent and adsorbed (kJ/mol).As indicated in Fig. 10 and Fig.11

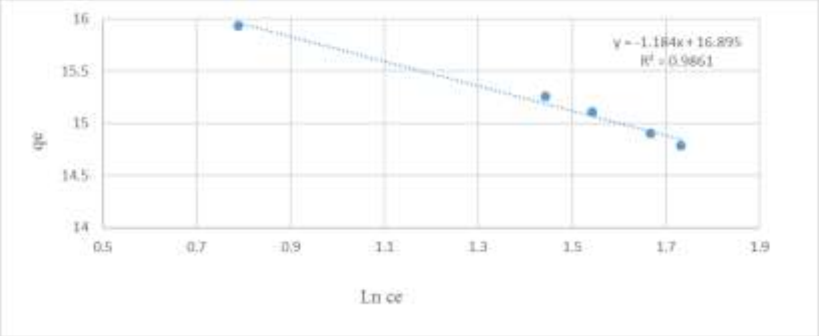

Fig10. *Temkin isotherm for the adsorption of Cr (VI) using GLP*

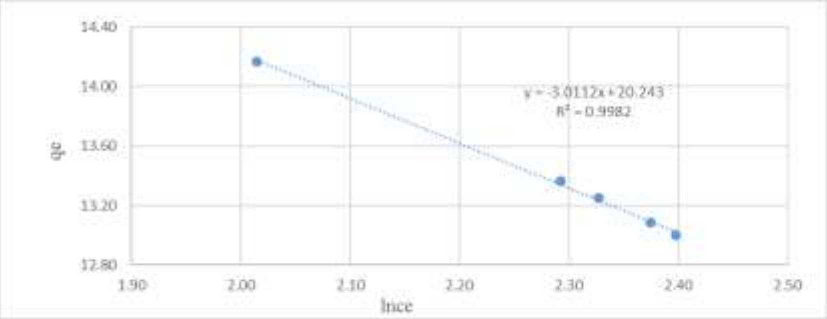

Fig11. *Temkin isotherm for the adsorption of Cr (VI) using GLC*

Isotherm is an important factor in the design of absorption systems. Isotherm as a major factor in determining the capacity of an adsorbent and is intended to optimize the use of absorbent. [25; 29]. Isotherms as a major factor in determining the absorbent capacity and is intended to optimize the use of adsorbents. Absorbent surface, as homogeneous as adsorbent surface Langmuir [25]. Describes the grape leaf powder. It is based on values obtained for the absorption coefficient is 0.98 percent chromium inferred.

4. CONCLUSION

This study investigate the appropriate capacity of untreated grape leaves powder and carbon as a natural adsorbent to remove Cr (*IV)* ions from aqueous solution with great emphasis on its potential for effluent treatment processes. Specifically, the following conclusions can be drawn from the results of this study. The removal of Cr (*IV)* from aqueous solution strongly depends on the pH value, adsorbent dosage, and initial Cr (*IV)* concentration. The maximum adsorption capacity for both of adsorbent was obtained at pH 1.5. Increasing in adsorbent dosage may rise up the Cr (*IV)* adsorption which is because of increasing in number of adsorption sites.

The Fraundlich, Langmuir and temkin models were used to adopt the data and to estimate the models parameters. Langmuir isotherm was in great compatibility with experimental data which has been obtained based on monolayer sorption over the surface of the adsorbent (R2 =0.999) isotherm. The optimal time for powdered grape leaves were found to be 60 minutes, and 90 minutes for carbon; optimum concentration of grape leaves powder was 25 milligrams per liter while carbon was 50 grams per liter. The adsorbent weight of powdered grape leaves and carbon goes up to 0.3 g, and 0.5g respectively, to which the temperature was preserved at 40 ° C. the wide surface area, even without activating substance, may be considered as an effective alternative to activate carbon for the removal of chromium and lead to conversion. These results confirm the idea that the GLP is a more effective adsorbent in comparison with the GLC regarding the removal of Cr (VI) from aqueous solution.

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