BUT

Adsorption of Chromium (IV) by a Low Cost Adsorbent Prepared from Neem Leaves

A.S. Kovo, S.C. Olu and E.S. Gwatana

Department of Chemical Engineering, Federal University of Technology, Minna

Abstract: The adsorption capacity of Neem Leaves powder (NLP) used as a low-cost adsorbent for the removal of Chromium (VI) from aqueous solutions was investigated. During the adsorption process, batch technique was used. The effects of initial metal ion concentration, adsorbent dose, temperature, pH and agitation/contact time on adsorption rate at constant solution pH of 6.4, under a constant temperature of 30°C were studied. The results were analyzed using three adsorption isotherm models; Freundlich, Langmuir and Temkin. Evaluating the correlation coefficients showed that Langmuir isotherm described the data more appropriately than the other isotherms. The adsorption capacity (q_m) from Langmuir isotherm for Chromium (VI) was found to be 125.83mg g^{-1}. The effectiveness of Neem Leave Powder (NLP) in the adsorption of the heavy metal (Chromium VI) from aqueous solution, kinetic studies showed that a pseudo second order model was more suitable than the pseudo first order model. It was concluded that Neem Leave Powder (NLP) can be used as an effective adsorbent for the removal of Chromium (VI) from aqueous solutions. The adsorption process was observed to be exothermic. The negative value of Gibb free energy indicates feasibility and spontaneity of the system while the negative values of the entropy and enthalpy indicate randomness and the exothermic nature of adsorption, respectively.

INTRODUCTION

In recent year's toxic metals level in fresh waters have increased gradually due to release of untreated industrial effluent and municipal wastewaters into nearby fresh waters [1]. Chromium being a heavy metal which is often found in high proportion in untreated municipal wastewater and industrial effluent discharged from different industries such as leather tanning, electroplating, metal coating industries and paint industries. Mining, metal finishing and leather tanning are the major industrial activities that lead to chromium pollution [2].

Adsorption through the use of solid adsorbents can effectively and efficiently remove pollutants from both aqueous and gaseous municipal and industrial waste discharge and therefore, it is considered environmentally significant. It has been reviewed by number of resaerchers [3-8] that Activated carbon is the most popular adsorbent and it has been right from time traditionally used for the adsorption of odor, taste and colors, which are known as trace pollutants [9]. Its high removal capacity and versatility have expanded its scope of application in the area of treatment of numerous industrial waste streams. With these other commercial adsorbents, with increased reversibility, have been recently reviewed although their versatility and high removal capacity is generally not greater than those of activated carbon, but they are advantageous for certain applications.

Such low cost adsorbents, [10, 11] have been found that in laboratory scale they are applied in the treatment of various pollutants from water and wastewater.

The aqueous form of chromium can be majorly found as Chromium (III) and Chromium (VI) [2]. At low concentration Chromium (III) can be regarded as a biological-element since it is an important constituent in metabolism of plants and animals [2]. On the other hand, Chromium (VI) is very toxic even at very low concentration and it can result in to genetic alternation in

---

Corresponding Author: A.S. Kovo, Department of Chemical Engineering, Federal University of Technology, Minna.
                            E-mail: kovoabdulsalami@yahoo.com.

plants and animals [2]. The adsorption of Chromium (VI) on so many locally prepared low cost adsorbents have been studied extensively as an alternative process for adsorbing Chromium (VI) from polluted fresh water [1], industrial effluent and municipal wastewater. Activated carbon being the most studied adsorbent and its high capacity for adsorbing Chromium (VI) is dependent upon the solution pH [12]. In the recent years the adsorption of Chromium (VI) on several low cost biological-adsorbents has been worked upon extensively. Some of the low cost biological-adsorbents studied include Eucalyptus, Agave lechugilla biomass; yohimbe and grape tree. The outcomes of the study have shown that these biological-adsorbents have a very high capacity of adsorbing Chromium (VI) from Chromium polluted water [1, 13].

The element Chromium occurs naturally in rocks, volcanic dust, gases, soil, plants and animals. Chromium (0) is the most common forms of chromium. Chromium (III) occurs freely in the environment and as an important nutrient that helps the use of protein, fat and sugar by the body. Chromium (VI) and chromium (0) are majorly fixed into the environment by industrial processes [14]. The element chromium (Cr (0)) is used for casting of steel [13]. Chromium (VI) and chromium (III) are used in chrome dyes and pigments, plating, wood preserving and leather tanning. Chromium (III) and Chromium (VI) is the form in which chromium enters the Air, water, soil [15]. Chromium compounds are present mostly in air in the form of fine dust particles, which gradually settle over land and water. Chromium is strongly attached to soil and only a small amount dissolves in water and penetrate deeper into soil particles and into underground waters. Skin ulcer is majorly caused by contact with some certain chromium (VI) compounds [16]. Some people sensitivity to chromium (VI) or chromium (III), results in an allergic reactions consisting of severe redness and swelling of the skin [17].

Adsorption is as a result of attraction forces between the individual atoms and ions of an adsorbate at the surface or interface or as a result of electromagnetic interactions [18]. The sum total dispersion, electrostatic and functional group interactions widely states the affinity of an adsorbent for a specific adsorbate is termed chemisorption. Series of parameters, affect adsorption [18]. For the adsorbate, molarity, molecular structure, molecular size, molecular weights, molecular polarity, configuration or steric form and competitive adsorption or the nature of background are important. Surface area, physicochemical nature of the surface, the availability of the surface to adsorptive molecules, the physical size [19],

form of the adsorbent particles are the valuable characteristics of the adsorbent that determine equilibrium capacity and rate, other parameters such as pH and temperature can also influence adsorption to a large extent [20], the accumulation of solute at the surface of a solid is essentially based on adsorbate, van der waal forces are responsible for adsorbent interaction involving permanent dipoles, induced dipoles and quadruples [21].

MATERIAL AND METHOD

Preparation of Adsorbent: Neem leaves, were harvested from a tall matured Neem tree at Federal university of Technology minna Gidan kwano campus, Minna Niger state, Nigeria. Repeatedly washed with ordinary water to remove soluble impurities, dust and poured into a perforated bowl for the water to drain and then allowed to dry under room temperature or a shade. For the leaves to become crisp, the leaves were placed in an air oven at 80–90°C for 4hours (not to decompose the active principle, high temperature range should not be used [22] and therefore, the drying of the leaves is done only at 30–40°C above the ambient temperature), which was then grinded or blended into a fine powder in a mechanical grinder or blender. The (NLP) Neem Leaf Powder, sieved fraction was, less than or equal to 75 im, were selected for use as the adsorbent. These selected fraction was again washed 8 times with ordinary water till the washings is free of color and turbidity and finally with distilled water. After which the (NLP) Neem leave powder was dried for 4 days at room temperature, the Neem Leaf Powder (NLP) was preserved in glass bottles for use as an adsorbent.

Raman Spectroscopy Studies: IR and Raman are the most common vibrational spectroscopies for assessing molecular motion and finge printing species. Based on *inelastic* scattering of a monochromatic excitation source routine energy range between: 200 - 4000 cm^{-1}.

Adsorption Studies: The batch mode operation was used to study the removal of Chromium (VI) from the prepared Cr (VI) solution. 1.2 g adsorbent was placed in a conical flask with 50ml solution of metal ions of desired concentration. The mixture was shaken in temperature controlled water bath shaker for 120 minutes at 240rpm. The mixture was then filtered using (Whatman filter paper No. 41) and final concentration of metal ion was determined in the filtrate by atomic absorption spectrophotometer (AAS). The amount of metal ions adsorbed was calculated by subtracting final concentration from initial concentration.

Effect of pH: The effect of pH on the Adsorption of Cr (VI) was studied by batch process as follows: 50ml of the prepared metal ion solution was taken in beaker. 6.4 was the natural pH of the aqueous solutions of potassium dichromate prepared the desired pH of solution was adjusted by adding dilute solution of 0.1M HNO$_3$ and 0.1M NaOH. 50ml of the metal ion solution was taken in a conical flask and was treated with 1.2 g of Adsorbent, the pH ranges between 2.4-12 the final concentration of metal ions in this solution was then determined using Atomic Adsorption spectrophotometer (AAS) respectively.

Effect of Contact Time/ Agitation: A series of six 250ml conical flasks, each having 1.2 g adsorbent and 50ml of the prepared metal ion solution was shaken in temperature controlled water bath shaker at 240 rpm and at the predetermined time intervals (20, 40, 60, 80, 100 and 120min) the solution of the specified flask was taken out and filtered. The concentration of metal ions in the filtrate was determined by AAS. The amount of metal adsorbed in each case was then determined as described earlier.

Effect of Adsorbent Dose: A series of six 250ml conical flasks each containing 50ml of the prepared metal ion solution (1000mgl^{-1}) were treated at the same temperature by varying the amount of sorbent (0.2–1.2 g). The flasks were shaken in temperature controlled water bath shaker at 240 rpm and after equilibrium (2 hours) the solutions were filtered. The amount of metal ions in filtrate was then determined by AAS.

Effect of Temperature: A series of six 250ml conical flasks each containing 50ml of the prepared metal ion solution (1000mg l^{-1}) was treated at different temperatures ranging between (30-55°C) by keeping the amount of sorbent constant at 1.2 g and the natural pH of 6.4. The flasks were shaken in temperature controlled water bath shaker at 240 rpm and after equilibrium (2 hours) the solutions were filtered. The amount of metal ions in filtrate was then determined by AAS.

Effect of Initial Concentration: A series of six 250ml conical flasks each containing 50ml of the prepared metal ion solution of different initial metal ion concentration of the range within (70.7, 141.5, 212.24, 282.99, 353.74 and 424.49 mg dm^{-3}) equivalent to K$_2$Cr$_2$O$_7$ concentration of (200, 400, 600, 800, 1000 and 1200 mg dm^{-3}). (50mg l^{-1}) were treated at the same temperatures and the same amount of adsorbent (1.2 g) and pH of 6.4. The flasks were shaken in temperature controlled water bath shaker at 240

rpm and after equilibrium (2 hours) the solutions were filtered. The amount of metal ions in filtrate was then determined by AAS.

Blank sample where ran und similar condition of concentration, temperature, pH without adsorbent in all cases to correct any adsorption on the internal surface of flask.

The percentage of Chromium removal (R%) was determined by the expression

$$R\% = \frac{(E_i - E_e)}{E_i} \times 100 \tag{1}$$

where E_i and E_e are the initial and final concentration of Chromium in the solution respectively, q_e the adsorption capacity of an adsorbent which is obtained from the mass balance on the sorbent in a system with solution volume V is often used to acquire the experiment adsorption capacity of all the adsorbent for each concentration of Chromium ions at equilibrium were calculated as thus

$$q_e(mg\ g^{-1}) = (\frac{E_i - E_e}{M}) \times V \tag{2}$$

where V is the volume of solution and (M) is the mass of adsorbent in grams used

RESULT AND DISCUSSION

Raman Spectroscopy Analysis: Raman spectroscopy measurements for Neem leaves powder are shown in Fig. 1. The broad and strong bands around 2000-3200cm^{-1} were due to vibration of –OH, C=C-H, etc. At the wavelength neem leaves powder at 1200-2000 cm^{-1} (Fig. 1), corresponding to the vibration of the cyano group. On the other hand, more new bands appeared at wavelength less than 1000cm^{-1}in the Neem leaves powder (Fig. 4.1), which were characteristic of the –C=N, –C=N and –N–OH groups, respectively.

Effect of Agitation/Contact Time: The study of the kinetic of Cr (VI) Adsorption on (NLP) was carried out as a batch experiment with initial concentration of Cr (VI) metal ions of 353.74 mg l^{-1} at 303 K with 50ml of six different Cr (VI) samples of the constant concentration when the agitation time was varied from 20 to 120 minutes at intervals of 20 minutes in each case. A gradual increase in the extent of adsorption with time was observed (Fig. 2). The percentage Cr (VI) adsorption increased from 99.5 to 99.75% in the time interval of 20 to 120 minutes for an
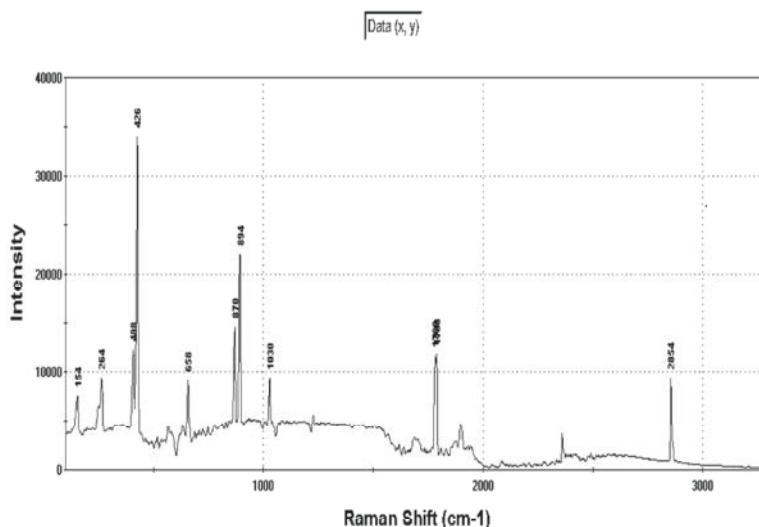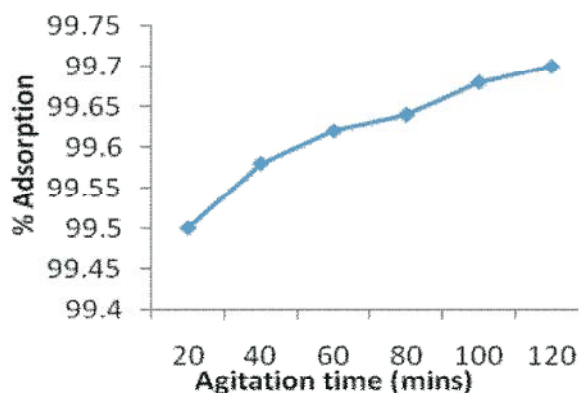
Fig. 1: Raman spectroscopy of Neem Leaves Powder

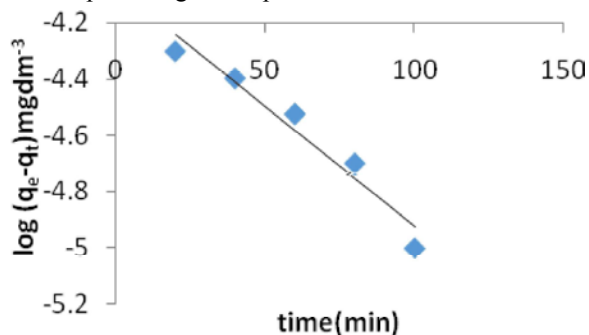Fig. 2: Effect of agitation time of adsorption on percentage adsorption

Fig. 3: Plot for pseudo first order kinetics

amount of 1.2 g NLP per dm^3. Such behavior is expected in a batch reactor with either constant adsorbent amount or varying initial adsorbate concentration or vice versa, based on the fact that the adsorbate have enough time to react with the adsorbent as the contact time increases [23].

Kinetic Study

First Order Kinetics: In this present work, the adsorption extent changed very slightly after 100 min and applying Lagergren pseudo first order kinetics, equilibrium conditions could be assumed at 100 min. The Lagergren's plots linearity range calculated to be, (Fig. 3, R value 0.95), this was obtained by plotting $\log(q_e-q_t)$ (mg dm^3) vs agitation time for the adsorption of Chromium (VI) from a prepared aqueous solution of concentration 353.74 mg dm^3 of the metal ions at 303K for the six different samples at different agitation time and of the adsorbent amount, indicated that the adsorption process maybe following the pseudo first order kinetics. The calculated rate constant, from the slopes of the best-fit lines, was gotten to be19.57$\times10^{-3}$ min^{-1} and q_e=8.424 $\times10^{-5}$ not similar with the experimental value.It has been reported with very similar values for Chromium (VI) removal by *Dakiky* [24], *on* diverse kinds of adsorbents (cactus leaves 6.80$\times$10-3 min^{-1}, wool 3.96$\times10^{-3}$ min^{-1}, sawdust 9.00$\times$10-3 min^{-1}, olive cake 8.99$\times$10-3 min^{-1}, almond 8.80$\times$10-3 min^{-1}) at pH 2 and 30°C.

Describing the adsorption process for a large number of cases, Lagergren equation has been adequate [3, 10], although for a concrete mechanism of the adsorption process this equation does not provide such pictures. Besides, the experimental *log q$_e$*value of the present work, does not match with the *log q$_e$* value obtained from the intercept of the plot.

Second Order Kinetics: To give a good account of the kinetics of Chromium (VI) adsorption on Neem leave powder, the first order kinetics is thus inadequate.
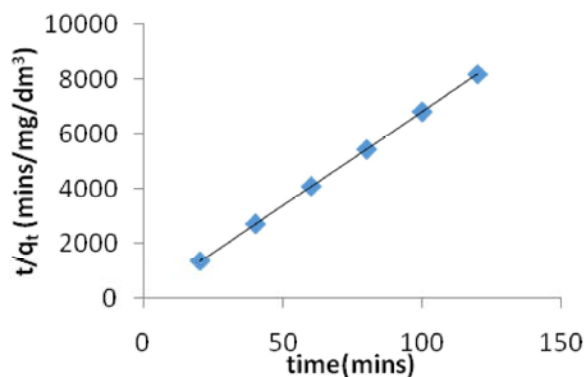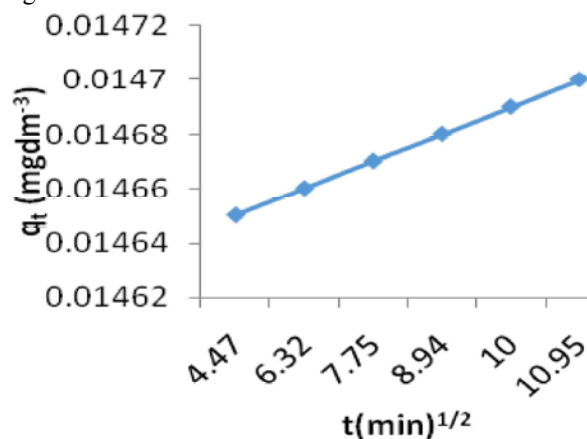
Fig. 4: Plot for the Pseudo-second order kinetics

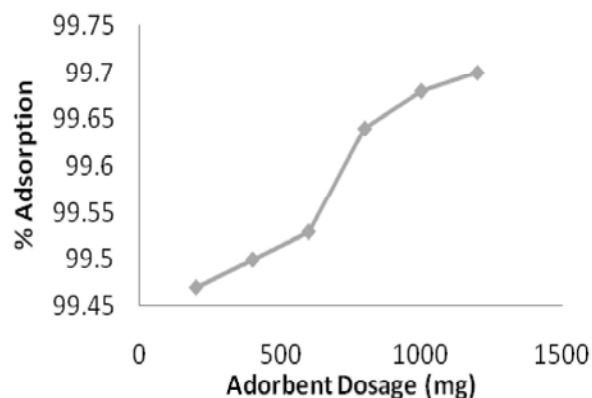

Fig. 5: Plot for intra-particle diffusion

Second order kinetics must be applied by plotting t/q_t vs t gave forth a better results (Fig. 4), with the second order rate constant k_2 gotten to be 984.09 mg^{-1}min^{-1} (R for the lines ≈ 0.99). There is also now good agreement between experimental q_e (0.0147) values and those obtained from the slopes of the second order plots as given in the figure below, (Fig. 4).

Intra-Particle Diffusion: Intra-particle diffusion mechanism of adsorption the approach towards equilibrium is governed by the equation $(D.t/r^2)^{0.5}$, in which D is the diffusivity within the particle and r is the radius of the particle. From the plot of q_t (amount adsorbed in *mg* per unit mass (*g*) of the adsorbent after a contact time of t minutes) vs $t^{0.5}$ (Fig. 5) k_p, value as the constant of adsorption is discovered to be 7.721×10^{-6} The intra-particle diffusion is thus a very slow process its significance cannot be over emphasized. After the metal ions are adsorbed initially on the surface of the Neem leaves powder particles, the metal ions are slowly been transported into the interior of the particles and the

kinetics of adsorption should be discussed in overall on the basis of both intra-particle diffusion and surface adsorption [25].
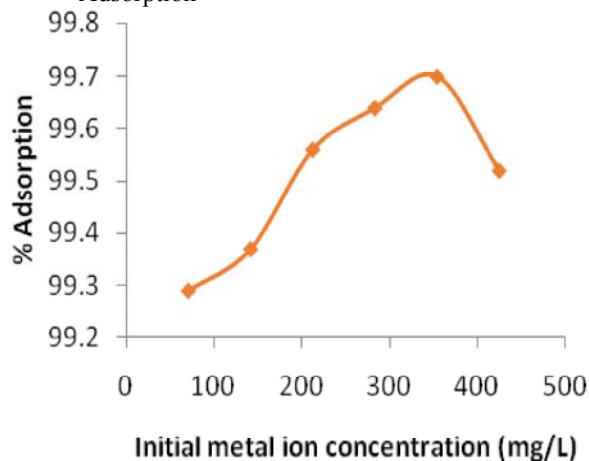
The intercept should have been zero by plotting t/q_t vs $t^{0.5}$ but the lines in the present work (Fig. 5) has the intercept of 0.0146. These proved that the mechanism for the adsorption process of Chromium (VI) on Neem leaves powder is not only governed by intra-particle diffusion. Adsorption process of chromium (VI) took place through initial diffusion followed by surface compound formation on a homogeneous mixture of wollastonites and fly ash [26]. A comparable condition cannot be ruled out in the present work as well. The metal ions diffuse from the aqueous solution to the exterior surface of the Neem Leaves Powder particles at a relatively high speed, then gradual diffuse into the interior surface and ultimately fix to the surface through chemisorptive bond formation.

Effect of Adsorbent Dosage: The amount of Neem Leaves Powder influenced the adsorption process of Chromium (VI). With Chromium (VI) concentration of 353.7 *mg dm*$^{-3}$, the% adsorption increased from 99.45 to 99.70% while increasing the Neem Leaves Powder amount between the range of 200 to 1200 *mg* per *dm*^{3} at a constant agitation time of 120 min at 303 K due to availability of more adsorption sites. On increasing the adsorbent dose from 200 to 1200 *mg dm*$^{-3}$ for constant Chromium (VI) metal ion concentration, the rate of adsorption process per unit mass indicated a decrease due to accessibility of fewer number of Chromium (VI) metal ions per adsorbent unit mass. Neem Leave Powder compared to some unconventional adsorbent has a larger adsorption capacity. Cactus leaves and pine needles at metal ion concentration of 0.1 *mg dm*$^{-3}$ at 303 K pH 2.0 adsorbents can respectively remove 19.8 and 42.9% [24]. Large number of OH-groups on the surface based cellulose plant material can bind easily to Chromium (VI) ions. Similar attribute can be apportioned to the large adsorption capacity of the NLP to easily access other groups for metal ion uptake and surface OH. The major chemicals contained in the Neem leaves, are namely, azadirachtin, meliantriol, nimbin, salannin and andnimbidin comprise of large number of Hydroxyl-groups that are probable to be the potential sorption sites for the metal ions. Fatty acids like linoleic acid, oleic acid, palmitic acid, steric acid, etc. are present in Neem Leaves [27]. FTIR measurements also indicated the existence of a large number of functional groups, OH, COOH, etc., in Neem leaves and these groups may give Neem leaves powder the excellent sorption properties it has [26].
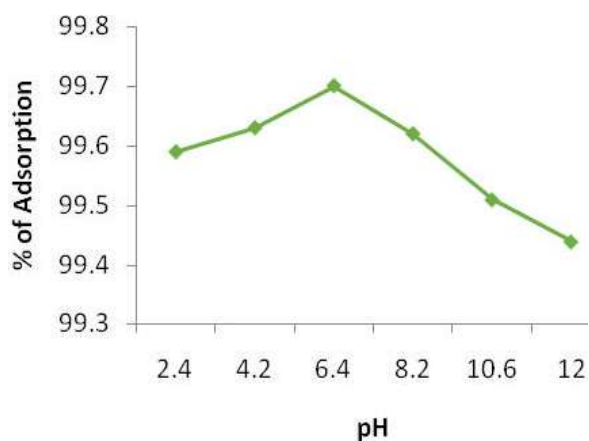
(V=50ml=0.05*l*, T=30°C, t=120mins, C$_o$=1000 *mg l^{-1}* = 353.74 *mg l^{-1}* of Cr metal Ions)

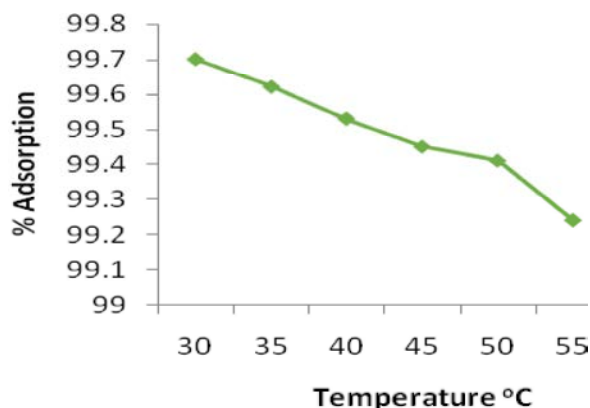Fig. 6: Effect of adsorbent dose on percentage Adsorption

(V=50ml=0.05L, T=30°C, t=120mins, M=1.2g)

Fig. 6: Effect of Initial concentration on percentage Adsorption

(V= 50 *ml* =0.05 *l*, T=30°C, t=120 min, M=1.2g, C$_o$=1000 *mg l^{-1}* =353.74 *mg l^{-1}* of Cr metal Ions)

Fig. 7: Effect of pH on Percentage of Adsorption

(V=*50ml* =0.05 *l*, t=120min, M=1.2g, C$_o$=1000 *mg l^{-1}*=353.74 *mg l^{-1}* of Cr metal Ions)

Fig. 8: Effect of Temperature on percentage adsorbed

Effect of Initial Concentration of Metal Ions: The effect of initial concentration of chromium is shown in (Figure 7). Results from these plots indicate that% removal decreases from 99.7 (353.7 *mg g^{-1}*) to 95.5% (424.5 *mg g^{-1}*) as the initial concentration of chromium is increased from 70.75 to 424.5 *mg l^{-1}* for 1.2 *g* of 75*ìm* size adsorbent at equilibrium agitation time of 120 minutes. However, the change in% removal increased for initial concentration between 70.72 to 353.74 *mg l^{-1}*. Maintenance a fixed number of binding sites in the dosage can be attributed as evidence to such a behavior while increasing the concentration. This kind of behavior are not usually found in literature but they are bound to happen only if the concentration of initial metal ion concentration needed exceeds the number of available sorption sites in the adsorbent [28]. The% removal of chromium is found to be maximums at (99.7%) for 1.2 *g* of 75 *μ*m adsorbent sizes, where the adsorption sites on the fixed adsorbent mass had been exhausted; while, the% adsorption starts decreasing to 99.5%.

Effect of pH: pH is an important factor controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of adsorbate.The effect of pH on adsorption of chromium is shown in Figure 4.8 the% removal of chromium increases from 99.59 to 99.70% for 1.2 g of 75*μ*m adsorbent with an increase in pH from 2.4 to 12 as similarly reported earlier [13]. It is conformed that adsorption increases with the decrease in acidity. At low pH, hydrogen ions compete with chromium ions for appropriate sites on the adsorbent. As pH approaches to 7, the competition of hydrogen ions becomes negligible and more chromium ions are bound to the adsorbent.

Table 1: Kinetic parameters

Pseudo-First order			Pseudo-second order			Intra-particle diffusion		
R^2	$q_e (mg\ dm^{-3})$	slope	R^2	$q_e (mg\ dm^{-3})$	$K_2 (mg^{-1} min^{-1})$	Kp	intercept	R^2
0.95	8.424×10^{-5}	19.57×10^{-3}	0.99	0.014705	984.09	7.72×10^{-6}	0.014613	0.99

Table 3.2: Coefficients calculated from Langmuir, Freundlinch and Temkin isotherm

Parameters	Langmuir isotherm			Feundlich isotherm				Temkin isotherm		
	R	$q_m (mg\ g^{-1})$	$b(dm^3m\ g^{-1})$	R_l	R	$K_f (dm^3\ g^{-1})$	n	A_T	b_T	R
Agitation time	0.99	104.6	0.00069	0.999	0.64	0.0148	-62.85	0	-0.0567	0.93
Adsorbent dose	0.99	128	0.0012	0.998	0.85	0.0123	0.405	1.048	89.9	0.97
Initial metal conc	0.98	126	0.0023	0.99	0.79	0.0111	0.469	2.38	12.0	0.98
pH	0.99	104.5	0.0021	0.997	0.94	0.0147	245.1	0	-0.0613	0.96
temperature	0.99	166.0	0.016	0.974	0.98	0.0147	202.02	0	-0.072	0.94

The values of k_f and n for the different parameters obtained from the intercept and slope of the plots of *log q_e vs log C_e* are also presented in Table 3.2. The values of k_f was calculated to be 14.8, 12.3, 11.1, 14.7, 14.7 mg/g for Agitation time, Adsorbent dose, Initial metal ion concentration, pH and Temperature respectively. k_f Is a measurement of adsorption capacity, all the values

The% removal decreases as pH increases beyond 7. The maximum removal of chromium was reported at a pH value of 6.4 for this present work. With chitosan as adsorbent [29], the maximum uptake capacity (50 $mg\ g^{-1}$) was noted at a pH of 5. The fungi biomass removed 64 $mg\ g^{-1}$ at a pH of 4.8 [30]. The maximum removal of chromium was reported at a pH of 4 with cationic starch maleate [31].

Effect of Temperature: The effect of temperature on the adsorption of Cr (VI) on Neem leaves powder is depicted in Fig. 8 The percentage of adsorption at temperatures range from 30 to 55°C and pH = 6.4 plotted in this figure indicated that the Cr (VI) adsorption capacity of the Neem leaves powder diminished while increasing the temperature from 30 to 55°C. At an initial metal ion concentration of 353.74 $mg\ dm^{-3}$, the percentage adsorption of Cr (VI) adsorbed on the Neem Leaves Powder diminished steadily when the temperature was raised from 30 to 35°C and 35 to 40°C, respectively. Roberto *et al*. [1] reported that the adsorption capacity of the organobentonite decreased while increasing the temperature because the adsorption is exothermic. The heat of adsorption for the adsorption of Chromium (VI) on a bentonite modified with HDTMA was estimated to be ΔH_{ad} = -35.5 $kJ\ mol^{-1}$ this is similar to the report in this present work.

Isotherm Study
Langmuir and Freundlich Isotherm: Chromium (VI) adsorption on Neem Leave Powder isotherm was studied using both Langmuir Isotherm and Freundlich Isotherm. The adsorption coefficients and the correlation coefficients are given in Table 3.2. The Langmuir plots have good linearity (R: 0.99 to 1.00). The Langmuir

monolayer adsorption capacity (q_m) was calculated to be 104.6, 128, 126, 104.5 and 166 $mg\ g^{-1}$ for agitation time, adsorbent dose, initial metal ion concentration, pH and temperature respectively, for the Neem Leaves Powder amount varying from 0.2 to 1.2 g dm^{-3} for adsorbent dose and for the remaining parameter the adsorbent dose was kept constant at 1.2 $g\ dm^{-3}$. The adsorption equilibrium parameter, b, was also calculated respectively for the individual parameter studied to be 0.00069, 0.0012, 0.0023, 0.0021 and 0.016 $dm^{-3}\ g^{-1}$. The dimensionless parameter, R_L, remained between 0.974 and 0.999 ($0 < R_L < 1$) compiling with the requirement for a favorable adsorption process of n are between -62.85, 0.405, 0.469, -245.1 and -202.02. The values of n in the range of 2–10 represent good adsorption. From the results obtained, it is clear that the adsorption study is not too good [32]. The comparison of the experimental value with the calculated value from the equilibrium isotherm for chromium (VI) adsorption using Neem leaves powder as adsorbent. It is obvious that the adsorption capacities calculated from Langmuir isotherm are much closer to the experimental values of q_e than that of Freundlich isotherm. From Table 3.2, it also appears that Langmuir isotherm fitted the experimental results over the experimental parameters with a higher coefficient of correlation than that of Freundlich isotherm. These results indicated that the adsorption of Chromium (IV) onto Neem leaves powder as adsorbent follows Langmuir Isotherm better than Freundlich.

Temkin Isotherm: Temkin adsorption potential, A_T, of Neem Leaves Powder for Chromium (VI) adsorption are 0, 1.048, 2.38, 0 and 0 for Agitation time, Adsorbent dose, Initial metal ion concentration, pH and Temperature respectively, indicating a lower Neem Leaves Powder-

metal ion potential for Chromium (VI) probably due to its small ionic radius. The Temkin constant, b_T, related to heat of Adsorption for the Chromium (VI) metal ions were -0.0567, 89.9, 12, -0.0613 and -0.072 $kJ\,mol^{-1}$ for agitation time, Adsorbent dose, Initial metal ion concentration, pH and Temperature respectively. It has been reported [10], that the typical range of bonding energy for ion-exchange mechanism is 8-16 kJ/mol. The values in this study indicates a weak interaction between adsorbate and sorbent, supporting an ion-exchange mechanism for the present study. Dada *et al.,* [33] reported some estimated values as follows $A_T = 1.075\,l\,g^{-1}$, B=25.34 $J\,mol^{-1}$ which is an indication of the heat of sorption indicating a physical adsorption process and the R^2=0.62. Comparing this with the present work Agitation time, pH and Temperature with R^2 0.93, 0.98 and 0.98 are chemosorbed. While Adsorbent dose and Initial metal ion concentration with R^2= 0.64 and 0.98 are physical adsorption process.

Thermodynamic Studies: The thermodynamic parameters such as enthalpy change $\Delta H°$, change in entropy $\Delta S°$ and Gibb free energy $\Delta G°$ are helpful in determining the spontaneity, feasibility as well as the endothermic or exothermic nature of the adsorption process [34]. The thermodynamic parameters can also be correlated to the distribution coefficient by equations (3 and 4) as shown below:

$$\log\frac{q_e}{C_e} = \frac{\Delta S°}{2.303R} - (\frac{\Delta H°}{2.303R})\frac{1}{T} \tag{3}$$

$$\Delta G° = -RT\ln K_c \tag{4}$$

where $\Delta S°$ and $\Delta H°$ are the standard entropy and enthalpy for the adsorption process, q_e denotes the rate of adsorption ($mg\,g^{-1}$), $K_c = \dfrac{C_{ad}}{C_e}$, C_{ad} is the quantity of Chromium adsorbed and C_e denotes the quantity of chromium in the solution at equilibrium [35].

Fig. 9 is the plot of *log (q_e/C_e)* against *1/T* for 1000 ($mg\,l^{-1}$) initial concentration of Chromium (VI). The intercept and slope are used to evaluate the entropy change ΔS and enthalpy change ΔH, respectively. The values for entropy and enthalpy change is -4.715 and -118.766 ($kJ\,mol^{-1}$) for NLP sample. The values of change in enthalpy calculated from the plot suggest that the adsorption is exothermic in nature. The negative values of change in entropy also suggest decreasing randomness at the liquid-solid interphase. The change in Gibb's free
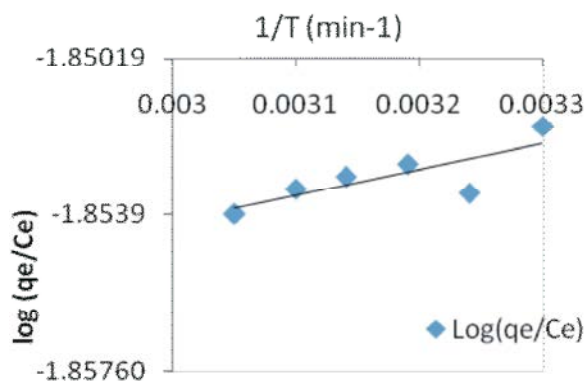

Fig. 9: Relationship between *1/T* and *log (q_e/C_e)*

energy values obtained via the above equation (4.2) are -615.96, -1217.44, -1659.57, -1846.74 and -2569.38 ($kJ\,mol^{-1}$). The negative values denoted a spontaneous and a feasible process.

CONCLUSION

The results of the study reveal that Neem Leaves Powder can be converted into an adsorbent with good adsorption capacity instead of its medicinal use it has been known for in time passed. The Neem Leaves Powder was used to study the removal of Chromium (VI) from aqueous solution and the adsorption percentage increased with an increase in Agitation time, Adsorbent Dose, increases with increase in Initial metal ion concentration to the maximum level and start decreasing after attaining it maximum adsorption capacity, adsorption is favorable at pH of 5-6.4, but decreased with the increase in temperature.

The studies of adsorption isotherms suggested that Langmuir isotherm generated the better agreement with the experimental data of Chromium (VI) adsorbed by Neem Leaves Powder than Freundlich isotherm. The values of the maximum adsorption capacity q_m calculated from Langmuir model were also closer to the experimental values of q_e than that of Frenudlich model, when studying the parameters. Some of the maximum adsorption capacity like Adsorbent Dose with Initial concentration of metal ion indicated the adsorption process of Chromium (VI) onto the Neem Leaves Powder was exothermic. And from Temkin isotherm coefficient of correlation there is a poor Neem Leaves Powder-metal ion interaction and adsorption process for Agitation time, pH and Temperature are chemosorbed while that for Initial metal ion concentration and adsorbent dose are physical adsorption process.

A pseudo-second-order model was more suitable than a pseudo first-order model with correlation coefficients greater than 0.999, which confirmed the exothermic nature of the adsorption process.

The intra-particle diffusion is a slow process and that the adsorption process is governed by slow transport into the interior of the particles, so the overall kinetics is based on both intra-particle diffusion and surface adsorption.

The adsorption process was observed to be exothermic. The negative value of Gibb free energy indicates feasibility and spontaneity of the system while the negative value of the entropy and enthalpy indicate randomness and the exothermic nature of adsorption. This also indicates that an increase in temperature decreases the overall sorption rate as well as amount of chromium (IV) ion adsorbed from aqueous solution by NLP.

REFERENCE

1. Roberto Leyva-Ramos, Araceli Jacobo-Azuara, Oliva L. Torres-Rivera, Rosa M. Guerrero-Coronado, Maria S. Berber-Mendoza and Pedro Alonso-Davila, 2008. Adsorption of chromium (vi) from water solution onto Organobentonite J. Environmental Engineering Management, 18(5): 311-317.

2. Bradl, H.B., C. Kim, U. Kramar and D. Stüben, 2005. Interactions of Heavy metals. In H.B. Bradl Ed., Heavy Metals in the Environment: Origin, Interaction and Remediation. Elsevier Ltd., London, UK, pp: 104-107.

3. Ho, Y.S. and G. Mckay, 1998. A comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents, Transactions Industria Chemical Engineering, 76B: 332-340.

4. Hamideh Radnia, Ali Asghar Ghoreyshi and Habibollah Younesi, 2011. Isotherm and Kinetics of Fe(II) Adsorption onto Chitosan in a Batch Process, Iranica Journal of Energy and Environment 2(3): 250-257, DOI: 10.5829/idosi.ijee.2011.02.03.1837

5. Bharathi Kandaswamy Suyamboo and Ramesh Srikrishna Perumal, 2012. Equilibrium, Thermodynamic and Kinetic Studies on Adsorption of a Basic Dye by Citrullus Lanatus Rind, Iranica Journal of Energy and Environment, 3(1): 23-34, DOI: 10.5829/idosi.ijee.2012.03.01.0130

6. Sanaz. Monemtabary, Mojtaba Shariati Niasar, Mohsen Jahanshahi and Ali Asghar Ghoreyshi, 2013. Equilibrium and Thermodynamic Studies of Methane Adsorption on Multi-Walled Carbon Nanotube, Iranica Journal of Energy and Environment, 4(1) Special Issue on Nanotechnology: 17-23, DOI: 10.5829/idosi.ijee.2013.04.01.03

7. Mahalakshmi, K., S.K. Suja, K.Yazhini, S. Mathiya and G. Jayanthi Kalaivani, 2014. A Novel Approach to Investigate Adsorption of Crystal Violet from Aqueous Solutions Using Peels of Annona Squamosa, Iranica Journal of Energy & Environment, 5(2): 113-123, DOI: 10.5829/idosi.ijee.2014.05.02.02

8. Seyed Mahmoud Mehdinia, Khalilollah Moeinian and Tayyabeh Rastgoo, 2014. Rice Husk Silica Adsorbent for Removal of Hexavalent Chromium Pollution from Aquatic Solutions, Iranica Journal of Energy & Environment, 5(2): 218-223, DOI: 10.5829/idosi.ijee.2014.05.02.15

9. Thomas, W. John, 1998. Crittenden, Barry, in Adsorption Technology and Design, Butterworth, Heinemann, Oxford.

10. Ho, Y.S. and G. Mckay, 1999. A comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents, Trans. IChemE., 76B: 332-340.

11. Bailey, S.E., T.J. Olin, R.M. Bricka and D.D. Adrian, 1999. A Review of Potentially Low Cost Sorbents for Heavy Metals, Walter Res., 33: 2469-2479.

12. Sh.Shahmohammadi-Kalalagh, H. Babazadeh, A.H. Nazemi and M. Manshouri, 2011. Isotherm and Kinetic Studies on Adsorption of Pb, Zn and Cu by Kaolinite. Caspian Journal of Environmental Sciences, 9(2): 243-255.

13. Sharma, A. and K.G. Bhattacharyya, 2004. Adsorption of Chromium (VI) on Azadirachta Indica (Neem) Leaf Powder, Adsorption, 10: 327-338.

14. ATSDR, 2013. Chromium Fact Sheet, Agency for Toxic Substances and Disease Registry (ATSDR), USA http://www.atsdr.cdc.go.

15. Monika Jain, V.K. Garg, K. Kadirvelu, 2009. Chromium (VI) removal from aqueous system using Helianthus annuus (sunflower) stem waste. Journal of Hazardous Materials, 162(1): 365-372.

16. Vinodhini V. and Nilanjana Das, 2009. Mechanism of Cr (VI) Biosorption by Neem Sawdust, American-Eurasian Journal of Scientific Research, 4(4): 324-329. ISSN 1818-6785.

17. US Department of Health and Human services, 2011. Toxicological profile for Chromium, Public Health services Agency for Toxic Substances and diseases Registry. Washington, DC.

18. Shuguang Deng, 2006. Sorbent Technology. Chemical Engineering Department, New Mexico State University, Las Cruces, New Mexico, U.S.A.

19. Gregg, S.J. and K.S.W. Sing, 1982. Adsorption, surface area and porosity, Academic Press, London.

20. Rifaqat Ali Khan Rao, Moonis Ali Khan, 2009. Biosorption of bivalent metal ions from aqueous solution by an agricultural waste: Kinetics, thermodynamics and environmental effects. Colloids and Surfaces A: Physicochem. Eng. Aspects, 332: 121-128.

21. Yu Jiang, Hao Pang and Bing Liao, 2009. Removal of copper(II) ions from aqueous solution by modified bagasse. Journal of Hazardous Materials, 164(1): 1-9.

22. Kraus, W., 1995. Biologically Active Ingredients, in The Neem Tree, H. Schmutterer (Ed.), pp: 35-92, VCH, Weinheim.

23. Chu, K.H., 2002. Removal of Copper from Aqueous Solution by Chitosan in Prawn Shell: Adsorption Equilibrium and Kinetics, Journal of Hazardous Materials, B90: 77-95.

24. Dakiky, M., M. Khamis, A. Manassra and M. Mereb, 2002. Selective adsorption of Cr (VI) in industrial wastewater using low cost abundantly available adsorbents. Advances in Environ. Res., 6: 533-540.

25. Wu, Feng-Chin, Tseng, Ru-Ling and Juang and Ruey-Shin, 2000. Comparative Adsorption of Metal and Dye on Flake- and Bead-Types of Chitosans Prepared from Fishery Wastes, Journal of Hazard Materials, B73: 63-75.

26. Panday, K.K., G. Prasad and V.N. Singh, 1984. Water Research, 19: 869-873.

27. Skellon, J.H., S. Thorburn, J. Spence and S.N. Chatterjee, 1962. The Fatty Acids of Neem Oil and their Reduction Products, Journal of Scientific Food Agriculture, 13: 639-643.

28. Mohanty, K., M. Jha, B.C. Meikap and M.N. Biswas, 2005. Removal of chromium (VI) from dilute solutions by activated carbon developed from Terminalia arjuna nuts ctivated with zinc chloride, Chemical Engineering Sciences, 60: 3049-3059.

29. Sarin, V. and K.K. Pant, 2005. Removal of chromium from industrial waste by using eucalyptus bark. Bioresource Technology, 97: 15-20.

30. Keskinkan, O., M.Z.L. Goksu, M. Basibuyuk and C.F. Forster, 2004. Heavy metal adsorption properties of a submerged aquatic plant, Bioresource Technology, 92: 197-200.

31. Xing, G.X., S.F. Zhang, B.Z. Ju and J.Z. Yang, 2006. Study on adsorption behaviour of crosslinked cationic starch maleate for chromium (VI), Carbohydrate Polymer, 66: 246-251.

32. McKay, G., M.S. Otterburn and A.G. Sweeney, 1980. The removal of colour from effluent using various adsorbents-III. Silica: rate processes, Water Research, 14: 15-20.

33. Dada, A.O., A.P. Olalekan and A.M. Olatunya, 2012. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherms Studies of Equilibrium Sorption of Zn^{2+} Unto Phosphoric Acid Modified Rice Husk (IOSR-JAC), 3: 38-45.

34. Xiao-ming, L., W. Zheng, D. Wang, Q. Yang, J. Cao, X. Yue, T. Shen and G. Zeng, 2010. Removal of Pb (II) from aqueous solutions by adsorption onto modified areca waste: Kinetic and thermodynamic studies. Desalination, 258: 148-153.

35. Aksu, Z., 2002. Determination of equilibrium, kinetics and thermodynamic parameters of the batch Biosorption of nickel(II) ions onto chlorella vulgaris, process Biochemistry, 38: 89-96.

Persian Abstract

چکیده

ظرفیت جذب پودر برگ نیم که به عنوان یک جادب ارزان قیمت برای حذف کروم از محلول‌های آبی استفاده می شود، مورد بررسی قرار گرفت. در طول فرایند جذب تکنیک ناپیوسته مورد استفاده قرار گرفته است. اثر غلظت اولیه یون فلزی ،میزان جاذب، دما ، pH ،اختلاط/زمان تماس روی سرعت جذب در ثابت ۶/۴ و دمای ثابت ۳۰ درجه سانتیگراد و pH مورد مطالعه قرار گرفت.نتایج با استفاده از ۳ مدل جذب هم دما، فرندلیچ ، لانگمایر و تمکین مورد ارزیابی قرار گرفت.ارزیابی ضرایب تصحیح نشان داد مدل هم دمای لانگمایر داده هارا به طور مناسب تری نسبت به سایر مدل ها عرضه می کند. ظرفیت جذب از مدل هم دمای لانگمایر برای کروم شش ظرفیتی ۱۲۵/۸۳ میلی گرم بر گرم بود. میزان موثر بودن پودر برگ نیم در جذب فلزات سنگین از محلول های آبی،مطالعات سینتیکی نشان داد که مدل شبه مرتبه ۲ از مدل شبه مرتبه ۱ مناسب تر بود. نتیجه گیری شد که پودر برگ نیم جاذب موثری برای حذف کروم شش ظرفیتی از محلول آبی را دارد.مشاهدات نشان میدهد که فرایند جذب گرما زاست. مقدار منفی انرژی آزاد گیبس نشانگر مقرون به صرفه بودن و خود به خودی بودن فرایند است. در حالیکه میزان منفی انتروپی و انتالپی به ترتیب نشانگر ماهیت تصادفی و گرمازای جذب هستند.