Study of the Kinetics and Thermodynamics of Adsorption of Hexavalent Chromium on the Luffa Cylindrica Cords

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ABSTRACT: *In the present work, the objective is to determine the potential use of natural materials, Luffa cylindrica cords for the removal of Chrome (VI) through the adsorption batch process under different experimental conditions. The determination of the concentrations of Chrome (VI) has been performed using a UV - Visible spectrophotometer. Adsorption studies were carried out under various parameters such as contact time, pH, initial concentration, and temperature. The results obtained show that Luffa cylindrica cords / Chrome (VI) have an adsorption capacity 29.98 mg/g. The adsorption process was rapid and reached equilibrium in 60 min of contact at 343K and pH 7.7. The different adsorption models Langmuir, Freundlich, Temkin, and Elovich were used for the mathematical description of the adsorption equilibrium, and it was found that the very well - equipped experimental data for the Langmuir model (R^2=0.9700), the pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data. The experimental data fitted very well the pseudo-second-order kinetic model (R^2= 0.982) and also followed the model of intraparticle diffusion (K_{dif} vary from 0.687 to 4.040 mg/(g min$^{1/2}$) for concentrations between 25 and 150 mg/L), whereas diffusion is not the only rate - control step. The thermodynamic parameters study show that the negative value of $\Delta H°$ (-11.49 kJ/mol) indicated that the adsorption of Chrome (VI) on Luffa Cylindrica cords was exothermic, the reaction was accompanied by a decrease in entropy (- 0.033 kJ/K. mol). The Gibbs free energy increased from -0.171 to -1.722 kJ/mol, respectively for Chrome (VI) when the temperature was increased from 296 to 343 K. The studied system shows that the adsorption process is spontaneous. The physical properties of the biosorbent were determined by FT-IR analysis and X-RD.*

KEYWORDS: *Luffa cylindrica cords; Cr (VI); Adsorption, Modeling; FT-IR; X-RD.*

INTRODUCTION

Heavy metals are placed among the most important environmental pollutants that have changed into a global concern due to their toxicity and carcinogenetic properties. These metals, even in trace amounts, accumulate in the body of creatures and their food cycle [1-4]. Examples of heavy metals include arsenic, cadmium, chromium, copper, lead, mercury and zinc [5, 6]. Generally, heavy metals have densities above 5g/cm^3. As the heavy metals cannot be degraded or destroyed, they are persistent in all parts of the environment. Human activity affects the natural geological and biological redistribution of heavy metals through pollution of the air, water, and soil [7, 8]. One of the most applicable heavy metals is chromium widely used in many industries including electroplating, dyeing, tannery, and fertilizer producing. This metal exists in the environment mainly in the form of trivalent and hexavalent forms. Hexavalent chromium is really toxic with its adsorption in potable water being nine times as much as the adsorption of trivalent chromium [9-11]. Moreover, the carcinogenicity of the hexavalent chromium has also been confirmed by the World Health Organization [12]. The international cancer research agency has placed hexavalent chromium in the first group of carcinogen substances [13]. Hexavalent chromium can cause serious problems in the performance of the liver, kidneys, and lungs. The short term effects of exposure to chromium involve burning and inflammation in the upper respiratory tract and dermatological burning resulting in ulcers and scars. On the other hand, lung cancer and kidney damages can be mentioned as long-term effects of being exposed to chromium [14].

The maximum allowable limit for chromium in potable water is 0.05 mg/L [15] according to Iranian industrial standard and research Institute, while World Health Organization has specified it as 0.01 mg/L [12]. Various methods have been reported including, conventional methods for treating effluents, such as precipitation, electro dialysis, ion exchange resins, reduction, and so on are both costly and ineffective, particularly when there is a very low concentration of heavy metals. By comparison, biosorption processes offer the advantages of low operational costs and of minimising the volume of chemical and/or biological waste sludge as well as a high degree of efficiency in decontaminating very diluted effluents. Biosorption is an alternative technique for removing heavy metals from aqueous solutions, based on the property of a certain class of biomass to accumulate this kind of pollutant through mechanisms, such as physical adsorption, complexing and ion exchange. The most commonly used natural biosorbents are totally renewable, their cost is low and their use and handling involve no additional risks; they may also be specifically selective for different pollutants and are generally disposed of by incineration [16].

Many materials, such as waste red mud and fly ash, tea-industry waste, calcite and hydroxyapatite, waste materials as refuse concrete, waste paper and charcoal, and natural indigenous rocks as andesite, limestone, granite and nitrolite, olive cake, bagasse fly ash, and rice husk ash, the orange barks, the algae, plants dried and olive stone waste have been tested for Cr (VI) removal from water systems by various researchers [17].

Luffa cylindrica cords, mainly consists of cellulose, hemicelluloses and lignin; of composition (60%, 22% and 10.6% by weight, respectively) [18]. Because of its unique structure, Luffa Cylindrica has been used as an efficient adsorbent or as a carrier for immobilization of some microalgal cells for the removal of water pollutants [19, 20]. In this study, Luffa Cylindrica cords were investigated as an alternative biosorbent for removing of Chromium ion from aqueous solutions, the sorption capacity of Luffa cylindrica cords for hexavalent chromium ions has been investigated by determining the pH in the solution, effect and contact time, the equilibrium isotherm at various temperatures. In each system four isotherms, the Langmuir, Freundlich, Elovich and Temkin have been analyzed. Kinetic studies have been carried out to study the effect of temperature. Physical characteristics of LCC were characterized before and after adsorption using FT-IR and X-RD.

EXPERIMENTAL SECTION

Preparation of the biosorbent

Luffa cylindrica cords were washed with boiling distilled water for 30 min. These cords were then placed in a solution of NaOH (12%) for 15 min and washed again with tap water. They are whitened with bleach 12% for 3 h at ambient temperature after which the cords are rinsed with distilled water several times. The cords of Luffa cylindrica were oven dried at 105°C for 120 min, then crushed and sifted. Samples are ready for adsorption.

Preparation of solutions

Stock solution of Cr (VI) ions with a concentration of 1000 mg/L was prepared by dissolving $K_2Cr_2O_4$ (analytical reagent grade) in distilled water. The desired Cr (VI) concentrations were prepared from the stock solution by making fresh dilutions for each sorption experiment and the experimental solutions were obtained by diluting the stock solution to the required concentrations (5 to 50 mg/L). For experiments at different pH, the acidity of Cr (VI) solution was adjusted by addition of drops of 0.1M (HNO_3) and 0.1 M (NaOH) solution.

Analysis

Fourier Transform Infrared Spectroscopy, FT-IR (IR Prestige-21, Shimadzu, Japan) was used to identify the different chemical functional groups present in the LCC. The analysis was carried out using KBr and the spectral range varying from 4000 to 600 cm. The FT-IR spectra of the free unloaded LCC were compared with those obtained for LCC loaded with Cr (VI). Powder diffractograms of the LCC samples were obtained with an X Pert PHILIPS diffractometer with PW3373/Cu LFF radiation at 40 kV and 50 mA. The diffractograms were used to identify the compounds and to verify crystalline structure. They were compared with LCC loaded with Cr (VI). Diffractograms were obtained by varying angle (2θ) from $3°$ to $90°$.

Adsorption experiments

The method used for the establishment of the adsorption isotherm method is to put in a water bath fitted with a stirrer, a series of flasks with which we introduce a volume (V = 200 mL) solution of the adsorbate (Cr (VI)) known concentration (25, 50, and 150 mg/L) and a mass (m = 1 g) of the adsorbent of well-defined size ($0.08 \leq dp$ (mm) ≤ 0.63), and specific surface area 22.48 m^2/g at different temperatures (296, 313 and 343 K) with pH 7.7. For a given contact time corresponding to equilibrium, we recover the filtrate solution for passing the UV-visible spectrophotometer.

Adsorption kinetic experiments were used to investigate the effect of contact time and determine the kinetic parameters. For these tests, 1 g of LCC were added to 200 mL Cr (VI) solutions with different initial concentrations. The mixture was agitated on an electromagnetic stirrer at 350 rpm. At predetermined time intervals (0 - 250 min), 10 mL samples were taken out

and filtered. The same methods were used to determine the residual Cr (VI) concentration. Each measurement of Cr (VI) concentration was repeated three times.

The adsorption amount at time t, qt (mg/g) was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t) V}{m} \tag{1}$$

Where qt is the amount of Cr (VI) taken up by the adsorbent (mg/g); Ct (mg/L) is the concentration of Cr (VI) solution at time, t (mg/L), C_0 (mg/L) is the initial concentration of Cr (VI). V is the volume of Cr (VI) solution (L), and m is the weight of adsorbent used (g).

$$Percent\ removal = \frac{(C_0 - C_f)}{C_0} \times 100 \tag{2}$$

Where C_i and C_f represent the initial and final (after adsorption) Cr (VI) concentrations, respectively.

RESULTS AND DISCUSSION

Characterization of adsorbent

FT-IR Studies

To explore the characteristics of the biosorbent FT-IR analysis of Luffa cylindrica cords were performed at the range of 4000 - 400 cm^{-1} as shown in Fig. 1. The FT-IR spectrum presented a broad band located around 3330 cm^{-1} which is assigned to O–H stretching vibrations of hydrogen bonded hydroxyl groups. In fact, the hydroxyl groups are present in the primary components of wood: cellulose, hemicelluloses and lignin [21].

The peak at about 2900 cm^{-1} was attributed to the asymmetric and symmetric stretching vibrations of CH_2 and CH_3. The band around 1501 cm^{-1} was associated with C=C and C=O stretching in the aromatic ring. The peak at 1023 cm^{-1} may be due to C–O stretching vibrations [22]. Also it is important to notice that the band intensities decreased in the FT-IR spectrum of Cr (VI) loaded LCC because the functional groups of the LCC surface have been occupied with Cr (VI). This study demonstrated that hexavalent chrome ion was adsorbed and penetrated into the interlayer space of the LCC.

X-Ray diffraction

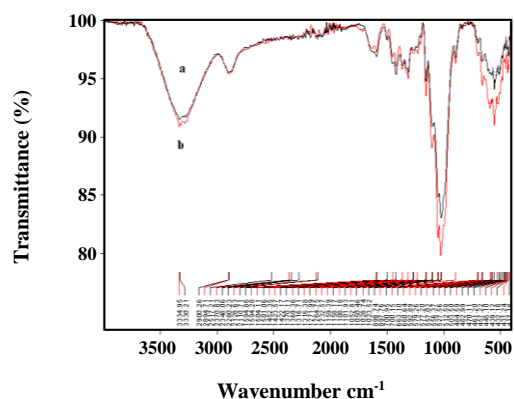X-RD patterns of LCC before and after Cr (VI) adsorption (T=343 K, pH=7,7, C_0=150 mg/L) are shown in Fig. 2.

Fig. 1: FT-IR spectra of (a) raw LCC and (b) LCC loaded Cr (VI) sample.

Fig. 2: X-Ray diffraction patterns of LCC before (a) and after (b) adsorption.

The X-RD patterns of LCC raw and LCC loaded with Cr (VI) were shown in Fig. 2. The LCC raw at 2θ scale is shown peaks at 22.52° and 15.72° with relative intensities of 2800 and 1400, respectively. Similarly, LCC loaded with Cr (VI) is shown peaks at 22.32° and 15.88° with relative intensities of 1136 and 731, respectively. The percentage crystallinity (X_C (%)) and crystallinity index (C.I.) were calculated as follows [23, 24].

$$X_C\ (\%) = \frac{I_C}{I_C + I_A} \times 100 \tag{3}$$

$$C.I. = \frac{I_C - I_A}{I_C} \tag{4}$$

Where IC is peak intensity of crystalline phase, IA is peak intensity of amorphous phase. The percentage crystallinity of LCC raw and LC cords loaded with Cr (VI) were observed as 66.76 and 60.85, while the crystallinity index as 0.50 and 0.36.

It was observed that the intensity of the peak in LCC loaded with Cr (VI) is decreased on the adsorption. The decrease in intensity of peak during the adsorption process is indicated a decreased in crystallinity of LCC loaded with Cr (VI). However, the LC loaded with Cr (VI) is shown broadening of the peak after adsorption due to convergence of the cords towards more disordered system [25].

It has been observed that (Table 1) a slight decrease in percentage crystallinity of the cords on adsorption copolymerization resulted in increase in randomness or disorder in the crystal lattice of cellulose cords.
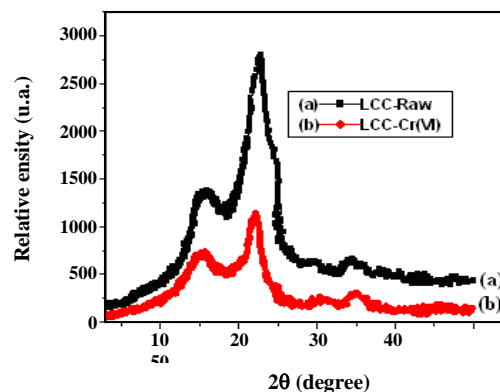
This was due to incorporation of Cr (VI) ion on the active sites of backbone during grafting and cords became more amorphous and resulted in impaired crystalline structure [26, 27].

Optimization of adsorption parameters

The optimization of different adsorption parameters such as pH of solution, Cr (VI) concentration, temperature, dose of LCC and particles size of LCC at different time intervals was carried out for Cr (VI) onto Luffa Cylindrica cords.
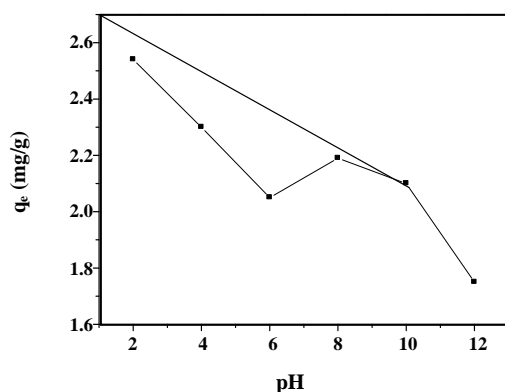
Effect of pH

Many studies suggest that pH is an important factor in the adsorption process [28, 29] variations in pH could change the characteristics and availability of metal ions in solution as well as the chemical status of the functional groups responsible for biosorption. Some experiments were therefore performed at 343 K with 150 mg/L solutions to study the Cr (VI) adsorption on LCC as a function of solution pH.

The results for the study of the effect of pH on Cr (VI) adsorption are shown in Fig. 3. It is clear that a progressive increase in pH 2 to 12 causes a lowering in the adsorption capacity.

This Chrome adsorption behavor can be explained by the fact that during the pH adjustment of the solution containing the hexavalent chromium ion; the LCC undergo accordingly possible alteration of the ionic character of their surfaces and the aggregation state of the Cr (VI).

Research Article

***Table 1: Percentage crystallinity and crystallization index of LCC raw and LCC loaded with Cr (VI).***

Sample	2θ (°)		Intensity			
	Crystalline peak	Amorphous peak	I_C	I_A	XC (%)	C.I
LCC raw	22.52	15.72	2800	1400	66.67	0.50
LCC loaded with Cr (VI)	22.32	15.88	1136	731	60.48	0.36

Fig. 3: FT-IR spectra of (a) raw LCC and (b) LCC loaded Cr (VI) sample.

Fig. 4: X-Ray diffraction patterns of LCC before (a) and after (b) adsorption.

The ion exchange sites are mainly protonated and are less available for ion exchange. Within this pH range, the ion exchange process is the major mechanism for the removal of metal ion from the solution. Earlier similar results have reported that the optimal pH for Cr (VI) adsorption was around [30].

Effect of adsorbent dose

The effect of the adsorbent dose on the amount adsorbed of chrome was studied at 343K and pH of 7.7 by varying the adsorbent amounts from 0.125 to 7.5 g/L. For all these runs, initial concentration of hexavalent chromate ion was fixed as 150 mg/L. The analysis was shown that the adsorption of Cr (VI) is increased as the adsorbent dosage increased from 0.125 to 7.5 g/L due to the limited availability of the adsorbing species number for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is apparent that with higher dosage of adsorbent there would be greater availability of exchangeable sites from metals ions. The significant increase in uptake was observed when the dose was increased from 0.125 to 1.75 g/L; any further addition of the adsorbent than this dose would not cause any significant change in the adsorption. These results are clearly indicated that the LCC dosages
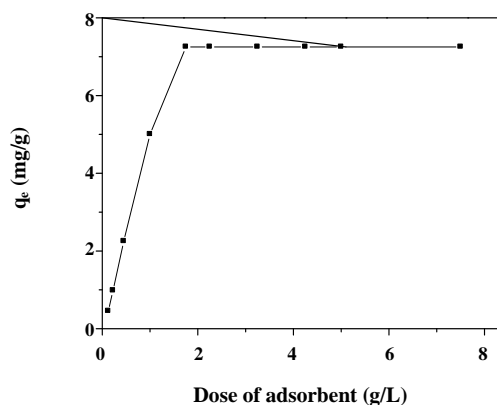
must be fixed at 1.75 g/L, Fig. 4 which is the dosage that corresponding to the minimum amount of adsorbent that is led to constant Cr (VI) removal for the entire experiments [31].

Effect of particles size

The contact surface between any biosorbent and the liquid phase played an important role in the adsorption phenomenon. According to Fig. 5 the results show that the amount of chromium adsorbed is increased with the reduction of the particle diameter, which is probably due to the increase in the number of active sites and the increase of the biosorbent surface. The maximum adsorption capacity is 50mg/g was reached using the fine particle (diameter less than 0.08 mm).

Effect of contact time

The results obtained from the biosorption rate tests are shown in Fig. 6, the evolution of the adsorbed quantity of Cr (VI) per gram of LCC as a function of the contact time at initial concentration 150 mg/L as a Cr (VI), showing that the amount of adsorbate fixed on each material increases with the increase of the content of the solution in Hexavalent chromium. A rapid adsorption is observed at the beginning and then a spreading with
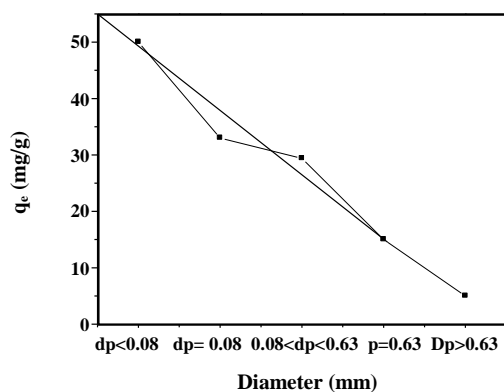
Fig. 5: Effect of the diameter of biosorbent particle (dp) on Cr (VI) adsorption onto LCC: C₀= 150 mg/L, pH=7.7, m=1g; T=343K, contact time=250 min and agitation rate=350 rpm.

Fig. 6: Variation of the amount of Cr (VI) adsorbed as a function of the contact time for LCC: pH 7.7, C₀ = 150mg/L, m = 1g, V = 200ml, T = 343K and ω = 350 rpm

saturation. A rapid increase in the adsorption capacity of the heavy metal occurs within a few minutes ($\approx$5 minutes), due to the adsorption of Cr (VI) to the surface of the particles of each adsorbent. This first phase constitutes the essential part of the phenomenon of adsorption because the kinetics of fixation is limited by the low residual concentration of heavy metal. In the second stage, the occupation of deep adsorption sites requires diffusion of the adsorbate within the micropores of the adsorbent. A second, slower phase is observed which can last from 10 to 50 minutes. After this phase, a saturation plateau. Generally, all of these results revealed that equilibrium occurs after 60 minutes respectively for the Hexavalent chromium solution. Similar results have been reported by other groups such as *Sari et al.* [32] and *Gupta et al.* [30].

Effect of initial Cr (VI) concentration

Adsorption of Cr (VI) was measured at given contact times for four different initial Cr (VI) concentrations of 25, 50 and 150 mg/L. From Fig. 7, the plot reveals that the amount of Cr (VI) removal is higher at the beginning. This is probably due to larger surface area of the LCC being available at beginning for the adsorption of Cr (VI) ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. Most of the maximum amount of Cr (VI) removal was attained after about 250 min of shaking time at different initial concentrations. The increasing contact time increased the Hexavalent chromium adsorption and it remained constant after
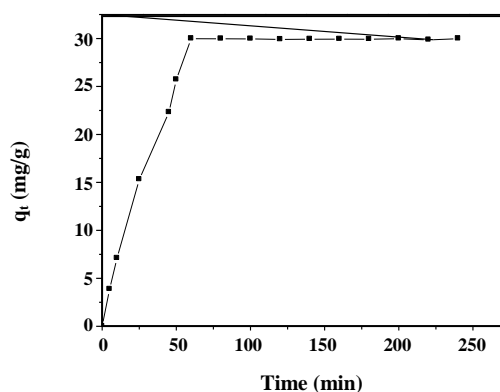
equilibrium reached in 60 min for different initial concentrations. Usually, the contact time is selected at the material saturation or above, because these times correspond to pseudo equilibriums. The same phenomenal was observed for others materials [33, 34].

Effect of temperature

The initial Hexavalent chromium concentration provides an important driving force to overcome all mass transfer limitations of Cr (VI) between the aqueous and solid phases.

Therefore, a higher initial Cr (VI) concentration will enhance the adsorption process. Fig. 8 shows the effect of initial hexavalent chrome ion concentration on the equilibrium adsorption capacity (q_e) of Cr (VI) on LCC at different temperatures. It was clear to see that the q_e values increase with the increase in the initial concentrations of the solution. The maximum equilibrium (q_e) values were determined as 8.75, 17.9 and 29.98 mg/g for 150 mg/L initial Cr (VI) concentrations at 296, 313, and 343 K, respectively. Similar endothermic nature of the adsorption process has been reported for other adsorbent systems [30], [35], [36]. The adsorption capacity for the system (Cr (VI) / LCC) increases with increasing the temperature from 296 to 343 K. The best removal efficiency (29.98 mg/g and 93.07%) was obtained at temperature of 343 K.

Adsorption isotherm models
Isotherm modeling

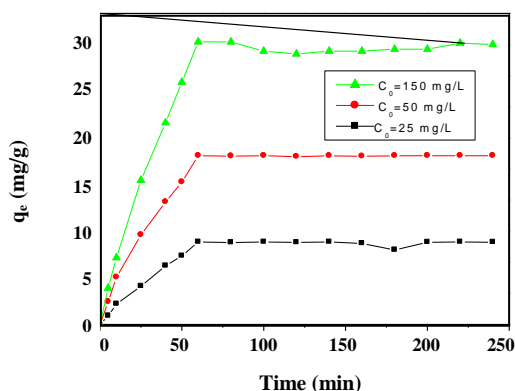Adsorption isotherm models are widely used to describe the adsorption process and investigate

Fig. 7: Effect of Contact time on Cr (VI) Removal onto LCC: pH 7.7, m = 1 g, 0.08 ≤ dp (mm)≤0.63, V = 200 ml and equilibrium time= 60 min.

Fig. 8: Effect of temperature on the amount adsorbed by the LCC / Cr (VI): pH 7.7, m = 1 g, 0.08 ≤dp(mm) ≤0.63 and V = 200 ml.

mechanisms of adsorption. Adsorption isotherms were calculated based on the well-known Langmuir, Freundlich, Temkin and Elovich models. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites, using uniform strategies of adsorption [37]. The linear form of the Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (5)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the sorption capacity of adsorbent at equilibrium (mg/g), q_m and K_L are the maximum hexavalent Chromium ions adsorbed per unit mass of the adsorbent (mg/g) and Langmuir constant, in relation to energy of sorption which quantitatively indicates the affinity between the adsorbent and hexavalent Chromium ions (L/mg), respectively [17].

The favorable or unfavorable of the adsorption system can be determined based on the essential characteristic of the Langmuir model which can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as follows:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (6)$$

Where K_L is the Langmuir constant and C_0 is the initial concentration. The value of separation factor indicates the nature of adsorption process. R_L values indicate the adsorption process to be irreversible (R_L=0),
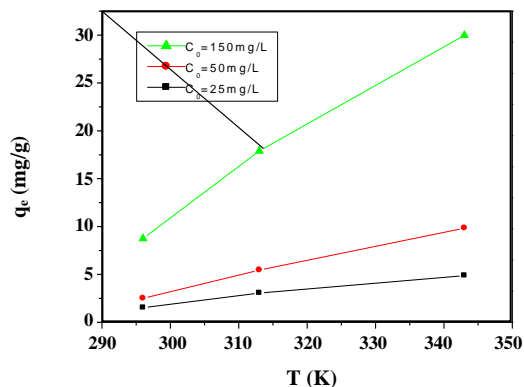
favorable ($0<R_L<1$), linear (R_L=1), or unfavorable ($R_L>1$) [38, 39].

The adsorption intensity of the hexavalent chromium ions towards the adsorbent can be determined using the Freundlich model The Freundlich equation is purely empirical based on sorption on heterogeneous surface, which is commonly described by the following equation [40]:

$$q_e = K_F C_e^{1/n} F \qquad (7)$$

Where q_e is the sorption capacity of adsorbent at equilibrium (mg/g), K_F (mg$^{(1-n)}$.L^n/g) and $1/n_F$ are the Freundlich constants in relation to adsorption capacity and adsorption intensity, respectively. The Freundlich equilibrium constants were evaluated from the intercept and the slope, respectively, of the linear plot of log q_e versus log C_e based on experimental data. The Freundlich equation can be linearized in a logarithmic form for the determination of the Freundlich constants as follows [41]:

$$Ln(q_e) = Ln(k_F) + \frac{1}{n_F} Ln(C_e) \qquad (8)$$

Where the constant K_F shows the adsorption capacity and the constant n indicates the adsorption intensity. They can be determined from the plot of Ln (q_e) vs Ln (C_e) [42, 43].

Temkin's model rests on the assumption that during the adsorption gas phase, the heat of adsorption due to interactions with the adsorbate decreases linearly with the recovery rate θ. From q_e plotted as a function of Ln C_e, B_T, and K_T values can be determined [44]:

$$q_e = \frac{RT}{B_T} Ln (K_T \cdot C_e) \tag{9}$$

Where R is the perfect gas constant (8.314 J/(mol K)), T is the absolute temperature (K), B_T is the variation in energy of adsorption (J/mol), and K_T is the constant of Temkin (L/mg).

Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate-adsorbent [45]. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation [46]. The linear form of this equation is given by [45]:

$$q_t = \frac{1}{\beta_{El}} Ln (\alpha_{El} \beta_{El}) + \frac{1}{\beta_{El}} Ln (t) \tag{10}$$

Where α_{El} is the initial adsorption rate (mg/g min), and the parameter be is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The Elovich coefficients could be computed from the plots q_t vs. Ln (t). The initial adsorption rate, and the desorption constant, β_{El}, were calculated from the intercept and slope of the straight-line plots of q_t against Ln (t).

The plots of C_e/q_e vs. C_e for the adsorption of Cr (VI) at 296, 313, and 343 K according to the linear form of the Langmuir isotherm is shown in Fig. 9.

Table 2 summarizes the constants of the Langmuir, Freundlich, Elovich and Temkin isotherms obtained from the slope and the interception of the plots of each isotherm at different temperatures. The values of R^2 exceed 0.9 for the three models of Langmuir, Freundlich, and Elovich, suggesting that the three models with near experimental results.

From Table 2, the values of 1/n were found to be less than 1. The low value of the linear correlation coefficient, R^2, indicated the unsuitability of Temkin isotherm model. The values of R^2 for Freundlich model (0.706, 0.866, and 0.881 at 296, 313, and 343 K, respectively) were high, indicating that this model can be used to characterize the equilibrium adsorption. However, Freundlich model was not the best model in this study. Langmuir models were fitting well with the isotherm data at various temperatures with the highest R^2 values, compared to Elovich, Temkin and Freundlich models.
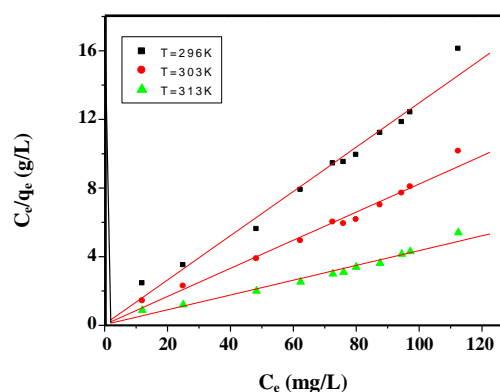

Fig. 9: Linearization of the Langmuir equation for adsorbing Cr (VI)/ LCC: pH 7.7, C_0=150 mg/L, V= 200 mL, and m=1 g.

The Langmuir fit is consistent with strong monolayer sorption onto specific sites. The maximum adsorption capacities (q_m) of LCC for Cr (VI) were 7.752, 12.240, and 23.202 mg/g at 296, 313, and 343 K, respectively. The similar phenomena are also observed in adsorption of copper onto the orange skin [47] and in adsorption of copper and lead on tea waste [48].

The R_L values were found to be less than 1 and greater than 0 for all experiments carried out at different initial concentrations and temperatures (Table 2). It is found that the adsorption of Cr (VI) on LCC is a favorable phenomenon. Thus, LCC seems to have a good affinity for hexavalent chromium removal and its adsorption capacity increased as the temperature increases.

Moreover, as shown in Table 3, we made a comparison between our experimental results of Cr (VI) adsorption on LCC surface with others studies reported in the literature using some lignocellulosic materials. From this table, the results of our new raw adsorbent (LCC) show that it has an acceptable potential for removing of Cr(VI) from water with a maximum adsorption capacity of 29.98 mg/g compared to several materials shown in this table.

However, other lignocellulosic materials applied in other studies have shown much higher adsorption capacities, such as Brazilian-pine fruit wastes: 240 mg/g [49], Palmaria palmata: 33.79 mg/g [50] and Grape stalk: 59.8 mg/g [51]. These differences adsorption capacity of *hexavalent chromate* ion can be attributed to the adsorbent properties such as structure, functional groups, and specific surface area. Furthermore, the chemical and thermal treatments usually applied to these materials in order to increase their adsorptive behavior can be envisaged.

Table 2: Parameters of different adsorption models for Cr (VI) / LCC.

T(K)	Freundlich			Langmuir				Temkin			Elovich		
	K_F	$1/n_F$	R^2	q_m (mg/g)	K_L (L/g)	R^2	R_L	K_T (L/g)	B_T	R^2	α_{El} (mg/g.min)	β_{El} (g/mg)	R^2
296	1.563	0.272	0.866	7.752	1.963	0.974	0.003	1.132	537.935	0.884	0.661	0.336	0.949
313	1.969	0.234	0.881	12.240	1.421	0.981	0.005	1.514	453.762	0.817	1.494	0.170	0.963
343	2.582	0.233	0.706	23.202	1.026	0.970	0.006	1.641	277.214	0.675	2.646	0.110	0.942

Table 3: Cr (VI) adsorption by lignocellulosic materials.

Adsorbent material	q (mg/g)	pH	References
Luffa Cylindrica Cords	29.98	7.7	This study
Palm flower	4.90	4.5	[33]
Tea dust	29.39	2.0	[52]
Cupressus lusitanica Bark	15.0	1.5	[53]
Palm stems	2.44	2.0	[54]
Posidonia oceanica fibers	3.34	2.0	[55]
Oak tree (treated)	1.74	3.0	[56]
Ceratocystis paradoxa MSR2	2.125	4.5	[57]

Kinetics studies

The rate constant for surface adsorption of Cr (VI) ions onto LCC are also studied under the light of the pseudo-first-order rate expression of Lagergren model [58]. The integrated form of the Lagergren equation is given by:

$$Log(q_e - q_t) = Log q_e - \frac{k_1}{2.303}t \tag{11}$$

Where q_e and q_t are the amounts adsorbed at equilibrium and at time, t (mg/g), and k_1 is the rate constant of the pseudo-first-order adsorption (1/min).

The pseudo-second-order kinetic model (12) can be represented in the following form [59]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{12}$$

Where k_2 is the rate constant of the pseudo-second order adsorption (g/mg min).

The kinetics of adsorption of the adsorbate on the adsorbent was verified at different initial concentrations (25, 50, and 150 mg/L).

The validity of each model was determined by the SSE (%), given by:

$$SSE(\%) = \frac{1}{N}\sqrt{\sum_N \left(q_{e,exp} - q_{e,cal}\right)^2} \tag{13}$$

Where *N* is the number of trials. Low value indicates a better SSE smoothing.

Most adsorption reactions take place through multi-step mechanism comprising (i) external film diffusion, (ii) intraparticle diffusion, and (iii) interaction between adsorbate and active site. Since the first step is excluded by shaking the solution, the rate-determining step is one of the other two steps. *Weber* and *Morris* [60] described the intraparticle uptake of the adsorption process to be proportional to the half power of time:

$$q_t = K_{dif} t^{1/2} \tag{14}$$

With: k_{dif}: rate constant intraparticle diffusion (mg/g.min$^{1/2}$).

The kinetic parameters for adsorption of hexavalent chromium ions presented in Table 3 were calculated from plots of log (q_e-q_t) vs. t (Fig. 10) and the plots of t/q_t vs. t (Fig. 11). For the system studied (Cr (VI) /LCC), we have two distinct phases. One is attributed to the diffusion in the mesopores or macropores, the second part, in the absence of micropores systems tend towards equilibrium.
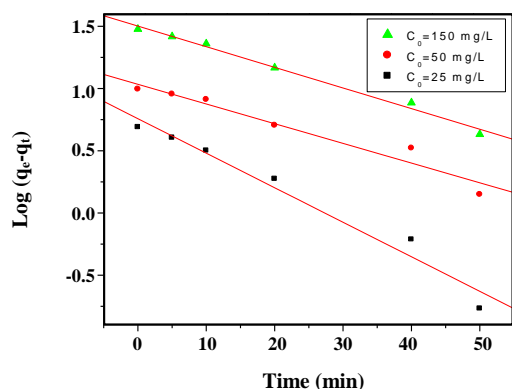
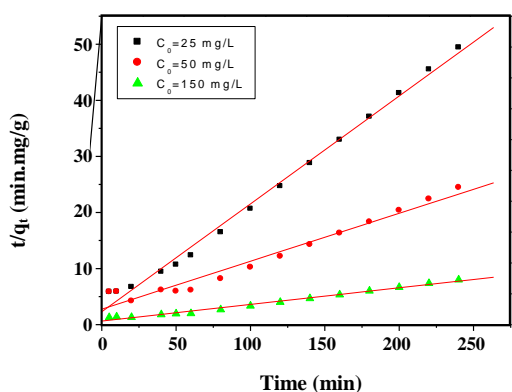**Fig. 10: Linearization of the kinetic model of pseudo-first-order, at T = 343 K g.**

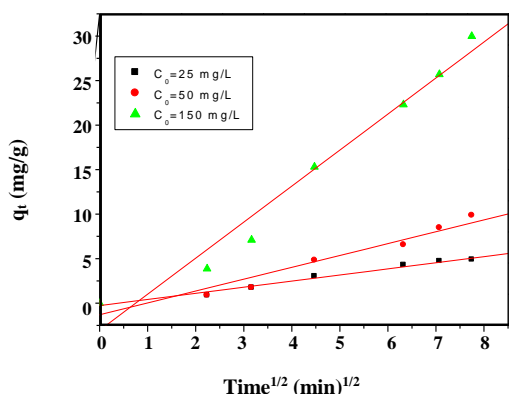**Fig. 11: Linearization of the kinetic model of the pseudo-second-order for the system Cr (VI) / LCC, at T = 343K.**

Fig. 12: Application of simplified model intraparticle diffusion for the adsorption of Cr (VI) on LCC, T = 343 K.

The values of the diffusion rate constants (K_{dif}) are calculated by the linearization of the first phase described by equation (12).

According to Fig. 12, the curves (linear) do not pass through the origin. This shows the dual nature of the adsorption phenomenon. The intercept is due to the presence of an external resistance transfer material which gives the thickness of the boundary layer.

The results of Table 4 show that the second-order rate constant k_2 decreased with increasing concentrations. The correlation coefficients for the second-order kinetic model were between 0.982 and 0.997. Moreover, the experimental q_e (exp) values agree well with the calculated ones. On the other hand, the correlation coefficients for the pseudo-first-order kinetics ($0.975 < R_2 < 0.995$) were lower than that from pseudo second-order one. Furthermore, the values of k_1 obtained from the former had no obvious trend of rise or fall with increase in concentration. Similar results have been reported by Dhanakumar et al. [8]. These results indicate that the adsorption system of hexavalent chromium ion obeyed a pseudo-second-order kinetic model. The pseudo-first-order and pseudo-second-order kinetic models could not identify the diffusion mechanism.

We observe that the diffusion rate constants increase in the same direction as the initial concentration of Cr (VI) (Table 4). Indeed for initial concentrations between 25 and 150 mg/L, the values of K_{dif} vary from 0.687 to 4.048 mg/(g min$^{1/2}$) for the Cr (VI)/ LCC system.

Thermodynamic studies

The original concepts of thermodynamics assumed that in an isolated system, where energy cannot be gained or lost, the entropy change is the driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. The Gibbs free energy change, $\Delta G°$, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if $\Delta G°$ is a negative quantity. The value of $\Delta G°$ can be determined from the following equation:

$$\Delta G^0 = -RT \, Ln\left(k_L\right) \qquad (15)$$

Where K_L is the adsorption equilibrium constant, R is the gas constant (8.314 J/mol K), and T is the absolute temperature.

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Table 4: Pseudo-first-order and Pseudo-second-order kinetic parameters for the adsorption of Cr (VI) onto LCC.

Cr (VI) (mg/L)	Pseudo-first-order					Pseudo-second-order				Intraparticle diffusion	
	$q_{e, exp}$ (mg/g)	$q_{e, cal}$ (mg/g)	K_1 (min^{-1})	R^2	SSE	$q_{e, cal}$ (mg/g)	K_2 (g/mg.min)	R^2	SSE	K_{dif} (mg/g.min$^{1/2}$)	R^2
25	4.870	5.724	0.064	0.985	0.285	5.20	0.016	0.997	0.110	0.687	0.991
50	9.841	10.814	0.036	0.975	0.324	11.695	0.003	0.982	0.627	1.332	0.972
150	29.982	31.747	0.038	0.995	0.588	33.784	0.001	0.993	1.27	4.048	0.985
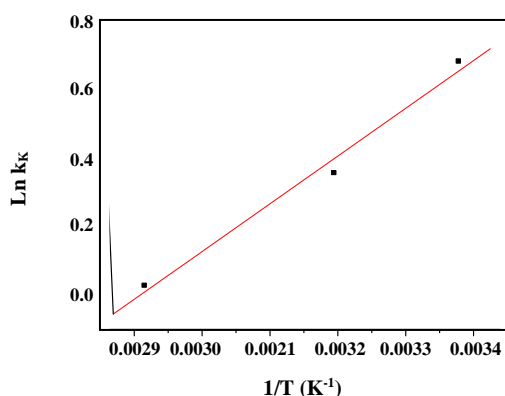
Fig. 13: Relationship between Langmuir sorption equilibrium constant and temperature for Cr (VI) / LCC; C_0= 150 mg/L.

A convenient form of the Van't Hoff equation then relates K_L to the standard enthalpy and entropy changes of adsorption, ΔH^o and ΔS^o, respectively [61]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (16)$$

(10) can be written as:

$$Ln\left(k_L\right) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R}\cdot\left(\frac{1}{T}\right) = -\frac{\Delta G^0}{R}\cdot\frac{1}{T} \qquad (17)$$

Where the values of $\Delta H°$ and $\Delta S°$ can be determined from the slope and the intercept of the plot between Ln (K_L) vs (1/T) (Fig. 13). The $\Delta G°$ values were calculated using equation (16). The values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the biosorption of Cr (VI) onto LCC at different temperatures (296, 313, and 343 K) are given in Table 5.

The negative ($\Delta G°$) values of Gibb's free energy represent that the adsorption undergoes thermodynamically feasible reaction and also spontaneous in nature [6]. The negative $\Delta H°$ value (-11.490 KJ / mol) shows that the nature of adsorption is exothermic. The negative $\Delta S°$ value (- 0.33 KJ / mol.K) suggests a decrease in the randomness at the Solid/solution interface during adsorption of hexavalent chromium on to LCC [62]. A similar trend was observed for adsorption of Cr (VI) by Ceratocystis paradoxa MSR2 [57]. The $\Delta G°$ values obtained in this study for the hexavalent chromate ion are < - 10 kJ/mol, which indicates that physical adsorption was the predominant mechanism in the sorption process [63].

CONCLUSIONS

This study shows that Luffa cylindrica cords, an abundant natural source, can be used effectively and efficiently for the removal of hexavalent chromium ion from aqueous solutions. Equilibrium data were fitted to Langmuir, Freundlich, Elivoch and Temkin isotherms, and the equilibrium data were best described by the Langmuir isotherm model ($R^2 = 0.975$), with a maximum monolayer adsorption capacity of 29.98 mg/g, at 60 min. The adsorption kinetics is best described by the pseudo-second-order ($R^2 = 0.982$).

The thermodynamic parameters for the adsorption of Cr (VI) onto Luffa cylindrica cords were also determined. The negative sign of $\Delta G°$ confirms the feasibility and the spontaneous nature of the adsorption process and physical reaction.

The negative sign of $\Delta S°$ shows the decreased randomness at the solid - solution interface during adsorption, and the negative sign of $\Delta H°$ indicates that the adsorption process is exothermic.

Therefore, the potential use of Luffa cylindrica cords for industrial wastewater treatment is real and represents interesting prospects to investigate, particularly for solutions containing organic species at very low concentrations.

Nomenclatures

LCC	Luffa cylindrica cords
Cr (VI)	Hexavalent Chromium (VI)
SEE	Sum of squared errors
vs	Versus

Table 5: Thermodynamic parameters for the adsorption of Cr (VI) ions onto LCC different temperatures.

T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
296	- 1.722		
313	-1.161	- 11.49	- 0.033
343	0.171		

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