Biosorption of hexavalent chromium metal ions from an aqueous solution of leaves and bark of *Cinnamomum verum* via green route

Benish Saeed¹ · Humera Anwer¹ · Sumra Naqvi¹ · Asma Siddiqui¹ · Sobia Hashim¹

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Abstract

In present research work *Cinnamomum verum* leaves (CL) and barks (CB) are exploited to encounter their effectiveness against the concentration of hexavalent chromium (Cr^{+6} metal ions) through biosorption process. To achieve this goal optimal conditions were set and broken into various parts such as; doses of adsorbents, concentrations of adsorbates, variations in contact and stirring time (5–100 min), temperatures (10 °C to 50 °C) and pHs from acidic to basic range (1 to 12). Thermodynamic parameters were also applied to validate the assay, which shows that the process is endothermic with positive ΔH° values, while negative values of ΔG° proved the spontaneous nature of sorption. Moreover, Lagergren's kinetic equations were employed, which suggest that the observed reaction process followed the dynamics of pseudo-second order. Equilibrium adsorption isotherms namely Langmuir and Freundlich have been applied to study the adsorbate materials attraction towards Cr^{+6} metal ions. The determined adsorption capability, i.e. q_e was found to be 11.33 and 26.85 mg/g acquired by CL and CB at 30 °C and 40 °C, respectively. FT-IR spectrums of loaded and unloaded metal ions were taken, which confirmed the participated functional groups of herbal plants in biosorption process. EDX analysis revealed the presence of Cr^{+6} metal ions after biosorption process. Furthermore, irregularities on surface of adsorbent material obtained from SEM images have provided more support to results for validation.

Keywords *Cinnamomum verum* leaves · *Cinnamomum verum* bark · Cr^{+6} metal ions · Thermodynamics study · Adsorption dynamics · Adsorption isotherms

1 Introduction

Industrialization and mining actions, rapidly increases the heavy metals contamination in aquatic systems [25, 44]. It's a well-known fact that even at very low concentration heavy metals are highly toxic to humans [14, 15]. They encounter human body in different ways, such as by inhalation, skin contact or using of those vegetables, which grew in sewage water or industrial effluents, etc. Consequently, they disturbed the metabolic processes and destroyed social health by accumulating in living creatures [17, 22]. Many synthetic mediators have been

used to take out the heavy metals from the body, but they had shown an adversarial side effects as per medical evidence. However, herbs have no side effects and they can be used conveniently as an alternative to those synthetic mediators [56].

Chromium is counted as one of the most significant pollutant amongst top sixteen toxic metals, due to its carcinogenic appearances towards humans [20]. However, trivalent chromium present in water and food in trace volume seems benign. While hexavalent chromium is mutagenic, not essential for mammals and has no biological confirmation [16, 36].

✉ Humera Anwer, humera.fuuast@gmail.com; Benish Saeed, beenishahmed781@gmail.com; Sumra Naqvi, sumra.naqvi@gmail.com; Asma Siddiqui, asmasiddiqui1091@gmail.com; Sobia Hashim, sobiahashim6@gmail.com | ¹Department of Chemistry, Federal Urdu University Art, Science and Technology, Gulshan-e-Iqbal Campus, Karachi 75300, Pakistan.

Therefore, an extensive time duration disclosure of Cr^{+6} metal ions above the proposed level caused severe damage to chief bio-systems [38], organs and skin of the body like, circulatory system, liver and kidney impairment, nerve dermatitis [28], nasal septum perforation [39], skin ulceration [10], skin cancer [34] and lung cancer etc. [24]. Several types of allergic responses have also been familiar like swelling and redness to the skin [9].

Subsequently, over the wide range of pH Cr^{+6} oxyanions are soluble in water and can easily accumulate into underground water and pollute the consumption water [21, 23, 27, 31, 37, 43, 45–47, 57]. Permitting to the world health association in 2008 the authorized boundary of Cr^{+6} metal ions in consumption water that is 0.05 mg/L [52]. The EPA (Environmental Protection Agency) of USA fixed a concentrated pollutant limit up to 38 $\mu\text{g/L}$ for entire chromium in taking water [54, 55].

Bioinorganic with the unison of green chemistry (which is new efficacious and unfurl branch of chemistry), encourages the designs of product and process that omit or lessen the usage and propagation of hazardous constituents which are harmful for human, animals, plants and the environment.

Among several biodegradable adsorbents plants have productive, constructive, powerful and virtual qualities. They do not only make our environment fresh and striking but also they have been using in culinary, medicinal and some spiritual purposes since long ago [41]. They are combusted patently after adsorption and desorption mechanisms and their microstructure can be investigated comprehensively [32].

Ayurveda was the most ancient cure of a system which is still widely used in Asian countries [12]. Modern medicinal techniques in amalgamation of Ayurveda bring high quality, quick action herbal products with good bioavailability. Different combinations of herbs, amino acids and other nutritional supplements found to be healthier substitutes of chelating agents. They may take longer time to clear the toxic metals and unsafe chemicals from the body, but safer to use with no or minor side effects. In contrast, chelation therapy is the treatment to remove the heavy metals and toxic chemicals in clinical toxicology, but can prove incurable [19].

In the current research, CL and CB are used as natural adsorbents under optimize conditions at vitro level. CL is often known as Bay leaf. It is also used for culinary and medicinal purposes. CB is a common spice used in both sweet and savory items of food. It is employed in cookery as condiment and flavoring the material. In Mexico, it is used in the preparation of chocolate specially [49].

Hence, existing paper concentrated to investigate the adsorption of Cr^{+6} metal ions by the leaves and bark of *Cinnamomum verum* at the optimize parameters. The

mechanism of biosorption was studied by the number of isotherms and thermodynamics. Kinetics was also established to determine the efficacy of assay. Moreover, sophisticated instrumental techniques were used to support the obtained results.

2 Experimental process

2.1 Chemicals

Analytical grade chemicals were utilized during the investigation work. Double deionized water (D.I water) was used for the preparation of samples and stock solutions. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7 \approx 99.0\%$) by ACS reagent, Diphenyl Carbazide (DPC $\approx 98.0\%$) from ph. Eur. Reagent, HCl (37% with 1.2 g/mL density at 25 °C), NaOH pellets analytical ACS reagent (with $\approx 98\%$), Sodium chloride ($\text{NaCl} \approx 99.0\%$) H_2SO_4 (99.999%) and Acetone (with $\approx 99.9\%$) were obtained from Sigma Aldrich. All the chemicals were used as per received.

2.2 Instrumentation

Pulverized and weighed the adsorbent samples through an electric grinder (Kenwood) and weighing balance (ER-120A). pH of stock and sample solutions were maintained by the pH meter (HANNA pH 211). An electrical Thermo-Shaker (Model: MS-100) was cast off to agitate the sample solutions. SPR (surface plasmon resonance) analysis was inspected by Visible spectrophotometer (Jenway 6310; 320–900 nm) to quantify the Cr^{+6} metal ions adsorption,. For FTIR spectrum, Fourier transform Infrared Spectroscope (model NICOLET 67000) was used. Scanning Electron microscope (model JSM 6380A) by ASEM of JEOL Japan used to study the surface of adsorbents. Chemical composition of biosorbents analyzed by EDS Spectroscopy (model JMV 54175) between 0 and 10 kV.

2.3 Preparation of stock solution

All glassware was cleaned initially by soaking in acidified water (0.1M HCl) and washed carefully using tap water which followed by D.I water and acetone. A stock solution of Cr^{+6} metal ions of 0.1M was made via taking an appropriate quantity of $\text{K}_2\text{Cr}_2\text{O}_7$ in a 100 mL volumetric flask (acidified it with one drop of HCl (0.1M)) and filled up to the mark with D.I water. Serial dilutions were also made as per desire employed concentrations. H_2SO_4 (0.1M) stock solution was made in 50 mL which was further used for making up the complex solutions of Cr^{+6} with Diphenyl carbazide (DPC) in the series. For this purpose, 25% DPC was taken into service by making in 100 mL of volumetric

flask for complexation. Priory 0.257 g of DPC was dissolved in 50 mL of acetone and later made up it with D.I water up to the mark.

2.4 Preparation of biosorbents

Commercially available CL and CB were bought from the Metro super store of Karachi, Pakistan and were used directly without any reform. Both adsorbents were washed initially with plenty of tap water then rinsed with D.I water to remove the deposits of dust. The CB and CL were then desiccated in oven for overnight at 105 °C. Dehydrated adsorbents were grinded in grinder to acquire a larger surface area and then sieved (20 to 200 µm) to attained the same particle size of adsorbents throughout the testing because variable particle sizes may influence the result [48]. Different particle sizes of adsorbents by (20, 50, 100 and 200 µm size) were separated through the concerned sieve to select the favorable particles size for maximum adsorption.

2.5 Biosorption procedure

At ambient temperature, the percent biosorption was examined onto both of adsorbents by using the batch technique. The fixed amount of adsorbents CL and CB were added separately into 25 mL of Cr⁺⁶ metal ions solution of 0.1 M concentration in an Erlenmeyer flask. These mixtures were shaken thoroughly in electrical shaker for particular time (30 min) with a rotating speed of 120 rpm. After that mixture was filtered using wattman filter paper (1442—25 ashless grade 42 with 12.5 cm and 2.5 µm pore size) through suction pump. Finally, the un-adsorbed concentrations of Cr⁺⁶ metal ions were measured by making complex with a fixed amount of DPC. Solutions were made up with H₂SO₄ (0.1M) up to the mark [3]. The results were analyzed by Visible spectrophotometer at 540 nm. All the experiments were repeated in triplicate manner and mean values were used for calculations and displays.

2.6 Analysis of Cr⁺⁶ metal ions solution

The un-adsorbed concentration of Cr⁺⁶ metal ions in the supernatant liquid sample (after filtration) was analyzed by the Visible spectrophotometer through DPC assay. The difference in concentrations from original to obtained is measured by the support of the following equation;

$$q_t = V(C_o - C_e) / M \quad (1)$$

whereas q_t (mg/g) is the Cr⁺⁶ metal ions up taking power of adsorbents after a certain time, V (L) is the volume of Cr⁺⁶ metal ions in solution in contact with the biosorbents,

C_o and C_e (g/L) are the initial and remaining concentration of Cr⁺⁶ metal ions respectively and M (g) is the extent of adsorbents used throughout the experimentation.

However, the deletion percentage of Cr⁺⁶ metal ions from the solution were measured as;

$$\%R = C_o - C_e / C_o \times 100 \quad (2)$$

while R is the deduction percentage of Cr⁺⁶ metal ions from the mixture solution, C_o and C_e (g/L) are the concentrations at initial level and after achieving equilibrium respectively.

2.7 Zero-point charge determination

For determination of zero-point charge (ZPC), NaCl of 0.01 M as an electrolyte added in HCl/NaOH (0.1 M) solutions. Tests were performed by introducing 25 mL of electrolyte into the 10 beakers and later the initial pH was maintained to the required values in the range of 2–12. Optimized amounts of CL and CB were added into each beaker separately and kept for 48 h under agitation. After 48 h, the adsorbents were filtered and measured the final pH of each beaker. The graph was plotted between final against initial pH to get the ZPC of each adsorbent [51].

3 Results and discussion

3.1 Biosorption studies

3.1.1 Particle size

To analyze the influence of particle size of biomasses for adsorption of Cr⁺⁶ metal ions, different mesh sizes were checked for getting maximum adsorption. Experiments were done on 20, 50, 100 and 200 µm sizes of both biosorbents i.e. CL and CB. Results presented that uptake of Cr⁺⁶ metal ions were gradually increased from larger to smaller size of adsorbents particles. It means as particle size reduces the system got a greater surface area for biosorption with reduction in the external mass transfer resistance. Experimental outcomes shown the best result were collected at the 20 µm size of both adsorbents particles Fig. 1a.

3.1.2 Adsorbents dose

The adsorbent quantity is an essential element, which encourages metal ions up take from the original concentration caused by the availability of unoccupied tie positions. In present research effect of adsorbent doses were supported to find out the optimum adsorption of Cr⁺⁶

Fig. 1 Optimized parameters **a** Particle size variation **b** Effect of Adsorbents **c** Effect of Adsorbate **d** Effect of Contact & Stirring Time **e** Effect of pH **f** Effect of Various Temperature with respect to time **g** Zero-point charge CL and CB

metal ions with a changeable quantity of CL and CB from 0.424 g/L & 0.468 g/L to 10.020 g/L & 8.812 g/L respectively at optimized conditions. The amount of Cr^{+6} metal ions bio-sorption increases from 21.6 to 53.5% and 30 to 76.5% for CL and CB as shown in Fig. 1b respectively. The results revealed that the percent adsorption of Cr^{+6} metal ions risen as per the amount of adsorbent increases till a maximum plateau of adsorption was attained. It may have caused by the restricted accessibility of adsorbing specie for a greater surface sites of adsorbent [8]. However, in contrary conditions high adsorbent dosage begun screening effect and shielded the binding sites of adsorbent [13, 40]. The greatest adsorption was noted at 7.6 g/L and 6.4 g/L of CL and CB respectively.

3.1.3 Adsorbate concentration

The biosorption of Cr^{+6} metal ions on CL and CB were between the concentrations of $8.4429\text{e-}4$ to $6.207\text{e-}3$ (g/L). While the applied concentrations of herbs were 5.2 g/L and 6.0 g/L for CL and CB respectively. The adsorption ability decreases from 50.52 to 28.91% and 63.41 to 60.66% for CL and CB Fig. 1c. These results exposed the progressive decline in the electrostatic communication in the middle of adsorbate and active locations of adsorbents. As Cr^{+6} metal ion concentration increases the power of adsorption decreases due to less adsorption situations. Hence, smaller numbers of available surface sites decline the adsorption volume [30].

3.1.4 Contact time

Deduction of Cr^{+6} metal ions adsorption was improved by the rise of interaction time of adsorbate and adsorbent from 5 to 100 min. Each mixture of metal ion solution with CL and CB acquires equilibrium at 90 and 66 min with 69.01 and 76.52% of adsorption efficiency respectively. The deduction of Cr^{+6} metal ions from aqueous solution was found to be time dependent behavior, when all further parameters were kept constant. As an economical fact of view, these effects shown excessive significance for wastewater treatment.

3.1.5 Stirring time

The outcomes described the variation in adsorption arisen at different time intervals from 5 to 100 min at constant similarity as above. Optimum adsorption of Cr^{+6} metal ions was at 60 and 55 min with 66.96 and 77.5% for CL and CB. Rapid and progressive change appeared in adsorption process which reveals that equilibrium has achieved fast with stirring during the equal time intervals Fig. 1d.

The above results also shown that the nonstop stirring facilitate the active sites for adsorption of Cr^{+6} metal ions process. The results displayed that the steadiness between adsorbate and adsorbent has attained rapid during stirring time as related to simple interaction time.

The abstraction of Cr^{+6} metal ions by biosorption procedure during mechanical stirring may follows the metal ions travel from the bulk of the solution to adsorbent surface mechanism more swiftly. This may lead to metal ion transmission was occurred from next to the periphery surface layer of the adsorbent and Intra-particle diffusion of metal ions occurred into the internal stomas of adsorbent [7].

3.1.6 pH

Most favorable adsorption of Cr^{+6} metal ions examined by regulating pHs. Difference in pH is directly influencing the competitive power of H^{+} ions with metal ions for the active empty sites of the absorptive surface [50]. The significance of pH on the adsorption of Cr^{+6} metal ions for both CL and CB were studied between the range of 1 to 11. Results are indicated, that maximum adsorption was achieved at acidic pH 1.6 and 2.7 at 99.42 and 99.51% adsorption of CL and CB Fig. 1e.

As per reported in literature that the acidic medium following species of chromium were coexisted i.e. HCrO_4^{-} , CrO_4^{2-} , $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ and $\text{Cr}_2\text{O}_7^{2-}$ but only $\text{Cr}_2\text{O}_4^{2-}$ is stable and existed at above 8 pH so if the pH decreases the equilibrium shifts to dichromate [42].

Thus at extremely low pH these species are at risk to adsorb on the dynamic protonated positions of adsorbent [18, 53].

According to the literature survey of plants, they contain a great range of functional groups like phenol and alcohol [11]. However, in acidic medium the phenolic group of bio-sorbent become protonated due to electrostatic force of attraction and may interact with the HCrO_4^{-} ions. Therefore, according to results, it shows that the chemisorption process may have occurred at higher acidic pHs. While at higher pHs the bio-sorbent's surface may have becomes more negative, which creates repulsion between surface and HCrO_4^{-} ions and down the rate of adsorption [29].

3.1.7 Temperature variation with time

The influence of temperature by varying time is another non neglected factor because it provides information related to the surface interaction nature of adsorbent and adsorbate. For this purpose, experiments of percent

adsorption of Cr^{+6} metal ions done by altering temperature from 10 to 50 °C at comparable time breaks from 10 to 60 min. Consequently, the percent adsorption of metal ions increased from 26.57 to 76.64% and 41.22 to 87.59% for CL and CB respectively as temperature and varying time periods increased from lower to higher range. Early attainment of equilibrium exposes the adsorption route of Cr^{+6} metal ions is endothermic in manner [1].

By the rise of temperature, process of adsorption increases, which can be due to increase of strong interaction forces between adsorbent and metal ions. These obtained results also supported the chemisorption process, as similar behavior was also supported by earlier workers Fig. 1f.

3.1.8 Zero-point charge (ZPC)

Initial pH of CL and CB moves from 12.10 and 12.19 to 11.07 and 11.01 correspondingly, implying that both of adsorbents have a positive surface charge. It means they were acidic in a form which directly attract or adsorb the negative ions from the solution and reduces its pH from high to low.

The point of transition of the adsorbent material where the surface charge becomes negative from positive i.e. The point where it turns from acidic to basic and at this point the charge of the surface will be zero. According to experimental results 6.32 and 6.54 are points of transition for CL and CB Fig. 1g.

3.1.9 Characterization

The FTIR measurement were carried out to assess the participated biomolecules of CL and CB which are responsible for Cr^{+6} metal ions bio-sorption. The key frequencies of vibrations and their comparable groups that associated to Cr^{+6} metal ions are directed in Table 1.

It seems that there were some deviations in absorption peak frequencies between free and Cr^{+6} loaded infrared spectrum. The noticeable shift scene at the site of $-\text{OH}$ and $-\text{NH}_2$ stretching vibrational group ranging from 3290 and 3336 to 3330 and 3335 cm^{-1} in CL and CB. While CL showed a slight change in peak from 1436 to 1418 cm^{-1} because of a minor association with $\text{C}-\text{OH}$ bending group. CB exposed another change from 1248 to 1242 cm^{-1} . This can also attribute to the stretching vibration of the $\text{C}-\text{OH}$ group. These transfersals proposed that there was a typical procedure happened amongst ionizable functional groups and Cr^{+6} metal ions. Therefore, the strong shift in peak locations of $-\text{OH}$ and $-\text{NH}_2$ stretching, vibration indicated that Cr^{+6} metal ions was interected by carboxyl, hydroxyl and amide functional groups present on the outside surface of both adsorbents. Nevertheless, remaining differences in peaks shifting among all three adsorbents revealed the diverse levels of degree of association Fig. 2.

Moreover, the SEM images of CL and CB before adsorption show the bearing of many empty seats and tiny holes on the surface. Since high surface area and porous structures were the basic parameters for an effective adsorbent. However, after treatment with Cr^{+6} metal ions the vacant places of adsorbent were filled [2, 6, 33] (Fig. 3a–d).

The localized elemental information of both adsorbents CL and CB determined by EDX analysis (Fig. 3e–h). The obtained spectrum results showed the presence of Cr^{+6} metal ions in treated sample which indicates the successful adsorption of Cr^{+6} metal ions. However, presence of the other small metal ions impurities may have arisen due to the number of other plant constituents [3].

3.1.10 Adsorption isotherms

Isotherms are prerequisite requirement which are needed to understand the adsorption mechanism [26]. The observational data with various temperatures of each adsorbent were analyzed to understand the adsorption manner of

Table 1 Main frequencies of vibrations and their corresponding groups

S.No	<i>Cinnamomum leaves</i>		<i>Cinnamomum bark</i>		Bonds indicative
	Controlled (cm^{-1})	Cr^{+6} loaded (cm^{-1})	Controlled (cm^{-1})	Cr^{+6} loaded (cm^{-1})	
1	3290	3330	3336	3335	R-OH group or $-\text{NH}_2$ group
2	2920	2921	2917	2917	CH- symmetric and asymmetric stretching
3	2360	2360	2360	2360	stretching vibrations of $-\text{NH}_2^+$, $-\text{NH}^+$ and $-\text{NH}$ groups of biomass
4	1615	1615	1635	1636	$\text{C}-\text{COO}-$ and $\text{C}=\text{C}$ stretching associated to the aromatic bond
5	1436	1418	1456	1457	$\text{C}-\text{OH}$ bending and stretching vibration of phenols respectively
6	1015	1015	1034	1038	CO vibration of alcoholic group
7	–	–	1733	1732	stretching vibration of $-\text{CO}$ of carboxylic group
8	–	–	1158	1157	CN stretching vibration of amine

Fig. 2 FTIR Spectrum **a** Unloaded and loaded Cr^{+6} CL **b** Unloaded and loaded Cr^{+6} CB

the finest fitted theoretical model. The data was collected at room temperature, 10°, 20°, 40° and 50 °C. All temperatures were used to calculate Langmuir Fig. 4 and Freundlich Fig. 5 isotherms to get comparative analysis.

Following is the linearized Langmuir isotherm equation was utilized.

$$\frac{C_e}{x/m} = \frac{1}{q_m} C_e + \frac{1}{q_m \cdot K_L} \quad (4)$$

Here, $\frac{x}{m}$ is the extent of Cr^{+6} metal ions adsorbed for every unit mass of the adsorbent. C_e is the equilibrium concentration of Cr^{+6} metal ions. While, q_m is the single layer capacity that deals with the saturated amount of Cr^{+6} metal ion in solid phase. However, K_L is the constant for Langmuir binding. The measures of q_m and K_L were assigned by the slopes and intercepts of linear plots between $\frac{C_e}{x/m}$ and C_e . Moreover, values of K_L indicated the greater adsorption aptitude of bio-sorbents towards metal ions [4].

For calculation of the Freundlich isotherm following linearize equation was used.

$$\log \frac{x}{m} = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where $\frac{x}{m}$ or q_e is the quantity of adsorption over each gram of adsorbent and C_e is the concentration at equilibrium of metal ions. K_F and $\frac{1}{n}$ are the empirical constant associated to sorption capability and strength of Freundlich isotherm individually. They rely on the parameters of adsorbate, adsorbent, pressure and temperature. The isothermal diagram between $\log \frac{x}{m}$ and $\log C_e$ shows a straight line with positive intercepts and slopes. Values of constant parameters of both aforementioned adsorption isotherms were listed in Table 2.

3.1.11 Thermodynamic parameters

Thermodynamic factors, the enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°) in adsorption are useful tools to define the nature of the adsorption mechanism whether it is endothermic or exothermic. These limits were calculated with the following equation,

$$\ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

$$K_c = \frac{C}{C_e} \quad (8)$$

where, K_c is the constant of equilibrium, C (mg/L) is the adsorbent concentration while C_e (mg/L) is the concentration of adsorbate at equilibrium condition. R is the gas constant and T is the temperature in Kelvin. ΔH° and ΔS° values were calculated by the help of slopes and intercepts as in Table 3. There were gradual increases in the K_c values as temperature intensify which revealed the endothermic character of adsorption for both biosorbents Fig. 6. The negative figures of free energy (ΔG°) indicated that it was a spontaneous process and no energy barrier in sorption process was involved. The values of ΔG° came to be more negative as temperature increases, which pointed towards greater driving force. These results exhibited the highest adsorption volume as temperature growths. The activation of adsorbent surface or enlargement of pore size attributed greater adsorption capacity at greater temperature [35].

Similarly, the plus values of ΔH° indicated the bio-sorption manner was endothermic. It occurs spontaneously only when entropy of the system increases and the values of ΔH° are lesser than $T\Delta S^\circ$ values. ΔS° values are positive which confirmed the increase in randomness with the addition of temperature at the solid surface and Cr^{+6}

Fig. 3 SEM results of **a, b** controlled and sample of CL and **c, d** controlled and sample of CB respectively. EDX results of **e, f** controlled and sample of CL and **g, h** controlled and sample of CB correspondingly

metal ions solution border throughout adsorption phenomenon [5].

For the adsorption of Cr^{+6} metal ions on adsorbents, the change in activation energies were estimated via following Arrhenius equation:

$$\log K_d = \log A - (E_A / 2.303 RT) \quad (9)$$

where K_d is the sorption rate constant (g/mol s), E_A is the energy of activation (J/mol), A is the Arrhenius factor (g/mol s), R is the gas constant (J/K mol) and T is the

temperature. Activation energy values shown the chemical forces are regarded in the sorption process and probability of the mechanism Fig. 7. The values of its constant elements are prescribed in Table 4.

3.1.12 Kinetic modeling

Kinetic mechanism of adsorption was investigated by Lagergren's, kinetic representations for pseudo-first and pseudo-second order Fig. 8a, b. The experimental data

Fig. 3 (continued)

for both adsorbents were used to predict the adsorption kinetics. It was tested by the following equations;

For pseudo first order reaction, the equation is

$$\log(q_e - q_t) = \log q_e - K_1/2.303 \quad (10)$$

For pseudo second order reaction, the equation is

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (11)$$

where K_1 for pseudo first order and K_2 for pseudo second order rate constants. At time t (min) the quantity of

Fig. 4 Langmuir Isotherm for CL and CB

Fig. 5 Freundlich Isotherm for CL and CB

sorption is q_t (mg/g) whereas, q_e (mg/g) is the amount of sorption at equilibrium. In pseudo first order the chart was designed between $\log(q_e - q_t)$ and t while in pseudo second order, it was in between t/q_e and t . Adsorption kinetics were investigated with the fixed concentration of Cr^{+6} metal ions solution and bio-sorbents dose. Sample mixtures were kept for 5 to 100 min with different breaks of time, as mentioned in Table 5. The summarized results of estimating values of equilibrium sorption capacities (q_e) for CL and CB, do not agree with the experimental values in front of a pseudo first order. However, the determined quantities of equilibrium sorption capacities in pseudo

second order plot have shown worthy agreement with the experimental values for the same sorbents respectively.

To excuse the second order kinetics, Elovich equation was employed by assuming actual solid surfaces to be energetically heterogeneous Fig. 9a. Elovich equation is expressed as

$$q_t = \alpha + \beta_E \ln t \quad (12)$$

where α is the preliminary adsorption rate (mmol/g.min) and β_E is associated with the energy of activation for chemisorption and degree of surface exposure (g/mol). Elovich equation is simplified by; if $\alpha \cdot \beta_E t \gg 1$ and taking into account, the boundary environments $q_t = 0$ at $t = 0$, the calculation improves as,

$$q_t = \frac{1}{\beta_E} \ln(\alpha \beta_E) + \beta_E \ln t \quad (13)$$

Validity of Elovich equation was tested by plotting values of q_t verses $\ln t$. If a straight line is obtained, the parameter β_E is estimated from the gradient of the slope and the intercept of the line made the value of initial sorption rate α . If Elovich equation is valid, it favors the assumption that chemisorption mechanism can describe adsorption rate as represented in Table 5.

According to Weber Morris Equation,

$$q_t = k_i \sqrt{t} + C \quad (14)$$

The Intra- particle diffusion step controls the degree of adsorption and the up taking of adsorbate differs with the square root of contact time. Therefore, adsorption proportions often calculate for values of adsorption capacities as a function of the square root of interaction time Fig. 9b. Where k_i is the intra-particle diffusion constant and C is a measure of the thickness of the borderline film.

Table 2 Constant parameters of Langmuir and Freundlich adsorption isotherms

Adsorbents	Temperature	Langmuir Isotherm			Freundlich Isotherm	
		q_m (mg/g)	KL	RL	n	KF (mg/g)
CL	Room	11.331	-0.633	1.000	1.299	8.68E-01
	10 °C	1.666	-3.074	1.000	0.480	4.03E-11
	20 °C	4.500	-6.222	1.000	1.096	8.48E-05
	40 °C	6.343	-10.911	1.000	1.791	7.50E-03
	50 °C	6.663	-11.881	1.000	1.904	1.15E-02
CB	Room	17.320	-1.231	1.000	1.124	1.74E+01
	10 °C	10.716	-3.310	1.000	1.052	2.21E-09
	20 °C	17.484	-6.455	1.000	1.876	3.59E-07
	40 °C	26.855	-19.302	1.000	4.787	2.19E-05
	50 °C	26.064	-19.580	1.000	3.992	1.26E-05

Table 3 Values of ΔG° , ΔH° and ΔS° at various temperatures with different adsorbents

Thermodynamics											
Adsorbents	Temperature	10 min		20 min		30 min		50 min		60 min	
		ΔG°		ΔG°		ΔG°		ΔG°		ΔG°	
CL	10 °C	−1.22	ΔH°	−3.53	ΔH°	−6.00	ΔH°	−7.04	ΔH°	−8.34	ΔH°
	20 °C	−19.73	145.05	−20.95	135.77	−21.84	154.41	−23.74	226.49	−25.37	−316.37
	40 °C	−22.58	ΔS°	−24.60	ΔS°	−27.50	ΔS°	−34.82	ΔS°	−49.37	ΔS°
	50 °C	−25.80	0.54	−26.42	0.51	−31.62	0.58	−42.90	0.84	−53.54	1.16
CB	10 °C	−19.69	ΔH°	−26.61	ΔH°	−28.78	ΔH°	−36.26	ΔH°	−37.39	ΔH°
	20 °C	−34.64	214.72	−38.83	207.61	−43.08	239.17	−48.19	274.14	−53.48	267.15
	40 °C	−49.28	ΔS°	−55.52	ΔS°	−59.39	ΔS°	−67.16	ΔS°	−68.94	ΔS°
	50 °C	−53.76	0.84	−59.57	0.83	−68.02	0.95	−81.76	1.10	−83.70	1.08

Fig. 6 Thermodynamic plots at different time periods **Fig. 7** Graphical representation of Arrhenius Equation at different time periods

4 Conclusion

In this study, the optimizations and feasibility of different factors like variations of concentration, mass, stirring time and pH along with thermodynamic study and kinetic

Table 4 Values of Arrhenius Equation factors

Arrhenius equation			
Adsorbents	Time	A	E _A
CL	10 min	6.84E+02	1.45E+02
	20 min	5.01E+02	1.36E+02
	30 min	1.19E+03	1.54E+02
	50 min	2.68E+04	2.27E+02
	60 min	1.32E+06	3.16E+02
CB	10 min	2.73E+04	2.15E+02
	20 min	2.59E+04	2.08E+02
	30 min	1.11E+05	2.39E+02
	50 min	6.37E+05	2.74E+02
	60 min	5.37E+05	2.67E+02

modeling were investigated for the bio-sorption of hazardous Cr^{+6} metal ions. Therefore, the rate of adsorption of Cr^{+6} metal ions decreases as a result of gain in the initial adsorption of solution, while the opposite trend was attained in the case of removal of metal ion from aqueous solution due to the presence of specific adsorption places of both bio-sorbents i.e. CL and CB. In case of variable dose of both adsorbents vices versa tendency obtained due to the gradual increase in adsorption sites with fixed Cr^{+6} metal ion concentration. However, lower than 3 pH of solution shows the appreciable amount of adsorption. In the considered Cr^{+6} metal ion concentration range, biosorption capacities raised with growing initial Cr^{+6} metal ion concentrations and temperatures. In

Fig. 8 **a** Pseudo first Order Kinetics **b** Pseudo Second Order Kinetics

the isotherm models dual parameters were worn to report mathematically the biosorption equilibrium of Cr^{+6} metal ions to CL and CB. It was realized that the biosorption equilibrium data contoured mutually well to Langmuir and Freundlich isotherms. The appropriateness of the Kinetic study, pseudo-first-order, pseudo-second order, intra particle diffusion and Elovich plot for the biosorption of Cr^{+6} metal ions onto CL and CB were scrutinized. The pseudo-second-order kinetic model agrees very well with the dynamical performance for the biosorption of Cr^{+6} metal ions against CL and CB. Results of ΔG° , ΔH° and ΔS° displayed the adsorption is possible, which is spontaneous, endothermic and irreversible in manner under the examined conditions. Hence, between both *Cinnamomum Verum* leaves and bark the percent adsorption discloses that bark has a greater tendency for the elimination of Cr^{+6} metal ions as compare to its leaves.

Table 5 Values of constant parameters of Pseudo first order and Pseudo Second order along with Intra particular diffusion and Elovich Plot

Kinetic modeling										
Adsorbents	Temperature	Pseudo 1st order		Pseudo 2nd order		q_e (exp)	Intra particle diffusion		Elovich plot	
		K_1	q_e	K_2	q_e		C	K_p	α	β
CL	Room	8.35E-03	8.13E-06	1.32E+04	1.24E-05	1.57E-05	6.26E-06	5.92E-07	4.52E-06	1.59E-06
	10 °C	3.09E-03	1.15E-05	3.07E+04	6.51E-06	1.57E-05	3.40E-06	3.59E-07	2.17E-06	9.69E-07
	20 °C	-3.80E-03	6.02E-06	5.24E+04	8.95E-06	1.57E-05	7.16E-06	1.94E-07	6.62E-06	4.88E-07
	40 °C	1.20E-02	9.31E-06	8.54E+03	1.26E-05	1.57E-05	5.26E-06	7.35E-07	3.36E-06	1.80E-06
	50 °C	1.37E-02	9.16E-06	7.79E+03	1.33E-05	1.58E-05	5.36E-06	8.00E-07	3.26E-06	1.97E-06
CB	Room	9.45E-03	1.67E-05	7.27E+03	3.46E-05	4.07E-05	2.02E-05	1.46E-06	1.55E-05	4.04E-06
	10 °C	5.49E-03	2.27E-05	1.20E+04	2.56E-05	4.07E-05	1.52E-05	1.22E-06	1.24E-05	2.95E-06
	20 °C	7.41E-03	1.76E-05	1.19E+04	3.08E-05	4.07E-05	2.07E-05	1.14E-06	1.83E-05	2.69E-06
	40 °C	8.27E-03	1.25E-05	1.87E+04	3.39E-05	4.07E-05	2.61E-05	9.31E-07	2.40E-05	2.25E-06
	50 °C	1.39E-02	1.18E-05	1.38E+04	3.67E-05	4.07E-05	2.62E-05	1.26E-06	2.34E-05	3.03E-06

Fig. 9 **a** Elovich plot **b** intra particle diffusion

Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

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