

## EFFECTIVE CHROMIUM (VI) REMOVAL FROM CONTAMINATED WATER BY CHEMICALLY MODIFIED *LITCHI CHINENSIS* SEED POWDER: CHARACTERIZATION, KINETIC AND ISOTHERM STUDIES

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### Abstract

In this work, Litchi chinensis seed powder has been chemically modified to charred Litchi chinensis seed powder (CLCS) for removal of Cr(VI) from the simulated wastewater. The adsorption capacity of CLCS for Cr(VI) was determined in batch experiment method. The materials were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), and fourier transform infrared (FTIR) spectroscopy. Biosorption behaviour was investigated using isotherm and kinetic models. CLCS demonstrated a noteworthy adsorption capacity for Cr(VI), with a maximum adsorption capacity of 69.93 mg/g at pH 2.0. The Cr(VI) adsorption onto CLCS was found to follow pseudo-second-order kinetics and the experimental data best fitted with Langmuir isotherm model. According to the results, Cr(VI) can be removed from acidic wastewater using CLCS as an adsorbent. The results indicate that further studies and modification are necessary to improve the efficiency of the CLCS, and its feasibility at normal pH conditions.

Keywords: Adsorption, Biosorbent, Hexavalent chromium, Litchi seed, Wastewater treatment

DOI: <https://doi.org/10.3126/ije.v12i2.65442>

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## 1. Introduction

Water pollution is a global concern, causing detrimental impacts on human health (WHO & UNICEF 2000; Georgaki & Charalambous, 2023). Direct discharge of effluents, chemical exposure, suspended particles, and oxygen depletion are the main pollutants of water. Heavy metals make up the majority of chemical pollutants and are one of the main causes of water pollution due to their toxic properties and carcinogenicity (Miao et al., 2015). Consumption of heavy metals beyond the bio-recommended limit results in adverse health consequences known as heavy metal bio-toxicity (Verma, 2017). Because they tend to bioaccumulate, heavy metals are hazardous. Heavy metals can enter a water system through a variety of channels, including industrial and consumer waste, and acid rain, which decomposes soil and discharges heavy metals into streams, rivers, lakes, and groundwater. Lowered energy levels, allergies, altered blood chemistry, and inflammation in the liver, kidneys, lungs, and other crucial organs are all possible effects of heavy metal poisoning. Prolonged exposure can cause gradually developing physical, muscular, and neurological disorders. Multiple prolonged exposures to some metals may potentially cause cancer (Verma, 2017).

Chromium is among the most found heavy metals in wastewater. This metal comes in contact with drinking water due to natural as well as anthropogenic causes. Natural causes can be erosion or geochemical phenomena whereas, anthropogenic causes include industrial sources such as fertilizers and pesticide production, alloying, dying, tanneries, and electroplating (Mahmoud, 2020; Suganya et al., 2019). Among various valency states of chromium, trivalent and hexavalent chromium are the most common (McNeill et al. 2012; Moffat et al., 2018). Cr(III) is a vital essential element, but Cr(VI) is harmful, as it may have a key role in the body's respiratory, digestive, urinary, gastrointestinal, immunological, and reproductive dysfunctions (Georgaki & Charalambous, 2023). The USEPA has set a 0.1 mg/L permissible contamination limit for total chromium (VI) in drinking water (USEPA, 2002), and the limit is 0.05 mg/L according to WHO (Cotruvo, 2017).

Adsorption, ion exchange, redox reaction, and membrane technology are a few of the techniques being researched and utilized to remove toxic heavy metals from the aqueous environment (Abdel-Galil et al., 2021; Labied et al., 2018; Ortega et al., 2017; Abejon et. al., 2015). However, because of the need for costly equipment, lack of sensitivity, poor removal efficiency, and other factors, most of the preceding remedies can only be employed to a certain extent (Aryal et al., 2022; Aryal et al., 2019; Homagai et al., 2023; Saha et al., 2011). The adsorption method has become increasingly common due to the accessibility of less expensive components to produce inexpensive adsorbents (Bingol et al., 2004; Bashyal et al., 2023; Poudel et al., 2024). Agricultural residues (peels, seeds, husks, etc.) are discovered to have ion exchange and adsorptive abilities since they are rich in several functional groups. Also, they are cheap and readily available. Both their raw and modified forms can be used as efficient biosorbents. Our research group has reported

several other studies on the Cr(VI) sequestration using different biomass such as pomegranate peels (Rai et al., 2023) and Arundo donax stem (Bhattarai et al., 2022). The authors hypothesize that litchi seed, an abundant biowaste, also can be modified to an efficient adsorbent for removing pollutants from water. The raw biomasses in the previous studies did not show a significant adsorption capacity, but their efficiency improved after they were treated with an acid. This might be due to the ring opening of the surface functional groups present. In reference to previous studies, raw biomass has been modified to CLCS using conc. H<sub>2</sub>SO<sub>4</sub>. The present study aims to broaden the understanding on the efficacy of easily available biomass such as agricultural wastes for the adsorptive removal of Cr(VI) from wastewater. It is anticipated that the results obtained will support the reports from similar studies reported earlier. Additionally, H<sub>2</sub>SO<sub>4</sub> treatment may promote Cr (VI) removal. The objective of the study was to synthesize charred biomass derived from Litchi chinensis seed to investigate its effectiveness in eradicating Cr(VI) from aqueous solution. The study aimed to investigate the discrepancy in the biosorption behaviour of the biomass at variable pH, adsorbent dose, and contact time, followed by a study on the reusability of the spent biosorbent.

## **2. Methods**

### **2.1. Preparation of solution**

Most of the chemicals were of the analytical-grade (AR) grade and were utilized without further purification. Calculated amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> crystals were dissolved in deionized (DI) water to make the stock solution of Cr(VI), which were further subjected to dilution process to obtain working solutions.

### **2.2. Preparation of adsorbent**

Lychee seeds were collected from Kalimati, Kathmandu, and were washed several times before drying in daylight for two weeks. The dry seeds were ground and separated to obtain a fine powder of 120 µm particle size. The powder was then referred to as raw Litchi chinensis seed powder (RLCS). Furthermore, three-fourths of the dry RLCS powder were treated with conc. H<sub>2</sub>SO<sub>4</sub> at a 1:2 g/mL ratio (solid: liquid). The acid alteration of the RLCS creates ideal circumstances for the opening of the cellulose ring in the sorbent, which is high in cellulose content. Additionally, this results in adequate micro-porosity and increases the surface area (Homagai et al., 2010). The charred RPP was washed until neutral pH, dried, and further sieved to 120 µm and was named as (charred Litchi chinensis seed powder) CLCS.

### **2.3. Adsorbent characterization**

The salt titration method was employed using different concentrations of NaCl to evaluate the point of zero charge (pH<sub>PZC</sub>) of CLCS. SEM (JEOL, JSM-6701F, Japan) images were used to investigate the morphology of RLCS, CLCS, and Cr(VI) adsorbed CLCS. The FTIR spectrometer (IR Affinity -1S-SHIMADZU

spectrometer, Kyoto, Japan) was utilized to examine the functionality of the biosorbents. Their crystal structures were studied using XRD pattern (X-ray diffractometer, Rigaku Co., Japan).

## 2.4. Batch biosorption tests

For the biosorption investigations of both RLCS and CLCS, 20 mL of a solution of known Cr(VI) content with 20 mg of the sorbent was used. To achieve equilibrium, the mixture was stirred for 24 hours at 140 rpm. The remaining Cr(VI) ion concentration was then determined from the filtrate after the solution had been filtered. A dual-beam UV-visible spectrophotometer (Labtronics, LT-2802, India) was employed to spectrophotometrically measure equilibrium and initial chromium(VI) concentrations. 1,5-Diphenylcarbazide (DPC) was used for measuring Cr(VI) in the solution. In an acidic media, DPC was added to Cr(VI) to form Cr(III)-DPCA (Diphenyl carbazone). Equilibrium data were obtained through batch adsorption tests at variable contact times, initial Cr(VI) concentration, and pH at room temperature. All experiments were accomplished in triplicate and the findings were represented as average.

Equations 1 and 2 calculated the biosorption capacity ( $q_e$ ) (mg/g) at equilibrium and percentage of biosorption (%A), respectively.

$$q_e = \frac{C_o - C_e}{M} \times V \quad (1)$$

$$\% A = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Here, 'Co' and 'Ce' in mg/L, denote the initial concentration and equilibrium time concentration of metal, respectively. 'M' in grams is the mass of the sorbent, and 'V' in liters is the volume of the solution (Hameed & Ahmad, 2009; Uzun et al., 2003; Poudel et al., 2022).

### 2.4.1 Biosorption kinetics

With a preliminary Cr(VI) concentration of ~20 mg/L and biosorbent dosage of 1 g/L, kinetic experiment of Cr(VI) adsorption onto SPP@Zr was performed. The pH was held constant at 2.0 during the experiment. The sample from each flask was filtered after a certain length of time, and the Cr(VI) concentration was analyzed. Calculations were made to determine the biosorption capacity of Cr(VI) at a certain time (t). The kinetics of the biosorption phenomenon were studied using pseudo-1st-order (PFO) and pseudo-2nd-order (PSO) kinetic models. PFO linear equation and PSO linear equation are represented by equations 3 and 4, respectively (Lagergren, 1998; Ho, 2006).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \times t \quad (4)$$

Here, 'qt' (mg/g) denotes the biosorption capacity at time 't', 'k1' (mg/g.min) denotes the pseudo-1st-order rate constant, and 'k2' (g/mg.min) denotes the pseudo-2nd-order rate constant (Ucun et al., 2003).

### 2.4.2 Adsorption isotherm

With a range of starting Cr(VI) concentrations (5 to 250 mg/L), a dosage of 1 g/L and solution pH of 2.0, a biosorption isotherm experiment was conducted. At 298 K, the flasks were swirled for 12 h. Following biosorption, samples were filtered, and the equilibrium Cr(VI) concentrations were analyzed. Cr(VI) adsorption behavior was modeled using the Freundlich and Langmuir isotherms. Freundlich isotherm describes the multilayer adsorption on sorbent's heterogeneous sites. This isotherm model is linearly expressed through Equation 5 (Freundlich, 1907)

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (5)$$

The Freundlich exponent, 'n', defines the intensity of adsorption, and the adsorption capacity is denoted by the Freundlich constant, 'KF' (mg/g).(L/mg) 1/n.

The monolayer adsorption on the adsorbent's surface is described by the Langmuir isotherm model. Equation 6 gives it a linear expression (Langmuir, 1916).

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{C_e}{q_{max}} \quad (6)$$

Here, 'q<sub>max</sub>' (mg/g) denotes the maximal biosorption capacity, and 'b' (L/mg) is the Langmuir constant.

### 2.5 Desorption studies

The effectiveness of the CLCS for biosorption was tested numerous times using a sorption-desorption cycle. The adsorbed quantity of Cr(VI) was intended to determine the equilibrium concentration. For this, 40 mL of chromium (VI) solution was mixed with 40 mg of CLCS and the mixture was agitated for 24 hours at optimum pH. After filtration, the residue was subjected to desorption by mixing it with 40 mL of 1.0 M NaOH solution and agitating the mixture for another 24 hours. Variable concentrations of sodium hydroxide were employed as an eluent for the study.

Equation 7 gives the percentage desorption (%D) of chromium.

$$\% D = \frac{A_d}{A_a} \times 100 \quad (7)$$

Here, 'Ad' is the amount desorbed whereas, 'Aa' is the adsorbed amount (mg/g) of metal ion (Paudyal et al., 2020; Poudel et al., 2021). Figure 1 revealed the adsorbent preparation method followed by the adsorption-desorption cycle.

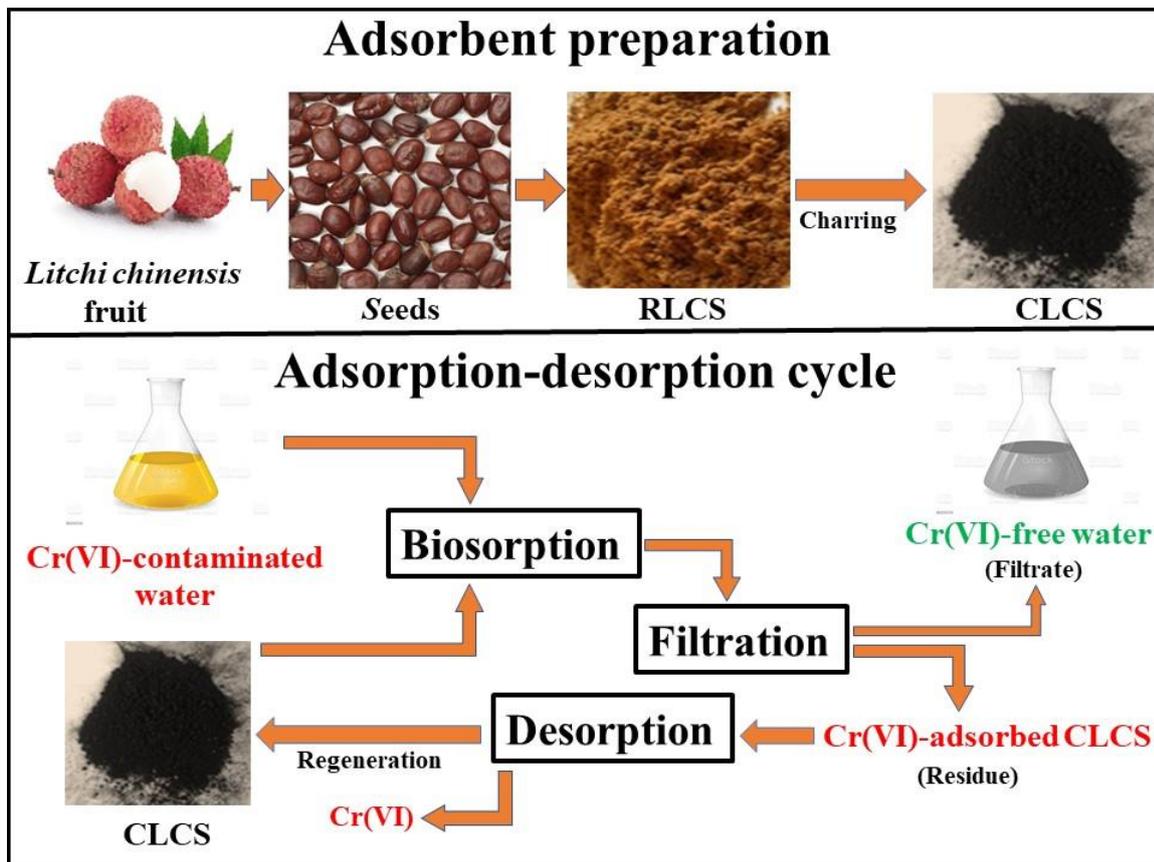


Figure 1: Flowsheet illustrating the biosorbent preparation and biosorption-desorption cycle.

### 3. Results and discussion

#### Characterization

Figure 2 illustrates the plots for the mass titrations using 0.01M, 0.05M, and 0.1M NaCl solution, demonstrating that the  $pH_{PZC}$  of CLCS is 4.0. The result signified that the biosorption of oxyanion of chromium species is favoured at a pH lower than 4.0. Whereas the cationic species are preferably adsorbed at pH conditions above the  $pH_{PZC}$  value (Bhattarai et al., 2022; Labied et al., 2018).

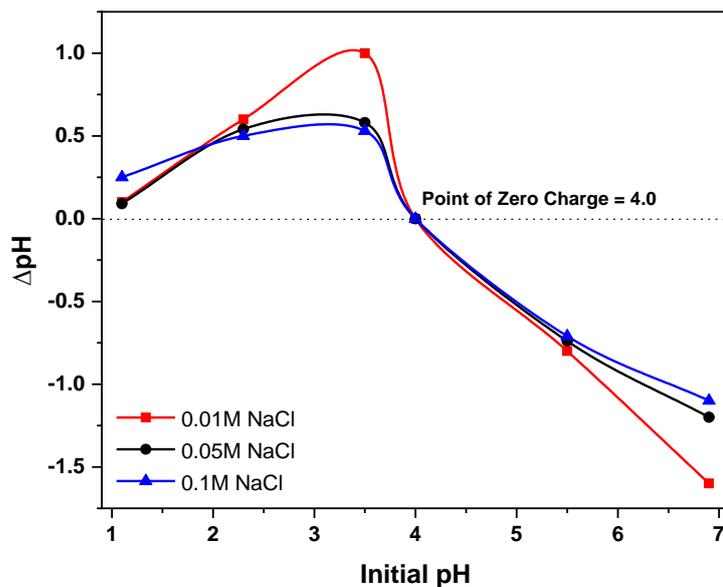


Figure 2: Determination of point zero charges (pHPZC) of CLCS using 0.01, 0.05, and 0.1 M NaCl.

Figure 3 illustrates the FTIR spectra of the raw, charred, and metal-adsorbed biosorbent. A broader peak at 3332.99 cm<sup>-1</sup> shows the existence of the -OH group in RCLS. It shifted to 3375.43 cm<sup>-1</sup> after charring and disappeared after Cr(VI) uptake. Peaks at 2924.09 cm<sup>-1</sup> in RCLS and 2920.23 cm<sup>-1</sup> in CLCS attributed to -CH stretching vibrations, which disappeared in Cr(VI)-adsorbed CLCS. A peak at 1620.21 cm<sup>-1</sup> in RCLS, shifting to 1589.34 cm<sup>-1</sup> in CLCS, and disappearing after metal adsorption can be correspond to C=O stretching vibrations (Rai et al., 2023). Furthermore, a peak at 1018.41 cm<sup>-1</sup> in RLCS shifted and slightly deformed in CLCS. The observed factors indicated the chemical modification of the adsorbent and successful Cr(VI) adsorption.

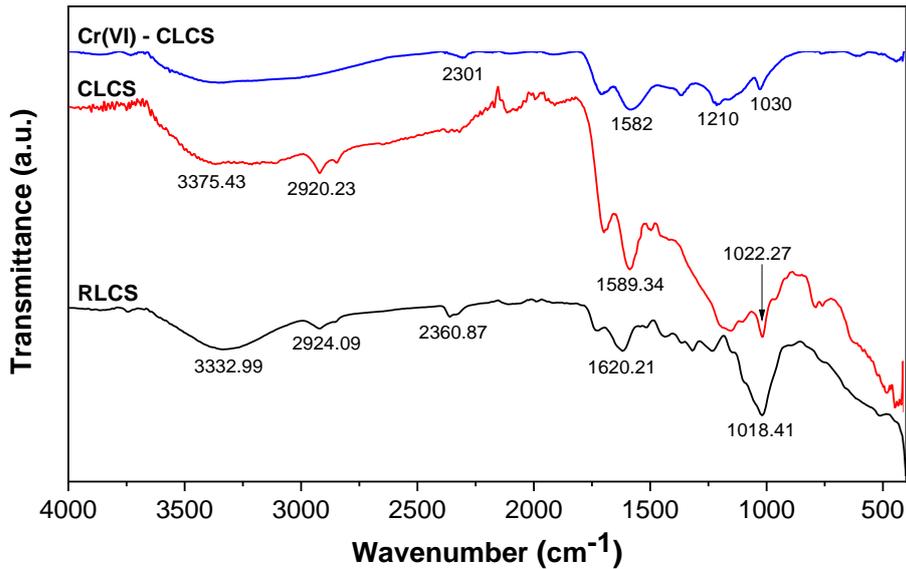


Figure 3: FT-IR spectra of RLCS, CLCS, and Cr(VI)-CLCS.

The SEM images of RLCS, CLCS, and chromium(VI) adsorbed CLCS are displayed in Figure 4. It was observed that the RLCS's uniform, smooth surface had much fewer pores and voids. In contrast, the charring process produced rough surfaces with larger pores and voids CLCS, which made the adsorbent more welcoming toward metal ions. The surface roughness of the metal-loaded CLCS was decreased due to Cr(VI) biosorption.

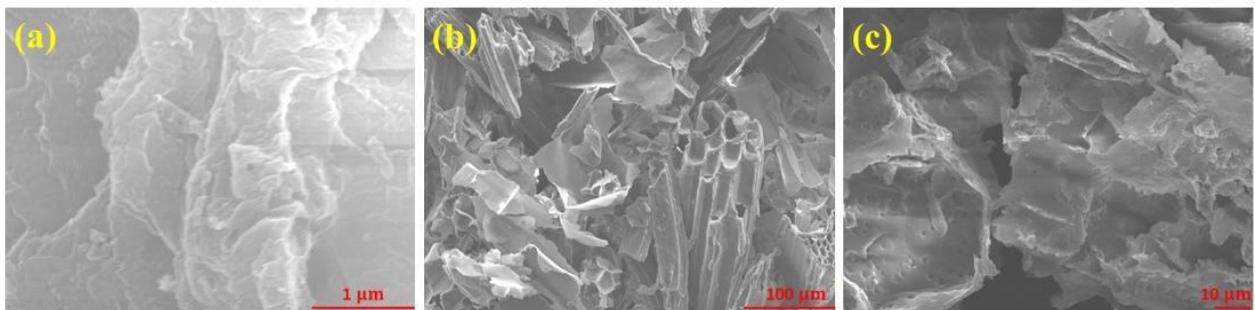


Figure 4: SEM images of RLCS (a), CLCS (b), and Cr(VI)-CLCS (c).

Figure 5 shows the XRD pattern of the adsorbents. A somewhat intense peak was observed at the 2-theta value of around 20° to 25° in RLCS, which signifies the occurrence of crystalline cellulose in the RLCS. Upon charring, the peak seemed to broaden, signifying the conversion of the crystalline structure to amorphous. The amorphous structure is more favorable for the uptake of Cr(VI). After chromium was adsorbed onto CLCS, the peak narrowed, which may have been caused by the sorbent's increased particle size.

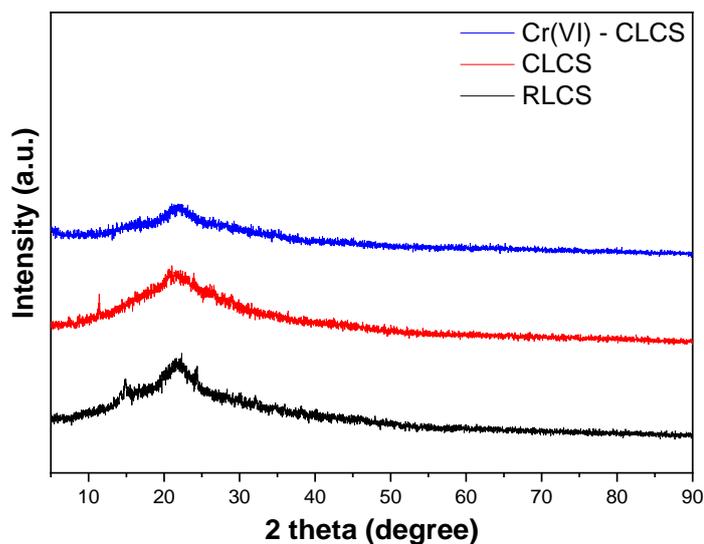


Figure 5: XRD diffractogram of raw, charred and Cr(VI)-adsorbed biosorbent.

### Effect of pH

The pH studies were performed by taking 20 mL of Cr(VI) solution with 20 mg of the RLCS and CLCS in conical flasks and maintaining preliminary pH values from 1.0 to 7.0, before adding the biosorbent. Each sample was shaken using a mechanical shaker at room temperature. The equilibrium pH was evaluated by utilizing a digital pH meter. The filtrate was utilized for the analysis of final Cr(VI) concentration. The removal rates of both the adsorbents rose from pH 1 to 2 but subsequently fell as pH climbed further, indicating the value of 2 as the ideal pH. The maximum Cr(VI) elimination at the optimal pH is shown in Figure 6 to be 19.9% for RLCS and 70.3% for CLCS. Further research was done for the charred adsorbent only because there is a significant difference between the removal efficacies of RLCS and CLCS. In acidic circumstances, chromium is typically found as anions, such as  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ , or  $\text{HCr}_2\text{O}_7^-$ . More particularly, when the pH rises, the primary form of  $\text{HCrO}_4^-$ , which is found in solutions with pH values between 1 and 3, is changed to  $\text{CrO}_4^{2-}$  and  $\text{HCr}_2\text{O}_7^-$ . The key difference is that the adsorbent surface can more readily absorb  $\text{HCrO}_4^-$  because it has larger adsorption energy than the other two forms (Ball & Nordstrom, 1998; Rai et al., 2021). Thus, it can be concluded that the biosorption efficiency for biosorbent is substantially linked to the sorption of  $\text{HCrO}_4^-$ . Additionally, Cr(VI) ions and  $\text{OH}^-$  ions compete for adsorption sites on adsorbent surfaces when pH of a solution rises. This rivalry reduces the adsorbent's ability for absorption and hinders the adsorption capacity. Similar results for the hexavalent chromium removal using bio-adsorbents have been reported in previous studies with the optimum pH being 2.0 (Bhattarai et al., 2022; Pant et al., 2022; Rai et al., 2021). The pH of 2.0 was fixed for the experiments that followed.

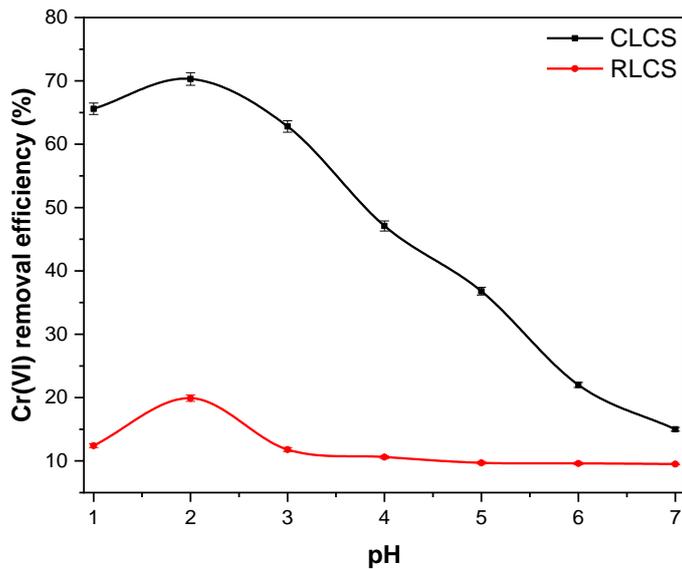


Figure 6: Impact of pH on Cr(VI) uptake by raw and charred biosorbent.

### **Influence of contact time**

To study the impact of contact time throughout a time range, 25 mg of CLCS and 25 mL of 20.12 mg/L of Cr(VI) solution at pH 2.0 were taken in several conical flask and shaken vigorously at room temperature. We carried out biosorption experiments with different contact periods. Each flask's sample was filtered after a set period of time, and the equilibrium Cr(VI) concentration was analyzed. Figure 7 depicts the Cr(VI) sorption onto CLCS over 10 minutes to 24 hours. After 240 minutes, it was discovered that the metal adsorption and adsorption percentage onto CLCS were constant, suggesting the equilibrium period for the maximum sorption.

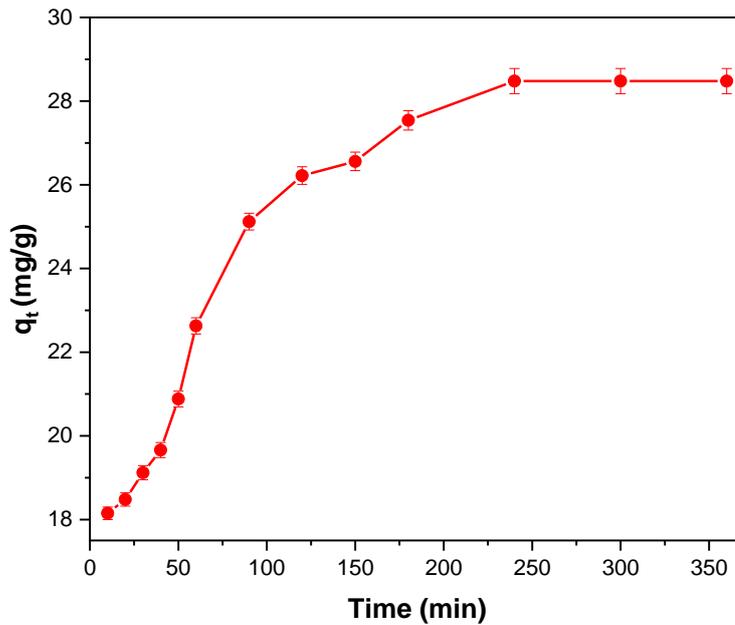


Figure 7: Impact of contact time on biosorption.

### Biosorption kinetics

The chromium (VI) biosorption on CLCS was inspected by PFO, and PSO kinetic models. When plots in Figure 8 were analysed, the PSO model, with a higher value of correlation coefficient, best described the adsorption process. The result showed that the biosorption is influenced by chemisorption. The findings were shown to be consistent with other research that employed a variety of biomass-based adsorbents to adsorb hexavalent chromium (Bhattarai et al., 2022; Homagai et al., 2023; Rai et al., 2021). Table 1 displays the derived values for the kinetic parameters.

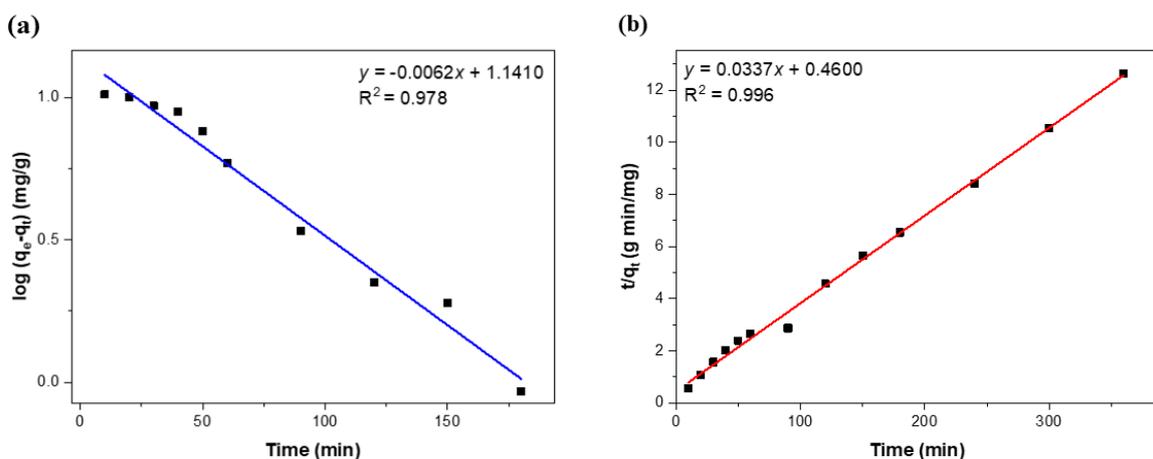


Figure 8: (a) PFO, and (b) PSO kinetic plots.

Table 1: Calculated kinetic parameters for Cr(VI) bisorption onto CLCS.

$q_{exp}$ (mg/g)	PSO			PFO		
	$K_2$ (mg.min/g)	$q_e$ (mg/g)	$R^2$	$K_1$ (min-1)	$q_e$ (mg/g)	$R^2$
28.48	$1.05 \times 10^{-3}$	29.674	0.996	$1.43 \times 10^{-2}$	13.836	0.978

### Adsorption isotherm

Figure 9 shows the Freundlich and Langmuir isotherm plots (linear) for the biosorption process. From the isotherm study, the maximal chromium (VI) adsorption onto CLCS was found to be 69.93 mg/g at the optimum pH of 2.0. The Langmuir correlation coefficient ( $R^2$ ) value was found greater than the Freundlich correlation coefficient value, proving the better fitness of the Langmuir model than the latter. This indicated the adsorption to be unimolecular and the adsorbent surface to be homogenous (Langmuir, 1916; Dong et al., 2011). The determined isotherm parameters are enumerated in Table 2. Table 3 compares the Cr(VI) biosorption capacities of various biosorbents with the CLCS.

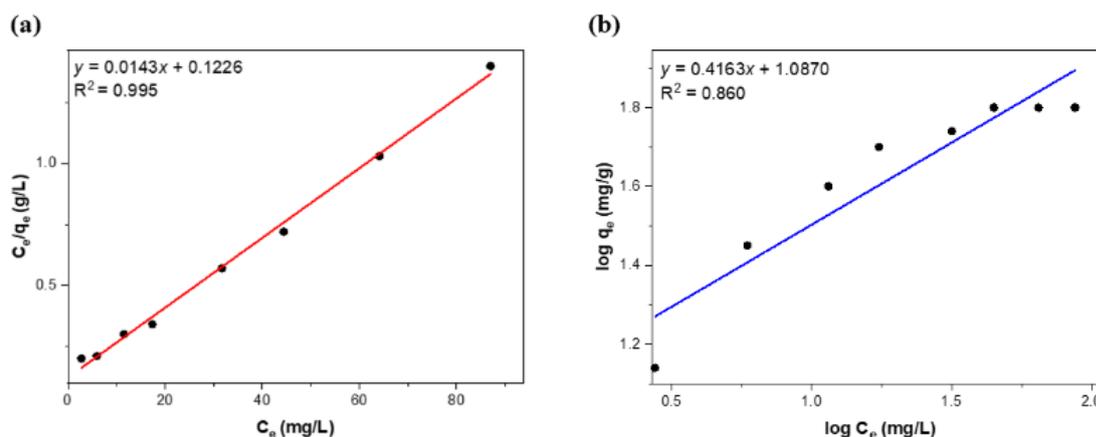


Figure 9: (a) Langmuir, and (b) Freundlich isotherm plots.

Table 2: Calculated isotherm parameters.

Langmuir			Freundlich		
$q_{max}$ (mg/g)	$b$ (L/mg)	$R^2$	$K_F$ (mg.g-1)(L.mg-1) <sup>1/n</sup>	$n$	$R^2$
69.930	0.117	0.995	12.22	2.402	0.860

Table 3: Maximum Cr(VI) biosorption capacity of CLCS in comparison to that of other previously reported biosorbents.

SN	Bio-adsorbent	pH	Adsorption capacity (mg/g)	Reference
1	Peanut shell	2.0	4.32	(Ilyas et al., 2013)
2	Banana peel	1.5	10.42	(Parlayici & Pehlivan, 2019)
3	Carbon slurry	2.0	15.24	(Gupta et al., 2010)
4	Cactus fruit	2.0	18.50	(Fernández-López et al., 2014)
5	Giant reed	3.0	18.80	(Ammari, 2014)
6	FeCl <sub>3</sub> - treated pomelo peel	2.0	21.55	(Wang et al., 2020)
7	Pomegranate peel	3.0	28.28	(Abdel-Galil et al., 2021)
8	Coconut husk	2.0	29.00	(Tan et al., 1993)
9	Waste newspaper	3.0	59.88	(Dehghani et al., 2016)
10	Charred Litchi chinensis seed powder	2.0	69.93	Present study

### Impact of adsorbent dosage

Adsorbent dosage studies were carried out by using a different mass of adsorbent for the adsorption process in which concentration and volume of metal solution were kept constant during each adsorption process. Here, we have used different dosage of adsorbent (0.2 to 3.0 g/L of CLCS) in different reagent bottle where 20 ml of 20 mg/L Cr(VI) solution was used at pH 2.0 and shaken for 24 hours and filtered using Whatman filter paper, then concentration before and after adsorption were analysed using a spectrophotometer. The quantity of the adsorbent metal ion rises with the dose of the sorbent because surface-active sites are more readily available. The correlation between the dosage of CLCS and the remaining Cr(VI) concentrations is depicted in Figure 10. The results exposed that 2.60 g/L of CLCS dropped the residual chromium concentration of the solution from 20 mg/L to 0.05 mg/L. With an increasing dose of CLCS, Cr(VI) was totally remediated from water. The WHO has set a limit of 0.05 mg/L for the maximum content of Cr(VI) in drinking water. The results are found agreeing to the findings of previous studies (Pant et al., 2022; Rai et al., 2023).

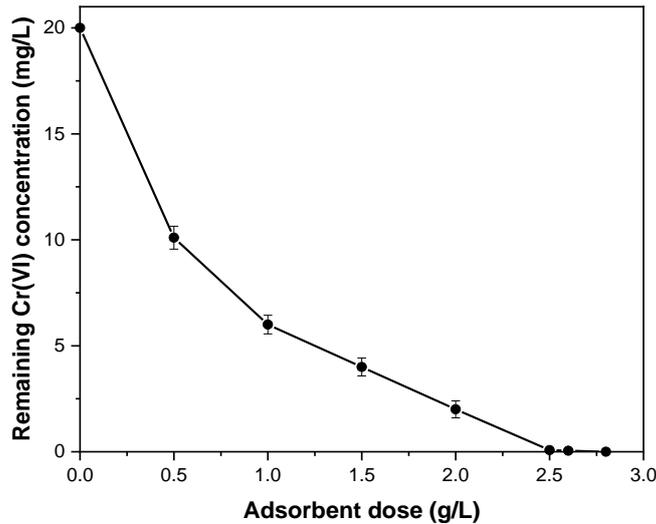


Figure 10: Impact of adsorbent dose.

### Desorption studies

As an eluent for the desorption study, several NaOH solution concentrations were used. Figure 11(a) depicts the effect of NaOH concentration on CLCS. It was found that the rate of desorption increased to 96% from 19% when the NaOH concentration was raised from 0.05M to 1M and remained constant as the concentration was raised further. This indicated that 1.0 M of NaOH was the ideal concentration for desorption. The performance of CLCS following a few consecutive adsorption-desorption cycles is shown in Figure 11(b). In the first cycle, the removal efficiency was 69.12%; however, it fell to 67.03%, 64.46%, and 60.87% in successive cycles. The findings demonstrated that CLCS can be successfully regenerated for certain cycles. The reduction in removal effectiveness might be brought about by the occlusion of certain adsorbent pore openings, and a reduction in the number of binding sites on the surface of the (Ma et al., 2019).

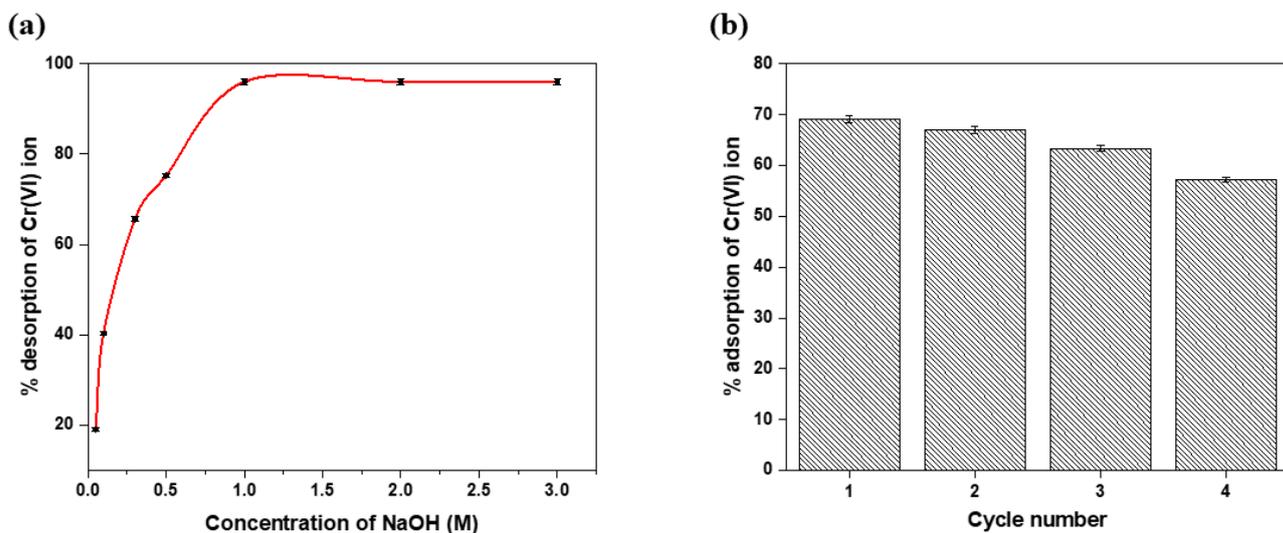


Figure 11: (a) Percentage desorption of Cr(VI) at varying NaOH concentrations, and (b) Variation in Cr(VI) biosorption ability of CLCS after consecutive adsorption-desorption cycles.

## Conclusions

The charred Litchi chinensis seed powder was prepared by treating dry lychee seed powder with concentrated sulphuric acid. The charred biosorbent (CLCS) showed greater adsorption efficiency than the uncharred one (RLCS). CLCS had the greatest sorption at a pH of 2.0, while its  $pH_{PZC}$  was found to be 4.0. At the ideal pH, CLCS demonstrated maximum Cr(VI) biosorption capacity of 69.93 mg/g, and the equilibrium was obtained at 4 hours at room temperature (25°C). The kinetics data best agreed with the PSO model and the isotherm data best fitted with the Langmuir model. Desorption studies revealed that CLCS can be revived and salvaged for numerous cycles before its disposal. The results suggested that the CLCS can also be a good adsorbent like other biomasses reported in earlier researches, for the Cr(VI) removal from aqueous solution. Further studies are necessary to improve the efficiency of the CLCS and its feasibility at normal pH conditions. The acid modification process has its drawbacks, as the use of sulphuric acid is harmful to the environment. Therefore, there is a need for further research on the development of environmentally green biosorbents with greater removal efficiency at natural pH conditions.

## Conflict of interest statement

The authors declare no conflict of interest.

## Authors' contribution statement

**R. Rai, M. Pokhrel:** Performed the experiments; Analyzed and interpreted the data; Wrote the paper. Ram

**D. Khadka, J. Baral:** Performed the experiments; Analyzed and interpreted the data. **D. R. Paudel, S. K.**

**Gautam:** Conceived and designed the experiments; Analyzed and interpreted the data. **M. R. Pokhrel:** Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data. **B. R. Poudel:** Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

### Acknowledgment

The authors would like to acknowledge the Department of Chemistry Tri-Chandra Multiple Campus, Tribhuvan University, for the laboratory facility, and Dr. Prakash Chandra Lohani, Jeonbuk National University, South Korea for XRD and SEM analysis.

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