



Biosorption of Cr(VI) by *Theobroma cacao* pericarp

Miguel Fernández-Pezua¹ · Carmencita Lavado-Meza¹ · Leonel De la Cruz-Cerrón² · Francisco Gamarra-Gómez³ · Elisban Sacari-Sacari³ · Carmen Lavado-Puente¹ · Juan Z. Dávalos-Prado⁴

Received: 6 May 2024 / Accepted: 9 September 2024 / Published online: 4 October 2024
© The Author(s) 2024

Abstract

This paper reports a comprehensive study of *Theobroma cacao* pericarp (TCP) residues, which has been prepared, characterized, and tested as an inexpensive and efficient biosorbent of Cr(VI) from aqueous solutions. The maximum adsorption capacity of TCP obtained at optimal conditions (pH = 2, dose = 0.5 g L⁻¹, C₀ = 100 mg L⁻¹) was $q_{\max} = 48.5 \text{ mg g}^{-1}$, which is one of the highest values reported by the literature. Structural and morphological characterization has been performed by FTIR, SEM/EDX, and pH_{PZC} measurements. FTIR analysis revealed the presence of O–H, –NH, –NH₂, C=H, C=O, C=C, C–O, and C–C functional groups that would be involved in the Cr(VI) biosorption processes. The experimental equilibrium data of biosorption process were successfully fitted to non-linear Langmuir ($R^2 = 0.95$, $\chi^2 = 11.0$), Freundlich ($R^2 = 0.93$, $\chi^2 = 14.8$), and Temkin ($R^2 = 0.93$, $\chi^2 = 14.7$) isotherm models. Kinetics experimental data were well adjustment to non-linear pseudo-2nd ($R^2 = 0.99$, $\chi^2 = 2.08$)- and pseudo-1st-order kinetic models ($R^2 = 0.98$, $\chi^2 = 2.25$) and also to intra-particle Weber-Morris ($R^2 = 0.98$) and liquid film diffusion ($R^2 = 0.99$) models. These results indicate that Cr(VI) biosorption on heterogeneous surfaces as well as on monolayers of TCP would be a complex process controlled by chemisorption and physisorption mechanisms. The thermodynamic results indicate that the Cr(VI) biosorption on TCP is a feasible, spontaneous, and endothermic process. TCP can be regenerated with NaOH and reused up to 3 times.

Keywords Cr(VI) biosorption · *Theobroma cacao* · Agricultural waste · Langmuir isotherms · Heavy metals

Introduction

In many places of the world, population growth and uncontrolled industrialization generate wastewater, whose discharges with poor or no treatment contaminate water

resources (Quitian 2021). Wastewater contains several contaminants, among them heavy metals (Soon et al. 2022; Pérez-Marín et al. 2024) that can pass not only into the food chain but also into the atmosphere. These contaminants (such as Cr, Hg, Cd, and Pb) represent one of the most pressing global problems, due to their high degree of toxicity and persistence in ecosystems, causing negative effects on the health of the population and the environmental (Murga and González 2020; Tejada-Tovar et al. 2020).

Chromium (Cr) is a heavy metal found in wastewater in both trivalent (III) and hexavalent (VI) forms (Quitian 2021); the latter being the most toxic, due to its high solubility and mobility in biological systems (Mishra et al. 2020), while the trivalent form (III) is rather considered a micro-nutrient with important functions in the metabolism of sugars and lipids (Oliveira 2012). Cr(VI) is used in the fabric factory, metal finishing, metallurgy, chrome electroplating, glass manufacturing, wood preservation, dye manufacturing, and tanning (Wang et al. 2023). Exposure to this metal in humans can cause respiratory, gastrointestinal, immunological, hematological, reproductive, dermal, ocular, genetic, and particularly with carcinogenic effects (Wise et al. 2019),

Responsible Editor: Tito Roberto Cadaval Jr

✉ Juan Z. Dávalos-Prado
jdaalos@iqfr.csic.es

Miguel Fernández-Pezua
76828087@uniscjsa.edu.pe

- ¹ Faculty of Engineering, Professional School of Environmental Engineering, Universidad Nacional Intercultural de la Selva Central Juan Santos Atahualpa (UNISCJA), La Merced, Chanchamayo 1285, Peru
- ² Faculty of Engineering, Universidad Continental (UC), Huancayo 12004, Peru
- ³ Nanotechnology Laboratory, Faculty of Engineering, Universidad Nacional Jorge Basadre Grohmann (UNJBG), Tacna 23001, Peru
- ⁴ Instituto de Química Física “Blas Cabrera”, CSIC, 28006 Madrid, Spain

since Cr (VI) and Cd are categorized, according to International Agency for Research on Cancer, as “Group 1” carcinogen. Therefore, Cr(VI) is one of the metallic species that poses a serious environmental problem and has harmful health effects that make its elimination essential.

Currently, there are several techniques for the treatment and removal of Cr (VI) from contaminated aqueous systems: precipitation, redox, ion-exchange, filtration, reverse osmosis, electrochemical treatment, membrane technologies, recovery by evaporation and adsorption, and others (Pabón et al. 2020; Dev et al. 2024). Several of them have disadvantages such as high operational costs, high reagent and energy consumptions, and low selectivity and in some cases can be counterproductive, because can yield polluting sludge (Pari 2020). The adsorption process is considered an effective method for the removal of numerous pollutants due to the high efficiency, low operating cost, ease of operation, good selectivity, availability, and sustainability of the process. However, the high cost of conventional and commercial adsorbents, including those with activated-carbon, is a disadvantage that drives the search for new economical, highly effective, reusable, and environmentally friendly adsorbents capable of replacing conventional and commercial ones. Biological techniques, based on biosorption, bioreduction, and bioaccumulation processes are considered as economical and environmentally beneficial techniques (Xie 2024). Particularly, agricultural materials such as agro-industrial waste materials show potential biosorption capacity for various pollutants (Bhatnagar and Sillanpää 2010). So, these biosorbent materials constitute an effective, economic, and ecological alternative for the removal heavy metals such as Cr(VI) from aqueous solutions, due to their structural composition, availability in abundance, renewable nature, and low cost (Miranda 2019). The composition of agro-industrial waste materials includes lignocellulosic compounds (cellulose, hemicellulose, and lignin) containing a variety of polar functional groups (–OH, –COOR, –CO, etc.) that enhance their metallic adsorptive capacities (Pérez et al. 2020; Dev et al. 2024). The literature reports studies of a wide variety of agricultural by-products on Cr(VI) biosorption employing, e.g., olive leaves *Chemlali* pruning waste (Rzig et al. 2024), *Phoenix dactylifera* coir wastes (Rambabu et al. 2021), coffee grounds (Silva 2021), banana peel (Pari 2020), eucalyptus leaves (Miranda 2019), water hyacinth (Tejada et al. 2020), *Sargassum tenerrimum* (Bazzazzadeh et al. 2020), gliricidia leaf (Suganya et al. 2019), *Colocasia esculenta* leaves (Nakkeeran et al. 2016), and Teff straw (Tadesse et al. 2014).

It is important to mention that the search and evaluation of lignocellulosic biosorbents for Cr(VI) removal is a promising area of research (Dev et al. 2024), and the potential use of chemically modified lignocellulosic wastes, as efficient and low-cost biosorbents (Jamshaid et al. 2017; Nigam et al.

2019; Zhang et al. 2020), for large-scale removal of heavy metal ions from wastewater, is an interesting environmental challenge.

In Peru, the Junín zone is one of the regions with the highest cocoa production (29,774 T year^{−1}). The process of obtaining cocoa beans generates large quantities of waste, called pericarps (MIDAGRI 2022), which if not properly treated can become an environmental problem (Sanchez 2018; Vásquez et al. 2019). It is known that the cocoa pericarp contains cellulose, hemicellulose, lignin, and ash that favor the adsorption of Cr (VI) (Sánchez 2016; Pérez et al. 2020) and also of Pb(II) and Cd(II) (Lavado-Meza et al. 2023a, c). Therefore, this material is promising since it may be susceptible to suitable chemical modifications to be used as a low-cost and highly effective biosorbent for removing various heavy metals from wastewater.

In this context, the goals of this work are the following: (i) Prepare *Theobroma cacao* pericarp agro-industrial waste (TCP) collected from Junin-Peru region. (ii) Characterize TCP, regarding the morphology and surface structure by means SEM/EDX, FTIR, and pH_{PZC} measurements. (iii) Evaluate the parameters (dose, pH, and initial Cr(VI) concentration) that affect the biosorption capacities of TCP to remove Cr(VI). (iv) Study the kinetic, thermodynamic, and mechanisms of the biosorption process.

Methods and materials

Preparation of TCP biosorbent

The preparation of the biosorbent was carried out according to the procedures described by Pari (2020) and Lavado-Meza et al. (2023b). *Theobroma cacao* pericarp waste (TCP) was collected from Alto Huacará (Chanchamayo province) located at Junín region in Peru. It was washed with plenty of deionized water, dried at 70 °C for 48 h. After that, the dried sample was ground and sieved using a 70 mesh.

Characterization of TCP biosorbent

Point of Zero Charge pH (pH_{PZC}) evaluation was carried out following the procedure described by Lavado-Meza et al. (2023b): It was prepared a mixture of 1 g of TCP biosorbent with 50 mL of aqueous solutions at different initial pHs (pH₀) ranging from 2.0 to 9.0. The acid dilutions were prepared from 1 M HNO₃ solution, while the basic dilutions from 1 M NaOH. After 24 h of equilibrium, the final pHs (pH_f) were measurements by means a potentiometer (HANNA HI1271 CHECKER). pH_{PZC} was determined from the intersection of ΔpH (= pH₀ – pH_f) curve with pH₀ axis.

Fourier transform infra-red spectrophotometer (FTIR, Bruker Invenio R/Platinum ATR, Ettlingen, Germany) was

used to identify, over a range of 4000 to 500 cm^{-1} , the functional groups present on the surface of TCP, before and after Cr adsorption. The morphology and elemental analysis of these surfaces were also performed using scanning electron microscopy, coupled with energy dispersive X-rays (SEM/EDX, Thermo Scientific Co, Eindhoven, The Netherlands).

Biosorption experiments

Batch experiments were carried out using $\text{K}_2\text{Cr}_2\text{O}_7$ solution, varying Cr(VI) concentrations between 10 and 150 mg L^{-1} . The dose of TCP biosorbent was varied in the range of 0.5 a 3 g L^{-1} and adjusted to a pH in the range of 2.0 to 6.0 by adding 0.01 M HNO_3 or 0.01 M NaOH . The solutions, at room temperature, were stirred at 300 rpm for $t = 120$ min, and the samples were extracted and filtered at certain time intervals. The Cr(VI) concentrations, before and after adsorption, were evaluated following ASTM D1687–02 (2007), where Cr(VI) reacts with diphenylcarbazide in an acidic medium to produce a reddish purple color, which intensity—proportional to the concentration of Cr(VI)—is measurement using UV/VIS spectrophotometer (UV-1900i, UV visible spectrophotometer, Shimadzu, Japan) at the maximum absorption wavelength (λ_{max} , 540 nm). All biosorption experiments were replicated three times. Both, adsorption capacity q_e ($\text{mg} \cdot \text{g}^{-1}$) and removal efficiency %RE, were calculated by using Eqs. (1) and (2), respectively (Araújo et al. 2018; Lavado-Meza et al. 2023c).

$$q_e = \frac{(C_0 - C_e)}{M} \times V \quad (1)$$

$$\% \text{RE} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where C_0 and C_e (mg L^{-1}) are initial and equilibrium final Cr(VI) concentrations, respectively; V (in L) is the volume of solution; and M (in g) is the TCP biosorbent mass.

Both isothermal-adsorption and kinetic experimental data were adjusted to the different models described in Table 1. Biosorption thermodynamic functions, such as standard Gibbs energy (ΔG^0), enthalpy (ΔH^0), and entropy changes (ΔS^0), were evaluated using the Eqs. (3) and (4) (Van't Hoff equation) (Mosaffa et al. 2024a):

$$\Delta G^0 = -RT \ln(K_c) \quad (3)$$

$$\ln(K_c) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (4)$$

where K_c is the equilibrium constant, $K_c = C_{\text{es}}/C_e$; C_{es} and C_e are the equilibrium Cr(VI) concentrations in the biosorbent

and in the solution, respectively. R is the universal gas constant, and T (in K) is the temperature of the solution.

Desorption-regeneration experiments

Desorption or regeneration experiments were carried out using 0.1 M NaOH and water distilled as eluents. 0.5 g of TCP previously loaded with Cr(VI) under optimal conditions (pH 2, $C_0 = 100 \text{ mg L}^{-1}$) then filtered, washed, and dried at 80 °C for 3 h was subjected to desorption process by adding 25 mL of each eluent and stirring at 100 rpm for 1 h. After that, the regenerated TCP was rinsed with distilled water many times before being dried and reused again. The desorption or regeneration efficiency (%D) of TCP was determined using Eq. (5) (Lavado-Meza et al. 2023c).

$$\%D = \frac{\text{Cr (VI) desorbed from biomass}}{\text{Cr (VI) adsorbed on biomass}} \times 100 \quad (5)$$

Results and discussion

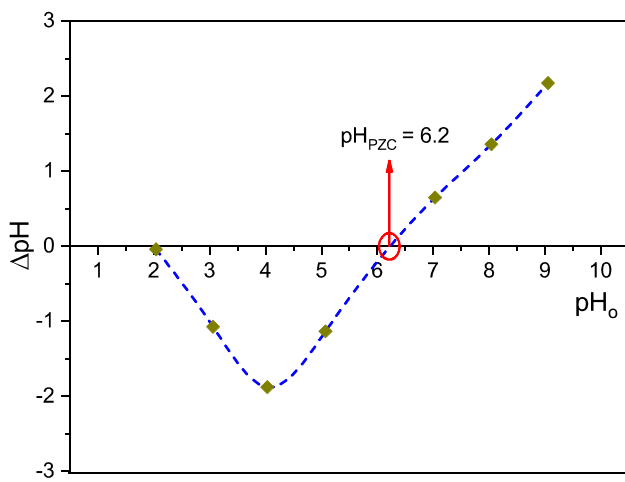
Biosorbent properties, pH_{PZC} measurement, and pH effects

In Fig. 1, the ΔpH ($= \text{pH}_0 - \text{pH}_f$) vs. pH_0 curve is depicted, where can be seen the pH_{PZC} value equal to 6.2. It indicates that the surface of the TCP is positively charged at $\text{pH} < 6.2$ or negatively charged at $\text{pH} > 6.2$. For the 1st case, the TCP surface favors the electrostatic attraction of anions, while for the 2nd case, favors the attraction of cations. Our pH_{PZC} value is very close to that reported by Sánchez (2016) ($\text{pH}_{\text{PZC}} = 6.9$) and Machado (2017) ($\text{pH}_{\text{PZC}} = 7.0$) for cocoa-pericarp biosorbents.

Figure 2 shows the pH influence on the Cr (VI) adsorption capacity (q_e) of the TCP. It can be appreciated that q_e decreases with increasing pH, being the highest value at pH 2. At this pH, and according to the value of $\text{pH}_{\text{PZC}} = 6.2$, the surface of the TCP biosorbent would be positively charged due to the protonation of the active sites (formed by amino and carboxyl groups) which would strongly attract the anions of Cr (VI) such as HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ (Mondal et al. 2019; Ren et al. 2022). Increases in pH would induce a less positive biosorbent surface that would decrease the adsorption of Cr(VI) anions (Blázquez et al. 2014; Mondal et al. 2019; Li et al. 2021; Narayanasamy et al. 2022; Ren et al. 2022). A more detailed explanation was given by Park et al. (2005), Verma et al. (2021), and Pertile et al. (2021) who included reduction process of Cr(VI) to Cr(III) following one of two proposed mechanisms: (1) Cr (VI) is directly reduced to Cr (III) in aqueous phase by contact with the

Table 1 Models used for the Cr(VI) biosorption onto TCP

Model	Equation	Parameters	References
Isotherm adsorption models			
Langmuir	$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$	q_e : adsorption capacity at equilibrium (mg g ⁻¹) $q_{\max}$: maximum adsorption capacity (mg g ⁻¹) K_L : Langmuir constant related to the affinity between sorbent and sorbate (L mg ⁻¹) C_e : adsorbate concentration at equilibrium (mg L ⁻¹) R_L : Separation factor	(Araújo et al. 2018; Mzinyane et al. 2023; Mosaffa et al. 2024b)
Freundlich	$q_e = K_F C_e^{1/n}$	K_F : equilibrium constant (mg g ⁻¹) (L mg) ^{1/n} n : constant related to the affinity between sorbent and sorbate	
Temkin	$q_e = \frac{RT}{B} \ln(A_T C_e)$	R : universal gas constant (J mol ⁻¹ K ⁻¹) T : temperature (K) A_T : Temkin's equilibrium constant (L mg ⁻¹) B : adsorption energy variation (J mol ⁻¹)	
Kinetic models			
Pseudo-1st order	$q_t = q_e (1 - e^{-k_1 t})$	q_e : adsorption capacity at equilibrium (mg g ⁻¹) q_t : amount of Cr(VI) retained per unit mass of biosorbent at time t (mg g ⁻¹) k_1 : the first-order kinetic constant (1 min ⁻¹)	(Mzinyane et al. 2023; Mosaffa et al. 2024b)
Pseudo-2nd order	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	k_2 : rate constant adsorption (g mg ⁻¹ min ⁻¹)	
Weber Morris intra-particle diffusion	$q_t = k_{id} t^{0.5} + C$	k_{id} : intraparticle diffusion rate constant (mg g ⁻¹ min ^{-1/2}) C : constant	
Liquid film diffusion	$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_{fd} t + C$	k_{fd} : film-diffusion rate coefficient (min ⁻¹) C : constant	


Fig. 1 Evaluation of pH_{PZC} value for the TCP biosorbent

electron donating groups of the biosorbent; (2) previous anionic adsorption of Cr(VI), this is reduced to Cr(III) through electron-donating groups of the biosorbent, and then, Cr(III) ions are released by electrostatic repulsion with the positive biosorbent surface.

These results are comparable to those obtained for waste biosorbents such as eucalyptus (Miranda 2019), banana-peel (Pari 2020), coffee-bora (Silva 2021), gliricidia-leaf (Suganya et al. 2019), and water-hyacinth (Tejada et al. 2020), where at pH < 2.5 are reported high values of Cr(VI) adsorption capacities, q_e .

FTIR spectral analysis was done to identify functional groups present on the surface of TCP. Figure 3 shows typical FTIR spectra of TCP before and after Cr(VI) adsorption. The FTIR spectra of the unloaded-Cr samples show band positions at (i) 3330.2 cm⁻¹ assignable to O–H and

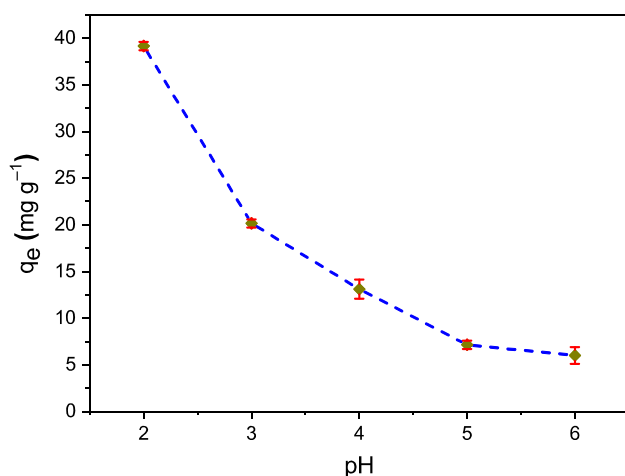


Fig. 2 pH influence on the Cr(VI) adsorption capacity q_e of TCP. Experimental conditions: $T=20\text{ }^{\circ}\text{C}$, sorption or contact time $t=120\text{ min}$, dose $=0.05\text{ g L}^{-1}$, $C_0=100\text{ mg L}^{-1}$

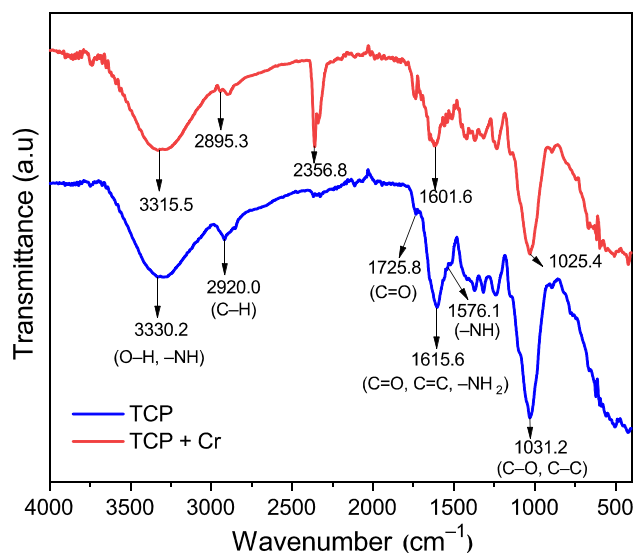


Fig. 3 FTIR spectra before (blue) and after (red) Cr(VI) adsorption on TCP, at pH 2, $C_0=100\text{ mg L}^{-1}$, $T=293\text{ K}$, $t_{sp}=120\text{ min}$, dose $=0.5\text{ g L}^{-1}$

N–H bond stretching vibrations in cellulose, hemicellulose, lignin, and pectin (Olu-owolabi 2012; Lavado-Meza et al. 2023b); (ii) 2920.0 cm^{-1} , attributed to stretching vibrations of C–H bonds in aliphatic acids and methyl and methylene groups (Olu-owolabi 2012; Rzig et al. 2021); (iii) 1725.8 cm^{-1} , would correspond to the C=O stretching vibrations of the hemicelluloses (Rzig et al. 2021); (iv) 1615.6 cm^{-1} , related to stretching vibrations of C=O in ketones and C=C bonds in carbonyl groups present in lignin (Pérez et al. 2020; Nursiah et al. 2023; Mosaffa et al.

2024b); (v) range of $1650\text{ to }1450\text{ cm}^{-1}$, would be related to the --NH_2 scissoring and --NH deformation bands (Suganya et al. 2019; Ren et al. 2022); (vi) 1031.2 cm^{-1} , attributed to stretching vibrations of C–OH in alcohols (Olu-owolabi 2012; Mosaffa et al. 2024a) and C–C bonds of carboxylic acids of polysaccharides (Pérez et al. 2020).

After biosorption, the (TCP+Cr) spectrum (Fig. 3) shows changes in the intensity and position of the most important bands described above. Thus, the bands move toward lower values (red-shifting) between 5.8 and 24.7 cm^{-1} . These changes reflect the interaction of Cr(VI) with the active sites of TCP biosorbent (Pérez et al. 2020; Rzig et al. 2021; Lavado-Meza et al. 2023a). The intense band at 2356.8 cm^{-1} would correspond to CO_2 present in the solution (Gök et al. 2022; Ni et al. 2023).

Figure 4 shows SEM micrographs and EDX analysis of the TCP before and after Cr(VI) sorption. TCP clean (Fig. 4a) shows a cracked surface with heterogeneous plates involving an irregular micro-rough structure that would facilitate the adsorption of Cr(VI) (Sanchez 2018). The morphology of the surface after Cr(VI) adsorption is different to clean surface, given that it is more compact, less rough, and heterogeneous (Fig. 4b). The EDX analysis of clean TCP shows C (48.63%), N (8.41%), and O (42.96%) peaks related to its lignocellulosic nature, while TCP loaded with Cr(VI) (TCP+Cr) shows Cr peak in addition to those mentioned, which is evidence of Cr (0.03%) adsorption on the TCP surface. Banchhor et al. (2021) reported similar results after loading with Cr(VI) the biomass of *Simarouba glauca* leaves.

Biomass dose effect

The dose of biosorbent has a significant impact on both, the equilibrium adsorption capacity (q_e) and removal efficiency (%RE) of Cr(VI). The effect of TCP doses, in the 0.5 to 3.0 g L^{-1} range, was investigated at $C_0=100\text{ mg L}^{-1}$, pH 2, $T=20\text{ }^{\circ}\text{C}$, and sorption time $t_{sp}=180\text{ min}$. The results of q_e and %RE are shown in Fig. 5. It can be appreciated that q_e decreases with an increasing biosorbent dose. In contrast, %RE increases. With an initial dose of 0.5 g L^{-1} , the maximum q_e value of 39.2 mg g^{-1} is obtained. These observations can be explained by the availability of active sites on the surface of the biosorbent. At low doses, there is a high concentration of Cr(VI) per unit mass of TCP, leading to rapid saturation of the active sites and higher q_e . However, at higher doses, there are more available but unsaturated sites, resulting in a lower q_e but higher %RE due to the increased contact area. Similar results of (q_e vs. biomass dose) were reported by Suganya et al. (2019) and Li et al. (2021) using, respectively, *Gliricidia-sepium* and lychee peel biosorbents

Fig. 4 Typical SEM morphology (left) and EDX analysis (right) of TCP, **a** before and **b** after Cr(VI) adsorption. pH 2, $C_0 = 100 \text{ mg L}^{-1}$, dose = 0.5 g L^{-1}

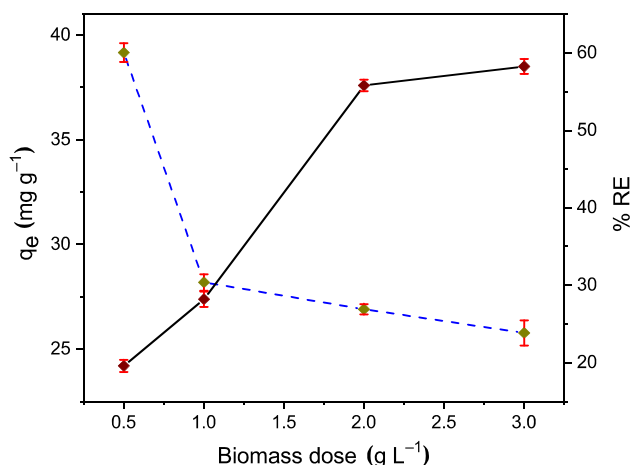
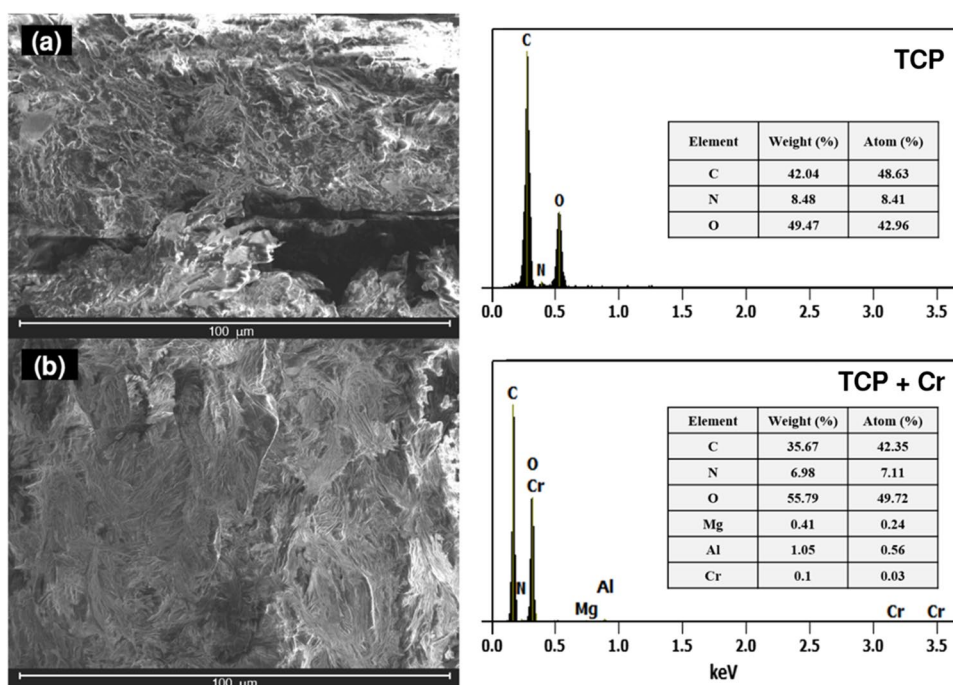


Fig. 5 Biomass dose of TCP vs. adsorption capacity q_e (dotted line) and removal efficiency %RE (continuous line) of Cr(VI) at pH 2, $C_0 = 100 \text{ mg L}^{-1}$, $T = 20^\circ \text{C}$ and sorption time $t_{sp} = 180 \text{ min}$

to remove Cr(VI). Then, and according to these authors, the minimum dose ($= 0.5 \text{ g L}^{-1}$) was considered as the most appropriate amount of TCP for optimal adsorption of Cr(VI).

Biosorption isotherm

Cr(VI) biosorption isotherm (q_e vs. C_e) was studied, under equilibrium optimal-conditions, in a range of initial Cr(VI) concentrations C_0 between 10 and 150 mg L^{-1} , at pH 2, dose = 0.5 g L^{-1} and contact time $t_{sp} = 120 \text{ min}$. It can be seen that q_e increases with the increase of C_e , reaching

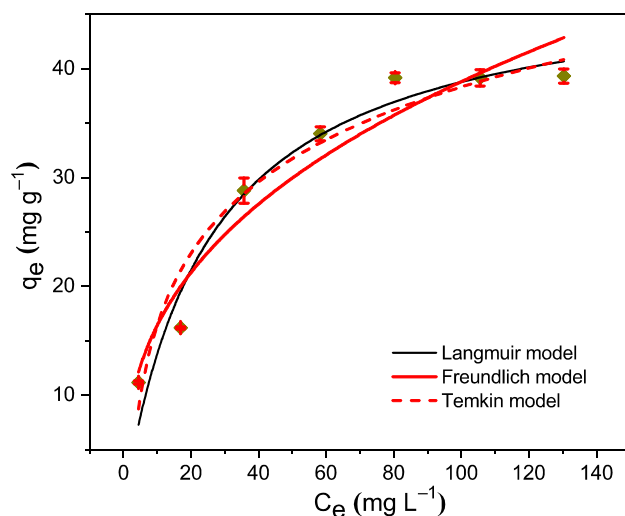


Fig. 6 q_e vs. C_e biosorption isotherm. TCP dose = 0.5 g L^{-1} , $t_{sp} = 120 \text{ min}$, $T = 20^\circ \text{C}$, pH 2

highest experimental value (39.2 mg g^{-1}) for $C_e > 80 \text{ mg L}^{-1}$ (see Fig. 6). This behavior can be attributed to the interaction of Cr(VI) cations with biosorbent surface. So, at lower Cr(VI) concentrations, reduced competition for active binding sites on the TCP adsorbent surface allows more vacant sites to be available, increasing its biosorption capacity q_e . However, as the initial C_e increases, excess Cr(VI) cations difficulty finding available binding sites and q_e slows its growth. At C_e higher than 80 mg L^{-1} , the q_e remains constant, indicating the saturation of binding

Table 2 Isotherm parameters of Cr(VI) biosorption on TCP

Models	Parameters	
Langmuir	$q_{\max}$ (mg g ⁻¹)	48.5 ± 3.5
	K_L (L mg ⁻¹)	0.04 ± 0.01
	R_L	0.45
	R^2	0.95
	χ^2	11.0
Freundlich	K_F (mg g ⁻¹) (L mg) ^{1/n}	6.9 ± 1.7
	N	2.6 ± 0.4
	$1/n$	0.38
	R^2	0.93
	χ^2	14.8
Temkin	A_T (L g ⁻¹)	0.6 ± 0.2
	B (J mol ⁻¹)	262.9
	R^2	0.93
	χ^2	14.7

sites on the TCP surface has been reached (Ren et al. 2022). The (q_e vs. C_e) experimental data were fitted (non-linear adjustments) to three models, Langmuir, Freundlich, and Temkin (see Fig. 6). The evaluated parameters are consigned in Table 2. The biosorption-isotherm data are well fitted with the three models ($R^2 \geq 0.93$, $\chi^2 \leq 14.8$), although the best fit, with highest correlation coefficient R^2 ($=0.95$) and lowest χ^2 ($=11.0$), was obtained with Langmuir model. The Langmuir parameters deduced were, a low value K_L equal to 0.04 L mg⁻¹ with maximum adsorption capacity $q_{\max}$ equal to 48.5 mg g⁻¹. The separation

factor value R_L ($=0.45$) is in the range of $0 < R_L < 1$, which provides the favorability of the adsorption process. The $1/n$ ($=0.38$) value obtained from the Freundlich isotherm, which is a measure of the intensity of biosorption or surface heterogeneity, is less than one ($0 < 1/n < 1$), indicating that the biosorption of Cr(VI) onto TCP is favorable (Mosaffa et al. 2024a). These values would indicate high affinity of Cr(VI) biosorption on monolayers of TCP (Pertile et al. 2021). However, as mentioned above, the acceptable adjustments with the Freundlich and Temkin models indicate that Cr(VI) biosorption would also occur in TCP multilayers of heterogeneous nature (Freundlich model). The adsorption would be predominantly a physisorption process given that Temkin parameter B ($=262.9$ J mol⁻¹) is less than 8000 J mol⁻¹ (Araújo et al. 2018; Moreira et al. 2019; Mahmoud et al. 2020; Hezam et al. 2022), and the Cr(VI) adsorbates would adhere to the TCP through weak van der Waals interactions. Therefore, all these results indicate that in reality the Cr (VI) biosorption on TCP is rather complex processes, where under the experimental conditions, heterogeneous surface as well as monolayer biosorption might coexist.

These results are comparable to those reported by Pari (2020), Mondal et al. (2019), Pant et al. (2022), and Daffalla (2023), where the isothermal Cr(VI) adsorptions are well fitted with Langmuir model. In Table 3, the maximum Cr(VI) biosorption capacities, $q_{\max}$, of different non-treated agro-industrial waste is consigned. The $q_{\max}$ of TCP is among the highest values, indicating that TCP is a promising biomass to remove Cr(VI) from contaminated aqueous media.

Table 3 Maximum Cr(VI) biosorption capacities, $q_{\max}$, of non-treated biosorbents coming from agroindustrial waste

Biosorbent	C_0 range (mg L ⁻¹)	pH	$q_{\max}$ (mg g ⁻¹)	References
Banana (<i>Musa acuminata colla</i>) peel	10–50	2	36.10	Pari (2020)
Litchi shell	50–100	3	25.78	Li et al. (2021)
Agro-waste <i>Cocos nucifera</i>	2–6	2	5.95	Kumari et al. (2021)
<i>Phoenix dactylifera</i> coir wastes	50–250	2	138.89	Rambabu et al. (2021)
<i>Sargassum tenerrimum</i>	5–50	2	37.7	Bazzazzadeh et al. (2020)
Eucalyptus (<i>Globulus labill</i>) leaves	5.5–52	3	16.84	Miranda (2019)
Mosambi (<i>Citrus limetta</i>) peel	5–30	2	3.62	Mondal et al. (2019)
<i>Theobroma cacao</i> shell	2.5–15	6	2.92	Pérez et al. (2020)
<i>Colocasia esculenta</i> leaves	20–100	2	47.62	Nakkeeran et al. (2016)
Orange (<i>Citrus sinensis</i>) peel	20–100	3	16.66	Tejada et al. (2015)
Leaves of <i>Tradescantia pallida</i>	50–200	2	64.67	Sinha et al. (2015)
<i>Artocarpus heterophyllus</i> peel	10–150	2	64.47	Saranya et al. (2018)
Teff straw	2.5–15	2	3.51	Tadesse et al. (2014)
<i>Prosopis cineraria</i> leaf powder	10–60	5	10.046	Singh et al. (2023)
Pine sawdust-cellulose fibers	20–100	6	9.78	Mzinyane et al. (2023)
Chemlali olive leaves	10–1000	3.9	21.2–40.3	Rzig et al. (2024)
Orange peels	10–100	2	5.46	Khalfaoui et al. (2024)
<i>Euryale ferox</i> Salisbury seed coat	5–25	2	13.64	Goswami et al. (2024)
<i>Theobroma cacao</i> pericarp	10–150	2	48.5	This work

Biosorption kinetics

The experimental kinetic data were fitted using three adsorption kinetic models (q_t vs. t), for both pseudo-1st and pseudo-2nd orders (see Fig. 7) (q_t vs. $t^{1/2}$) and $[-\ln(1 - q_t/q_e)]$ vs. t] for intra-particle diffusion and liquid film diffusion models (see Fig. 8). q_t is the Cr(VI) biosorption capacity or amount of Cr(VI) removed per mass unit of biosorbent, at contact time t . The parameters obtained after non-linear adjustments are reported in Table 4. The best fit of (q_t vs. t) is obtained with pseudo-2nd-order model ($R^2 = 0.99$, $\chi^2 = 2.08$), although the pseudo-1st-order model also fits very well ($R^2 = 0.98$, $\chi^2 = 2.25$). These results would indicate that the Cr(VI) biosorption is a complex process where both chemisorption and physisorption processes take place. According

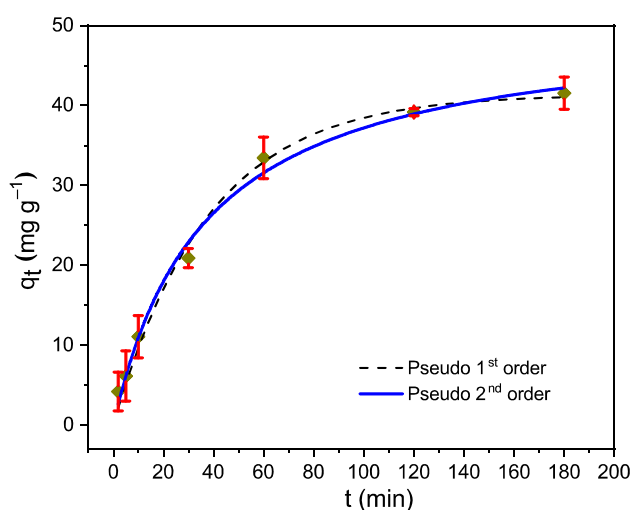


Fig. 7 Cr(VI) biosorption kinetics, q_t vs. t (contact time). pH 2, dose = 0.5 g L⁻¹, $C_0 = 100$ mg L⁻¹, $T = 20$ °C. Pseudo-1st-order (dotted line) and pseudo-2nd-order (solid line) adjustments

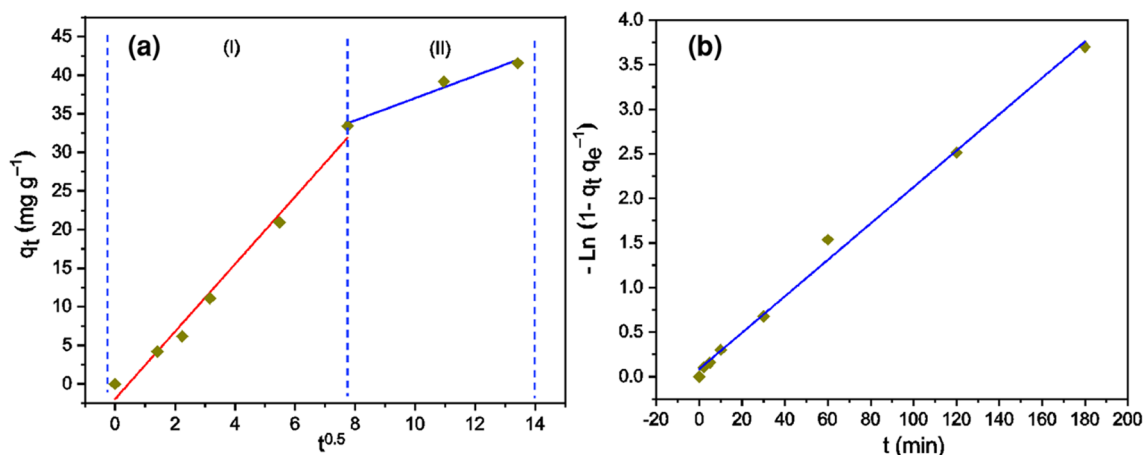


Fig. 8 **a** q_t vs. $t^{0.5}$ plot fitted with Weber-Morris intra-particle diffusion model; **b** $-\ln(1 - q_t/q_e)$ vs. t plot fitted with liquid-film diffusion kinetic model. pH 2, dose = 0.5 g L⁻¹, $C_0 = 100$ mg L⁻¹, $T = 20$ °C

to Park et al. (2005), Verma et al. (2021), and Pertile et al. (2021), the biosorption mechanism would involve anionic adsorption of Cr(VI) and its subsequent reduction to Cr(III) ions due to the presence of electron-donating groups in the biosorbent.

The (q_t vs. $t^{1/2}$) data were fitted with the intra-particle diffusion Weber-Morris model (see Fig. 8a) where two well-defined stages are distinguished: the first stage ($0 < t^{0.5} < 7.8$) shows a rapid growth of q_t at the time t (in minutes), which would be associated to a rapid external diffusion of Cr(VI), from aqueous solution to outer surface of the biosorbent (Datt et al. 2022). The second stage ($t^{0.5} > 7.8$) shows a growth of $q_t(t)$ almost three times slower than in 1st stage, indicating a gradual adsorption process, where Cr(VI) ions would diffuse from the surface into the pores of the biosorbent (Lavado-Meza et al. 2023d). The $[-\ln(1 - q_t/q_e)]$ vs. t] data were fitted with liquid film diffusion model (see Fig. 8b) which asserts that the rate-of adsorption is governed by adsorbate species transiting through a liquid layer surrounding the solid adsorbent (Mosaffa et al. 2023).

The fit of the data with both diffusion models is excellent ($R^2 \geq 0.98$). However, the fitting line does not pass through the origin, showing the incapacity of both Weber-Morris and liquid diffusion models to govern the rate-limiting step of the Cr(VI) biosorption process (Albadarin et al. 2011; Salam et al. 2014; Pant et al. 2022; Al-Odayni et al. 2023). The mechanism based on diffusion via the liquid layer would be applicable at low initial Cr(VI) concentration (Mosaffa et al. 2024a).

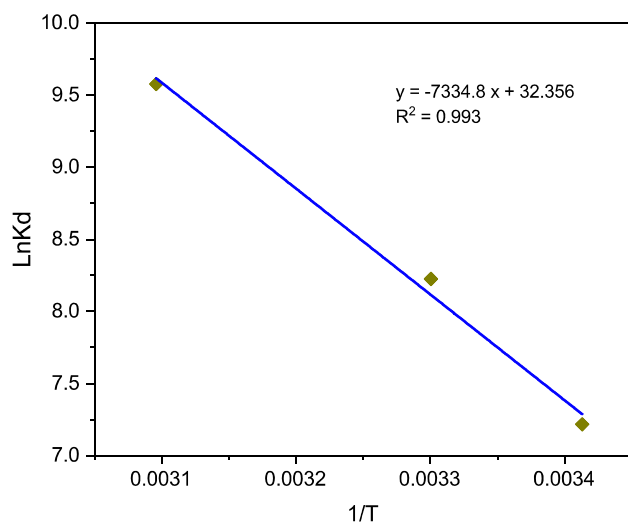
Biosorption thermodynamics

$\Delta G^0(T)$ values were calculated from Eq. (3); while ΔH^0 and ΔS^0 values were deduced from the Van't Hoff equation fit (Fig. 9). The results are consigned in Table 5 and

Table 4 Kinetic parameters of the Cr(VI) biosorption process

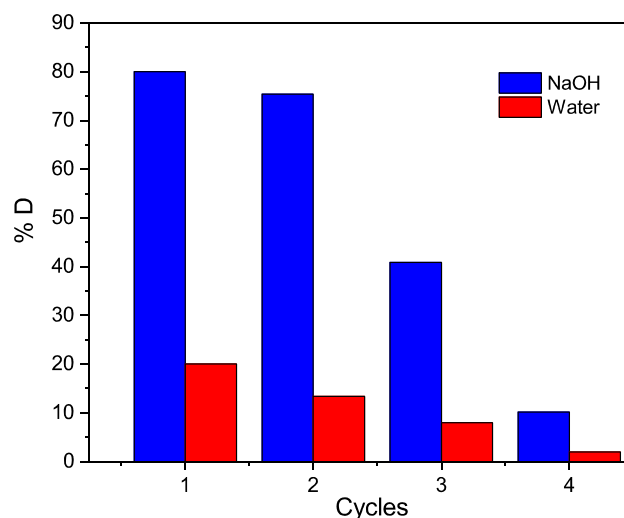
Kinetic models	Kinetic parameters	
Pseudo-1st order	$q_{e,cal}$ (mg g ⁻¹) ^a	42.6
	k_1 (l min ⁻¹)	0.03
	R^2	0.98
	χ^2	2.25
Pseudo-2nd order	$q_{e,cal}$ (mg g ⁻¹) ^a	41.4
	k_2 (g mg ⁻¹ min ⁻¹)	1.19
	R^2	0.99
	χ^2	2.08
Weber-Morris model	k_{dI} (mg g ⁻¹ min ^{-1/2})	4.37
	R^2	0.99
	k_{dII} (mg g ⁻¹ min ^{-1/2})	1.45
	R^2	0.98
Liquid diffusion model	k_{fd} (min ⁻¹)	0.024
	R^2	0.99

^a $q_{e,cal}$ is the calculated adsorption capacity

**Fig. 9** ($\ln K_d$ vs. $1/T$) plot for Cr(VI) biosorption onto TCP at pH 2, dose = 0.5 g L⁻¹, C_0 = 100 mg L⁻¹**Table 5** Thermodynamic parameters of Cr(VI) biosorption on TCP

ΔG^0 (kJ mol ⁻¹)		ΔH^0 (kJ mol ⁻¹)		ΔS^0 (J mol ⁻¹ K ⁻¹)
293 K	303 K	323 K		
-17.6	-20.7	-25.7	61.1	269.0

indicate that the Cr(VI) biosorption process on TCP can be characterized as spontaneous ($\Delta G^0 < 0$), endothermic ($\Delta H^0 > 0$), with increase in randomness ($\Delta S^0 > 0$) of biosorption at the solid–liquid interface. Similar results were found for Cr(VI) biosorption on treated-Juniperus procera leaves (Ali et al. 2019), mesoporous metal–organic

**Fig. 10** Desorption or regeneration efficiency (%D) of TCP biosorbent

structure (Babapour et al. 2022), derived of *Arundo donax* stem (Bhattarai et al. 2022) and agro-waste *Cocos nucifera* (Kumari et al. 2021).

Desorption or regeneration of TCP

The desorption or regeneration efficiency (%D) of a biosorbent is a crucial factor influencing the economics of the biosorption process, specifically the operating costs (Mosaffa et al. 2024a). Four desorption or regeneration cycles were carried out to evaluate the %D of TCP, using NaOH and distilled water as eluents (see Fig. 10). NaOH was the most efficient desorbent, with %D > 40% for the first 3 cycles. On the contrary, %D ≤ 20% was achieved with distilled water. The Cr(VI) desorption from the TCP surface in a basic pH environment would be due to a significant exchange among CrO_4^{2-} , dominant Cr(VI) species in alkaline solution, and OH^- cations (Rzig et al. 2021), although the regeneration effect of TCP was drastically reduced after the 3rd cycle. Therefore, TCP is a biosorbent with an appreciable reuse performance.

Conclusions

In the present study, the use of agricultural residues of *Theobroma cacao* pericarp (TCP) as an effective biosorbent of Cr (VI) ions from aqueous solutions was investigated. It has been determined the point of zero charge pH (pH_{PZC}) at 6.2. FTIR analysis showed the presence of functional groups such as O–H, C–H, C=O, C=C, C–O, C–C, $-\text{NH}_2$, and $-\text{NH}$ on the TCP surface, which favored

the Cr(VI) biosorption process. SEM/EDX analyses showed irregular and rough surface morphologies on TCP clean, which changed to more compact and homogeneous after Cr(VI) adsorption. Optimal Cr(VI) biosorption capacities, q_e , were determined at pH 2, biosorbent dose = 0.5 g L⁻¹ and initial Cr(VI) concentration C_0 = 100 mg L⁻¹. The adsorption isotherm data were successfully fitted with non-linear Langmuir model, although acceptable non-linear adjustments were also obtained with Freundlich and Temkin models. These results indicate that Cr(VI) biosorption on TCP is a process where heterogeneous surface as well as monolayer biosorption might coexist. It has been determined a maximum Cr(VI) biosorption capacity $q_{\max}$ equal to 48.5 mg g⁻¹, which is one of highest value among the non-treated agriculture waste biosorbents, reported in the literature. The adsorption kinetic data were well fitted with non-linear pseudo-2nd- and also with pseudo-1st-order models. These results would indicate that the Cr(VI) biosorption on TCP would be controlled by both, chemisorption and physisorption mechanisms. Intra particle diffusion model indicated a rapid diffusion of Cr(VI) ions from aqueous solution to outer surface of TCP and then a slow diffusion into its pores. However, both Weber-Morris and liquid diffusion models do not govern the rate-limiting step of the Cr(VI) biosorption. From thermodynamic point of view, the biosorption process is feasible and spontaneous ($\Delta G^0 < 0$); endothermic ($\Delta H^0 > 0$) with an increasing randomness ($\Delta S^0 > 0$) at the solid–liquid interface. The desorption-regeneration experiments, using NaOH as the eluent, showed that TCP can be reused (%D > 40%) up to 3 times.

Author contribution All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Miguel Fernandez-Pezua, Carmencita Lavado-Meza, Leonel De la Cruz-Cerrón, and Carmen Lavado-Puente. The characterization of the materials and their interpretation were carried out by Francisco Gamarra-Gómez and Elisban Sacari-Sacari. The first draft of the manuscript was written by Miguel Fernandez-Pezua and Juan Z. Dávalos Prado. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Funding Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature. Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature. The research leading to these results received funding from Universidad Nacional Intercultural de la Selva Central Juan Santos Atahualpa under Grant Agreement N° 041–2022-UNISCISA.

Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Albadarin AB, Al-Muhtaseb AH, Al-Iqat NA et al (2011) Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts. *Chem Eng J* 169:20–30. <https://doi.org/10.1016/j.cej.2011.02.044>
- Ali IH, Mesfer MK, Khan MI et al (2019) Exploring adsorption process of lead(II) and chromium(VI) ions from aqueous solutions on acid activated carbon prepared from *Juniperus procera* leaves. *Processes* 7:217. <https://doi.org/10.3390/pr7040217>
- Al-Odayni A-B, Alsubaie FS, Abdu NAY et al (2023) Adsorption kinetics of methyl orange from model polluted water onto N-doped activated carbons prepared from N-containing polymers. *Polymers* 15:1983. <https://doi.org/10.3390/polym15091983>
- Araújo CST, Almeida ILS, Rezende HC et al (2018) Elucidation of mechanism involved in adsorption of Pb(II) onto lobeira fruit (*Solanum lycocarpum*) using langmuir, freundlich and temkin isotherms. *Microchem J* 137:348–354. <https://doi.org/10.1016/j.microc.2017.11.009>
- Babapour M, Hadi M, Alimohammadi M et al (2022) Adsorption of Cr(VI) from aqueous solution using mesoporous metal-organic framework-5 functionalized with the amino acids: characterization, optimization, linear and nonlinear kinetic models. *J Mol Liq* 345:117835. <https://doi.org/10.1016/j.molliq.2021.117835>
- Banchhor A, Pandey M, Pandey PK (2021) Optimization of adsorption parameters for effective removal of hexavalent chromium using *Simarouba glauca* from aqueous solution. *Water Conserv Sci Eng* 6:127–144. <https://doi.org/10.1007/s41101-021-00106-z>
- Bazzazadeh R, Soudi MR, Valinassab T, Moradlou O (2020) Kinetics and equilibrium studies on biosorption of hexavalent chromium from leather tanning wastewater by *Sargassum tenerrimum* from Chabahar-Bay Iran. *Algal Res* 48:101896. <https://doi.org/10.1016/j.algal.2020.101896>
- Bhatnagar A, Sillanpää M (2010) Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review. *Chem Eng J* 157:277–296. <https://doi.org/10.1016/j.cej.2010.01.007>
- Bhattarai KP, Pant BD, Rai R et al (2022) Efficient sequestration of Cr(VI) from aqueous solution using biosorbent derived from *Arundo donax* stem. *J Chem* 2022:12. <https://doi.org/10.1155/2022/9926391>
- Blázquez G, Calero M, Ronda A et al (2014) Study of kinetics in the biosorption of lead onto native and chemically treated olive stone. *J Ind Eng Chem* 20(5):2754–2760. <https://doi.org/10.1016/j.jiec.2013.11.003>

- Daffalla S (2023) Adsorption of chromium (VI) from aqueous solution using palm leaf-derived biochar: kinetic and isothermal studies. *Separations* 10:260. <https://doi.org/10.3390/separations10040260>
- Datt B, Neupane D, Ram D, et al (2022) Efficient biosorption of hexavalent chromium from water by modified arecanut leaf sheath. *Helv. Chim. Acta* 105:2022. <https://doi.org/10.1016/j.heliyon.2022.e09283>
- Dev AM, Unni A, Mathew A et al (2024) An evaluation on the prospective application of lignocellulose based biosorbents for the separation of Cr(VI) from aqueous solution: a critical review. *Sep Sci Technol* 59(15):1–23. <https://doi.org/10.1080/01496395.2024.2371370>
- Gök G, Kocyigit H, Gök O, Celebi H (2022) The use of raw shrimp shells in the adsorption of highly polluted waters with Co²⁺. *Chem Eng Res Des* 186:229–240. <https://doi.org/10.1016/j.cherd.2022.07.041>
- Goswami M, Devi B, Das E et al (2024) A promising approach for the removal of hexavalent and trivalent chromium from aqueous solution using low-cost biomaterial. *Environ Monit Assess.* <https://doi.org/10.1007/s10661-024-12617-y>
- Hezam A, Yub N, Mahmoud M et al (2022) Removal of cadmium from aqueous solution by optimized rice husk biochar using response surface methodology. *Ain Shams Eng J* 13:101516. <https://doi.org/10.1016/j.asej.2021.06.002>
- Jamshaid A, Hamid A, Muhammad N et al (2017) Cellulose-based materials for the removal of heavy metals from wastewater – an overview. *ChemBioEng Rev* 4:240–256. <https://doi.org/10.1002/cben.201700002>
- Khalfauoui A, Benalia A, Selama Z et al (2024) Removal of chromium(VI) from water using orange peel as the biosorbent: experimental, modeling, and kinetic studies on adsorption isotherms and chemical structure. *Water* 16:742. <https://doi.org/10.3390/w16050742>
- Kumari B, Tiwary RK, Yadav M, Singh KMP (2021) Nonlinear regression analysis and response surface modeling of Cr(VI) removal from synthetic wastewater by an agro-waste Cocos nucifera: Box-Behnken design (BBD). *Int J Phytoremediation* 23:791–808. <https://doi.org/10.1080/15226514.2020.1858399>
- Lavado-Meza C, De la Cruz-Cerrón L, Asencios YJO et al (2023a) Alkaline modification of Arabica-coffee and Theobroma-cocoa agroindustrial waste for effective removal of Pb(II) from aqueous solutions. *Molecules* 28:683. <https://doi.org/10.3390/molecules28020683>
- Lavado-Meza C, De la Cruz-Cerrón L, Cisneros-Santos G et al (2023b) Arabica-coffee and theobroma-cocoa agro-industrial waste biosorbents, for Pb(II) removal in aqueous solutions. *Environ Sci Pollut Res* 30:2991–3001. <https://doi.org/10.1007/s11356-022-22233-3>
- Lavado-Meza C, De la Cruz-Cerrón L, Lavado-Puente C et al (2023c) Effective removal of Cd(II) from aqueous solutions using Theobroma cacao agro-industrial waste. *Molecules* 28:5491. <https://doi.org/10.3390/molecules28145491>
- Lavado-Meza C, De la Cruz-Cerrón L, Lavado-Puente C et al (2023d) Efficient lead Pb(II) removal with chemically modified Nostoc commune biomass. *Molecules* 28:1–16. <https://doi.org/10.3390/molecules28010268>
- Li L, Cao G, Zhu R (2021) Adsorption of Cr(VI) from aqueous solution by a litchi shell-based adsorbent. *Environ Res* 196:110356. <https://doi.org/10.1016/j.envres.2020.110356>
- Machado S (2017) Analisis del proceso de biosorción de cobre presente en efluentes líquidos utilizando bagazo de caña de azúcar y cascara de cacao. Universidad de Cuenca, Tesis de Pregrado
- Mahmoud AED, Fawzy M, Hosny G, Obaid A (2020) Equilibrium, kinetic, and diffusion models of chromium(VI) removal using Phragmites australis and Ziziphus spina-christi biomass. *Int J Environ Sci Technol* 18:2125–2136. <https://doi.org/10.1007/s13762-020-02968-7>
- MIDAGRI (2022) Observatorio de commodities cacao. Minist Desarro Agrar y Riego 1–22
- Miranda N (2019) Biosorción de cromo Cr(VI) de soluciones acuosas por la biomasa residual de hojas de eucalipto (Globulus labill). *Rev Didáctica Las Ciencias Nat UNA* 1:20–32
- Mishra S, Chen S, Saratale GD et al (2020) Reduction of hexavalent chromium by Microbacterium paraoxydans isolated from tannery wastewater and characterization of its reduced products. *J Water Process Eng* 39:101748. <https://doi.org/10.1016/j.jwpe.2020.101748>
- Mondal NK, Basu S, Sen K, Debnath P (2019) Potentiality of mosambi (Citrus limetta) peel dust toward removal of Cr(VI) from aqueous solution: an optimization study. *Appl Water Sci* 9:1–13. <https://doi.org/10.1007/s13201-019-0997-6>
- Moreira VR, Lebron YAR, Lange LC, Santos LVS (2019) Simultaneous biosorption of Cd(II), Ni(II) and Pb(II) onto a brown macroalgae Fucus vesiculosus: mono- and multi-component isotherms, kinetics and thermodynamics. *J Environ Manage* 251:109587. <https://doi.org/10.1016/j.jenvman.2019.109587>
- Mosaffa E, Banerjee A, Ghafari H (2023) Sustainable high-efficiency removal of cationic and anionic dyes using new super adsorbent biochar: performance, isotherm, kinetic and thermodynamic evaluation. *Environ Sci Water Res Technol* 9:2643–2663. <https://doi.org/10.1039/d3ew00464c>
- Mosaffa E, Patel D, Amiri N, Indravadan R (2024a) Bacterial cellulose microfibril reinforced hollow chitosan beads decorated with cross-linked melamine plates for the removal of the Congo red. *Int J Biol Macromol* 254:127794. <https://doi.org/10.1016/j.ijbiomac.2023.127794>
- Mosaffa E, Rishikumar I, Banerjee A et al (2024b) Comprehensive analysis of cationic dye removal from synthetic and industrial wastewater using a semi-natural curcumin grafted biochar/poly acrylic acid composite hydrogel. *RSC Adv* 14(11):7745–62. <https://doi.org/10.1039/d3ra08521j>
- Murga L, González O (2020) Evaluación de metales pesados en ríos y truchas Oncorhynchus mykiss de la región Pasco, Perú. *Rev Iberoam Ambient Sustentabilidad* 3:32–48. <https://doi.org/10.46380/rias.v3i2.93>
- Mzinyane NN, Mngqwu KM, Moukangoe KM (2023) Adsorption of hexavalent chromium ions using Pine sawdust cellulose fibres. *Appl Sci* 13:9798. <https://doi.org/10.3390/app13179798>
- Nakkeeran E, Saranya N, Giri Nandagopal MS et al (2016) Hexavalent chromium removal from aqueous solutions by a novel powder prepared from Colocasia esculenta leaves. *Int J Phytoremediation* 18:812–821. <https://doi.org/10.1080/15226514.2016.1146229>
- Narayanasamy S, Sundaram V, Sundaram T, Vo DVN (2022) Biosorptive ascendancy of plant based biosorbents in removing hexavalent chromium from aqueous solutions – insights into isotherm and kinetic studies. *Environ Res* 210:112902. <https://doi.org/10.1016/j.envres.2022.112902>
- Ni Z, Song Z, Bi H et al (2023) The effect of cellulose on the combustion characteristics of coal slime: TG-FTIR, principal component analysis, and 2D-COS. *Fuel* 333:126310. <https://doi.org/10.1016/j.fuel.2022.126310>
- Nigam M, Rajoriya S, Rani Singh S, Kumar P (2019) Adsorption of Cr(VI) ion from tannery wastewater on tea waste: kinetics, equilibrium and thermodynamics studies. *J Environ Chem Eng* 7:103188. <https://doi.org/10.1016/j.jece.2019.103188>
- Nursiah C, Desvita H, Elviani E et al (2023) Adsorbent characterization from cocoa shell pyrolysis (Theobroma cacao L.) and its application in mercury ion reduction. *J Ecol Eng* 24:366–375. <https://doi.org/10.12911/22998993/163167>
- Oliveira H (2012) Chromium as an environmental pollutant: insights on induced plant toxicity. *J Bot* 2012:1–8. <https://doi.org/10.1155/2012/375843>
- Olu-owolabi, (2012) Biosorption of Cd²⁺ and Pb²⁺ ions onto mango stone and cocoa pod waste: kinetic and equilibrium studies. *Sci Res Essays* 7(15):1614–29. <https://doi.org/10.5897/SRE11.2248>
- Pabón S, Benítez R, Sarria R, Gallo J (2020) Contaminación del agua por metales pesados, métodos de análisis y tecnologías de remoción. Una Revisión Entre Cienc e Ing 14:9–18

- Pant BD, Neupane D, Paudel DR, et al (2022) Efficient biosorption of hexavalent chromium from water by modified arecanut leaf sheath. *Heliyon* 8(4). <https://doi.org/10.1016/j.heliyon.2022.e09283>
- Pari Y (2020) Biosorción del cromo hexavalente en soluciones acuosas utilizando biomasa de cáscara de plátano (*Musa acuminata* colla). Universidad Nacional del Antiplano, Tesis de Maestría
- Park D, Yun YS, Jong MP (2005) Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp. *Chemosphere* 60:1356–1364. <https://doi.org/10.1016/j.chemosphere.2005.02.020>
- Pérez L, Paz I, Sandoval A, Peñaloza G (2020) Uso de cáscara de cacao (*Theobroma cacao*) para la remoción de cromo en solución acuosa. *Rev EIA* 17:1–13. <https://doi.org/10.24050/reia.v17i34.1393>
- Pérez-Marín AB, Ortuño JF, Aguilar MI et al (2024) Competitive effect of zinc and cadmium on the biosorption of chromium by orange waste. *Processes* 12:148. <https://doi.org/10.3390/pr12010148>
- Pertile E, Dvorský T, Václavík V, Heviánková S (2021) Use of different types of biosorbents to remove Cr(VI) from aqueous solution. *Life* 11(3):240. <https://doi.org/10.3390/life11030240>
- Quitian C (2021) Biosorción de cromo hexavalente con la utilización del carbón activo procedente de la borra de café. Universidad Distrital Francisco José de Caldas, Tesis de Grado
- Rambabu K, Thanigaivelan A, Bharath G et al (2021) Biosorption potential of *Phoenix dactylifera* coir wastes for toxic hexavalent chromium sequestration. *Chemosphere* 268:128809. <https://doi.org/10.1016/j.chemosphere.2020.128809>
- Ren B, Jin Y, Zhao L, et al (2022) Enhanced Cr(VI) adsorption using chemically modified dormant *Aspergillus niger* spores: process and mechanisms. *J Environ Chem Eng* 10:106955. <https://doi.org/10.1016/j.jece.2021.106955>
- Rzig B, Guesmi F, Sillanpää M, Hamrouni B (2021) Modelling and optimization of hexavalent chromium removal from aqueous solution by adsorption on low-cost agricultural waste biomass using response surface methodological approach. *Water Sci Technol* 84:552–575. <https://doi.org/10.2166/wst.2021.233>
- Rzig B, Guesmi F, Sillanpää M, Hamrouni B (2024) Biosorption potential of olive leaves as a novel low-cost adsorbent for the removal of hexavalent chromium from wastewater. *Biomass Convers Biorefinery* 14:12961–12979. <https://doi.org/10.1007/s13399-022-03356-6>
- Salam MA, El-Shishtawy RM, Obaid AY (2014) Synthesis of magnetic multi-walled carbon nanotubes/magnetite/chitin magnetic nanocomposite for the removal of Rose Bengal from real and model solution. *J Ind Eng Chem* 20:3559–3567. <https://doi.org/10.1016/j.jiec.2013.12.049>
- Sánchez N (2016) Biosorción en tanque agitado de Cd+2 y Pb+2 con cáscara de cacao. Universidad de Cuenca, Tesis de Pregrado
- Sanchez Y (2018) Adsorción de arsénico y antimonio en soluciones acuosas mediante aplicación lignocelulósica de cáscara de cacao. Universidad Técnica de Machala, Tesis de pregrado
- Saranya N, Ajmani A, Sivasubramanian V, Selvaraju N (2018) Hexavalent chromium removal from simulated and real effluents using *Artocarpus heterophyllus* peel biosorbent - batch and continuous studies. *J Mol Liq* 265:779–790. <https://doi.org/10.1016/j.molliq.2018.06.094>
- Silva M (2021) Capacidad de biosorción de cromo hexavalente en medio acuoso usando la borra de café. Universidad Nacional de Cajamarca, Tesis de Grado
- Singh M, Rayaz M, Rao A (2023) Application of novel phytosorbent to sequester chromium (VI) and lead (II) from aqueous phase: optimization, equilibrium and kinetics. *Environ Prog Sustain Energy*. <https://doi.org/10.1002/ep.14266>
- Sinha V, Pakshirajan K, Chaturvedi R (2015) Evaluation of Cr(VI) exposed and unexposed plant parts of *Tradescantia pallida* (Rose) D R Hunt for Cr Removal from Wastewater by Biosorption. *Int J Phytoremediation*. <https://doi.org/10.1080/15226514.2015.1045135>
- Soon WL, Peydayesh M, Mezzenga R, Miserez A (2022) Plant-based amyloids from food waste for removal of heavy metals from contaminated water. *Chem Eng J* 445:136513. <https://doi.org/10.1016/j.cej.2022.136513>
- Suganya E, Saranya N, Patra C et al (2019) Biosorption potential of *Gliricidia sepium* leaf powder to sequester hexavalent chromium from synthetic aqueous solution. *J Environ Chem Eng* 7:103112. <https://doi.org/10.1016/j.jece.2019.103112>
- Tadesse B, Teju E, Megersa N (2014) The Teff straw: a novel low-cost adsorbent for quantitative removal of Cr(VI) from contaminated aqueous samples. *Desalin Water Treat* 56:1–12. <https://doi.org/10.1080/19443994.2014.968214>
- Tejada C, Paz I, Acevedo D et al (2020) Adsorption of chrome (VI) and mercury (II) in solution using hyacinth (*Eichhornia crassipes*). *Biotechnol en el Sect Agropecu y Agroindustrial* 19:54–65. [https://doi.org/10.18684/BSAA\(19\)54-65](https://doi.org/10.18684/BSAA(19)54-65)
- Tejada Tovar C, Quiñones Bolaños E, Tejada Benitez L, Marimón Bolívar W (2015) Absorción de cromo hexavalente en soluciones acuosas por cáscaras de naranja (*Citrus sinensis*). *Prod + Limpia* 10:9–21. <https://doi.org/10.22507/pml.v10n1a1>
- Tejada-Tovar C, Villabona-Ortiz A, Ortega-Toro R (2020) Determination of kinetic parameters in the biosorption of chromium (VI) in aqueous solution. *Ing y Cienc* 16:129–143. <https://doi.org/10.17230/ingciencia.16.31.6>
- Vásquez ZS, de Carvalho Neto DP, Pereira GVM et al (2019) Biotechnological approaches for cocoa waste management: a review. *Waste Manag* 90:72–83. <https://doi.org/10.1016/j.wasman.2019.04.030>
- Verma R, Maji P, Sarkar S (2021) Comprehensive investigation of the mechanism for Cr(VI) removal from contaminated water using coconut husk as a biosorbent. *J Clean Prod* 314:128117. <https://doi.org/10.1016/j.jclepro.2021.128117>
- Wang H, Wang W, Zhou S, Gao X (2023) Adsorption mechanism of Cr(VI) on woody-activated carbons. *Heliyon* 9:e13267. <https://doi.org/10.1016/j.heliyon.2023.e13267>
- Wise JTF, Shi X, Zhang Z (2019) Toxicology of chromium(VI). In: *Encyclopedia of environmental health*, 2nd edn. Elsevier Inc., 1–8
- Xie S (2024) Water contamination due to hexavalent chromium and its health impacts: exploring green technology for Cr (VI) remediation. *Green Chem Lett Rev* 17:1–19. <https://doi.org/10.1080/17518253.2024.2356614>
- Zhang D, Xu W, Cai J et al (2020) Citric acid-incorporated cellulose nanofibrous mats as food materials-based biosorbent for removal of hexavalent chromium from aqueous solutions. *Int J Biol Macromol* 149:459–466. <https://doi.org/10.1016/j.ijbiomac.2020.01.199>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.