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1 **Adsorption-reduction of Cr(VI) onto unmodified and phytic acid-modified**
2 **Carob waste: Kinetic and isotherm modeling**

3
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23 **Abstract**

24 Carob waste (CW) is an agro-biomass material abundant in nature with potential use for eco-
25 friendly remediation. However, like many biomass-based adsorbents, it suffers from its low
26 adsorption capacity for organic/inorganic pollutants. Therefore, modification using physical
27 and/or chemical means is commonly applied to improve the adsorptive properties of biomass-
28 based adsorbents. In this study, carob waste (CW) and carob waste functionalized with phytic
29 acid (PA-CW), as an ecofriendly product, were applied for the first time for Cr(VI)
30 elimination. Various methods were applied for the material characterization like Fourier-
31 transform infrared spectroscopy, powder X-ray diffraction (PXRD), thermogravimetric
32 analysis (TGA and DTG), X-ray photoelectron spectroscopy (XPS), specific surface area and
33 porosity measurements. The results proved that both CW and PA-CW own appropriate
34 features for efficient adsorption. Each experiments revealed that the optimum parameters for
35 Cr(VI) (100 mg/mL) removal at 25°C were pH 2, 0.05 g and 0.025 g as adsorbent dose for
36 CW and PA-CW, respectively, over 120 min contact time. The kinetic of adsorption was well-
37 described by the pseudo-second order model, whereas the isotherm modeling fitted well the
38 modified Langmuir model. CW and PA-CW achieved respectively maximum adsorption
39 capacities of 212.4 and 387.9 mg/g, which are among the highest values so far reported for
40 biomass-based adsorbent materials. These results confirmed that CW and PA-CW could be
41 alternative cost-effective adsorbents even for high concentrations of Cr(VI) in industrial
42 wastewaters along with their reduction capacity.

43

44 **Keywords:** Carob waste; Phytic acid; Cr(VI) adsorption; Kinetic-isotherm; Thermodynamic
45 modeling.

46

48 **1. Introduction**

49 No one doubts that industrial development led to the well-being of human life. However,
50 this development created a large water pollution by different industrial contaminants, causing
51 damage to nature and living organisms. Among these pollutants, heavy metals are considered
52 recently as an urgent concern (Jaishankar et al., 2014; Mishra and Bharagava, 2016). In
53 addition to human activities such as textile, mining extraction industries and nuclear power,
54 heavy metals could be from natural origin like soil erosion and volcanic activities (Akpor et
55 al., 2014). Among these heavy metals, chromium (Cr) accounts for the seventh most abundant
56 element on earth (Jaishankar et al., 2014). It is commonly used in paint, textile dyes,
57 chemicals, metal corrosion inhibition, and pharmaceuticals. Chromium is present in the
58 environment in two stable oxidation forms, Cr(VI) and Cr(III). Owing to its high stability,
59 solubility and mobility, Cr(VI) is more toxic compared to Cr(III). As a consequence, Cr(VI)
60 can impact negatively enzyme activity and plant growth (Akpor et al., 2014). It is considered
61 as one of the 17 elements that cause a health threat to human (Mishra and Bharagava, 2016).
62 Therefore, Cr(VI) removal represents a primordial issue for researchers in the recent decade.
63 Several approaches have been applied for Cr(VI) elimination such as ion exchange (Ye et al.,
64 2016), membrane separation (Li et al., 2018), electrocoagulation (Vasudevan and Lakshmi,
65 2011; GracePavithra et al., 2019), adsorption (Halouane et al., 2017), photocatalysis
66 (Dehghani et al., 2016), and solvent extraction (Ning et al., 2014).

67 Adsorption efficiency has been approved and chosen in several studies, owing to its low
68 cost and simple design. Currently, non-conventional adsorbents like agricultural wastes
69 compete with the usual ones (charcoal, zeolites, and clays) in heavy metals removal, because
70 they are abundant and not expensive. Among these, groundnut shell (Babarinde and
71 Onyiaocha, 2016), acorn waste (Kuppusamy et al., 2017), pine cone (Almendros et al., 2015),

72 fruit peels and sugarcane bagasse (Chao et al., 2014), sawdust (Ouafi et al., 2017), and many
73 other biomass-based materials have been successfully applied for Cr(VI) elimination from
74 wastewater.

75 Even though agro-waste materials represent an appealing alternative to synthetic ones for
76 Cr(VI) adsorption, their adsorption capacity in raw form is generally feeble to compete with
77 the existing ones. Therefore, natural adsorbents are not used in their raw nature, but different
78 treatments are applied on the adsorbents' surface to enhance their adsorption capacity by
79 increasing their porosity, specific space area or by the introduction of new active sites. These
80 treatments are commonly based on chemical or physical agents and processes such as acids,
81 bases, high temperature, etc. (Schwantes et al., 2016; Heidarinejad et al., 2020). According to
82 our best knowledge, only a few studies were devoted on the nature and toxicity of the agents
83 used toward the environment. To limit secondary pollution, originating from the reagents
84 applied for adsorbent surface modification, it is mandatory to apply environmentally-benign
85 products (Gomez-Maldonado et al., 2019). In this context, phytic acid represents an
86 interesting option to functionalize adsorbent surface, because of its eco-friendly nature and
87 provides important active sites for heavy metals adsorption (You et al., 2016; Qin et al.,
88 2017).

89 Carob (*Ceratonia Siliqua* L.) waste is an abundant material that has been studied for dye
90 adsorption (Güzel et al., 2015; Reffas et al., 2016), but not yet examined for heavy metal
91 removal. This study aimed at the valorization of carob waste for Cr(VI) elimination and assess
92 the impact of its surface functionalization with phytic acid on the adsorption process. The
93 modified material with an eco-friendly agent like phytic acid was used for the first time as an
94 adsorbent for Cr(VI) removal. A systematic investigation of the effects of adsorbate
95 concentration, contact time, adsorbent dose, pH and temperature on the adsorption process of
96 Cr(VI) onto untreated and phytic acid-treated carob waste was undertaken.

97

98 **2. Materials and methods**

99 **2.1. Materials**

100 Carob (*Ceratonia Siliqua* L.) waste was obtained from carob factory in Bejaia, Algeria.
101 Sodium hydroxide (NaOH), potassium dichromate ($K_2Cr_2O_7$), and phytic acid (PA) were
102 procured from Sigma-Aldrich and used as-received. Hydrochloric acid (HCl) was obtained
103 from Fisher scientific. Sodium chloride (NaCl), sodium nitrate ($NaNO_3$), sodium sulphate
104 (Na_2SO_4), and trisodium orthophosphate dodecahydrate ($Na_3PO_4 \cdot 12H_2O$) were purchased
105 from Biochem.

106 **2.2. Adsorbent preparation**

107 The carob waste was already crushed into pieces of 2 cm in length and removed from its seeds
108 by the factory. In the laboratory, the carob waste was dried at 80 °C overnight, and ground to
109 fine particles using a disk mill. Then, part of the obtained powder was rinsed copiously with
110 distilled water to eliminate the color and the soluble substances, dried for 24 h at 80 °C and
111 stored for further use (named as CW).

112 **2.3. Modification with phytic acid**

113 Phytic acid-modified carob waste (PA-CW) was obtained by the same method used in (You et
114 al., 2016; Qin et al., 2017). In short, 2 g of dry CW was placed in 30 mL of Milli-Q water and
115 ultrasonicated for 30 min. Then, 1.2 g of urea and 2.1 mL of phytic acid were added and the
116 resulting mixture was kept under magnetic stirring for 3 h at 60°C. After cooling to room
117 temperature and centrifugation, the resulting powder was rinsed copiously with Milli-Q water
118 to neutral pH and three times with ethanol. Finally, the material was dried for 24 h at 60°C
119 and stored for further use.

120 **2.4. Adsorption tests and regeneration**

121 The adsorption experiments were conducted using the well-known and commonly used batch
122 method, owing to its simple design. The tests were performed in conical flasks containing 50
123 mL of the Cr(VI) solution and varying the pH, adsorbent amount and the Cr(VI) concentration
124 for an equilibrium time of 120 min at 25 °C. The mixture was shaken at 300 rpm. After each
125 experiment, the sample was withdrawn, the adsorbent was isolated by centrifugation (13000
126 rpm) during 3 min and the supernatant was analyzed using UV-visible spectrophotometry at
127 the $\lambda_{\max}=348$ nm to assess the residual Cr(VI) concentration. The obtained data allowed to
128 calculate the adsorption capacity (q_t , mg/g) and the amount of Cr(VI) removal (R) using the
129 following equations:

$$130 \quad q_t = \frac{(C_i - C_t)}{m} * V \quad (1)$$

$$131 \quad R(\%) = \frac{(C_i - C_t)}{C_i} * 100 \quad (2)$$

132 where C_i and C_t are respectively the Cr(VI) initial and equilibrium concentration (mg/L),
133 V denotes the volume (L) and m represents the mass of the adsorbent (g).

134 Adsorption kinetics and isotherms were studied in 200 mL beakers containing 100 mL of
135 different Cr(VI) concentrations and 0.1 g of CW or 0.05 g of PA-CW at pH 2 and 25°C.
136 Samples of 1.5 mL were taken out the solution at different time intervals to follow the
137 remaining Cr(VI) by the same method mentioned above. All experiments were acquired in
138 triplicate under the same experimental conditions to validate the empirical data.

139 The reusability of the adsorbents was assessed using the optimum parameters ([Cr(VI)]=100
140 mg/L, $V=50$ mL, [CW]=0.05 g or [PA-CW]=0.025 g, pH=2 and 25°C). After 120 min
141 adsorption, Cr(VI) desorption was carried out using a solution of NaOH (0.1 M) under
142 shaking for 4 h. These optimum parameters were maintained constant for each cycle.

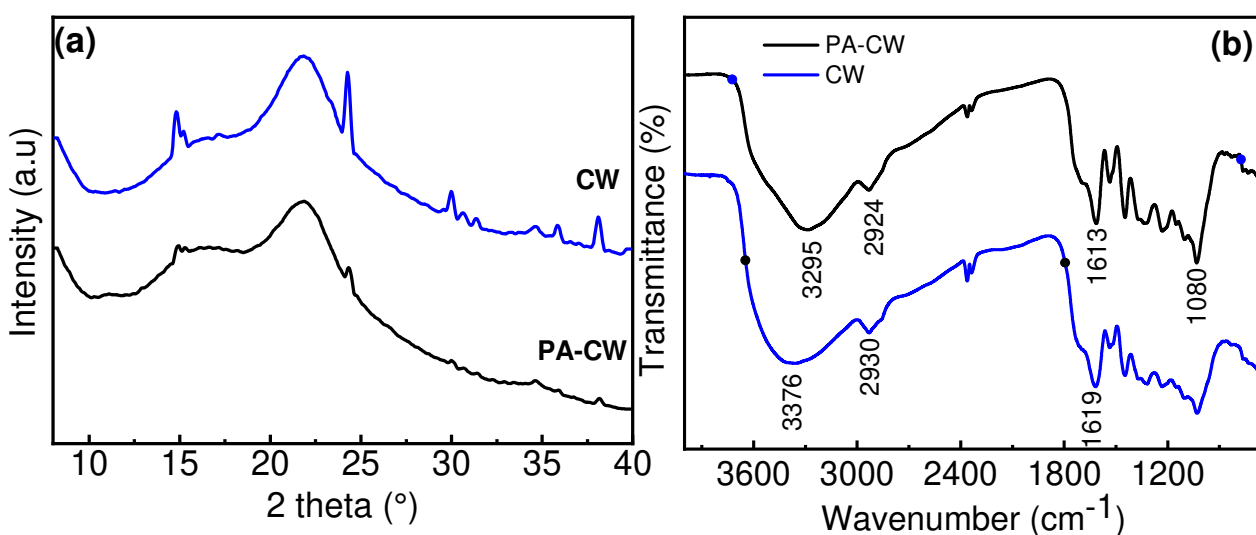
143 **2.5. Influence of co-existing anions**

144 The effect of interfering anions like Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-} (100 mg/L) on Cr(VI)
145 adsorption was studied using the optimum parameters ($[\text{Cr(VI)}]=100$ mg/L, $V=50$ mL,
146 $[\text{CW}]=0.05$ g or $[\text{PA-CW}]=0.025$ g, $\text{pH}=2$, contact time=120 min, $T=25^\circ\text{C}$).

147 3. Results and discussion

148 3.1. Characterization of CW and PA-CW

149 **Fig. 1a** and **S1** depict the crystal structure of raw CW, CW and PA-CW samples. The
150 XRD pattern of raw CW reveals two main peaks at 14.73° and 21.86° attributed to the
151 presence of cellulose (**Fig. S1**). In addition to cellulose peaks, the spectrum exhibits only a



152 few sharp peaks, signifying that the
153 pretreatment removed most of the impurities.

154
155 **Figure 1.** (a) XRD patterns of CW (blue) and PA-CW (black); (b) FTIR spectra of CW (blue)
156 and PA-CW (black).

157 The diffractogram of PA-CW comprises the typical cellulose peaks at 14.73° and 21.86° quite
158 similar to the CW precursor. From these results, it can be inferred that the pretreatment and
159 phytic acid modification of the CW reduced its crystallinity, meaning that the obtained

160 adsorbents are of amorphous nature. This characteristic is suitable for an effective adsorption
161 process (Güzel et al., 2015). Indeed, it has been observed that crystallinity affects the
162 adsorption capacity, the pollutant tends to adsorb onto amorphous regions rather than onto
163 crystalline ones (Gomez-Maldonado et al., 2019).

164 As seen in **Fig. 1b**, the FTIR plot of the CW displays many functional groups. It
165 comprises bands between 3280 and 3380 cm^{-1} which refer to OH stretching, and bands at
166 2930 cm^{-1} attributed to C-H of aliphatic groups. The peak at 1619 cm^{-1} is due to stretching
167 vibrations of C=O in the conjugated aldehyde and carboxylic acid groups, and the peak at
168 1447 cm^{-1} may be attributed to the C=O stretching in amide moiety. Besides, the bands at
169 1537 and 1231 cm^{-1} may be ascribed respectively to C=N and N-H stretching vibrations
170 (Pradhan et al., 2019). The FTIR spectrum of PA-CW reveals roughly similar features with a
171 slight shift of the characteristic wavenumbers due to phytic acid treatment. Furthermore, this
172 treatment is approved in comparison to FTIR plot of phytic acid, which shows peaks at 1080
173 and 1120 cm^{-1} attributed respectively to the stretching of P=O and P-O (Jahan et al., 2018).
174 Nevertheless, these peaks are also present in the CW spectrum at lower intensities, suggesting
175 the presence of phosphate groups before the phytic acid treatment.

176 The results of thermal analysis of CW revealed three mass losses (**Fig. S2**). The first mass
177 loss is related to the vaporization of free water at 100 °C, followed by two mass losses at 250
178 and 320 °C due respectively to cellulose and hemicellulose degradation. Furthermore, a slow
179 decomposition of lignin occurred at above 400 °C. Similar thermal behavior was observed for
180 PA-CW with a slight difference in the mass loss proportion related to the phytic acid (**Fig.**
181 **S2**). Quite similar interpretations were described by many researchers on agricultural waste
182 (Djilani et al., 2012; Sanchez-Silva et al., 2012).

183 The XPS survey spectra (**Fig. S3**) of CW and PA-CW samples confirmed the results of
184 FTIR by the presence of peaks due to phosphorus, carbon, nitrogen and oxygen at 136, 285,

185 400 and 532 eV, respectively (Sherwood, 2002; Ali et al., 2020). The atomic concentrations
186 of P_{2p} , C_{1s} , N_{1s} and O_{1s} in CW are 0.99, 79.10, 0.93 and 18.98 at%, respectively. For PA-CW,
187 the atomic concentrations of P_{2p} , C_{1s} , N_{1s} and O_{1s} were respectively 1.81, 72.30, 1.85 and
188 24.03 at%. The increase in O, N and P proportions after treatment is related to phosphate and
189 amine groups derived from phytic acid and urea.

190 The deconvolution of the core level of the C_{1s} of CW depicts four sets at 284.5 eV (63%),
191 286.0 eV (25%), 287.2 eV (9%) and 288.7 eV (3%), **Fig. 2**. These sets are attributed
192 respectively to C-C, C-O, C=O and C-OOH (Tadjenant et al., 2020). The O_{1s} plot can be
193 deconvoluted into three components at 530.8 eV (5%), 532.5 eV (90%) and 533.8 eV (5%)
194 corresponding respectively to C-OH, -C=O and P-OH groups (Ali et al., 2020). The N_{1s} band
195 of CW is curve-fitted with two components at 399.6 eV (79%) and 401.3 eV (21%) attributed
196 respectively to free $-NH_2$ and protonated amine group $-NH_3^+$ (Kehrer et al., 2019).

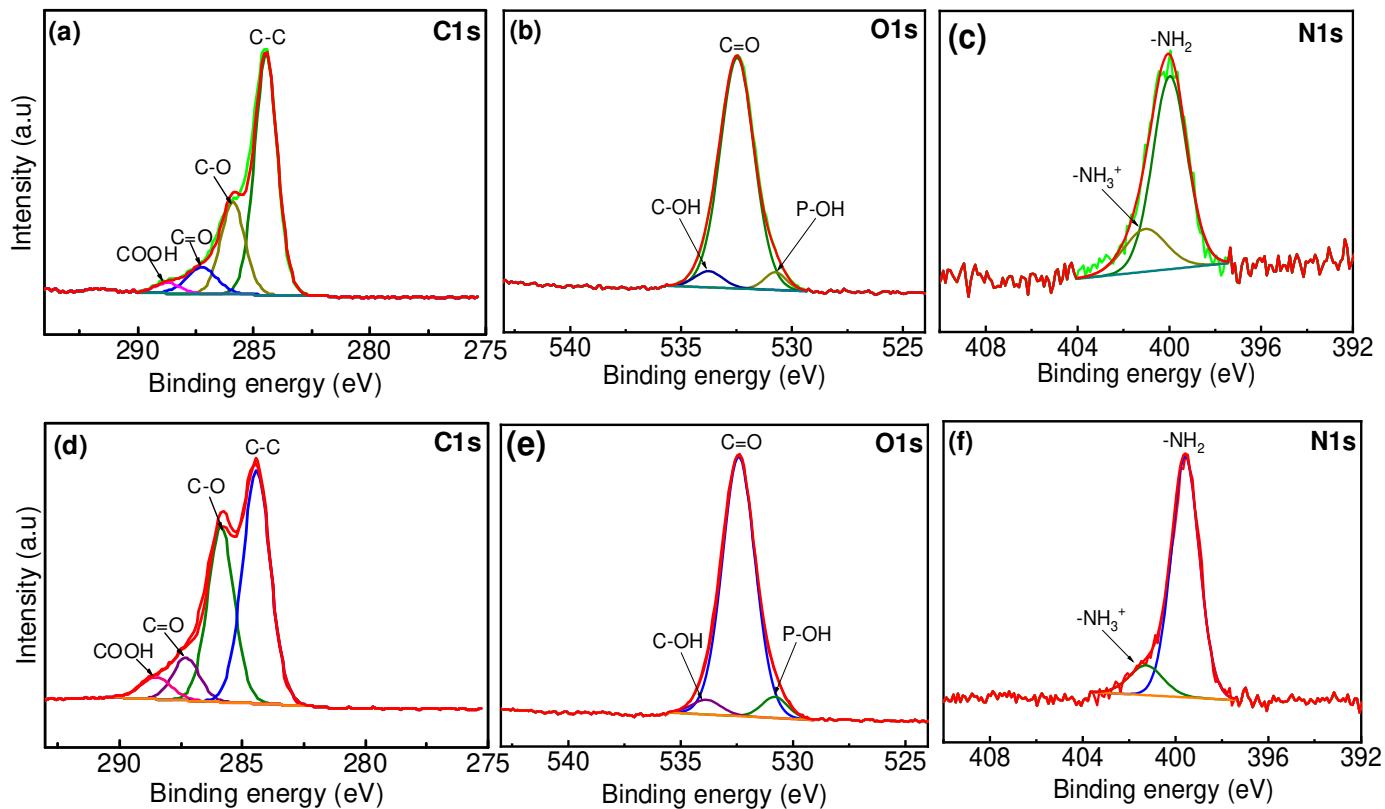
197 Similarly, the C_{1s} of PA-CW could be deconvoluted into four features at 284.5 eV (56%),
198 286.0 eV (28%), 287.2 eV (10%) and 288.7 eV (6%) related respectively to C-C, C-O and C-
199 OOH. The O_{1s} of PA-CW could be curve-fitted with two components at 530 eV (6%), 532.5
200 eV (89%) and 533.8 eV (5%) due respectively to C-H, C=O, and P-OH moieties. The
201 deconvolution of the N_{1s} of PA-CW reveals two sets of peaks at 399.6 eV (87%) and 401.3
202 eV (13%) ascribed respectively to $-NH_2$ and protonated amine $-NH_3^+$.

203 The specific surface area and porosity are important characteristics for an effective
204 adsorption, because they reflect the amount of active sites to retain the adsorbate (Almendros
205 et al., 2015). These features are determined by the standard BET method, which is used for a
206 wide range of fine powders and porous materials (Rouquerol et al., 2013). The N_2 adsorption-
207 desorption isotherms revealed that the isotherm has a type IV shape, according to the IUPAC
208 (International Union of Pure and Applied Chemistry) classification, characterized by an
209 hysteresis loop of H_3 -type related to non-rigid aggregates of plate-like particles (**Fig. S4**)

210 (Thommes et al., 2015). The surface area obtained for CW is 0.21 m²/g; this value is enhanced

211 by the phytic acid treatment to reach 4.1 m²/g for PA-CW. Literature data reported surface

212 areas ($0.5 < S_{\text{BET}} <$



213 5 m²/g) for agricultural waste used as adsorbents (Almendros et al., 2015).

214

215 **Figure 2.** Core level plots of (a) C_{1s}, (b) O_{1s}, (c) N_{1s} of CW; (d) C_{1s}, (e) O_{1s}, (f) N_{1s} of PA-
216 CW.

217 **3.2. Adsorption study**

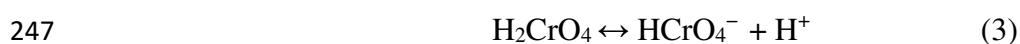
218 **3.2.1. Influence of pH**

219 The pH of the solution and resulting surface charge of the adsorbent have an important
220 impact on the adsorption mechanism (Rouquerol et al., 2013). The effect of pH (**Fig. S5**) on
221 the adsorption process was investigated at constant Cr(VI) concentration (100 mg/L) and
222 adsorbent amount (0.05 g/CW and 0.025 g/PA-CW) at 25 °C in the range of pH 2 to 8. For
223 both CW and PA-CW, the optimum pH was found to be 2 with an adsorption capacity of 98.0
224 and 196.5 mg/g, respectively. Thereafter, a sharp decrease was evidenced for Cr(VI) removal
225 by CW, when the pH was increased. However, a clear reduction of the adsorption capacity to
226 78.8 mg/g was noticed at pH \approx 4. For instance, this contrasts with PA-CW which exhibited
227 only a slight decrease of the adsorption capacity (\sim 6 mg/g) at pH \approx 4. The higher adsorption
228 capacity observed using PA-CW compared to CW could be explained by the presence of
229 more additional active sites like –OH, P=O and –NH₂ after phytic acid treatment in presence
230 of urea. In other words, at low pH, the predominant species present in the solution are HCrO₄⁻
231 (Zou et al., 2015), which are attracted to the positive sites formed by protonation of surface
232 moieties like amine, carboxyl and hydroxyl groups (Sathvika et al., 2019). Whereas at high
233 pH, repulsion forces occurred between the anionic molecules of the adsorbate and the
234 negatively charged surface, leading to adsorption capacity decrease (Kan et al., 2017).

235 The results were further validated by the determination of the point zero charge (PZC), as
236 shown in **Fig. S6**. The PZC values recorded for CW and PA-CW are respectively 5.4 and 4.4.
237 At pH < pH_{PZC}, the adsorbent surface is charged positively by the combination of excessive

238 protons (Dong et al., 2018), leading to enhanced adsorption capacity at low pH values of the
239 dominant HCrO_4^- species present in the solution phase. At $\text{pH} > \text{pH}_{\text{PZC}}$, the surface becomes
240 negatively charged and a decline of adsorption capacity was obvious. These observations are
241 in favor of Cr(VI) adsorption through electrostatic interactions between the negatively
242 charged chromium species (Eqs. 3-6) and the positively charged adsorption sites, resulting
243 from the protonation of the hydroxyl, phosphonate and amine groups on the adsorbent
244 surface.

245 The equilibrium reactions of different Cr(VI) species in aqueous media are summarized
246 below:



251 **3.2.2. Influence of initial concentration and contact time**

252 **Fig. S7** exhibits the study of contact time for different Cr(VI) concentrations (50-300
253 mg/L) at constant pH (2), and temperature ($25 \pm 2^\circ\text{C}$). The adsorption capacity increases
254 rapidly upon elevating the Cr(VI) concentration in the first 90 min, then slows down till it
255 reaches equilibrium at 120-180 min. This could be ascribed to the presence of available sites
256 on the adsorbent at the beginning (Khan et al., 2017). Thus, a contact time of 120 min was
257 selected as an equilibrium contact time, since longer times were not effective in improving the
258 adsorption capacity.

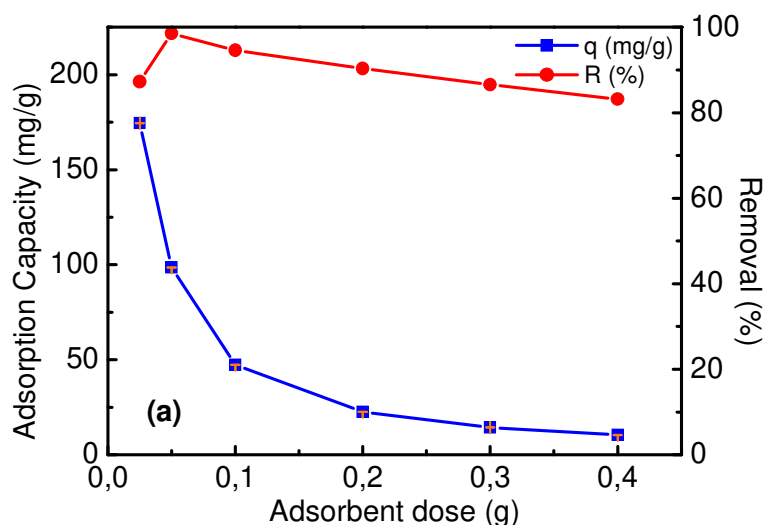
259 Furthermore, increasing the concentration of Cr(VI) from 50 to 300 mg/L causes an
260 enhancement in the adsorption capacity from 47.0 to 247.0 mg/g for CW and from 95.3 to
261 411.1 mg/g for PA-CW. This significant increase might be due to the maximum driving force
262 provided by the elevation of Cr(VI) concentration to face the mass transfer resistance of metal

263 ions due to collision with active sites during the adsorption process (Kuppusamy et al., 2016).

264 The same results were observed in previous studies (Saka et al., 2012; Yagub et al., 2014).

265 **3.2.3. Effect of adsorbent dose**

266 The influence of adsorbent dose was studied in 100 mL conical flasks using 50 mL of
267 fixed



268 concentration (100 mg/L) of Cr(VI) at pH 2 and $25\pm 2^\circ\text{C}$. The results in **Fig. 3** revealed that
269 the highest percentage of Cr(VI) elimination was achieved using 0.05 and 0.025 g of CW and
270 PA-CW with an adsorption capacity of 98.6 and 195.6 mg/g, respectively. Thereafter,
271 increasing of the adsorbent amount from 0.025 to 0.4 g caused a decline of the adsorption
272 capacity from 181.7 to 10.4 mg/g for CW and from 195.6 to 10.3 mg/L for PA-CW. This is
273 most likely due to the agglomeration of the biomass particles, and also to the presence of
274 more adsorbent than what it is necessary to remove the totality of the adsorbate (Ahmad et al.,
275 2017; Pradhan et al., 2019). On the other hand, an increase of the efficiency was observed
276 from 0.025 to 0.5 g in the case of CW, owing to the availability of exchangeable sites for ion
277 metals. Then a weak decline was noticed for both adsorbents upon increasing the adsorbent
278 dose due to the hidden sites, resulting from the reduction of the effective specific surface area
279 (Tadjenant et al., 2020).

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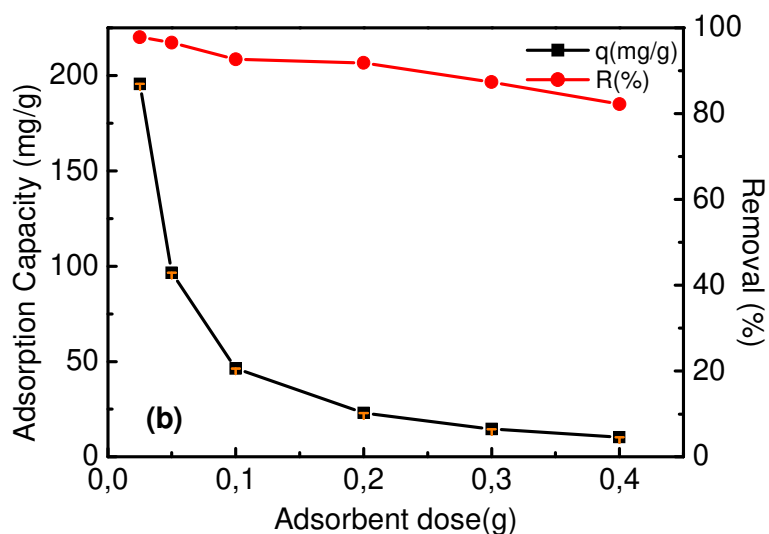
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288

289 **Figure 3.** Influence of adsorbent dose on Cr(VI) removal by (a) CW and (b) PA-CW.

290 3.2.4. Effect of temperature

291 The influence of temperature on Cr(VI) removal was assessed using 100 mg/L of Cr(VI)

292 solution, 0.1 g of CW or 0.05 g of PA-CW at pH 2 and various temperatures (25, 35 and

293 45°C) for a contact time of 180 min. As observed in **Fig. S8**, there is no difference in

294 adsorption capacity equilibrium even at high temperature. Though the difference was

295 observed on the equilibrium itself, it was achieved faster at 45°C (60 min) rather than at 35°C

296 (90 min) and 25°C (120 min). This could be due to an increase of the adsorbent particles or

297 the mobility of metal ions, resulting from the rise of temperature that provides a decrease of

298 the viscosity of the solution (Güzel et al., 2015; Nasseh et al., 2017).

299 3.3. Data modeling

300 3.3.1. Kinetic modeling

301 Kinetic models are investigated to study the mechanism controlling the adsorption

302 process, like mass transfer, residence time and sorption reactions (Ho and McKay, 1999)

303 using Laggragen (Ahmad et al., 2017), fist-order and second-order models expressed by the
304 relationships (7, 8) :

$$305 \quad \ln(q_t - q_e) = \ln q_e - k_1 t \quad (7)$$

$$306 \quad \frac{t}{q_t} = \frac{1}{k_1 q_e} + \frac{t}{q_e} \quad (8)$$

307 Where q and q_e represent the amounts (g) of solute sorbed per gram of adsorbent at any time
308 and at equilibrium, respectively, and k_1 (min^{-1}) and k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) denote
309 respectively the rate constants of the first-order and second-order.

310 The results obtained from the kinetic modeling are summarized in **Fig. 4, Tables S1** and **S2**.
311 The experimental values of adsorption capacity are closer to the ones found using the second
312 order model and the plots were linear with good correlation coefficients. Therefore, it is
313 considered that pseudo second order is an adequate model, which better fits the Cr(VI)
314 adsorption process onto both CW and PA-CW, as initially described for low initial
315 concentrations (Ho and McKay, 1999; Azizian, 2004a).

316 **Intra-particle diffusion model**

317 Intra-particle diffusion model expresses the relation between the adsorption capacity and
318 the square of time given by Webber and Morris equation:

$$319 \quad q_t = k_{id} t^{1/2} + C \quad (9)$$

320 Where k_{id} ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$) denotes the intra-particle diffusion rate constant and
321 C ($\text{mg} \cdot \text{g}^{-1}$) represents a constant related to the thickness of the boundary layer. This model
322 describes the mechanism of the particle diffusion through specific pores and the rate limiting
323 step (Largitte and Pasquier, 2016). The intra-particle diffusion is the rate limiting sequence of
324 the adsorption only if the plot of q_t vs $t^{1/2}$ is a straight line, which crosses the origin
325 (Ofomaja, 2010).

326 Two straight portions are noticed (**Fig. S9**), suggesting that the intra-particle diffusion is not
327 the only step controlling the adsorption process. The first segment refers to the external
328 diffusion through macropores and the second segment corresponds to the internal diffusion
329 through micropores (Güzel et al., 2015). The values of the constant k_{d1} are higher than those
330 of k_{d2} (refer to **Table S3** and **S4**) due to the important diffusion from the solution to the intra-
331 particle regions during the first stage, unlike to the second stage where the Cr(VI)
332 concentration gradient dropped significantly (Tadjenant et al., 2020).

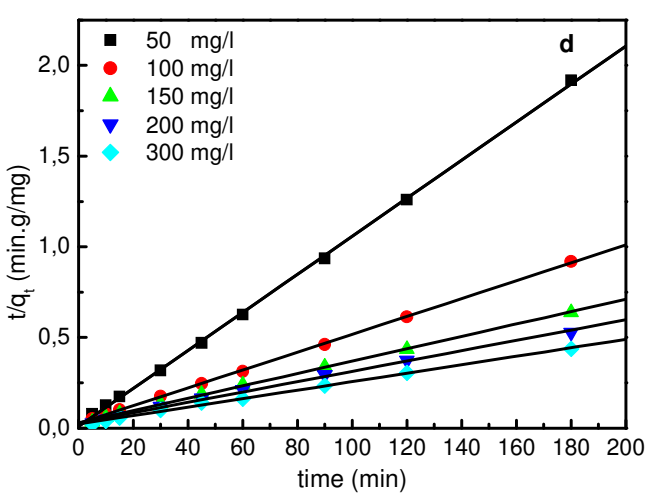
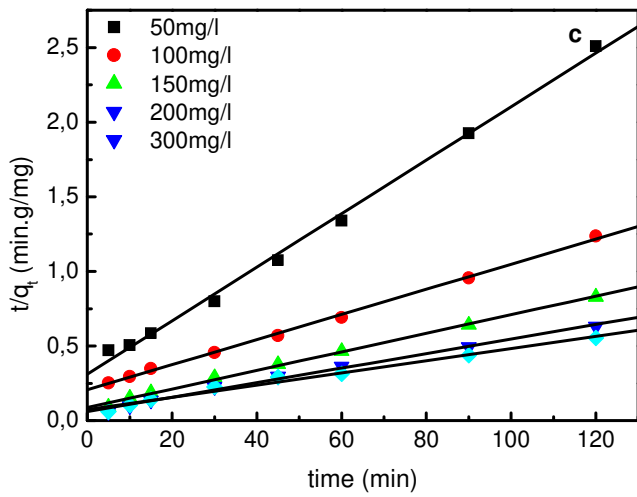
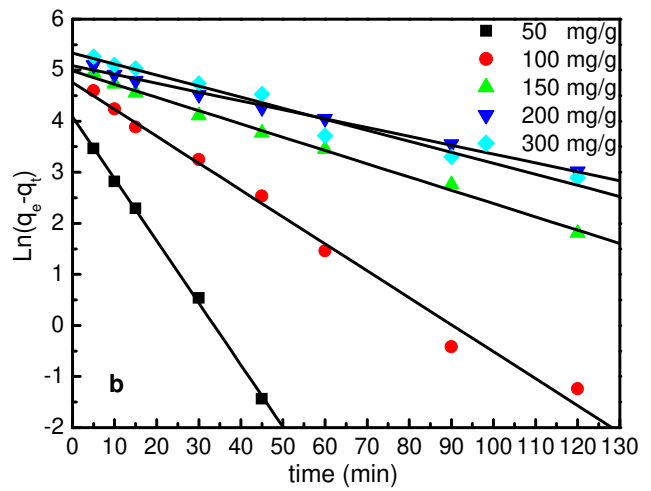
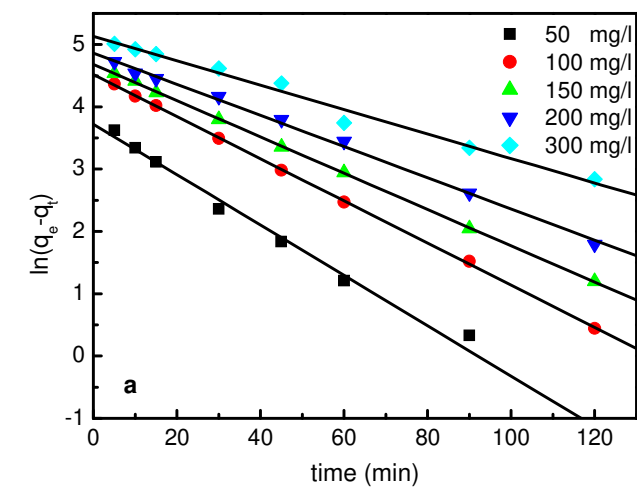
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339 **Figure 4.** The plots of pseudo-first order models of (a) CW, (b) PA-CW and pseudo-second
340 order models of (c) CW and (d) PA-CW for Cr(VI) removal.

341

342 3.3.2. Isotherm modeling

343 To gain more information on the adsorption process, it is necessary to view the link
344 between the amount adsorbed per unit mass of adsorbent (q_e) and the remaining
345 concentration of the adsorbate (C_e) at equilibrium. Many theoretical models are developed to
346 describe the adsorption isotherms. The most known ones are Langmuir and Freundlich
347 (Rangabhashiyam et al., 2014). For many years, the Langmuir model adapted is the classical
348 one used to describe the adsorption from gas phase. It consists of monolayer adsorption with
349 one kind of adsorbing sites, which can accommodate only one adsorbate molecule, and also
350 assumes that there is no interaction between the adsorbed molecules, thus the adsorption
351 energy is constant (Ruthven, 1984). A revised form of the Langmuir model was proposed in
352 2018. It provides an insight on the nature of adsorption and desorption processes in
353 condensate phases (Azizian et al., 2018). This model is expressed as:

$$354 \quad \frac{C_e}{q_e} = \frac{C_s}{K_{ML}q_m} + \frac{(K_{ML}-1)C_e}{K_{ML}q_m} \quad (10)$$

355 Where C_s denotes the saturation concentration of Cr(VI) in liquid phase ($45 \text{ mg} \cdot \text{L}^{-1}$), q_m the
356 maximum adsorption capacity and K_{ML} is the constant of modified Langmuir.

357 Hence, the commonly multilayer model used is Freundlich model. It assumes heterogeneous
358 surface and possible interactions between the adsorbed species (Rouquerol et al., 2013;
359 Hussain and Kharisov, 2016). It is expressed as:

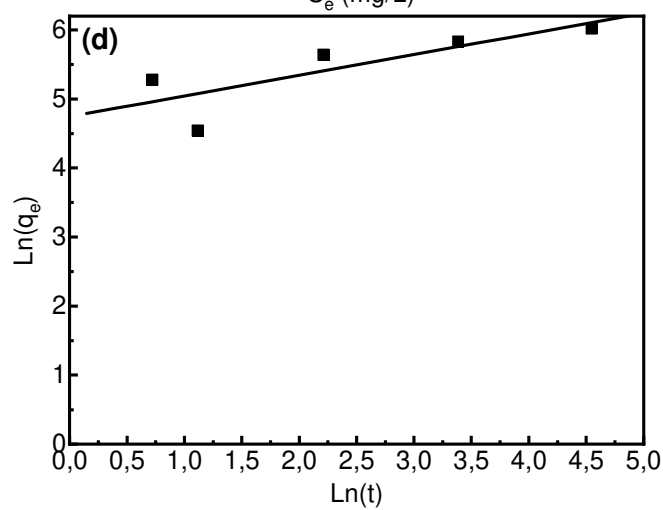
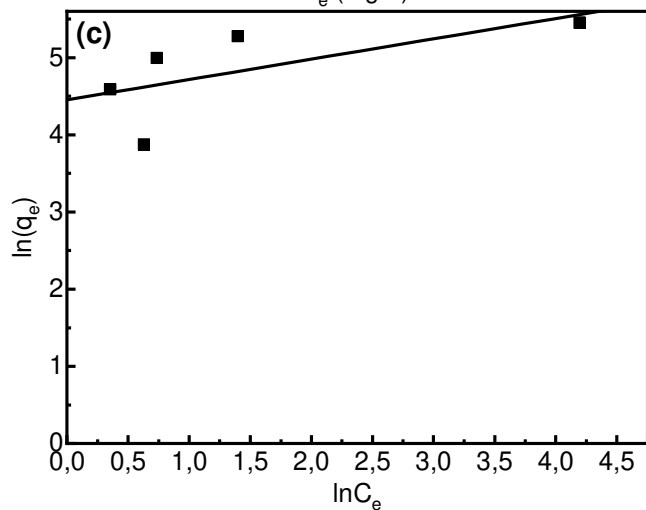
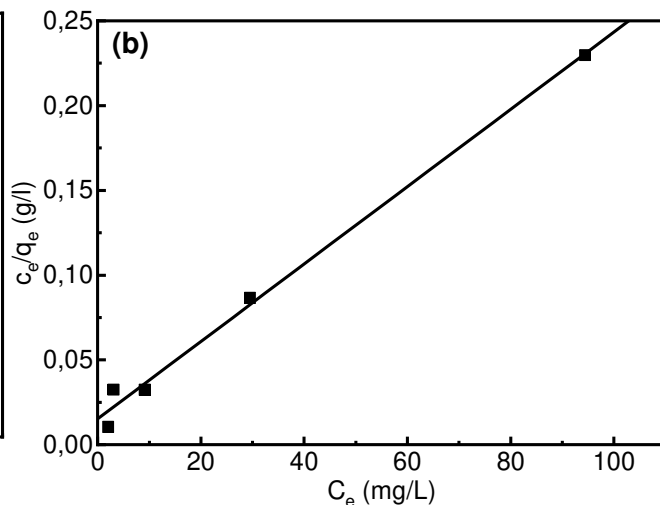
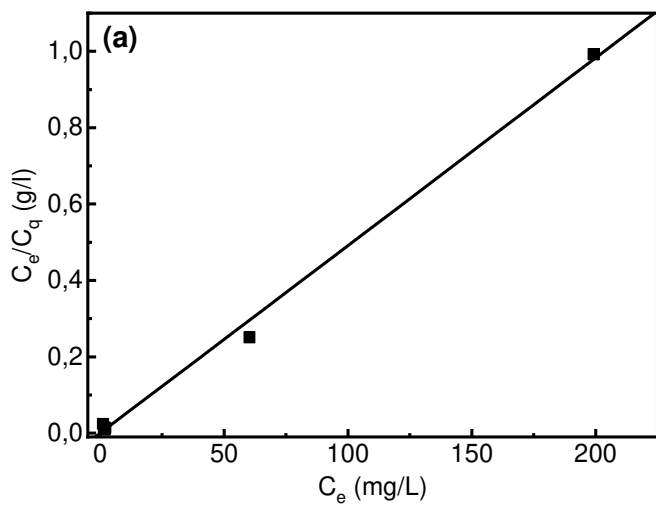
$$360 \quad \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (11)$$

361 Where K_f and n correspond to the Freundlich constant related to the adsorption capacity and
362 adsorption intensity, respectively.

363 From the results illustrated in the **Table S5** and **Fig. 5**, it could concluded that the Cr(VI)
364 adsorption onto CW and PA-CW follows the modified Langmuir model with a maximum
365 adsorption capacity of 212.4 and 387.9 mg/g, respectively.

366 A comparison of the adsorption capacities of Cr(VI) onto some natural adsorbents and the
367 one obtained from this study is depicted in **Table 1**. It could be clearly seen that Cr(VI)
368 adsorption onto CW and PA-CW are among the most effective processes realized in a short
369 time.

370



372 **Figure 5.** Langmuir model (a) CW, (b) PA-CW; Freundlich model (c) CW, (d) PA-CW for
 373 Cr(VI) adsorption.

374

375 **Table 1.** Comparison between results recorded for Cr(VI) adsorption onto carob waste (CW)
 376 and phytic acid-treated CW to the results of previous studies on natural adsorbents.

Adsorbent	q_{\max} (mg/g)	Kinetic model	Isotherm model	Contact time (min)	pH	Reference
PA-CW	387.9	2 nd order	Langmuir	120	2	This study
CW	212.4	2 nd order	Langmuir	120	2	This study
<i>Pistachiohull</i>	116.6	2 nd order	Langmuir	70	2	(Moussavi and Barikbin, 2010)
Tea waste	90.9	2 nd oredr	Langmuir	240	3.9	(Nigam et al., 2019)
<i>Melaleuca diosmifolia</i>	62.5	2 nd order	Langmuir	420	2-3	(Kuppusamy et al., 2016)
Acidically prepared rice husk carbon	47.6	2 nd order	Langmuir-Freundlich	120	2	(Khan et al., 2016)
Activated carbon from fox nutshell	46.2	2 nd order	Langmuir	60	2	(Kumar and Jena, 2017)
<i>Gliricidiasepium</i> leaf powder	35.7	2 nd order	Freundlich	160	2	(Suganya et al., 2019)
Banana Peel	10.4	2 nd order	Langmuir and Dubivin-Radeskevich	60	2	(Parlayici and Pehlivan, 2019)
Crambery	15.2					
Rosehup seed shell	6.8					
Sunflowers	7.9	2 nd order	Langmuir	120	2	(Jain et al., 2013)
Amalta leaves	4.5	2 nd order	Langmuir	360	4	(Ahmad et al., 2017)
Peanut shell	4.3					

377

378 **3.3.3. Thermodynamic study**

379 The determination of thermodynamic factors such as free energy ΔG° , enthalpy ΔH° and
380 entropy ΔS° allows to qualify the spontaneity of the adsorption process and the nature of
381 energy (exothermic or endothermic) (Pradhan et al., 2019). These parameters are given by the
382 following equations:

$$383 \quad K_d = \frac{q_e}{c_e} \quad (12)$$

$$384 \quad \Delta G^\circ = -RT \ln K_d \quad (13)$$

$$385 \quad \Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (14)$$

$$386 \quad \ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T} \quad (15)$$

387 Where T corresponds to the adsorption temperature (K) and R denotes the universal gas
388 constant ($J \cdot mol^{-1} K^{-1}$). From the data in **Figure S10** and **Table S6**, it could be deduced that
389 the process of Cr(VI) uptake is spontaneous and physical, owing to the negative charge
390 preceding the value of ΔG° which is less than 20 KJ/mol (Güzel et al., 2015).

391 Moreover, the negative value of ΔH° reveals that the nature of the adsorption is exothermic.
392 Whereas, the entropy ΔS° infers the randomness of the adsorbate molecules on the surface of
393 the adsorbent.

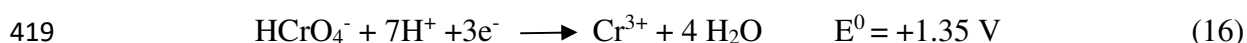
394 **3.3.4. Cr(VI) removal mechanism**

395 XPS analysis (**Fig. 6**) gives valuable information on the valence state of species on the
396 adsorbent surface before and after adsorption. The Cr_{2p} high-resolution XPS plots of the CW
397 (**Fig. 6a**) and PA-CW (**Fig. 6b**) after adsorption process revealed peaks ascribed to Cr_{2p1/2} and
398 Cr_{2p3/2} respectively at 588 and 579 eV associated with Cr(VI). Furthermore, the optimum
399 fitting after deconvolution of Cr_{2p} spectrum revealed two additional components at 575 and
400 585 eV ascribed to Cr(III) (Tadjenant et al., 2020). The results clearly suggest that Cr(VI)
401 adsorption is accompanied by its reduction to Cr(III). It is important to notice that Cr(III)
402 represents the highest portion on both adsorbents' surface (PA-CW: 88% and CW: 66%).

403 Therefore, Cr(VI) reduction to Cr(III) was higher using PA-CW than CW although both of
404 them are good adsorbents for Cr(VI) elimination.

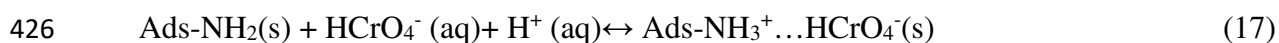
405 In addition, deconvolution of the C_{1s} of CW and PA-CW, after Cr adsorption (**Fig. S11**),
406 revealed the presence of a peak at 282.9 eV ascribed to C-Cr bond (Folkenant et al., 2015).
407 This peak, absent in the C_{1s} of the initial adsorbent materials, accounts for 13% and 19% after
408 Cr(VI) adsorption on respectively CW and PA-CW. In addition, the overall contributions of
409 different carbon moieties (C-OH, C=O and COOH) before and after Cr(VI) adsorption did not
410 vary significantly, while the C-H/C-C contribution decreased by about 18% and 11% for CW
411 and PA-CW, respectively (**Table S7**). Taken together, these results suggest that Cr(VI)
412 reduction took place through C-H sequential oxidation, as previously suggested by Zhuang et
413 al. (Zhuang et al., 2014) even though their XPS results did not provide any evidence for the
414 presence of C-Cr bonds.

415 Cr(VI) removal occurred by adsorption, reduction and/or adsorption-reduction, owing to the
416 different functional groups present on the adsorbent surface, as illustrated by XPS analysis in
417 **Fig. 2**. Cr(VI) reduction requires 3e⁻/7H⁺ (Eq. 16), signifying that this process is favorable in
418 acidic media.



420 XPS analysis provided a convincing evidence on Cr(VI) reduction to Cr(III) ions and their
421 adsorption of the adsorbents' surface. The appearance of C-Cr species in the C_{1s} XPS plot
422 indicates the involvement of C-H bond oxidation during Cr(VI) reduction to Cr(III).

423 Cr(VI) elimination occurred directly through Cr(VI) anions binding onto the positively
424 charged surface moieties of the adsorbents (Ads) involving electrostatic interactions (Eqs. 17-
425 19) (Park et al., 2008).



442 **Figure 6.** High resolution XPS plots of the Cr_{2p} of CW (**a**) and PA-CW (**b**) after Cr(VI)
443 adsorption.

444 3.3.5. Desorption study and interfering anion effect

445 In order to assess the practical utility of CW and PA-CW, desorption tests were conducted.
446 The regeneration of the adsorbents was performed up to 4 cycles using 0.1 M NaOH as the
447 eluent agent (Hsini et al., 2021). The results in **Fig. 7a** indicate that the removal of Cr(VI)
448 decreased upon increasing the number of cycles. The adsorption capacities of CW were found
449 to be 55.1, 33.6, 28.7 and 25.1 mg/g, while those of PA-CW were determined to be 109.0,
450 70.7, 54.2 and 49.3 mg/g, respectively for the first, second, third and fourth cycles of Cr(VI)
451 adsorption. The obtained data infer that, under our experimental conditions, the electrostatic
452 interactions of Cr species with the adsorbents' surface are sufficiently strong to be displaced
453 by 0.1 M NaOH, thus leading to only partial removal of the adsorbed chromium. Additional
454 experiments are required to optimize the desorption conditions to achieve full regeneration of
455 the surface i.e. total desorption of chromium species from the adsorbent surface.

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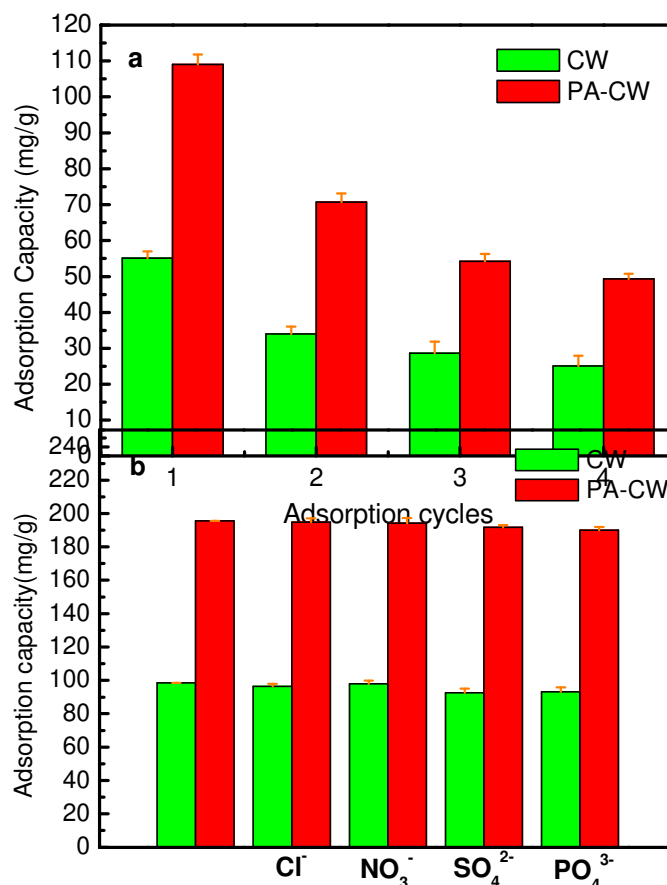
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469 **Figure 7.** (a) Effect of regeneration cycles and (b) effect of interfering anions on the

470 adsorption of Cr(VI) onto CW and PA-CW.

471 Furthermore, the influence of co-existing anions like Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-} on the

472 Cr(VI) removal on both CW and PA-CW was investigated (**Fig. 7b**). The results revealed that

473 these anions, when investigated at the same concentration as that of Cr(VI), did not have a

474 significant impact on the adsorption capacity. Indeed, only a slight decrease (2 – 6 mg/g) of

475 the adsorption capacity was recorded under our experimental conditions, suggesting the lack

476 of competition of these anions for binding the positively charged surface in presence of

477 chromium anions or the electrostatic interactions of Cr(VI) with the positively charged

478 binding sites on the adsorbents' surface are much stronger (Dong et al., 2018). The results

479 corroborate the data of the regeneration study.

480 **4. Conclusion**

481 The adsorption of Cr(VI) onto carob waste (CW) is a low cost technique to reduce and

482 remove this toxic contaminant. Our study demonstrated that agricultural CW can substitute

483 the classical adsorbents, owing to its important adsorption capacity of 212.4 mg/g.

484 Furthermore, the activation of the CW with phytic acid (PA) as an eco-friendly molecule

485 improved the specific surface area from 0.21 m^2/g to 4.1 m^2/g and enhanced the adsorption

486 capacity to 387.9 mg/g. The data gathered from different characterizations of CW and PA-

487 CW like FTIR, XRD, TGA and BET showed that both adsorbents have the required

488 properties like amorphous structure, favorable porosity and specific surface area for a
489 satisfying adsorption. The adsorption tests revealed that the optimum pH was 2 for both raw
490 CW and PA-CW at 25°C for 2h as equilibrium contact time. The data of kinetic study fitted
491 well the pseudo second order, whereas the isotherm modeling inferred that the modified
492 Langmuir model is the adequate model describing the adsorption process. Besides, the
493 thermodynamic results reflected that Cr(VI) adsorption onto CW and PA-CW is a
494 spontaneous and a physical adsorption process. XPS analysis of CW and PA-CW after Cr(VI)
495 adsorption evidenced that Cr(VI) was reduced to Cr(III), suggesting a reduction-adsorption
496 mechanism. To sum up, carob and phytic acid-treated carob wastes are effective for Cr(VI)
497 ions effective removal.

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Graphical Abstract

