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1 Investigation of chromate and nitrate removal by adsorption at the surface of an
2 amine-modified cocoa shell adsorbent

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11

12 **Keywords:** 3-aminopropyltriethoxysilane; cocoa shell; amine modified, physisorption;
13 chemisorption; heavy metals, nitrate, adsorption

14

15 **ABSTRACT**

16 Nitrate (NO₃⁻) and chromium (Cr(VI)) ions from contaminated aqueous solutions were
17 successfully adsorbed onto functionalized cocoa shell (ECAB, an agricultural waste material) *via*
18 chemical grafting of 3-aminopropyltriethoxysilane (APTES). The resulting adsorbent – ECAB-
19 APTES-HCl – was characterized by SEM, zeta potential, calorimetry, FTIR spectroscopy and
20 point of zero charge. The adsorption parameters were investigated to optimize the removal of
21 chromium and nitrate ions. The maximum removal efficiency stabilized at around 91-99% for
22 chromium and 58% for nitrate, for an initial concentration of 50 mg.L⁻¹ of the ions. The
23 adsorption process fitted well with both Freundlich and Langmuir isotherms, and with the
24 pseudo-second order model. Accordingly, adsorption onto ECAB-APTES-HCl involved both
25 physisorption and chemisorption. Desorption studies demonstrated that 82% of nitrate and 79.8%
26 of chromium were recovered in less than 2 hours. These results open onto the possible removal of

27 heavy metals from aqueous solutions in the absence of energy constraints, using low-cost
28 biomass relevantly functionalized for high adsorption efficiency.

29

30 **1. Introduction**

31 Nitrate (NO_3^-) and heavy metals such as chromium [Cr(VI)] are more and more utilized with the
32 continuous progress of industrialization. The water contaminants produced by industrial
33 manufacturing can not only directly damage the water ecosystem but also greatly threaten human
34 health because they are usually toxic, persistent, non-biodegradable, and accumulate in the food
35 chain [1-4].

36 The environmental hazards associated with these effluents are toxicity, bioaccumulation, and
37 effects on human health like skin irritation, dermatitis, conjunctivitis and painful colic if absorbed
38 orally [5-8]. In view of these environmental concerns and health issues, scientists have to develop
39 approaches and efficient adsorbents to remove heavy metal pollutants from wastewaters before
40 discharging them into natural water bodies. Numerous methods are available for nitrate and
41 heavy metal remediation from water, e.g., reverse osmosis, electrochemical methods, filtration,
42 ion exchange, flocculation, or coagulation [9-11]. Adsorption is one such method. It has several
43 advantages when compared to other methods such as ease of operation, improved efficiency,
44 limited cost, and reusability that reduces sludge disposal issues [12, 13].

45 Many adsorbents have already been evaluated, but, except for biomass and derivatives, most
46 materials have showed low adsorption capacities towards pollutants in aqueous solution [14-16].
47 Intensive research is being focused on promoting ecofriendly and low-cost agricultural waste
48 materials for water treatment. Biomass is widely available in nature, and growing interest is now
49 focused on its use as a promising source for the production of activated carbon and as a potential

50 alternative for adsorbing hazardous pollutants in aqueous solution [17-19]. However, biomass
51 materials remain a major issue as to surface functionalization and activation, and several studies
52 have already been carried out to overcome these shortcomings. The relatively limited number of
53 functional groups at the biomass surface seriously impedes the efficient use of numerous
54 adsorbents for practical applications in the removal of toxic molecules from water.

55 A relevant approach consists in functionalizing non-polluting biomass through impregnation
56 with polymers and amines. Adsorbent-pollutant interactions are an essential requirement in this
57 respect, and can be achieved using basic chemical functions of materials such as hydroxyl and
58 amine groups. Amine-enriched materials have already showed high affinity towards toxic
59 pollutants in water [20-22]. The improvement of their affinity was explained in terms of mere
60 incorporation of a vegetal source of -OH and -NH₂ groups. Unlike composite materials (zeolites,
61 metal-organic frameworks (MOFs), and others) tested in the removal of chromate and nitrate
62 ions, low-cost natural materials such as vegetal waste display low surface acidity and do not
63 require sophisticated modification procedures. The structure of all vegetal materials bears
64 terminal hydroxyl and amine groups but does not necessarily exhibit interesting affinity towards
65 organic and inorganic pollutants due to structure constraints. This is why vegetal waste
66 modification often turns out to be an essential requirement to improve affinity for pollutants.
67 Nitrate and heavy metal binding is required to use amine derivate to remove heavy metals from
68 water by adsorption. Structural groups like -COOH, -NH and -OH present in natural and
69 modified polymer (cellulose, chitosan, lignin) act as active sites for nitrate and heavy metal
70 binding by hydrogen bonding, hydrophobic interactions or complexation [23, 24].

71 The present study is focused on cocoa shell (ECAB), a byproduct of the cocoa industry.
72 ECAB was chemically modified by 3-aminopropyltriethoxysilane grafting through silanization,
73 followed by a protonation step. Such a chemical modification is supposed to improve the

74 adsorption properties of ECAB. Nevertheless, the role of amine in nitrate and chromium
75 adsorption onto a solid surface remains to be elucidated, more particularly on OH- and/or NH₂-
76 enriched solid surfaces, where competitive interactions can occur between pollutants and
77 adsorbent surfaces bearing -NH₂ and/or -OH and -COO⁻ groups. The originality of this approach
78 lies in (i) the attempts to induce both physical and chemical interactions to capture pollutants, and
79 (ii) a comparative study with our similar recently published work. For this purpose, the
80 comparison with our previous work was correlated with the surface properties and adsorption
81 performances [21, 25]. A comprehensive characterization through physicochemical techniques
82 such as FTIR and DSC spectroscopy, scanning electron microscopy and zeta potential provided
83 valuable insights. Moreover, the behavior of the adsorbents towards pollutants was examined in
84 terms of equilibrium isotherms and kinetic studies.

85

86 **2. Materials and methods**

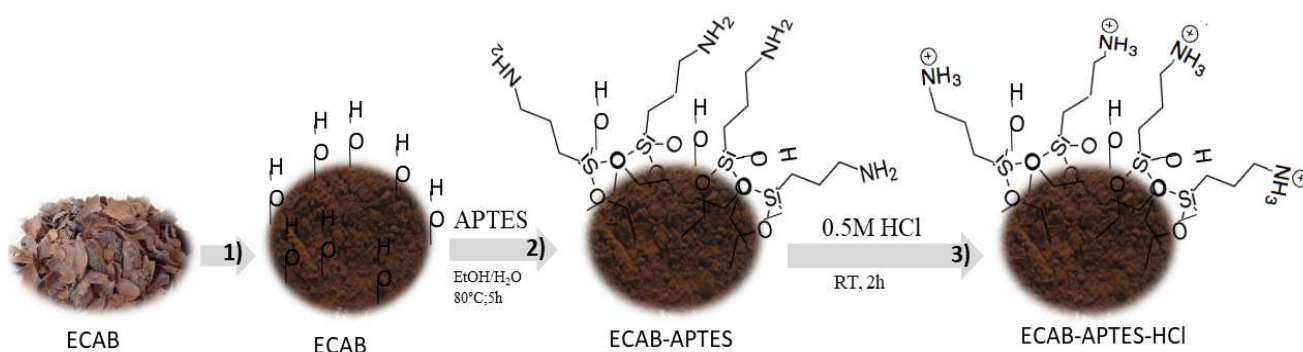
87 **2.1. Chemicals**

88 Potassium dichromate (K₂Cr₂O₇, 99%), sulfuric acid (95%), absolute ethanol (EtOH, 99%), 1.5-
89 diphenylcarbazide (C₁₃H₁₄N₄O, 98%), 3-aminopropyltriethoxysilane (APTES, 98%),
90 hydrochloric acid (37%), acetic acid (CH₃COOH, 96%), sodium hydroxide (98%),
91 ethylenediaminetetraacetic acid disodium salt (C₁₀H₁₄N₂Na₂O₈, 2H₂O, 99%), sodium nitrate
92 (NaNO₃, 99%), potassium nitrate (KNO₃, 99%), salicylic acid (C₇H₅NaO₃, 99%), sodium
93 phosphate monobasic monohydrate (H₄NaO₅P), and sodium azide (NaN₃, 99.5%) were purchased
94 from Merck (France) and used as supplied. All the solutions were prepared using double distilled
95 water (Merck, Millipore).

96 **2.2. Preparation and functionalization of modified cocoa shell**

97 The functional ECAB-APTES-HCl and ECAB materials were prepared as follows:

- 98 i) Firstly, cocoa shell was collected from a local farm managed by the IRAD (Institute of
 99 Agricultural Research for Development) at Yaoundé, Cameroon. It was cut, washed
 100 with acidic water (HCl , 1 mol.L^{-1}) to remove organic matter, sun-dried for 5 days and
 101 then heated at $70 \text{ }^\circ\text{C}$ overnight to remove moisture. Then it was ground and sifted at
 102 $160 \text{ }\mu\text{m}$. The resulting powder was named ECAB.
- 103 ii) Secondly, APTES was chemically grafted using water/ethanol 1:3 (V/V) as a solvent,
 104 and a mixture of ECAB/APTES 1:3 (W/W) at $80 \text{ }^\circ\text{C}$ for 5 hours. The synthesized
 105 product, named ECAB-APTES, was filtered ($0.45 \text{ }\mu\text{m}$ filter paper under vacuum
 106 (Fisherbrand)), washed several times, and then dried at $70 \text{ }^\circ\text{C}$ overnight [26].
- 107 iii) Finally, ECAB-APTES was acidified using HCl solution to protonate the amino
 108 groups and lead to positively charged ammonium moieties [27]: 1 g of ECAB-APTES
 109 was stirred in 100 mL of 0.5 mol.L^{-1} HCl for 2 h at room temperature. The acidified
 110 material, named ECAB-APTES- HCl , was recovered by filtration, washed several
 111 times, and then dried at $70 \text{ }^\circ\text{C}$ overnight (**scheme 1**).



112 ECAB ECAB ECAB-APTES ECAB-APTES-HCl

113 **Scheme 1:** Schematic illustration of the ECAB-APTES- HCl preparation procedure: 1)
 114 preparation of ECAB agricultural waste; 2) chemical grafting of APTES; 3) protonation step.

115

116 **2.3. Characterization of the material**

117 ECAB, ECAB-APTES and ECAB-APTES-HCl were characterized by scanning electron
118 microscopy (SEM), EDS (energy dispersive X-ray spectroscopy), Fourier transforms infrared
119 spectroscopy (FTIR), and differential scanning calorimetry (DSC); moreover, the points of zero
120 charge (pH_{pzc}) were determined. For SEM, adsorbents were metallized by a gold layer at 18 mA
121 for 360 s using a Biorad E5200 device. Then, SEM images were acquired using a ZEISS EVO 15
122 electron microscope. Two types of images were recorded: secondary ion images to observe the
123 morphology of the surface, and EDS images to evaluate the chemical contrast. FTIR analysis was
124 performed using a Tensor 27 (Bruker) spectrometer with a ZnSe ATR crystal in the 4000 – 500
125 cm^{-1} wavenumber range. For each spectrum, 20 scans were recorded with a resolution of 4 cm^{-1} .
126 DSC of the samples was carried out with a DSC – 131 Setaram, with a 20 °C to 500 °C
127 temperature range and a heating rate of 10 °C.min⁻¹. The zeta potential was measured for each
128 sample dispersion using the phase analysis light scattering (PALS) mode and a Malvern zeta sizer
129 nano ZS setup.

130 The pH values at the point of zero charge (pH_{pzc}) of ECAB, ECAB-APTES and ECAB-
131 APTES-HCl were determined by the solid addition method [28], using a Consort C 863
132 electronic multiparameter analyzer. The initial pH value (pH_i) of 50 mL of 0.1 mol.L⁻¹ of NaNO₃
133 solution was roughly adjusted in the 2 -12 pH range using 0.1 mol.L⁻¹ NaOH and HCl. Then, 0.1
134 g of each sample was placed in a 100-mL conical flask for 48 h to reach equilibrium at ambient
135 temperature. After that, the final pH (pH_f) of the solutions was measured, and pH_{pzc} was
136 determined as $\Delta\text{pH} = 0$ from a plot of ($\text{pH}_f - \text{pH}_i$) *versus* pH_i .

137 **2.4. Adsorption study**

138 Batch adsorption experiments were carried out at 300 rpm and at room temperature in 100-mL
139 shaking flasks containing 0.2 g of adsorbent and 50 mL of ions at different concentrations (from
140 50 to 400 mg.L⁻¹). The effects of different parameters (contact time, pH, initial concentration),

141 were also examined. Adsorption kinetics were obtained at $T = 20\text{ }^{\circ}\text{C}$ and $\text{pH}_i = 5.5$ and 4.5 for
142 nitrate and Cr(VI), respectively. After shaking for an appropriate time, ECAB and modified
143 ECAB samples were separated from the solution using $0.45\text{ }\mu\text{m}$ filter paper under vacuum
144 (Fisherbrand). Then, the solutions were analyzed by colorimetry with the 1,5-diphenylcarbazide
145 method ($\lambda = 540\text{ nm}$) for Cr(VI) [29] and with the sodium salicylate method ($\lambda = 415\text{ nm}$) for
146 NO_3^- [30], using a UV-visible spectrophotometer (SHIMADZU UV-1640). The influence of
147 competitive PO_4^{3-} ions was also evaluated. A mixture of 50 mg.L^{-1} of Cr(VI) and 50 mg.L^{-1} of
148 PO_4^{3-} ions was prepared and incubated with ECAB-APTES-HCl for 300 minutes. Then, 10 mL of
149 the mixture were filtered ($0.45\text{ }\mu\text{m}$ filter paper under vacuum (Fisherbrand)), mixed with
150 ammonium molybdate (1 mL) and hydrazine sulfate (0.4 mL) heated at $60\text{ }^{\circ}\text{C}$ for 30 min. Then,
151 the absorbance of the ammonium phosphomolybdate complex was measured at 830 nm.
152 The amounts of adsorbed Cr(VI) or NO_3^- (q_e in mg/g) at equilibrium were calculated using
153 equation (1),

$$154 \quad q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

155 where C_0 and C_e are the initial and equilibrium concentrations of Cr(VI) (mg.L^{-1}), respectively, V
156 is the volume of solution (L) and m is the mass of adsorbent used (g).

157 The adsorption yield was estimated using equation (2):

$$158 \quad E (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

159 **2.5. Desorption experiments**

160 Batch desorption experiments were conducted by stirring a solution of the adsorbent and 0.1
161 mol.L^{-1} NaOH for 180 minutes. When NaOH was used as an eluting agent, the interactions

162 between ECAB-APTES-HCl and Cr/nitrate were disrupted, and chromate/nitrate ions were
163 released into the eluent. Therefore, NaOH was selected to better compare and understand the
164 results with previously published ones [25]. Then, the solutions were filtered under vacuum and
165 analyzed by the 1,5-diphenylcarbazide method for Cr(VI) and the sodium salicylate method for
166 NO₃⁻ using a UV-Vis spectrophotometer. The amount of desorbed Cr(VI) et NO₃⁻ ions (q_{des} in
167 mg.g⁻¹) were calculated using equation (3) [31]

$$168 \quad q_{des} = \frac{C_{des} \times V}{m} \quad (3)$$

169 where C_{des} is the delivered concentration of Cr(VI) or NO₃⁻ (mg.L⁻¹), V is the volume of solution
170 (L) and m is the mass of adsorbent (g). Then, desorption yields were estimated using equation (4).

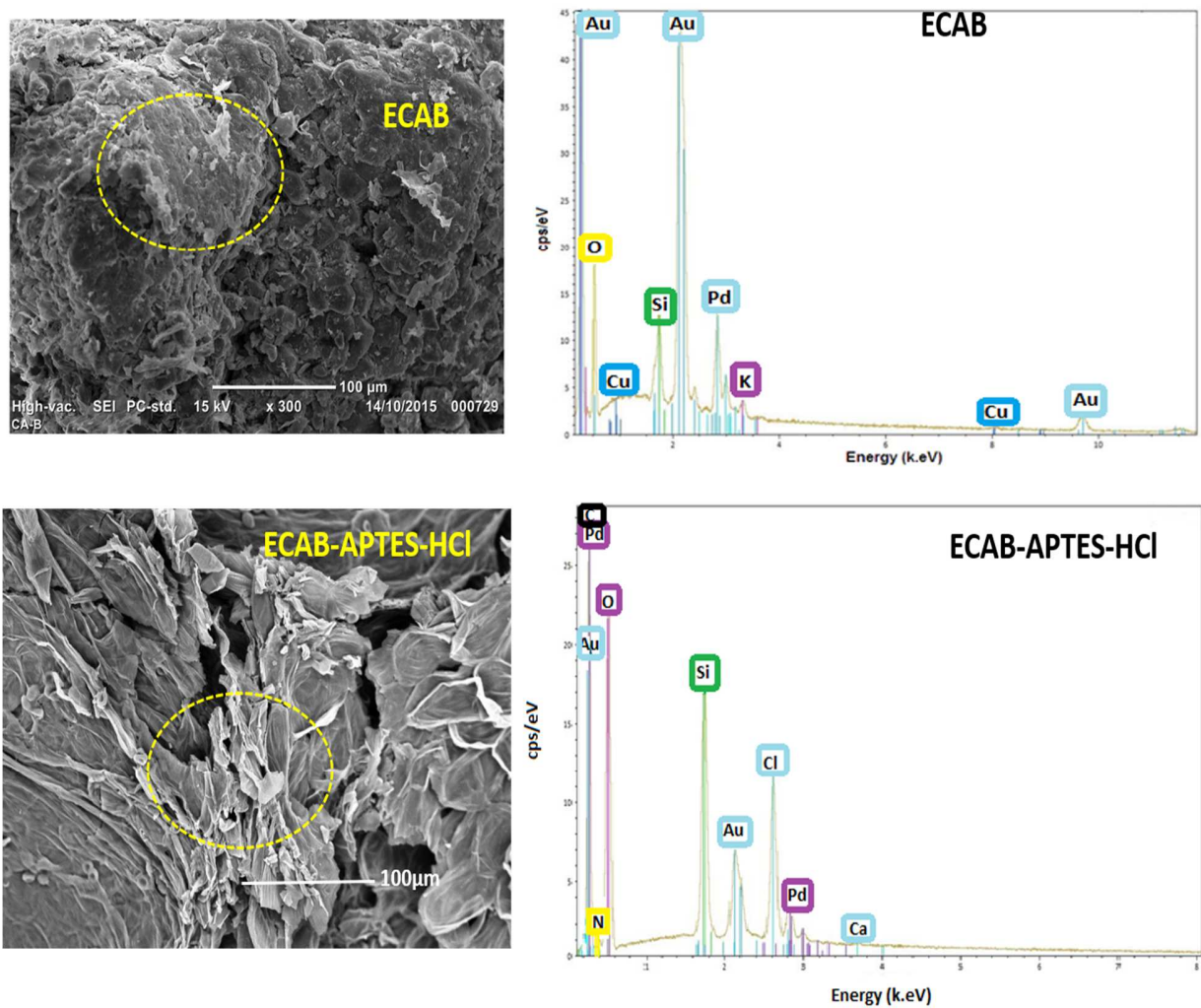
$$171 \quad \text{Percent of desorption} = \frac{\text{amount of desorbed NO}_3^- \text{ or Cr(VI)}}{\text{amount of adsorbed NO}_3^- \text{ or Cr(VI)}} \times 100 \quad (4)$$

172 **3. Results and discussion**

173 **3.1. Characterization**

174 The surface morphologies of ECAB and ECAB-APTES-HCl were analyzed by SEM microscopy
175 (**Figure 1a**). The surfaces of the untreated cocoa shell and modified cocoa shell were obviously
176 different. ECAB exhibited a smoother surface than modified ECAB. ECAB also presented
177 particle agglomerates coming from pectin, cellulose, lignin and wax, which were less visible after
178 APTES modification [32]. Foils corresponding to silane grafting were observed only on the
179 ECAB-APTES-HCl surface. HCl post-treatment caused holes to appear on the APTES foils
180 (**Figure S1**). This trend can be explained by the strong interaction between amino groups and
181 acidic protons.

182 To confirm the successful chemical grafting of APTES, the samples were analyzed by EDS
183 (**Figure 1**). The Au, Cu and Pd heteroatoms in the EDS spectra came from the metallization
184 process. After APTES modification, the peaks corresponding to carbon, oxygen and silicon were
185 more intense, confirming the presence of organosilane grafting. The peak at 2.6 keV was
186 assigned to chlorine from HCl treatment.

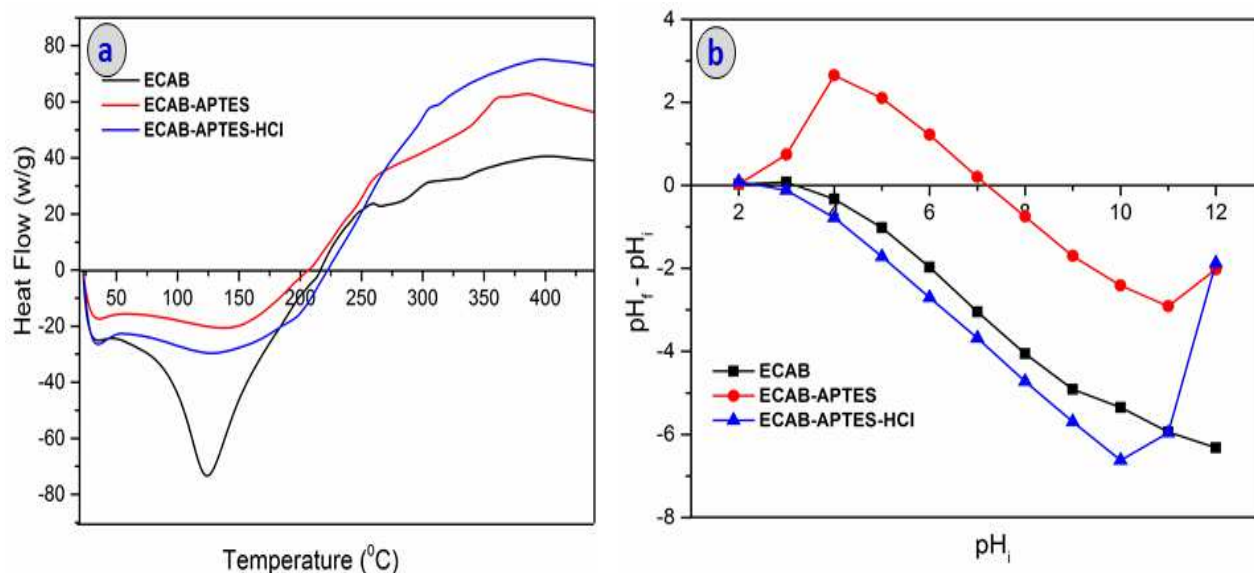


187
188 **Figure 1:** SEM images, with elemental composition and morphology of the ECAB and ECAB-
189 APTES-HCl adsorbents.

191 The ECAB adsorbent and its modified counterpart were characterized by FTIR analysis (**Figure**
192 **S2b**). The spectra of the APTES molecules is reported separately in **Figure S2a** to facilitate
193 comparisons and interpretations. The absorption bands of hydrolyzed APTES were described by
194 different vibrational modes related to NH₂, CH₂, and Si-O bonds. The peaks observed at 3300
195 cm⁻¹ and 3290 cm⁻¹ were associated to the asymmetric and symmetric stretching modes of NH₂,
196 respectively [33]. However, the band was related to the Si-OH groups at 3200 cm⁻¹, whereas the
197 stretching modes of CH₂ were observed at 2932 cm⁻¹ and 2883 cm⁻¹. In addition, the amine
198 function (NH₂) was observed at 1562 cm⁻¹ and 1484 cm⁻¹. The Si-O-Si bond was observed at
199 1130 cm⁻¹ and 1044 cm⁻¹ [33]. Regarding the initial adsorbent (ECAB), FTIR spectra displayed
200 distinguishable peak patterns in agreement with the literature [34]. The FTIR spectra of ECAB
201 presented a characteristic strong band at around 3350 cm⁻¹ associated with the stretching
202 vibration of the hydroxyl groups from cellulose, hemicellulose and lignin. Some bands at 2923
203 and
204 2881 cm⁻¹ corresponding to the stretching vibration of the -CH₂ groups were also present. The
205 band at around 1000 cm⁻¹ was associated to the oxygen functional groups C-O [35]. After APTES
206 grafting, the intensity of these bands was lower due to the formation of C-O-Si- bonds. New
207 bands at 1062 and 916 cm⁻¹ associated to the stretching vibration of Si-O-Si and Si-O-C,
208 respectively, confirmed this hypothesis [36]. Small bands at 709 and 644 cm⁻¹ assigned to the
209 stretching vibration of Si-C came from the propylsilane function. After acidic treatment, the
210 increase of the IR peak at 3336 cm⁻¹ was associated to the stretching vibration of NH₃⁺, whereas
211 peaks at 1720 and 1514 cm⁻¹ were assigned to the symmetric and antisymmetric stretching
212 vibration of N-H, respectively [37, 38]. Furthermore, new bands at 676 and 1180 cm⁻¹ attributed
213 to the stretching vibration of Si-C and C-N, respectively, confirmed the chemical grafting of
214 APTES and its protonation [38, 39]. Some visible changes on the FTIR spectra were observed

215 after the adsorption of chromate and nitrate (**Figure S2c**). The intensity of the peak at 1180 cm^{-1}
 216 corresponding to the C–N band was lower and even absent after Cr(VI) adsorption, confirming
 217 that the amino group was involved in the binding of anions. After nitrate adsorption, the peak at
 218 3336 cm^{-1} shifted to a higher wavenumber, indicating that NH_3^+ was involved in the interaction.
 219 Nitrate adsorption was also confirmed by the increase of the signal at 1400 cm^{-1} , which is
 220 characteristic of the NO_3 asymmetric stretching vibration.

221 DSC analysis in the $25 - 500\text{ }^\circ\text{C}$ temperature range was also performed to investigate the thermal
 222 stability of modified ECAB (**Figure 2a**). The endothermic peaks observed at around $126\text{ }^\circ\text{C}$ were
 223 attributed to the dehydration of the samples. From 200 to $250\text{ }^\circ\text{C}$, an exothermic peak
 224 corresponded to the degradation of cellulose, lignin and hemicellulose [26, 40]. In the $350 - 400$
 225 $^\circ\text{C}$ range, the two exothermic peaks at 363 and $392\text{ }^\circ\text{C}$ corresponded to silane degradation. Thus,
 226 APTES and APTES-HCl treatment increased the thermal stability of ECAB in the $250 - 400\text{ }^\circ\text{C}$
 227 range. All these results are in agreement with the literature and with SEM and IR data.



228
 229 **Figure 2:** DSC (a) and point of zero charge profiles (b) of ECAB, ECAB-APTES and ECAB-
 230 APTES-HCl.

231

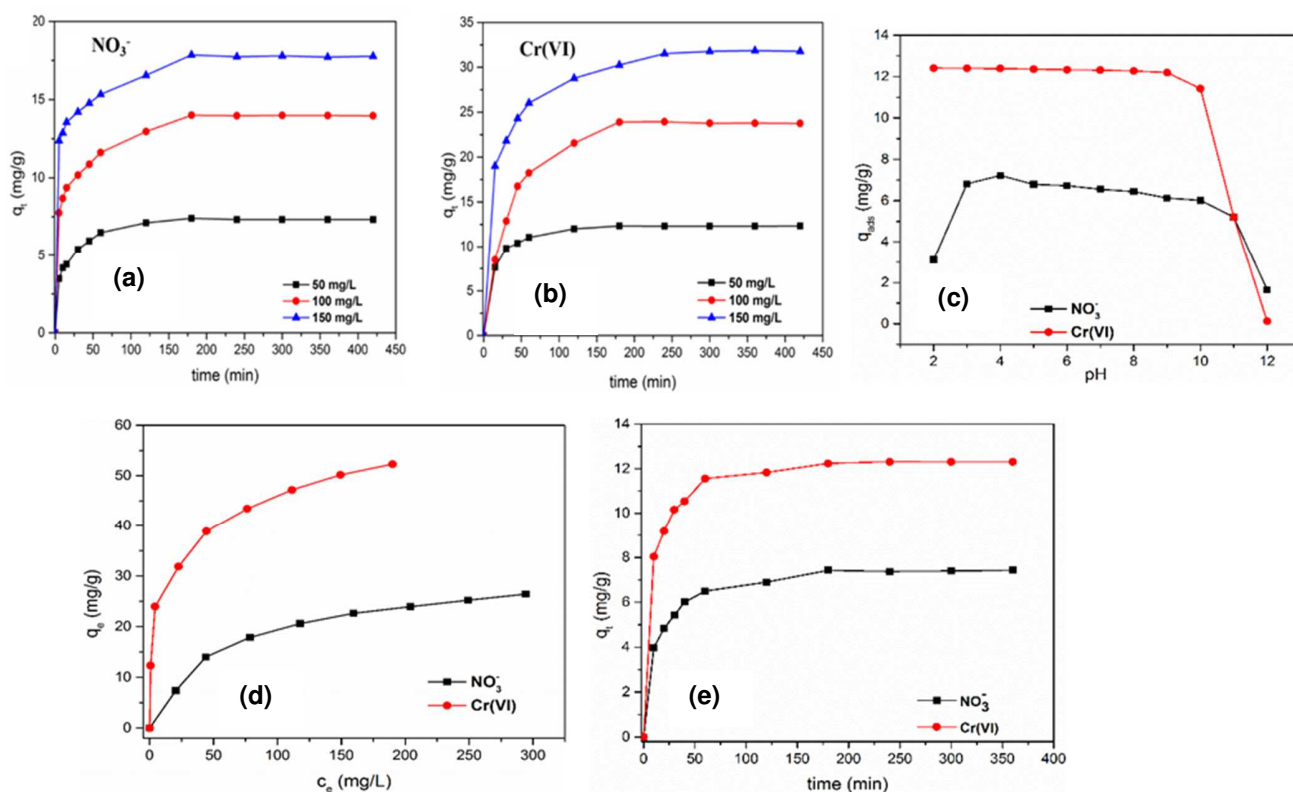
232 To determine the surface acidity of all adsorbents, their points of zero charge were measured
233 (**Figure 2b**). pH_{pzc} were found at pH values of around 3.4 for ECAB and 7.2 for ECAB-APTES.
234 When comparing the pH_{pzc} values of different adsorbents, it was clear that the lowest pH_{pzc} was
235 recorded for the initial material (ECAB), lower than that of other agricultural waste materials
236 such as olive stone (4.2) and sugar cane bagasse (5.7) [41].

237 ECAB was altogether negatively charged over a wide range of pH values, suggesting the
238 presence of functional groups (COO^- , OH^-) on its cellulose and lignin moieties. pH_{pzc} analyses of
239 ECAB-NH₂ indicated that APTES treatment affected the deprotonation of the cellulosic structure
240 with a positive surface charge over a wider pH range (2.0 - 7.2) than ECAB [42]. Therefore,
241 pH_{pzc} measurements confirmed the successful grafting of amino groups onto the ECAB surface.
242 These results are in agreement with those obtained by DSC, SEM and FTIR analyses. After
243 acidic activation, pH_{pzc} decreased from 7.2 for ECAB-APTES to 2.8 for ECAB-APTES-HCl,
244 indicating a lower surface charge. In addition, the zeta potential recorded at pH 7 shifted from -20
245 mV for ECAB to 0 mV for ECAB-APTES-HCl, suggesting high stability of the adsorbent.
246 Importantly, zeta potential (ZP) measurements performed after Cr(VI) and nitrate adsorption
247 indicated a negative ZP (-4 mV). This negative value confirmed that anions were adsorbed onto
248 ECAB-APTES-HCl. Consequently, functionalized ECAB could be a good candidate for Cr(VI)
249 and nitrate capture *via* electrostatic interactions.

250 **3.2. Adsorption study**

251 **3.2.1. Parameter effects**

252 **Figure 3** describes the amounts of Cr(VI) and NO₃⁻ adsorbed by different adsorbents as a
253 function of the contact time. The adsorption process was dependent on the initial amounts of
254 anions: the higher the initial anion concentration, the more anions were adsorbed. We evaluated
255 the adsorption yields of ECAB and ECAB-APTES as controls. The adsorption capacity of the
256 raw material ECAB was 0.94 mg.g⁻¹ for Cr(VI) and 1.04 mg.g⁻¹ for NO₃⁻ at an initial
257 concentration of 50 mg.L⁻¹. The weak adsorption yield recorded for ECAB can be explained by
258 the presence of substantial numbers of hydroxyl groups at its surface, which caused electrostatic
259 repulsion preventing the capture of pollutants. This result was confirmed by the ZP
260 measurements, where ECAB displayed negative values (-20 mV) due to the hydroxyl groups that
261 decreased the adsorption process. The adsorption capacities of ECAB-APTES were ~ 0 mg.g⁻¹
262 for Cr(VI) and 1.87 mg.g⁻¹ for NO₃⁻. For the same initial concentration of Cr(VI) and NO₃⁻, the
263 adsorption capacity of ECAB-APTES-HCl was 7 mg.g⁻¹ for Cr(VI) and 12 mg.g⁻¹ for NO₃⁻. The
264 profile of the adsorption curve of ECAB-APTES-HCl could be explained by a large amount of
265 active sites on the surface that were not totally in interaction with ions at low concentrations. The
266 adsorption rate proceeded in two steps, with a fast adsorption process from 0 to 60 minutes and a
267 lower rate later. First, all the adsorption sites of the adsorbent surface were available, and the
268 mass transfer of anions from the solution to the adsorbent was facilitated [40, 43, 44]. Then, the
269 adsorption rate decreased, and was lower in the presence of higher anion concentrations because
270 diffusion into the boundary film layer at the surface and into the structure was slower. The
271 equilibrium state was reached at t = 180 minutes for NO₃⁻ and t = 240 minutes for Cr(VI).



272

273 **Figure 3:** Effect of (a-b) the contact time, (c) the pH, (d) the initial concentrations, and (e) PO_4^{3-}
 274 on NO_3^- and Cr(VI) adsorption onto ECAB-APTES-HCl ($m = 0.2 \text{ g}$; 300 rpm ; $\text{pH}_i = 5.6$ for
 275 nitrate and 4.6 for chromate; $V = 50 \text{ mL}$).

276

277 The role of pH_i on Cr(VI) and NO_3^- adsorption was examined (**Figure 3c**). It revealed a pH-
 278 independent adsorption process within a large range of pH values. The maximum removal
 279 efficiency indeed stabilized at around 91 - 99% for chromium ions between pH 2 and pH 10. To
 280 clarify the mechanisms involved in these interactions, the diagram of Cr speciation in the pH
 281 range is presented in **Figure S3**. At higher pH values, the adsorption capacity plummeted from
 282 91% to 0.9%. Such a drop may result from a lower transfer of protons from the surface to the
 283 solution resulting in a negatively charged surface [29, 37, 43]. This drop may also come from the
 284 high amount of hydroxide ions, which competed with hydrogen chromate [37, 40, 45]. As for
 285 NO_3^- , maximum removal efficiency reached 57.8% at pH 4. In the 5 to 11 pH range, the

286 adsorption yield was close to the maximum value, indicating that the process was mainly pH-
287 independent. Similarly to Cr(VI) ions, NO₃⁻ ions were sensitive to high pH values due to the large
288 amount of hydroxide anions in competition in this context [28, 46]. So, in this work, the
289 adsorption mechanism of ECAB-APTES-HCl seemed to be sensitive to electrostatic interactions.

290 The amount of phosphate ions is limited in natural water bodies. However, phosphate ions
291 can be found in domestic or industrial water, so they were used to evaluate the effect of
292 coexisting ions on NO₃⁻ or chromate adsorption onto ECAB-APTES-HCl (**Figure 3e**).
293 Contaminated solutions were prepared with equal concentrations of NO₃⁻, phosphate or Cr(VI)
294 ions to carry out a competitive assay. The NO₃⁻ and Cr(VI) adsorption yields were not influenced
295 by the presence of phosphate ions. These results confirm that the adsorption process onto ECAB-
296 APTES-HCl is controlled by electrostatic interactions but also by the structural organization of
297 the ECAB-APTES-HCl surface. For nitrate, the negative charge is delocalized between the 3
298 oxygens, and this facilitates multiple electrostatic interactions with different positive charges
299 distributed across the surface of ECAB-APTES-HCl [47].

300

301 **3.2.2. Adsorption kinetics**

302 The kinetics of heavy metal and organic pollutant adsorption onto solid adsorbents are usually
303 investigated using pseudo-first order and pseudo-second order kinetic models. Our experimental
304 data were simulated by applying the pseudo-first order (Eq. (5)), pseudo-second order (Eq. (6)),
305 Elovich (Eq. (7)), and intra-particle diffusion (Eq. (8)) equations.

$$306 \log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303} \quad (5)$$

$$307 \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

308 $q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$ (7)

309 $q_t = k_{id} t^{1/2} + C_i$ (8)

310 where q_e and q_t (mg.g^{-1}) are the amounts of the adsorbate adsorbed *per* unit weight of adsorbent
311 at equilibrium time and time t (min), respectively; k_1 (min^{-1}), k_2 ($\text{g.mg}^{-1}.\text{min}^{-1}$), and k_{id}
312 ($\text{g.mg}^{-1}.\text{min}^{-0.5}$) are the pseudo-first order rate constant, pseudo-second order equilibrium rate
313 constant, and intra-particle diffusion rate constant, respectively; as regards Elovich coefficients, α
314 is the initial adsorption rate ($\text{mg g}^{-1}.\text{min}^{-1}$) and β is the desorption constant (g.mg^{-1}) during any
315 one experiment; C_i is the intercept related to the thickness of the boundary layer.

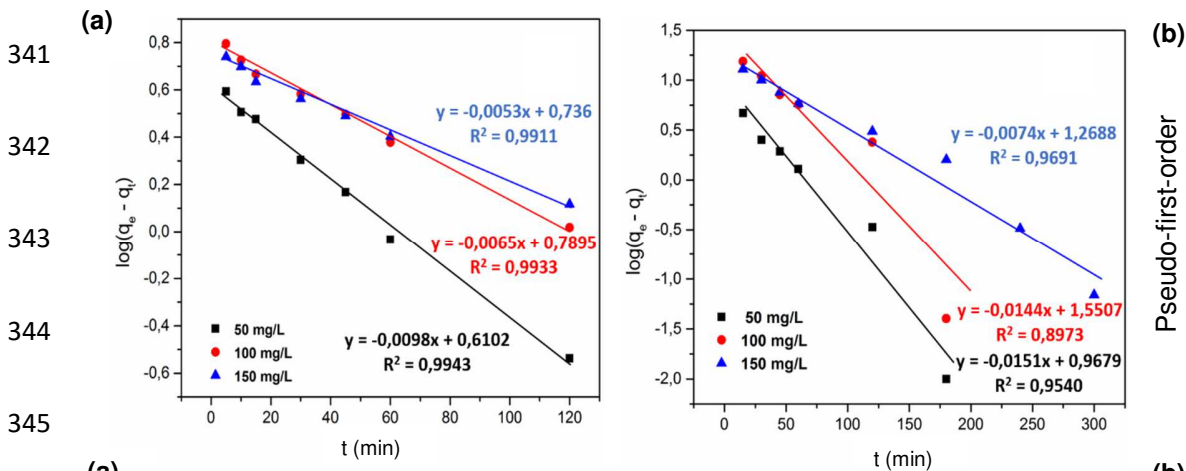
316 The pseudo-first order kinetic model generally suggested that adsorption occurred through
317 physisorption, whereas the pseudo-second order indicated that adsorption occurred through
318 chemisorption [48]. **Figure 4** and **Table 1** show that most of nitrate and heavy metal are adsorbed
319 onto functionalized ECAB. These datas fitted well with the pseudo-second order kinetic model,
320 as supported by the correlation coefficients. Therefore, for instance the ECAB adsorbent involved
321 chemisorption, as well as physisorption as estimated by the pseudo-first order model.

322 In this respect, other researchers created an intraparticle diffusion kinetic model that determines
323 the adsorption process of adsorbates [49, 50]. Mohan et al. assumed that intraparticle diffusion
324 was the best model describing the mass transfer of adsorbates [51]. Experimental data closely
325 fitted with this model ($R^2=0.98$), indicating that the intra-particle diffusion model could be
326 satisfactorily applied in 2 steps. The first step can be attributed to the diffusion of the ions
327 through the solution to the external surface of the adsorbent. The second step, describes the final
328 equilibrium where the intra-particle diffusion is limited. Thus, at the beginning, the rate of the
329 adsorption is controlled by intra-particle diffusion and then it was mostly due to chemisorption.

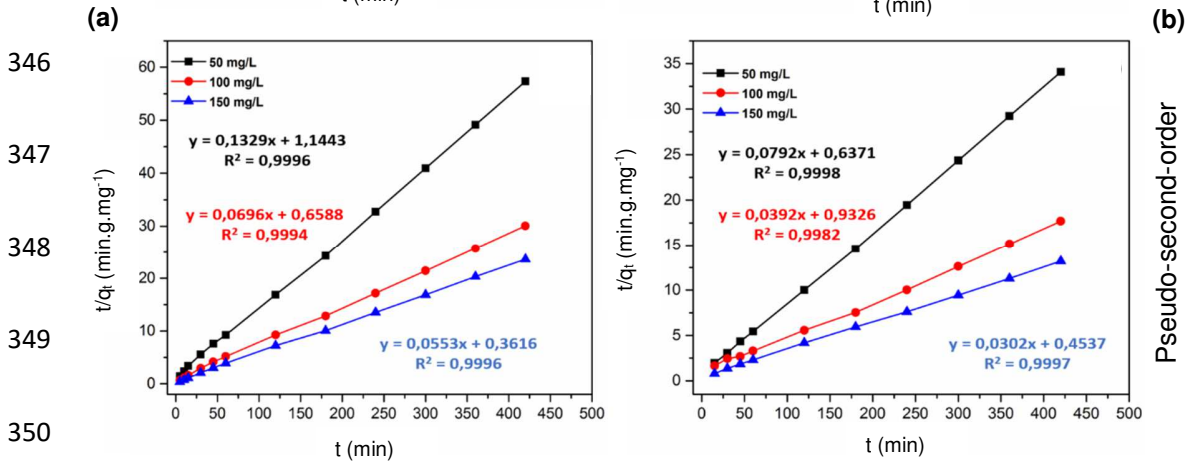
330 Regarding the intraparticle diffusion curves, a visible change in the slope was observed,
331 beginning at $t = \sim 10$ min. The results evidenced the existence of two adsorption types (i.e.,
332 physical and chemical). Afterward, physisorption was probably involved during the adsorption of
333 pollutants onto functionalized ECAB. In addition, a previously published work also reported
334 adsorption through physisorption [52]. Physisorption is an easily reversible phenomenon, which
335 improves the regeneration process. ECAB-APTES-HCl allowed for substantial regeneration of
336 both pollutants (*will be discussed in the following section*), suggesting the presence of weak
337 physisorption. Consequently, NO_3^- and Cr adsorption occurred via physisorption and
338 chemisorption.

339

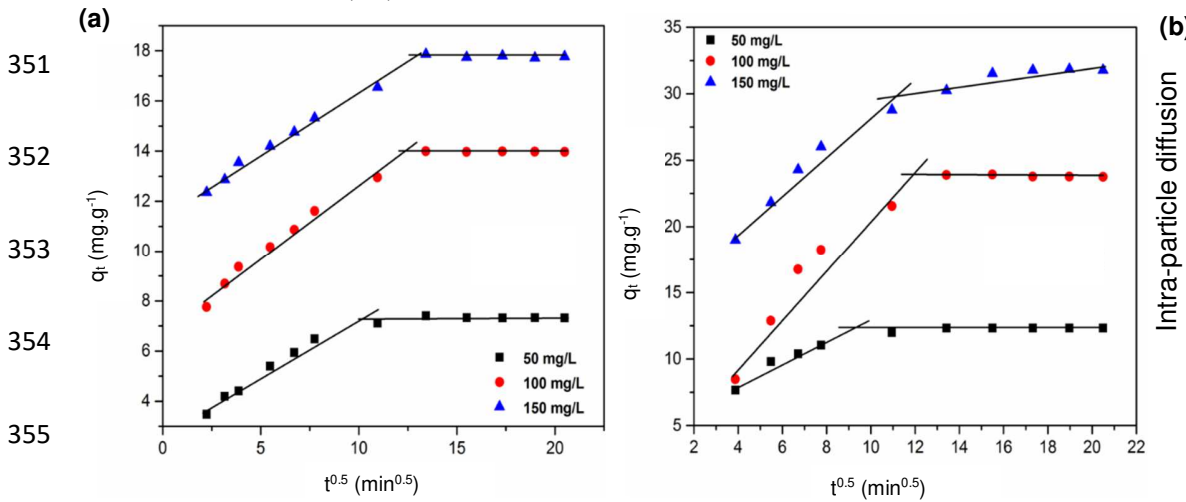
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345



350



356

357 **Figure 4:** Pseudo-first order, pseudo-second order kinetics and intra-particle diffusion model of
358 nitrate (a) and Cr (VI) (b) removal by ECAB-APTES-HCl.

359 **Table 1:** Summary of the kinetic parameters (k , R^2 , q_e) of NO_3^- and Cr(VI) adsorption onto
 360 ECAB-APTES-HCl. ($m = 0.2$ g, $\text{pH}_i = 5.6$ for nitrate and 4.6 for chromate, 300 rpm, $V = 50$ mL,
 361 room temperature).

Parameters/coefficients /constants	Concentration of NO_3^- (mg/L)			Concentration of Cr(VI) (mg/L)		
	50	100	150	50	100	150
$q_{e, \text{exp}}$ (mg.g⁻¹)	7.41	14.00	17.86	12.33	23.94	31.85
<i>Pseudo-first order</i>						
k_1 (min ⁻¹)	0.022	0.015	0.012	0.035	0.033	0.017
$q_{e, \text{cal}}$ (mg.g ⁻¹)	4.076	6.159	5.445	9.287	35.538	18.570
R^2	0.9943	0.9933	0.9911	0.9540	0.8973	0.9691
<i>Pseudo-second order</i>						
k_2 (g.mg ⁻¹ .min ⁻¹)	0.015	0.007	0.008	0.010	0.002	0.002
$q_{e, \text{cal}}$ (mg.g ⁻¹)	7.524	14.368	18.083	12.626	25.510	33.112
R^2	0.9996	0.9994	0.9996	0.9998	0.9982	0.9997
<i>Elovich</i>						
α (mg.g ⁻¹ .min ⁻¹)	9.656	44.422	900.848	79.014	3.017	35.398
β (g.mg ⁻¹)	1.072	0.646	0.719	0.785	0.218	0.248
R^2	0.9482	0.9772	0.9708	0.8734	0.9229	0.9749
<i>Intra-particle diffusion</i>						
k_{1d} (mg.g ⁻¹ .min ^{-1/2})	0.427	0.584	0.479	0.854	1.817	1.384
C_1 (mg.g ⁻¹)	2.841	6.850	11.485	4.642	2.952	14.360
R^2_1	0.9544	0.9796	0.9871	0.9427	0.9208	0.9574
k_{2d} (mg.g ⁻¹ .min ^{-1/2})	-0.01	-0.003	-0.012	0.027	-0.026	0.1989
C_2 (mg.g ⁻¹)	7.510	14.030	17.99	11.837	24.274	28.026
R^2_2	0.5668	0.3181	0.3662	0.5020	0.7176	0.6802

362

363 The diffusion mechanism involved in the adsorption process was predicted more precisely by
 364 calculating correlation factors. The correlation factor for nitrate showed estimated values ranging
 365 from 0.95 to 0.98, indicating that the intra-particle diffusion model could be satisfactorily applied
 366 for the first step of the nitrate adsorption process. Therefore, during the first 60 minutes, the
 367 adsorption process was mainly controlled by intra-particle film diffusion [23, 43, 53]. For Cr(VI),
 368 the adsorption process was also attributed to intra-particle diffusion during the first step, but other
 369 mechanisms were also probably involved because the correlation factor ranged from 0.92 to 0.95.

370 The second part of the curves corresponded to the slower process, when pore diffusion is the
371 limiting step because the main parts of the active sites are occupied [53]. The k_{id} constants were
372 consistently higher with Cr(VI) than with nitrate, indicating that the sorption process was more
373 intense and faster with Cr(VI) than with nitrate. This phenomenon could be explained by the
374 higher molecular weight of Cr(VI) anions as compared to nitrate anions [54].

375 In both cases, the intra-particle diffusion model was not the only rate-determining mechanism, as
376 the q_t versus $t^{0.5}$ curve did not go above zero. Therefore, other mechanisms such as mass transfer
377 from the bulk solution to the adsorption center underneath the adsorbent surface were probably
378 involved [55]. The mass transfer factor model developed by Fulazzaky *et al.* was applied to
379 Cr(VI) and nitrate data (**Figure S4**) [56]. The global mass transfer factors $(k_{La})_g$ of both ions
380 decreased quickly, confirming that the number of occupied active sites increased with time. The
381 low value of the external mass transfer factor $(k_{La})_f$ indicated that the process was controlled by
382 the internal mass transfer factor $(k_{La})_d$. Therefore, the adsorption rate was mainly controlled by
383 ion diffusion to the acceptor site of the adsorbent.

384

385 **3.2.3. Adsorption isotherms**

386 Exploring the adequate mechanisms involving adsorption onto functionalized ECAB requires
387 the study of adsorption isotherms. The most useful isotherms to investigate adsorption
388 equilibrium data are Freundlich and Langmuir isotherms. The adsorption data were fitted with
389 Freundlich (Eq 9), Langmuir (Eq 10), Temkin (Eq 11) and Dubinin-Radushkevich (Eqs 12-14)
390 models to optimize the design of the adsorption process and remove both anions from water.

391
$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (9)$$

392
$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}} C_e \quad (10)$$

393
$$q_e = B \ln A + B \ln C_e \quad (11)$$

394
$$\ln q_e = \ln q_{max} - B_D \varepsilon^2 \quad (12)$$

395
$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (13)$$

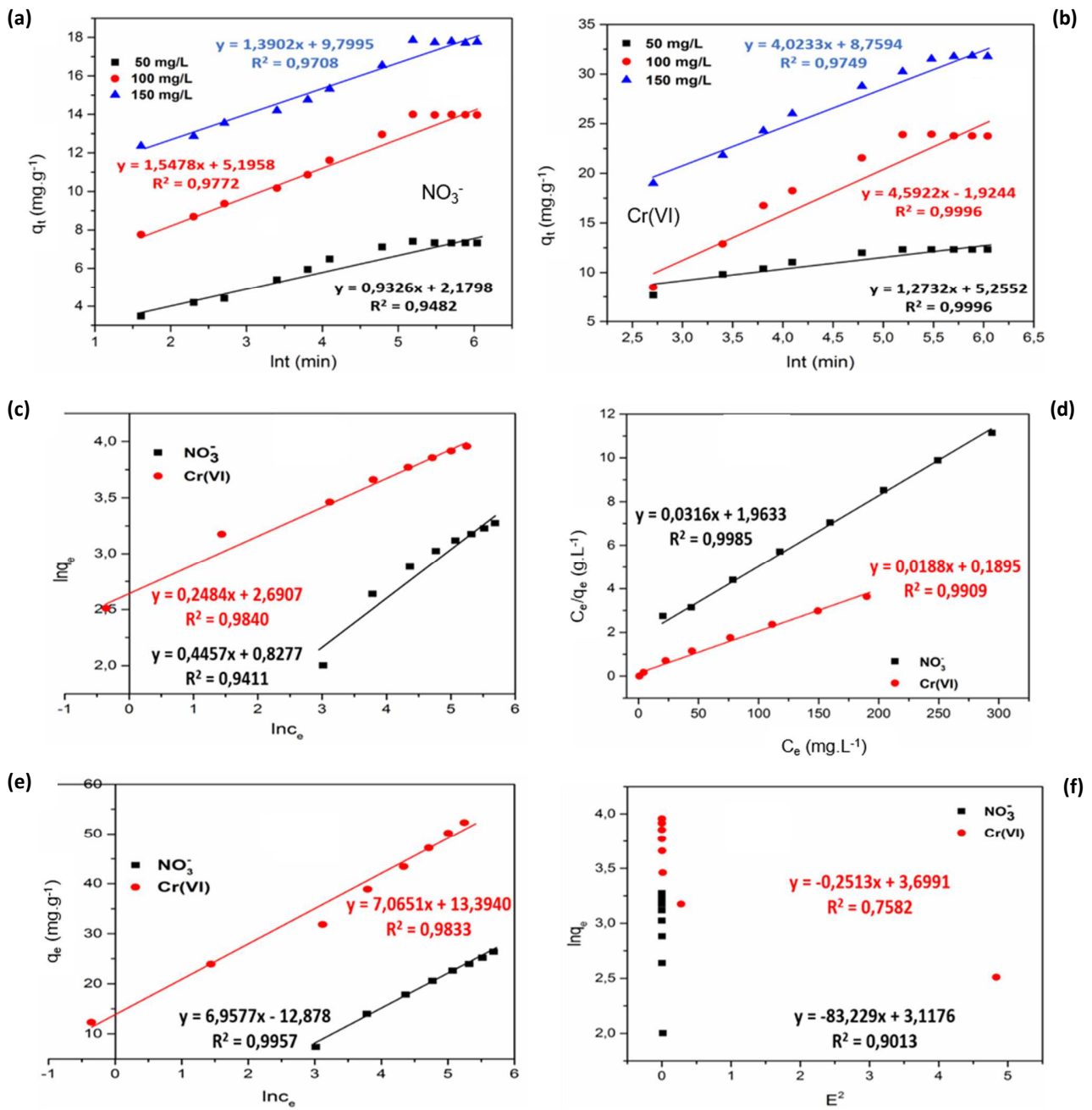
396
$$E = \frac{1}{\sqrt{2B_D}} \quad (14)$$

397 where q_e (mg.g⁻¹) and C_e (mg.L⁻¹) are the sorbate equilibrium concentrations in the solid and
 398 liquid phases, respectively; q_{max} (mg.g⁻¹) is the monolayer capacity of the sorbent; K_L (L.mg⁻¹) is
 399 a constant of the Langmuir isotherm. K_F (L.g⁻¹) is the Freundlich constant, and $1/n$ is the
 400 heterogeneity factor. B and A are the Temkin constants. B_D (mol².kJ⁻²) is the activity coefficient,
 401 useful to obtain the mean sorption energy E (kJ.mol⁻¹), and ε is the Polanyi potential. R is the gas
 402 constant (J.mol⁻¹.K⁻¹), and T is the temperature (K).

403 **Figure 5** shows the adsorption isotherms recorded for all adsorbates. **Table S1** presents the
 404 calculated isotherm constants and the square of the regression coefficients. The highest
 405 correlation coefficients were obtained with the Langmuir model, indicating that sorption was a
 406 chemical phenomenon that took place on a homogeneous surface through monolayer adsorption
 407 [23, 46]. Based on the Langmuir model, the maximum monolayer adsorption capacity was high
 408 and estimated to be 31.64 mg.g⁻¹ for nitrate and 53.19 mg.g⁻¹for Cr(VI). The fitting of the
 409 Freundlich model also gave a good correlation coefficient, indicating that the adsorption process
 410 of the two anions was reversible. This interpretation is in accordance with the low affinity
 411 constant (K_L) obtained from Langmuir data. K_F represents the adsorption capacity of the
 412 adsorbent and n_F the adsorption intensity. The high values of the two parameters confirmed that

413 ECAB-APTES-HCl had a good and strong adsorption capacity [43, 57]. The positive value of
414 the Temkin constants A and B indicated that the adsorption of nitrate and Cr(VI) was
415 endothermic and mainly occurred through physisorption [58, 59]. The Dubinin-Radushkevich (D-
416 R) model was used to estimate the apparent free energy of adsorption and the type of adsorption.
417 Based on the low value of the mean sorption energy E for nitrate and Cr(VI), D-R calculations
418 confirmed that biosorption was mainly physisorption. These results altogether confirmed again
419 the occurrence of both physisorption and chemisorption [60].

420 By comparing the results obtained in this work with those from numerous adsorbents reported in
421 the literature for removal of nitrate and Cr(VI), ECAB-APTES-HCl adsorbed more nitrate than
422 biochar or modified activated carbon did, indicating that this simple strategy of modification is an
423 efficient way to capture nitrate (**Table 2**).



424

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430

Figure 5. Elovich model (a-b) and equilibrium adsorption isotherms: (c) Freundlich, (d) Langmuir, (e) Temkin, and (f) Dubinin-Radushkevich models for NO_3^- and Cr(VI) adsorption onto ECAB-APTES-HCl ($m = 0.2$ g, $\text{pH}_i = 5.6$ for nitrate and 4.6 for chromate, 300 rpm, $V = 50$ mL, room temperature).

431 **Table 2:** Comparison of the results obtained in this work with other recently published studies

Biosorbent name	Functionalization	Capacity (mg/g)	Reference
NO₃⁻			
Modified granular activated carbon	[3-(methacryloylamino)propyl]-trimethylammonium chloride	26	[46]
Cellulose	epichlorohydrin	218.23 (293 K)	[5]
Giant reed	triethylamine	118.9	[61]
Corn stalks	ethylenediamine	65.36 (298 K)	[62]
Sugarcane bagasse biochar	ethylenediamine	28.21	[28]
PEG/chitosan and PVA/chitosan	polyethylene glycol and polyvinyl alcohol	50.68-35.03	[44]
Modified steel slag	aluminum hydroxide	16.40	[63]
Corn stalks	diethylamine	13.60	[64]
Modified cocoa shell	PEI-HCl	86.95	[25]
Modified cocoa shell	APTES-HCl	31.65	Present study
Cr(VI)			
Corn stalks	diethylenetriamine	200.00 (303 K)	[23]
Modified granular activated carbon	[3-(methacryloylamino)propyl]-trimethylammonium chloride	81.00	[46]
Spent mushroom (<i>T. lobayense</i>)	dodecyl dimethyl benzyl ammonium bromide	43.86	[65]
Sugarcane bagasse	iron(III)-impregnated	13.72	[66]
Brown algae	hydrochloric acid	52.63	[67]
<i>Lagerstroemia speciosa</i> bark	chemical treatment (H ₂ SO ₄ /formaldehyde)	24.39	[68]
Giant reed	triethylamine	135	[61]
<i>Lantana camara</i>	sulfuric acid	83.00	[69]
Masau stone	diethylenetriamine	87.32	[37]
Spent substrate (<i>Auricularia auricular</i>)	cetyl trimethyl ammonium bromide, immobilized by sodium alginate	27.25	[70]
Macadamia nutshell powder	HCl	44.83	[71]
	NaOH	42.44	
Modified cocoa shell	PEI-HCl	94.34	[25]
Modified cocoa shell	APTES-HCl	53.19	Present study

432

433 3.2.4. Thermodynamic parameters

434 Thermodynamic parameters such as ΔH° , ΔS° and ΔG° were determined based on Van't Hoff's

435 equations (15-19) to elucidate the adsorption process [72].

$$436 \quad \theta_e = \frac{q_e}{q_{max}} \quad (15)$$

$$437 \quad b = \frac{\theta_e}{C_e \times (1 - \theta_e)} \quad (16)$$

438
$$K_{aeq} = \frac{b \times Ma}{\gamma} \quad (17)$$

439
$$\ln(K_{aeq}) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (18)$$

440
$$\Delta G^\circ = -R \times T \times \ln(K_{aeq}) \quad (19)$$

441 where θ_e is the fraction of the surface coverage at equilibrium, q_e (mg.g⁻¹) is the amount of ions
442 adsorbed at equilibrium, q_{max} (mg.g⁻¹) is the maximum capacity of the adsorbent, b is the
443 isotherm constant, C_e (mg.L⁻¹) is the equilibrium concentration of ions in solution, K_{aeq} is the
444 equilibrium constant, Ma is the molecular weight of the adsorbent, γ is the activity coefficient, R
445 (8,314 J.K⁻¹.mol⁻¹) is the universal gas constant, and T (K) the absolute temperature. The values
446 of ΔG° , ΔH° and ΔS° were obtained from eq.19 and Figure S5, respectively; they are summarized
447 in Table 3. Nitrate and Cr(VI) adsorption presented different behaviors. The negative enthalpy for
448 nitrate proved that the adsorption process was exothermic, indicating that the total energy
449 absorbed in bond breaking was less than the total energy released by adsorbate-adsorbent bond
450 making. Therefore, nitrate adsorption was mainly driven by enthalpy. The negative value of
451 entropy implied a decrease of disorder at the solid-liquid interface associated with a strong
452 interaction at this interface during the adsorption process [73, 74]. Thus, the internal structure of
453 the adsorbent did not seem to be modified during adsorption [72]. Negative values of Gibb's free
454 energy indicated that nitrate adsorption was spontaneous which is in accordance with the fast
455 adsorption process observed in **Figure 3**.

456

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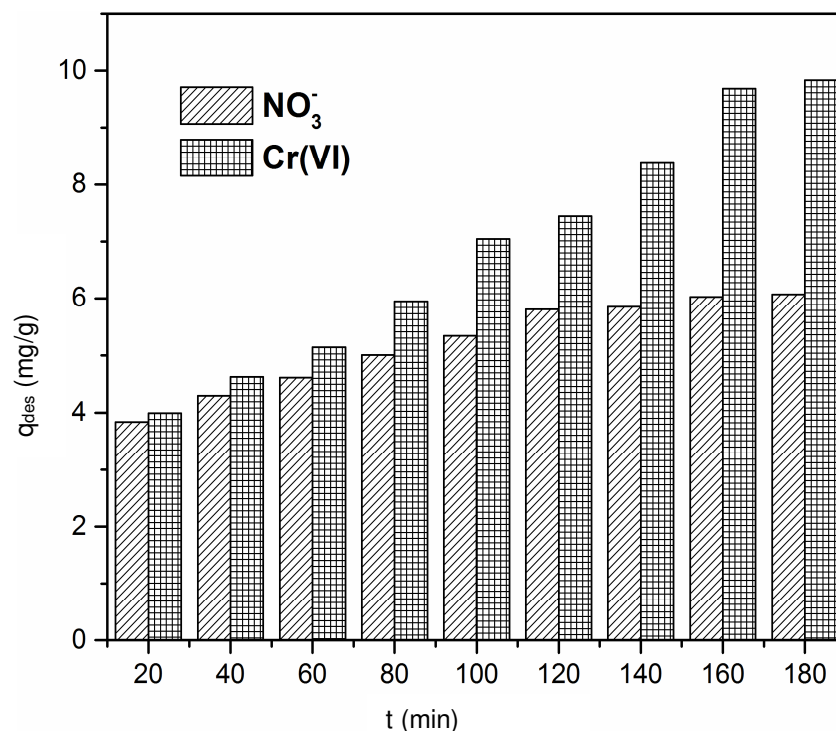
459 **Table 3:** Thermodynamic constants for NO₃⁻ and Cr(VI) adsorption onto ECAB-APTES-HCl
 460 (V = 50 mL, m = 0.2 g, 300 rpm).

	R ²	ΔH°(kJ.mol ⁻¹)	ΔS°(J.K ⁻¹ .mol ⁻¹)	ΔG°(kJ.mol ⁻¹)			
				293 K	303 K	313 K	323 K
NO ₃ ⁻	0.993	- 21.57	- 28.41	-13.21	-12.98	-12.78	-12.32
Cr(VI)	0.995	41.70	241.5	- 29.09	-31.36	-34.05	-36.25

461
 462 For chromium ions, the positive value of enthalpy implied that the adsorption process was
 463 endothermic and mainly controlled by physisorption [75]: the ions had to cause more than one
 464 water molecule to move. The positive value of entropy indicated some disorder at the liquid/solid
 465 interface, suggesting a spontaneous reaction and good affinity of the ions for ECAB-APTES-HCl
 466 [76]. ΔG° was negative, confirming the feasibility and the spontaneity of the adsorption process.
 467 Gibb's enthalpy decreased as the temperature increased, so that the diffusion of chromium ions
 468 across the external layer boundary and the internal pores was improved when temperature
 469 increased [75-77].

470 **4. Desorption of NO₃⁻ and Cr(VI)**

471 To be useful for industrial applications, the adsorbent should be reusable once saturated with
 472 pollutants. Regeneration of the adsorbent should be cheap, effective and harmless to its structure.
 473 Sodium hydroxide 0.1 mol/L was a good candidate to remove nitrate and chromium ions [78, 79]
 474 from ECAB-APTES-HCl (**Figure 6**). Respective recovery rates of 82% and 79.8% were reached
 475 in less than 2 hours. The desorption kinetic confirmed that the adsorption/desorption process was
 476 mainly controlled by both physisorption and chemisorption [60, 65]. IR analysis of ECAB-
 477 APTES-HCl after desorption studies evidenced a chemical composition of the surface
 478 comparable to that of ECAB-APTES-HCl.

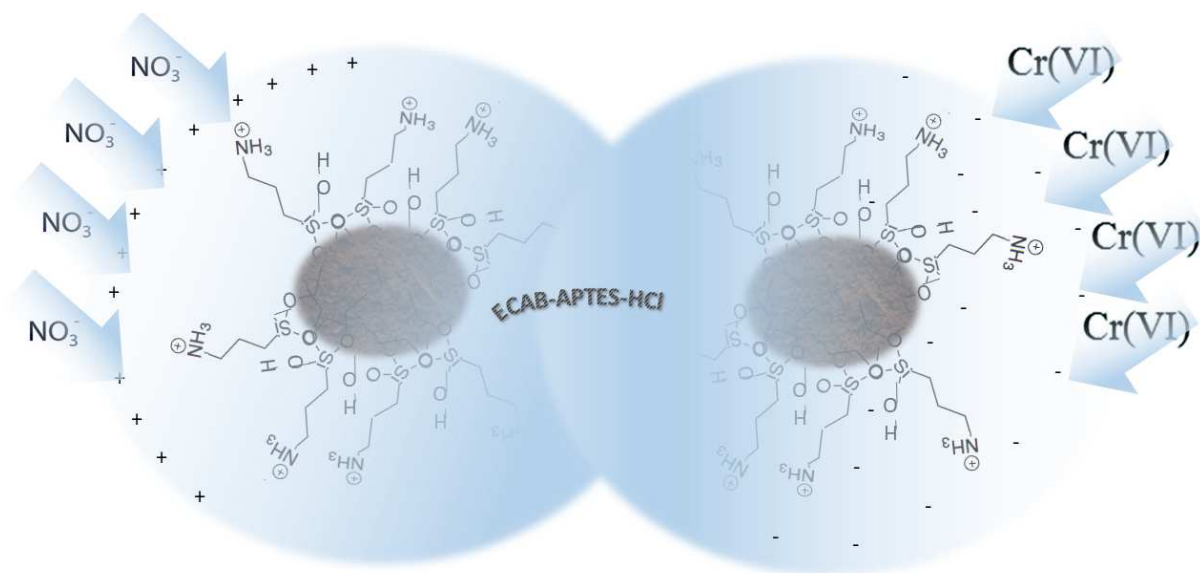


479
 480 **Figure 6:** Desorption of NO₃⁻ and Cr(VI) from ECAB-APTES-HCl (V = 50 mL; m = 0.2 g; 300
 481 rpm, pH_i = 5.6 for nitrate and 4.6 for chromate).

482
 483 **5. Proposed adsorption mechanism**

484 The above results show that adsorption is achieved through different steps. Firstly, the pollutants
 485 in aqueous solution cover the adsorbent, creating a film layer. Secondly, NO₃⁻ and Cr(VI) diffuse
 486 into the external surface. Thirdly, the pollutants diffuse into the internal adsorption site (**Scheme**
 487 **2**). Finally, adsorption occurs on the surface of ECAB-APTES-HCl [49, 80]. As the adsorption
 488 process involves both physisorption and chemisorption onto ECAB-APTES-HCl, heavy metal
 489 and NO₃⁻ adsorption can be postulated to take place as follows: (i) an electrostatic interaction
 490 occurs between the heavy metal ions (Cr(IV)) and oxygenic functional groups such as hydroxyl
 491 and carboxyl functional groups present on ECAB-APTES-HCl; (ii) protonation of the adsorbent
 492 introduces NH₃⁺ groups, and the surface becomes positively charged. The positively charged

493 surface slows down/ the interaction with Cr(VI), and NO_3^- adsorption is favored at the adsorbent
494 surface. In addition, the repulsion of Cr(VI) can result in complexation of the solution that
495 reduces chromium ions. In both cases [(i) and (ii)], the pH of the solution plays an important role
496 in the adsorption process: more H^+ ions are available in acidic media, and consequently more
497 NO_3^- is adsorbed, whereas more OH^- ions are available at high pH values and then Cr(VI) is
498 easily adsorbed. This is supported by the kinetic and isotherm studies, pH_{pzc} and ZP
499 measurements. The above results are in agreement with those obtained elsewhere [81].



500
501 **Scheme. 2.** Postulated mechanism of nitrate and chromium ion adsorption onto ECAB-APTES-
502 HCl.

503 Conclusion

504 Environment-friendly and cost-effective functional cocoa shell (ECAB) was prepared to remove
505 chromium and nitrate pollutants from aqueous solution. Modified ECAB was characterized by
506 FTIR, SEM, EDS, XRD, ZP and DSC, and the successful synthesis and functionalization of
507 ECAB-APTES-HCl was confirmed. Nitrate and chromate are adsorbed onto protonated ECAB-

508 APTES *via* physical and chemical interactions. Batch mode experiments of nitrate and Cr(VI)
509 adsorption were conducted to determine the kinetic parameters. More than 31 and 53 mg/g of
510 nitrate and Cr(VI) was adsorbed onto the functionalized ECAB-APTES-HCl. These
511 performances were promising in comparison to datas already published with modified vegetal
512 wastes of biochar. The results fitted well with Langmuir and Freundlich isotherms. Accordingly,
513 functionalized ECAB-APTES-HCl involves physisorption and chemisorption during the
514 adsorption process. The results show that the ECAB-APTES-HCl adsorbent can be used as an
515 efficient and low-cost alternative material to remove chromium and nitrate ions from wastewater.

516

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521

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