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Cynthia Sinyeue, Théophile Garioud, Monika Lemestre, Michaël Meyer, Frédérique Brégier, et al..
Biosorption of nickel ions Ni²⁺ by natural and modified Pinus caribaea Morelet sawdust. Heliyon,
2022, 8 (2), pp.e08842. 10.1016/j.heliyon.2022.e08842 . hal-03563781

HAL Id: hal-03563781

<https://unc.hal.science/hal-03563781>

Submitted on 22 Jul 2024

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Biosorption of nickel ions Ni²⁺ by natural and modified *Pinus caribaea* Morelet sawdust

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Highlights

- *Pinus caribaea* sawdust is an effective biosorbent of metallic trace elements.
- High Ni²⁺ removal efficiency was observed at pH 8 with 5g/L of biosorbent.
- Equilibrium adsorption was described by Freundlich and Langmuir isotherms.
- Pine sawdust is a reusable biosorbent with good desorption capacity.
- Efficiency of acidified and oxidized adsorbents.

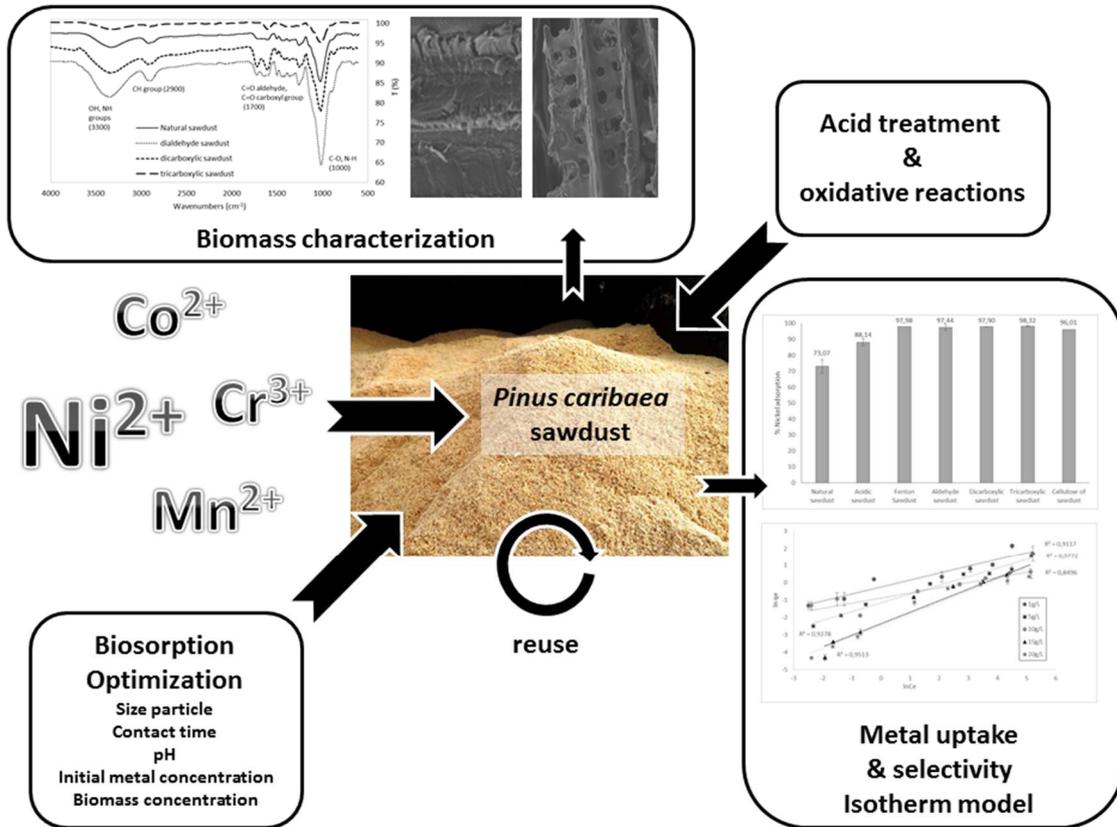
Abstract

The potential of *Pinus caribaea* Morelet sawdust for the removal of nickel ions (Ni²⁺) and other metallic trace ions (Co²⁺, Cr³⁺, Mn²⁺) from aqueous solutions was investigated under batch conditions. Several parameters such as size of particles, contact time, pH, initial metal and biomass concentrations, desorption conditions and reusability were evaluated on natural biomass. Biosorption was fast, effective (73%) and biomaterial can be reused after five cycles. To enhance the removal capacity of nickel, pine sawdust was modified by acidic and oxidative treatments. Cellulosic residues from sawdust sequential extraction showed great biosorption capacity (96%). In the presence of a metal mixture, oxidized sawdust had better selectivity for Cr³⁺ ions than for Ni²⁺. *Pinus caribaea* biomass could be an environmental, inexpensive and renewable material for the depollution of water laden with metallic trace elements.

Keywords (5): nickel, *Pinus caribaea* Morelet, modified sawdust, biomass recycle, water treatment.

36 Graphical abstract

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52 1. Introduction:

53 Pollution by trace metals and their bioaccumulation in ecosystems is a global problem.
54 Metals are particularly present in rivers and groundwater because of natural processes
55 (rocks alteration and soil erosion) and anthropogenic activities which lead to
56 uncontrolled discharges of urban, industrial and agricultural wastewater (Lakherwal et
57 al., 2014).

58 New Caledonia is a South Pacific island characterized both by soils naturally rich in
59 metallic trace elements and by nickel mining and industrial activities of worldwide
60 importance (Losfeld et al. 2015). One third of the main island is covered by ultramafic
61 rocks rich in transition elements as iron, nickel, cobalt, manganese or chromium which
62 can be released in surface waters (Gunkel-Grillon et al. 2014). In this archipelago, nickel
63 and chromium are two elements found in the urine of populations exposed to
64 concentrations above international reference values, in particular in children (St-Jean et
65 al. 2018).

66 To reduce the potential health risks associated to metals chronic exposure through the
67 consumption of drinking water and for the removal of trace metal elements in aqueous
68 solution, several treatment methods have been described (Lakherwal et al., 2014;
69 Volesky et al., 2001; Lin and Juang 2002). Among them, biosorption have the
70 advantages of being low cost, ecological, flexible, simple to implement and the
71 possibility to be reuse (Volesky et al., 2003; Torres et al., 2020; Gupta et al., 2015;
72 Demirbas et al., 2008; Veglio et al., 1997; Bailey et al., 1998).

73 Forestry by-products such as sawdust and bark have many advantages because they are
74 abundant, generally not toxic, and the macromolecules that compose them are known to
75 bind metal ions (Gupta et al., 2015, Basso et al., 2002, Shukla et al., 2002). In particular,
76 the biomass obtained from trees of the genus *Pinus* has been described as good
77 biosorbent for removing metallic trace elements (Gundogdu et al., 2009; Argun et al.
78 2005, Ucun et al., 2003). For example, the *Pinus halepensis* untreated sawdust traps
79 cadmium, copper and lead in aqueous solutions (Semerjian et al., 2010 and 2018). For
80 the removal of nickel (II) from aqueous environment, a review describes various
81 agricultural solid wastes used as biosorbent like peanut hulls, pine bark or pine cone
82 (Raval et al., 2016). Another example is the used of treated mahogany sawdust as
83 biosorbent for the removal of nickel from aqueous solution (Chanda et al., 2021).

84 In the context of the bioresource use and circular economy perspective, our work is
85 focused on *Pinus caribaea* Morelet, a native conifer from Central America and
86 Caribbean islands. This species was widely planted for timber production in tropical
87 regions including New Caledonia, where it is nowadays the most exploited wood. This
88 work investigates the use of sawdust from *P. caribaea* as a biosorbent material for Ni²⁺
89 removal and other metallic trace elements Co²⁺, Cr³⁺, Mn²⁺ ions from aqueous solutions.
90 This study allows the determination of optimal conditions (pH, contact time, initial Ni²⁺
91 and biomass concentration) based on batch experiments. Isotherms of Langmuir and
92 Freundlich have been compared and kinetic parameters have been calculated by pseudo-
93 second-order models. Extraction of parietal components of sawdust was carried out to
94 evaluate the biosorption capacity of cellulosic material. In addition, the selectivity of
95 sawdust has been evaluated according to four metals in solution (Ni²⁺, Cr³⁺, Co²⁺ and

96 Mn²⁺) taken separately or in mixture to take into account the behaviour of biosorbent in
97 more realistic conditions.

98 The impact of different chemical treatments of natural sawdust was furthermore
99 investigated in this work. Two treatments and three oxidations of sawdust were carried
100 out by acidic and oxidation methods. **The aim was to improve the capacity of nickel Ni²⁺**
101 **removal compared to the natural biomass.** The modification using an environmentally
102 friendly technique was chosen to evaluate the selectivity of this material.

103

104 **2. Materials and methods**

105 **2.1. Preparation of biosorbent material**

106 *2.1.1. Raw material*

107 Pine tree sawdust used in this work was from *P. caribaea* Morelet. The material for the
108 preparation of biosorbent was obtained from local garden center. Before use, pine
109 sawdust was washed in deionized water to remove surface impurities and then dried in
110 an oven (Memmert Universal Oven UF1060 marque) at 40 °C for 4 days. Then, sawdust
111 was ground into fine particle in a blender (Knife Mill GM 300) and sieved in a second
112 crusher (Polymix PX-MFC 90 D) to the particles size required (0.2 or 0.5 mm).

113 *2.1.2. Extraction of polymers*

114 The parietal polymers of wood were obtained through successive extractions. The first
115 step allows to get extractables like circulating sugars, tannins, mineral elements by an
116 80% hydroethanolic solution mixed with 10 g of sawdust powder. The solution was
117 stirred for 7 min through Soxhlet apparatus. The residue was obtained by filtration and
118 washed with ethanol 80%. For pectins, lignins, hemicelluloses and cellulosic residue
119 extractions, protocols have been used according to the literature (Astier et al. 2010).

120 *2.1.3. Modification of biomass*

121 Five biomass modifications have been carried out by washing the sawdust (5 g, 0.2 mm)
122 with different reagents following chemical protocols optimized from the literature
123 (Hachem et al., 2012; Astier et al., 2010; Varmat et al., 1995).

124 The acidic sawdust (S_H⁺) was obtained by washing the adsorbent material in a solution of
125 H₂SO₄ (0.1 M) under stirring for 2 h at 50 °C.

126 Fenton oxidized sawdust (S_F) was obtained by washing sawdust in 500 mL of water at
127 25 °C for 2 h. After filtration, a mixing solutions of hydrogen peroxide 50 mM and iron
128 sulfate 0.5 mM was equilibrated in biomass at pH 3 by adding H₂SO₄ solutions (0.1 M).
129 The solution was stirred at 25°C for 1 h. Finally, the biomass was filtered, washed and
130 then stirred in a H₂SO₄ solution (0.1 M) for 1 h.

131 The oxidation technics to get dialdehyde (S_{CHO}), di-carboxylic (S_{COOH(2)}) and tri-
132 carboxylic (S_{COOH(3)}) sawdust have been optimized from polysaccharide oxidation
133 described in the literature (Hachem et al., 2012; Varmat et al., 1995). Therefore, di-
134 carboxylic sawdust (S_{COOH(2)}) was obtained by reaction of 1.5 g of dialdehyde sawdust

135 (S_{CHO}) in 600 mL of sodium chlorite (0.3 M). Tri-carboxylic sawdust (S_{COOH(3)}) was
136 obtained from 3 g of S_{COOH(2)} in 300 mL of solution containing TEMPO (2,2,6,6-
137 tetramethylpiperidin-1-yl)oxyl) (0.24 mmol), sodium bromide (3.63 mmol) and sodium
138 hypochlorite (7.26 mmol). Aldehyde functions formed on the biomass after oxidation are
139 determined using the Cannizzaro reaction (Pommerening et al., 1992). Indeed, 100 mg
140 of modified sawdust was suspended in 20 mL of sodium hydroxide (0.1 M) and the
141 solution was stirred at 70°C for 15 min. The excess of sodium hydroxide was neutralized
142 by 0.05 M hydrochloric acid.

143 2.2. Characterizations of natural and modified adsorbent material

144 The functional groups on the surface of natural and modified biomass were identified by
145 Fourier Transform Infrared (FTIR) spectrometer, ATR Frontier by PerkinElmer
146 (spectrum range of 400 to 4000 cm⁻¹). The morphology and surface of natural and
147 modified sawdust particles were observed by a scanning electron microscope (SEM,
148 JSM-IT300 LV/LA).

149 The P_{H_{PZC}} (Point of zero charge) of natural sawdust was determined by adding amounts
150 of biosorbent at different pH values (Tran et al., 2017). In series of centrifuge tubes (50
151 mL), the pH was adjusted with 0.1 M HCl and 0.1 M NaOH as needed, to obtain the
152 appropriate pH range of 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11. These pH values are denoted as
153 the initial pHs (pH_i). 100 g of sample were added and solutions were completed with
154 deionized water. The solutions were shaken on a mechanical platform shaker at 250
155 rpm for 24 h and the final pH in each tube were measured and denoted as pH final (pH_f).
156 The P_{H_{PZC}} was obtained from the plot of ΔpH (= pH_f – pH_i) versus pH_i or the plot of
157 P_{H_f} versus P_{H_i}. Experiments were carried out in triplicate and the mean value was
158 recorded.

159 2.3. Preparation of metal ions solutions and analytical methods

160 A solution containing 5 g/L Ni²⁺ ions was prepared from a solution of Ni(NO₃)₂.6H₂O
161 (Sigma-Aldrich) in a volumetric flask with deionized water. The working solution was
162 carried out by appropriate dilutions with varying concentration (mg/L) of the mother
163 solution at a given pH. Other metals solutions were prepared in the same way from
164 solutions of Co(NO₃)₂.6H₂O, Cr(NO₃)₃.9H₂O and Mn(NO₃)₂.4H₂O respectively.

165 An Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES 730ES
166 Varian) was used to analyze metal ions concentrations in experimental aqueous
167 solutions. A reference scale of Ni²⁺ solutions at known concentrations was realized in
168 the range among 0.005 to 20 mg/L as a calculus base for the ICP-OES to determine
169 further concentrations. Samples with an initial Ni²⁺ concentration higher than 20 mg/L
170 were prepared by adequate dilution to avoid any error during the analyzing process.

171 2.4. Biosorption

172 The biosorption of Ni²⁺ on the pine sawdust was studied through batch technique by
173 studying the effect of particle size, pH, contact time and initial adsorbate concentration.
174 The general method was as follows: 10 mL of nickel solutions at varying concentrations
175 (0.5 to 1000 mg/L) was in reaction with biomass (1 to 20 mg) at pH 5 for the first batch.
176 Values of pH of solutions were adjusted to desire levels (pH = 1 to 9) using diluted
177 NaOH or HCl solutions.

178 The suspension in the tube was stirred at 25 °C on a mechanical platform shaker at 250
179 rpm for 16 h to reach equilibrium. The influence of contact time on adsorption efficiency
180 ~~and isotherm analysis~~ were investigated by shaking the tubes at different times (10 s to
181 360 min). Biomass was removed by vacuum filtration through 0.45 µm nitrocellulosic
182 membrane, and the concentration of Ni²⁺ ions in the filtrate was analyzed using ICP-
183 OES. All the biosorption experiments were repeated in triplicate.

184 Compared to the initial metal concentration, the adsorption efficiency in the following
185 Eq. (1) was calculated as a percentage of adsorbed metal in equilibrium. Adsorption
186 capacity is the amount of metal adsorbed per mass unit of sawdust according to Eq. (2).

187 (1) Metal removal efficiency (%) = $\frac{(C_i - C)}{C_i} \times 100$

188

189 (2) $q \text{ (mg/g)} = \frac{(C_i - C) \cdot V}{m}$

190

191 Where, C_i and C are the initial and equilibrium concentrations of metals ions (mg/L) in
192 the solution, q is the adsorption capacity (mg/g) or the mass of metal ion solution
193 adsorbed per unit mass of sawdust (mg/g), V is the volume of solutions (L) and m is the
194 sawdust mass (g).

195 2.5. Desorption

196 The Ni²⁺ ions retained by pine sawdust have been extracted by experiments in a batch
197 system by investigating different concentrations of two acids: hydrochloric acid (0.01,
198 0.1 and 0.5 M) and sulfuric acid (0.005, 0.05 and 0.25 M). Previously dried, the biomass
199 loaded with Ni²⁺ ions was stirred for 16 h in 10 mL of HCl or H₂SO₄ solutions. The
200 solution was filtered through 0,45 µm nitrocellulose membrane and analyzed by ICP
201 spectrometer to determine the amount of Ni²⁺ desorbed.

202 2.6. Adsorption isotherm models

203 The relationship between the amount of Ni²⁺ ions adsorbed and its equilibrium
204 concentration in aqueous solution was established by models of Langmuir and
205 Freundlich which are the most commonly used (Langmuir et al., 1918; Freundlich et al.,
206 1907). Experiments were conducted at different concentration of biomass (1 to 20 g/L)
207 with different Ni²⁺ initial concentration (0.5 to 200 mg/L).

208 2.7. Adsorption kinetics

209 Most adsorption systems were reported to follow a pseudo second-order kinetic models
210 (Ho et al., 1999). Experiments were carried out at various periods ranging from 10
211 seconds to 360 minutes at two pH values to study the effect of acidic and basic
212 conditions.

213 2.8. Biosorption of a mixture of metals (Co²⁺, Cr³⁺, Mn²⁺, Ni²⁺)

214 The biosorption capacities of natural and Fenton oxidized sawdust were assessed for the
215 removal of metal ions Co²⁺, Cr³⁺, Mn²⁺ and Ni²⁺ ions from aqueous solutions. Metal
216 solutions were evaluated separately and in a mixture under optimum parameters

217 previously determined (initial metal ion concentration = 5 mg/L (alone or in a mixture),
218 5 g/L of pine biomass, pH=8).

219 **2.9. Biomass recycling**

220 **To** evaluate the reusability of natural pine sawdust, biosorption-desorption cycles were
221 repeated five times using the same concentrations (5g/L of sawdust). 5 mg/L of initial
222 Ni²⁺ concentration solution **was used for biosorption** and desorption was performed with
223 10 mL of 0.1 M HCl solution for 16 h.

224 **3. Results and discussion**

225

226 **3.1. Physicochemical characterization of natural and modified sawdust**

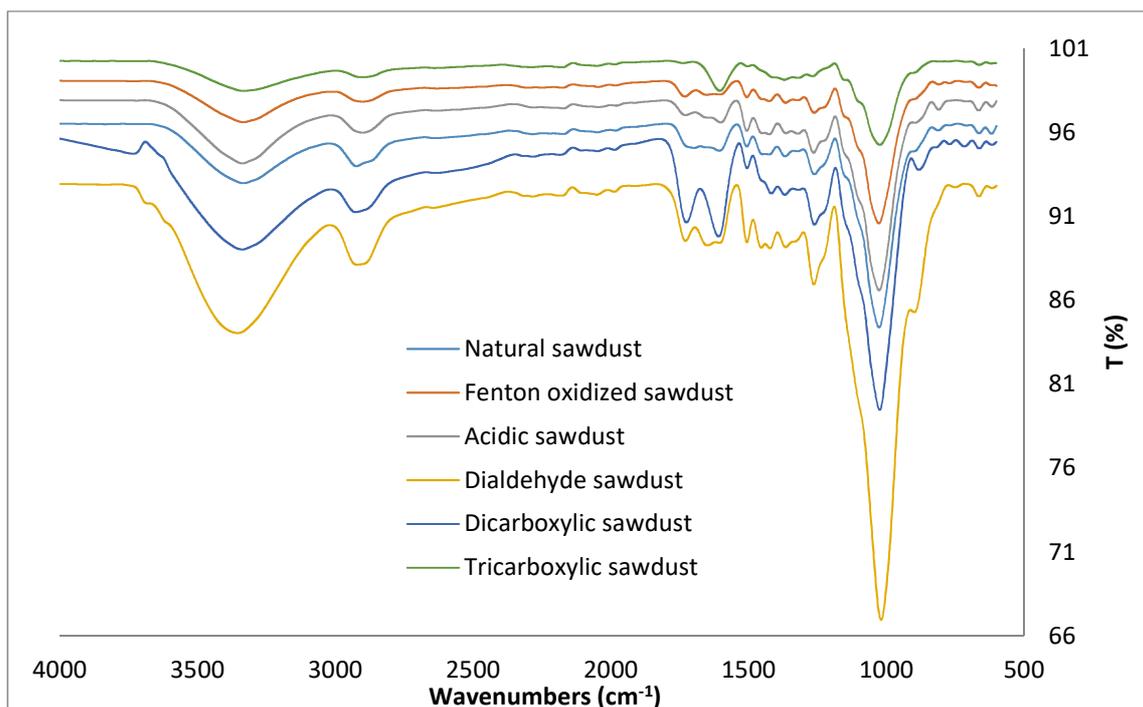
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228 *3.1.1. Fourier Transform Infrared (FTIR) Spectroscopy*

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230 The infrared spectra of the natural and modified pine sawdust were carried out to
231 determine the type of functional groups present in the sawdust surface (**Fig. 1**). All
232 spectra shared characteristic absorption bands around 1600-1700 cm⁻¹, 2900 cm⁻¹ and
233 3300 cm⁻¹ which has been assigned respectively to the stretching vibrations of carbonyl
234 group (C=O), C-H and OH stretching. Nevertheless, we can observe some modifications
235 after the different chemical treatments. Thus, aldehydes groups (S_{CHO}) **in pine sawdust** is
236 associated **to** bands around 2855-2849 cm⁻¹ (vibrational stretching of C-H bands) and
237 1700 cm⁻¹ (C=O) higher than natural sawdust (Stuart et al., 2005). Bands attributed to
238 COOH groups present at 1500-1600 cm⁻¹ (C=O), and 1200 cm⁻¹ (C-O) are higher in
239 dicarboxylic and tricarboxylic spectra. Generally, band intensities increase **in the same**
240 **direction as** the **sawdust** oxidation degree. The oxidation of aldehyde functions in
241 carboxylic acid function is reflected in a decrease of band intensity around 1740 cm⁻¹
242 versus a wide band around 1600 cm⁻¹ for dicarboxylic and tricarboxylic sawdust spectra.
243 The presence of band for dicarboxylic sawdust is translated by a non-complete reaction
244 because all aldehydes haven't been oxidized. The spectra of acidified sawdust allow to
245 observe a little increase in the intensity of the band around 1700 cm⁻¹ (C=O aldehyde) as
246 a sign of the disappearance of hemiacetal functions in acid treatment. For Fenton
247 oxidized sawdust, the band characteristic of aromatic rings (1600 cm⁻¹ stretching of
248 C=C) **was decreased** following degradation.

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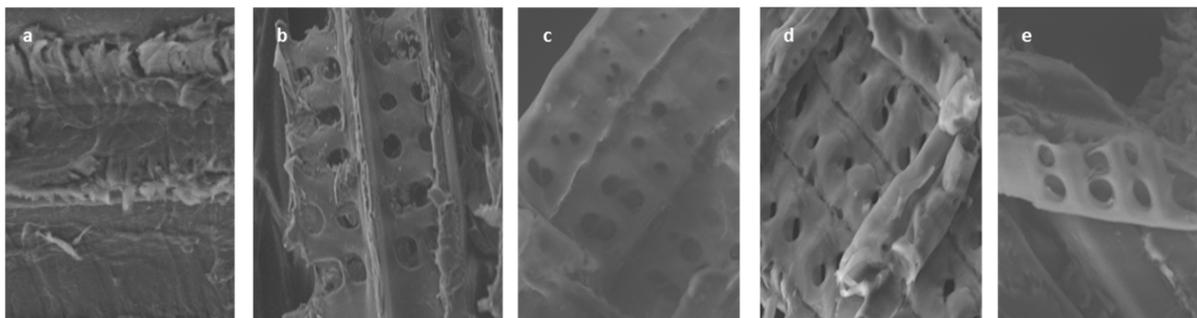
252 **Fig. 1.** FTIR spectra of natural, treated and oxidized sawdust

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3.1.2. Scanning Electron Microscopy (SEM) Analysis and Energy Dispersive X-Ray (EDX) Spectroscopy.

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The microscopic analysis SEM confirms the difference in structure between natural and modified sawdust (**Fig. 2**). Natural sawdust had fibrous and rough surface with heterogeneous structure similar to a spongy aspect. The obtained S_{H^+} presented many pits and fissures, possibly because of the powerful dehydrating of sulfuric acid. Oxidized sawdust S_F , S_{CHO} and S_{COOH} had irregular, heterogeneous surface characterized by cracks, the pore volume increase. Thus, oxidized reagents disturb the surface of sawdust making them more available to metals. The adsorption mechanism occurring in pores considers interactions such as electrostatic attraction, hydrogen bonding, surface precipitation, cation exchange. These interactions depend on the characteristics of the porous adsorbents and adsorbate (Tran et al., 2017).



267

268 **Fig. 2.** Characterizations by SEM of natural sawdust (a) at 1600x, treated SH+ (b), SF (c) at 650x
 269 and oxidized sawdust SCHO (d), SCOOH (e) at 650x.

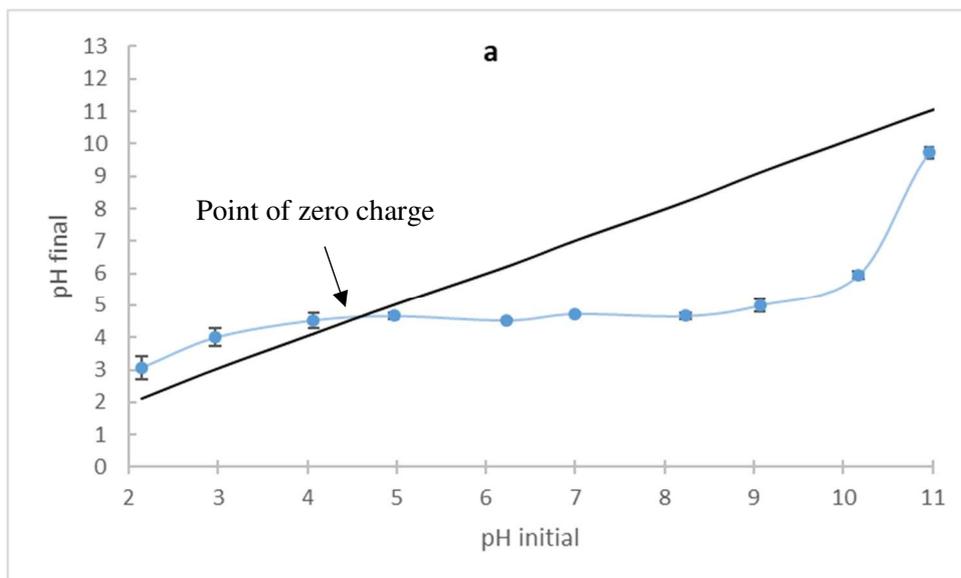
270 The EDX spectroscopy gives an overview of the sawdust elemental composition before
 271 and after nickel biosorption (Table 1s, Fig 1s and 2s in supplementary data). The natural
 272 sawdust contains atoms on its surface like carbon and oxygen present in the structural
 273 polymers of wood. Other elements are present such as minerals: calcium, manganese,
 274 silicon, iron or copper. These elements were naturally absorbed by the biosorbent in its
 275 environment. For example, manganese and calcium are found in *P. caribaea* needle
 276 samples in works of Carrions N. et al., 1987. Chlorine and nickel appear in addition on
 277 the sawdust after biosorption, chlorine comes from the HCl acid added during pH
 278 adjustment. This experiment shows that nickel is present on the surface of pine sawdust
 279 after biosorption of 5 mg/L of nickel solution. This element is not the only one present
 280 on the surface of the sawdust, which raises the question of the occupation of active sites
 281 (Supplementary Data).

282 *3.1.3. Point of zero charge determination*

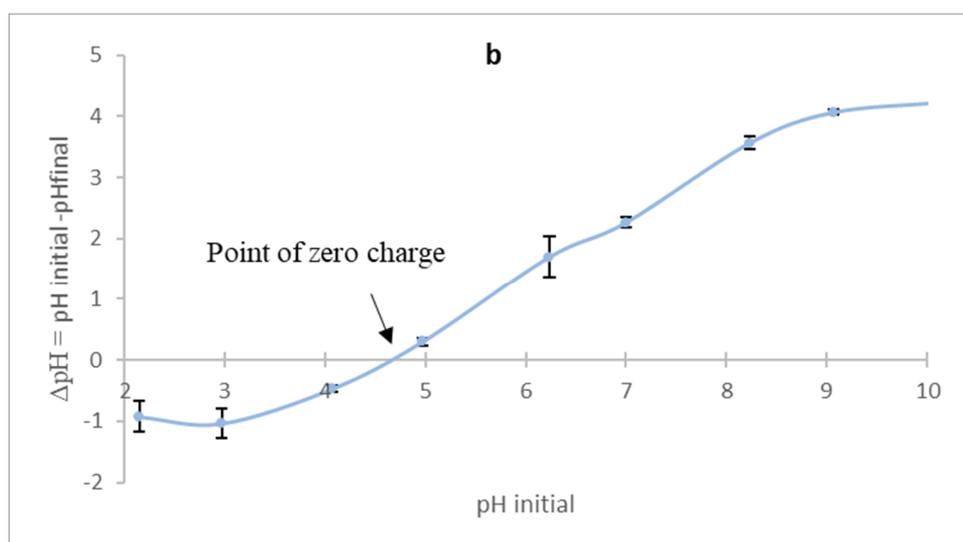
283

284 The point of zero charge (pH_{PZC}) of natural sawdust in aqueous solution was obtained by
 285 plotting pH final against pH initial or (pH initial – pH final) against pH initial according
 286 to **Fig.3**. For this biomass, the pH_{PZC} was around 4.6. At a pH less than pH_{PZC} , the
 287 biosorbent is protonated and the surface positively charged, is able to capture anions.
 288 When pH is higher than pH_{PZC} , the biosorbent surface is negatively charged and
 289 becomes a trap for the cations. The nickel (Ni^{2+}) is more easily trapped in basic
 290 environment. The mechanism involved is electrostatic interaction (Tran et al., 2017).

291



292



293

294 **Fig. 3.** Point of zero charge of natural sawdust, pH final against pH initial (a) and Δ pH against
 295 pH initial (b).

296

297 3.2. Modification yield and quantitative dosage

298

299

3.2.1. Modification yield

300 The mass yields obtained were 92.4, 93.8, 95.0 and 92.0% respectively for S_{H^+} , S_F , S_{CHO} ,
 301 and S_{COOH} . A low loss of mass was observed, the sawdust is reactive to oxidation even
 302 after several steps.

303

3.2.2. Quantitative determination of aldehyde functions (S_{CHO})

304

305 The oxidation reaction of polysaccharides by sodium hydroxide was confirmed through
 306 the determination of the aldehyde functions present on the sawdust. The Cannizzaro

307 reaction involves the action of base on the aldehyde functions leading to the
308 establishment of a stoichiometric ratio between the concentration of hydroxyl ions
309 consumed and the initial concentration of the dialdehyde groups. The aldehyde functions
310 rate was 12.7 mmol per gram of oxidized pine sawdust. Compared to the estimated value
311 (4.08 mmol) this value is higher, which suggesting that the oxidation was reacted on
312 other polysaccharides.

313

314 3.3. Factors affecting efficiency of Ni²⁺ biosorption on sawdust

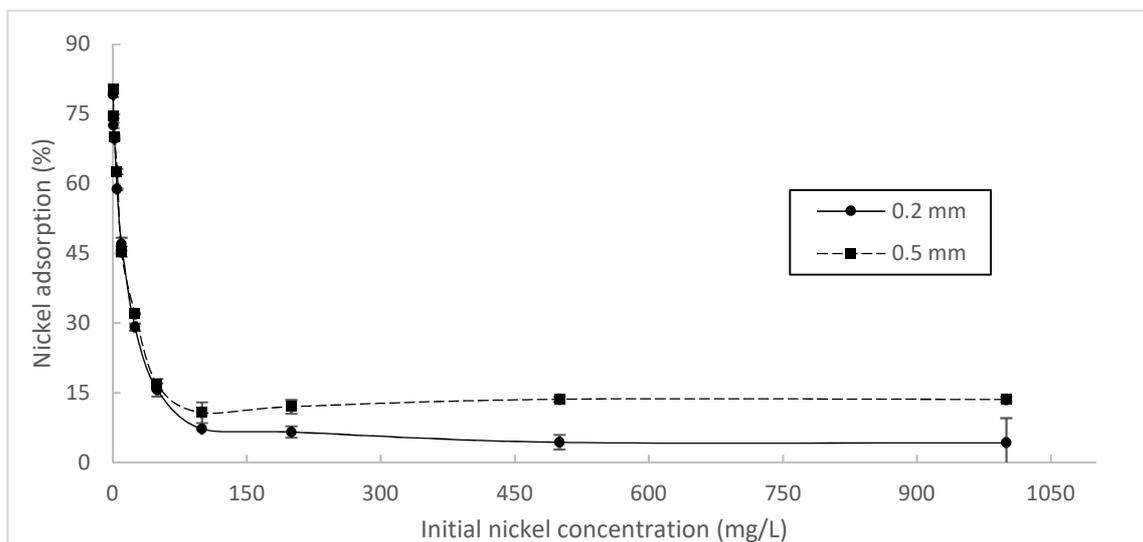
315

316 3.3.1. Initial concentration of Ni²⁺ and size of particles

317

318 High metal removal was attained (80%) at Ni²⁺ ions concentration of 0.5 mg/L (Fig.4).
319 The biosorption of metal ions has stabilized for higher concentration of Ni²⁺ because of
320 saturation of binding sites on the adsorbent. In this case, the additional number of metal
321 ions in solution was competing for a limited number of adsorption sites (Ucun et al.,
322 2003).

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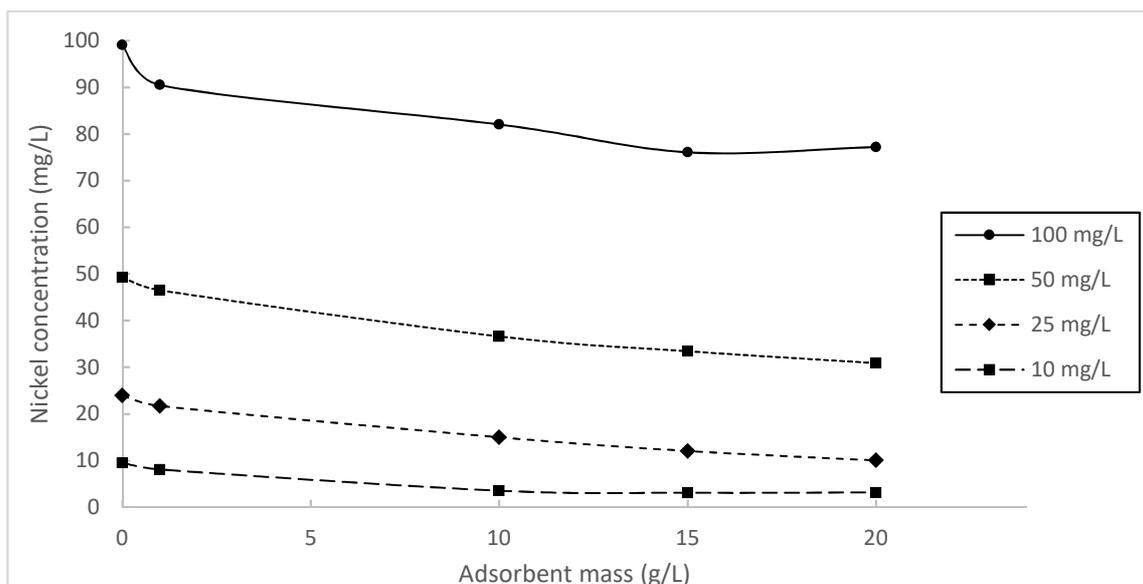
325

326 Fig. 4. Effects of initial concentration of Ni²⁺ and size of particles.

327

328 3.3.2 Adsorbent concentration

329 Experiments was carried out with sawdust concentrations ranging from 0 to 20 g/L and
330 different Ni²⁺ concentrations (10-100 mg/L) at pH 8 for 16 h. The percent removal of
331 metal ions was increased in the same direction than the mass of sawdust until a
332 quantitative retention for the adsorbent mass of 5 g/L in Fig. 5. It is apparent that the
333 Ni²⁺ adsorption evolves with the weight of sawdust because of an increase of availability
334 of exchangeable sites. At a moment, the maximum adsorption efficiency of a metal was
335 achieved even after additional added of binding sites from sawdust. Thus, the adsorption
336 efficiency decreases with the increases of the quantity of biomass.



337
338

Fig. 5. Effect of adsorbent mass.

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3.3.3. pH of suspension

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342

343 As an important parameter in the sorption process, pH can act on the functional groups
344 and the charges affecting interactions between ions in solution (Akmal et al., 2012).

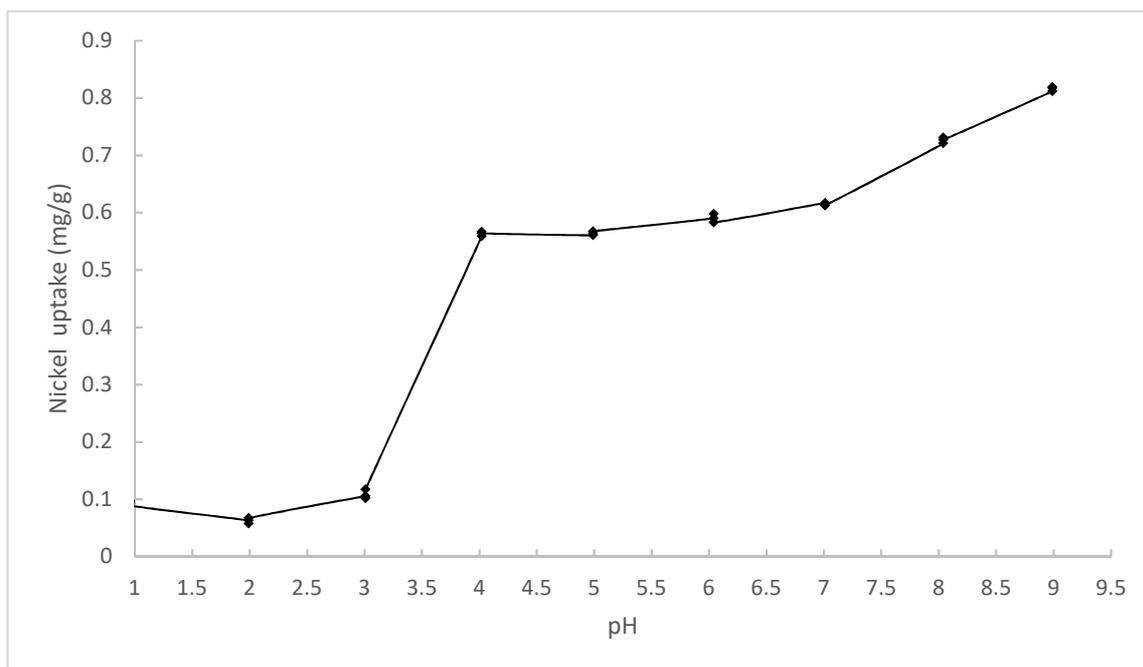
345 Under highly acidic conditions (pH 1-3), the amount of Ni²⁺ uptake was minimal (<0.2
346 mg/g) while the sorption was enhanced in the pH ranging of 3 to 9, showing a maximum
347 adsorption at pH 9 (Fig. 6). At lower pH values, high concentration of hydronium ions
348 are in competition with Ni²⁺ ions for the active sites on the sawdust surface positively
349 loaded. When pH increase, the competing effect of hydronium ions decreased, Ni²⁺ ions
350 have electrostatic attraction with the surface of sawdust, negatively loaded, allowing a
351 favorable process for the metal ions adsorption (Shukla et al., 2002 and 2005).

352 Nickel have four different species Ni²⁺, Ni(OH)⁺, Ni(OH)₂ and Ni(OH)₃ but the
353 predominant species is Ni²⁺ at pH 9 (Gonsalvesh et al., 2016). When the pH increased
354 above pH 9, the percentage of nickel removal decreased by the fact that soluble hydroxyl
355 complexes are formed at higher pH.

356 The increase observed around pH 4 seems to confirm the acidic character of the
357 unmodified pine sawdust surface that corresponds to pKa of aromatic carboxylic acids.
358 Indeed, Salazar J.J et al. described a high concentration of acid groups, mainly phenolic
359 groups present in the surface of the main components of pine sawdust (Salazar-Rabago
360 et al., 2017).

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Fig. 6. Effect of pH for the adsorption of 50 mg/L of Ni²⁺ in sawdust (5g/L).

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3.3.4 Contact time

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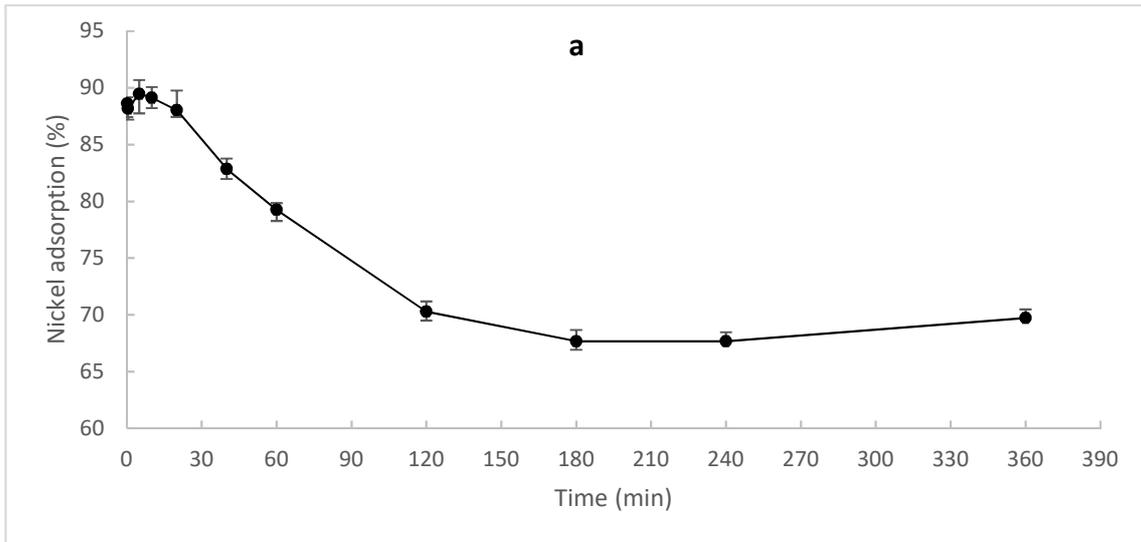
368

369 Under basic condition **Fig. 7(a)**, a maximum adsorption rate (90%) was achieved
370 instantly and then slowly decreased until equilibrium was reached (2 h, 70% of
371 biosorption). The formation of soluble hydroxyl complexes can lead to decrease of
372 adsorption (Shukla et al., 2005).

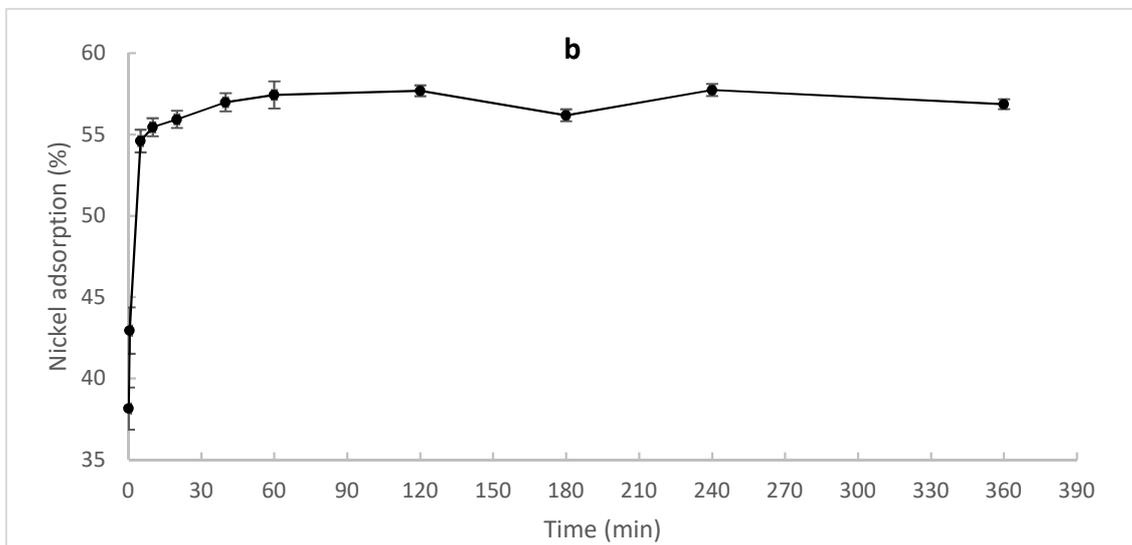
373 Under acidic condition (pH 4), the adsorption rate was increased during the first five
374 minutes and reach equilibrium after 1h according to **Fig. 7(b)**. An adsorption efficiency
375 of 57% was recorded for 50 mg/L. **The equilibrium in acidic conditions was reached**
376 **more rapidly but at lower percentage of adsorption as compared to the basic condition.**

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383 **Fig. 7.** Effect of contact time under basic (a, pH 8) or acidic (b, pH 4) conditions in 5g/L of
384 adsorbent.

385

386 3.4. Adsorption isotherms

387 3.4.1 Langmuir isotherm:

388

389 Langmuir isotherm is valid for monolayer adsorption capacity onto a surface containing
390 a finite number of equivalent adsorption sites. This model respects the following
391 assumptions: the number of active sites on the surface of the adsorbent is fixed and has
392 the same energy, desorption is possible, no other adsorption can occur on the occupied
393 site and no interaction between the adsorbed species. The following nonlinear and linear
394 forms (Eq. 3 and Eq. 4) model this isotherm (Langmuir et al., 1918).

395
$$(3) \frac{q_e}{q_{max}} = \frac{b.C_e}{(1+b.C_e)}$$

396

397
$$(4) \frac{C_e}{q_e} = \frac{1}{b} \cdot q_{max} + \frac{1}{q_{max}} C_e$$

398 Where q_e and q_{max} (mg/g) are the amount of metal ions adsorbed per unit mass of the
 399 adsorbent at equilibrium and at maximum respectively, b (L/mg) is the adsorption
 400 equilibrium constant related to the affinity of the binding sites and C_e (mg/L) is the
 401 adsorbate concentration at equilibrium.

402 The separation factor R_L is employed for isotherms that obey the Langmuir model at
 403 different initial adsorbate concentrations. This equation is presented below (Eq. 5).

404
$$(5) R_L = \frac{1}{1+b.C_0}$$

405

406 Where C_0 (mg/L) is the initial concentration of the adsorbate. The separator factor is
 407 commonly used to evaluate the adsorbent capacity. If $0 > R_L > 1$, the adsorption is
 408 favorable while if $R_L = 0$, $R_L = 1$ and higher than one, the adsorption is unfavorable (Fu et
 409 al., 2007).

410 **Table 1** presents the values of Langmuir parameters for nonlinear and linear modeling
 411 and separator factor R_L . The non-linear parameters were calculated according to the
 412 method described by Tran et al., 2017. The q_{max} values (number of active sites on the
 413 biosorbent) are higher when the concentration of sawdust is low and the R_L values are
 414 between 0 and 1 so the adsorption is favorable.

415

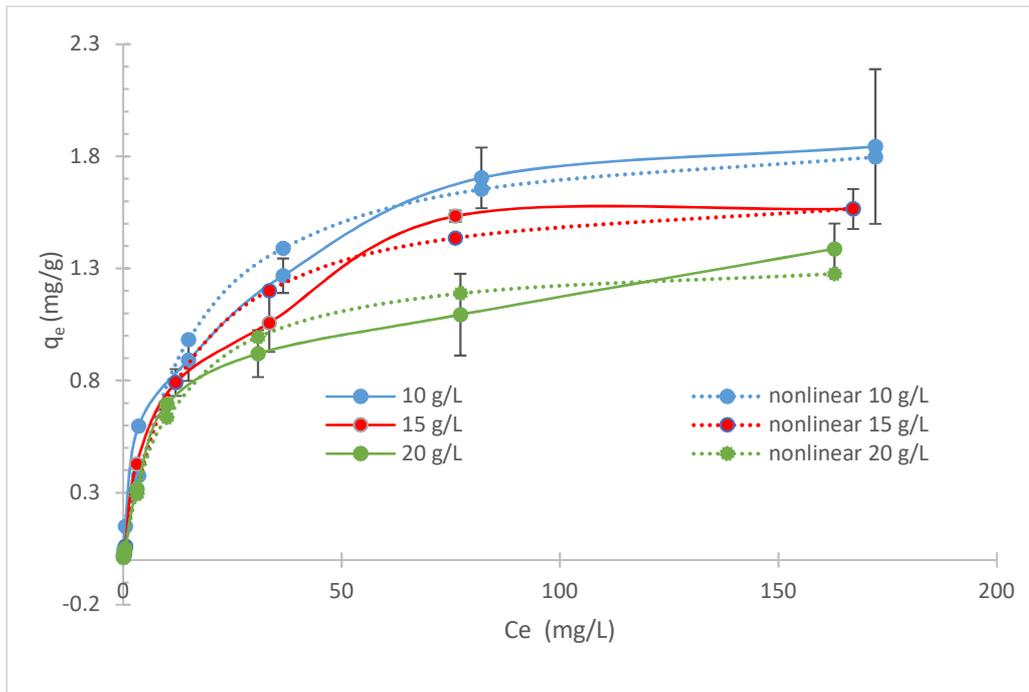
416 **Table 1.** Parameters of Langmuir isotherm models for Ni²⁺ adsorption on *P. caribaea* sawdust,
 417 comparison of linear and nonlinear models.

Sawdust (g/L)	Langmuir linear parameters			Langmuir nonlinear parameters		Comparison		R_L
	q_{max} (mg/g)	b (L/mg)	R^2	q_{max} (mg/g)	b (L/mg)	Δq_{max}	Δb	
1	5.692	0.067	0.869	7.274	0.018	1.582	0.049	0.937-0.982
10	1.890	0.097	0.994	1.952	0.067	0.062	0.03	0.597-0.912
15	1.705	0.071	0.994	1.696	0.073	0.009	0.002	0.478-0.484
20	1.439	0.073	0.988	1.367	0.086	0.072	0.013	0.366-0.407

418

419 The linearization used for Langmuir is the form ($C_e/q_e = f(C_e)$) which shows a reliable
 420 similarity with the nonlinear fit. The parameter values appear to be close for the linear
 421 and non-linear fit and the largest differences in values are found for low biosorbent
 422 concentrations (1g/L). Recent work has provided a critical analysis of the linear model.
 423 Indeed, the dispersion of the points is arranged according to a Gaussian distribution and

424 the error distribution is uniform at all points. However, according to a non-linear model,
 425 this rarely happens with adsorption isotherms. In our linearization, C_e is in both x and y
 426 and the correlation is overestimated. The linearization leads to a good fit but is not only
 427 significant of Langmuir hypotheses. Thus, high R^2 values do not prove that the
 428 Langmuir mechanism occurs exclusively and is no sufficient to compare the
 429 experimental values and isotherm parameters (González-López et al., 2021, Tran et al.,
 430 2017). Hence, the nonlinear model allows a reliability of the parameters (**Fig. 8**).



431

432 **Fig. 8.** Curves fitting of non-linear Langmuir equation.

433

434

3.4.2 Freundlich isotherm

435

436 The Freundlich isotherm implicates a removal of metal ions on a heterogeneous
 437 adsorbent surface. The model is suitable for multilayer adsorptions and describes a
 438 reversible adsorption process (Freundlich et al., 1907). The equation of Freundlich is
 439 expressed in nonlinear and linear forms in Eq. (6) and Eq. (7) respectively.

440

$$(6) q_e = K_f \cdot C_e^{1/n_f}$$

441

$$(7) \text{Log } q_e = \text{log } K_f + \frac{1}{n_f} \cdot \text{log } C_e$$

442 Where, K_f ((mg/g)/ (mg/L)ⁿ) is the constant related to adsorption capacity, n_f is the
 443 Freundlich equilibrium constant, a parameter related to adsorption intensity.

444 Linearization of Freundlich model by logarithmic form allows the determination of
 445 constants K_f and n_f by the plot of $\text{log } q_e$ versus $\text{log } C_e$.

446 The **Table 2** summarize Freundlich isotherms constants for Ni²⁺ adsorption in pine
 447 sawdust and allows the comparison of nonlinear and linear models. The K_f relative to the
 448 adsorption capacity increases when the biosorbent concentration is low. **These results**
 449 **showed the decrease of efficiency of Ni²⁺ removal despite the addition of adsorbent and**
 450 **the increased of Ni²⁺ concentration in solution.**

451 **Table 2.** Parameters of Freundlich isotherm models for Ni²⁺ adsorption on P. caribaea sawdust,
 452 comparison of linear and nonlinear models.

Sawdust (g/L)	Freundlich linear parameters			Freundlich nonlinear parameters		Comparison	
	K _f (mg/g)	n _f	R ²	K _f (mg/g)	n _f	ΔK _f	Δn _f
1	0.545	2.487	0.912	0.325	2.380	0.22	0.107
10	0.128	3.399	0.850	0.047	2.444	0.081	0.955
15	0.04	1.514	0.928	0.035	2.234	0.005	0.72
20	0.003	1.538	0.957	0.020	2.58	0.017	1.042

453

454 **The n_f values higher than 1 highlights a physical process. The values for the exponent n**
 455 **in the range of 0-10 suggest favourable adsorption (Kumar et al., 2006a). The K_f values**
 456 **is lower in the non-linear fit than linear fit. The comparison of the parameters shows that**
 457 **the values are close and the greatest difference is found for the concentrations of 1 and**
 458 **20 g/L.**

459 **3.5. Adsorption kinetic study**

460 **Kinetic models aim to understand the interactions between the adsorbent and the**
 461 **adsorbate, and to provide information on the complex mechanism of adsorption. The**
 462 **pseudo-second order models (PSO) is the most commonly used equation and suppose**
 463 **that the rate-limiting step involves chemisorption (González-López et al., 2021). The**
 464 **two equation (nonlinear and linear) Eq.8 and Eq. 9 respectively are presented below.**

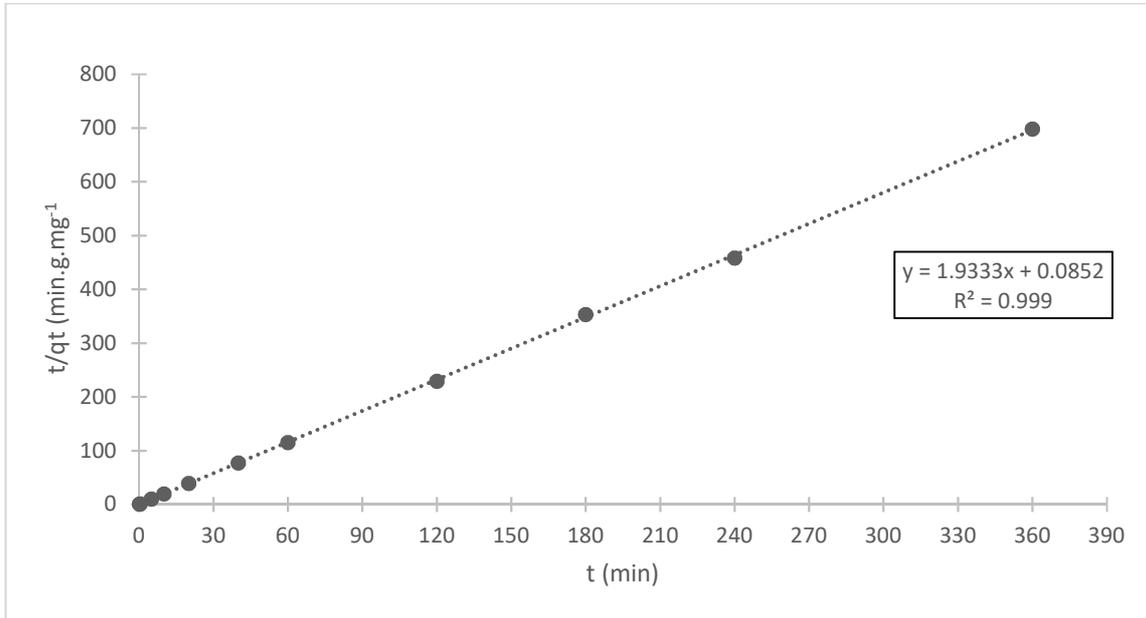
465 **(8):**
$$q_t = \frac{q_e^2 \cdot k^2 \cdot t}{1 + q_e \cdot k^2 \cdot t}$$

466 **(9):**
$$\frac{t}{q_t} = \frac{1}{q_e^2 \cdot k^2} + \left(\frac{1}{q_e} \cdot t\right)$$

467 **Where k (l/min) is the second-order rate constant, t (min) the time, q_t and q_e (mg/g) are**
 468 **the amounts of adsorbate uptake per mass of adsorbent at any time t (min) and at**
 469 **equilibrium respectively.**

470 **The linear form describes the kinetic of Ni²⁺ biosorption with a high correlation**
 471 **coefficient (R²> 0.999) for initial metal concentration of 5.0 mg/L according to **Fig. 9**.**
 472 **The linearized models help for predicting the initial k and q_e for non-linear models.**

473 Hence, the second-order rate constant (k) was 43.96 and the theoretical amount of
474 adsorbed metal ions at equilibrium was measured at 0.517 mg/g (q_e , calculated), whereas
475 the experimental value was 0.798 mg/g (q_e , experimental).

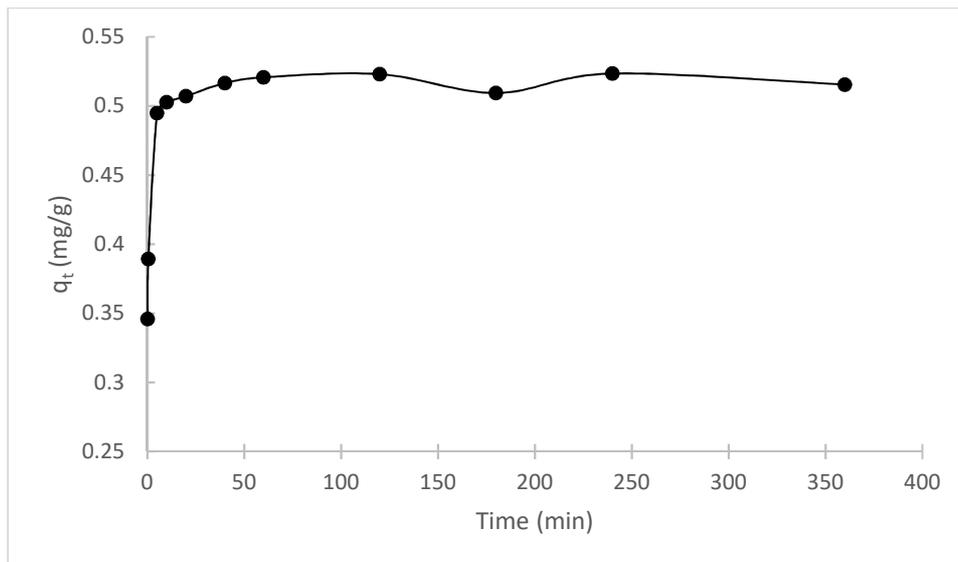


476

477 **Fig. 9.** Pseudo-second-order plot of Ni^{2+} adsorption on *P. caribaea* sawdust.

478

479 This linearized equation give a good fit but t is in the two axis so the correlation is
480 overestimating and could positively change the conditions (González-López et al.,
481 2021). Because of the error distribution, non-linear regression is preferred (**Fig. 10**).



482

483 **Fig. 10.** non-linear regression of Pseudo-second order in acid condition.

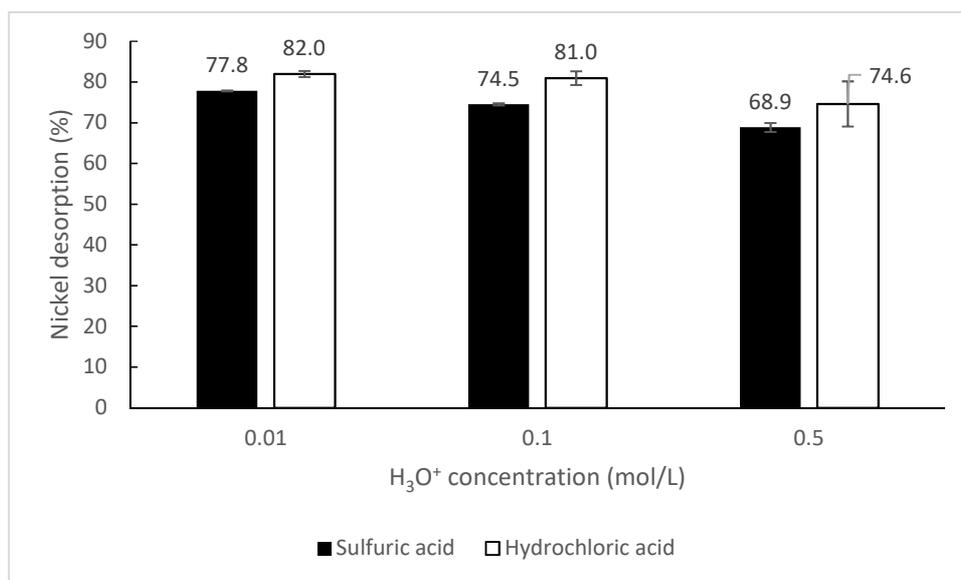
484 The maximal rate was obtained in the first minutes and the adsorption stabilizes.

485

486 3.6. Study of desorption of Ni²⁺ ions

487

488 After desorption, the biosorbent should recover its original form as well as its adsorption
489 capacities. Desorption process requires effective, cheap and non-destructive reagents for
490 the biomass. Dilute solutions of hydrochloric acid HCl and sulfuric acid H₂SO₄ were
491 selected as eluents to desorb Ni²⁺ ions from the metal-loaded pine biomass. Under acidic
492 conditions, protons displace metal cations such as Ni²⁺ from the binding sites of the pine
493 sawdust.



494

495 **Fig. 11.** Ni²⁺ desorption efficiency of sawdust with HCl or H₂SO₄ treatments.

496 The percentage of Ni²⁺ ions removal from pine sawdust surface with HCl was constant
497 (**Fig. 11**), but the highest desorption were observed for 0.01 and 0.1 M of HCl (82.0 and
498 81.0 % respectively). For 0.5 M of HCl, the Ni²⁺ desorption was bitten decreased. For
499 the three concentrations of H₂SO₄, the best rate of desorption is observed for a
500 concentration of 0.01 M showing that higher concentrations of sulfuric acid were less
501 efficient in releasing Ni²⁺ ions. Sulfuric acid globally presented lower desorption
502 capacities than hydrochloric acid. However, a complete desorption of Ni²⁺ ions **by using**
503 HCl or H₂SO₄ could not be obtained, which might be due to metal ions being trapped in
504 the intrapore of the sorbent's surface and therefore, difficult to be released (Serencam et
505 al., 2008). Finally, 0.1M of HCl was selected for the other experiments of this study.

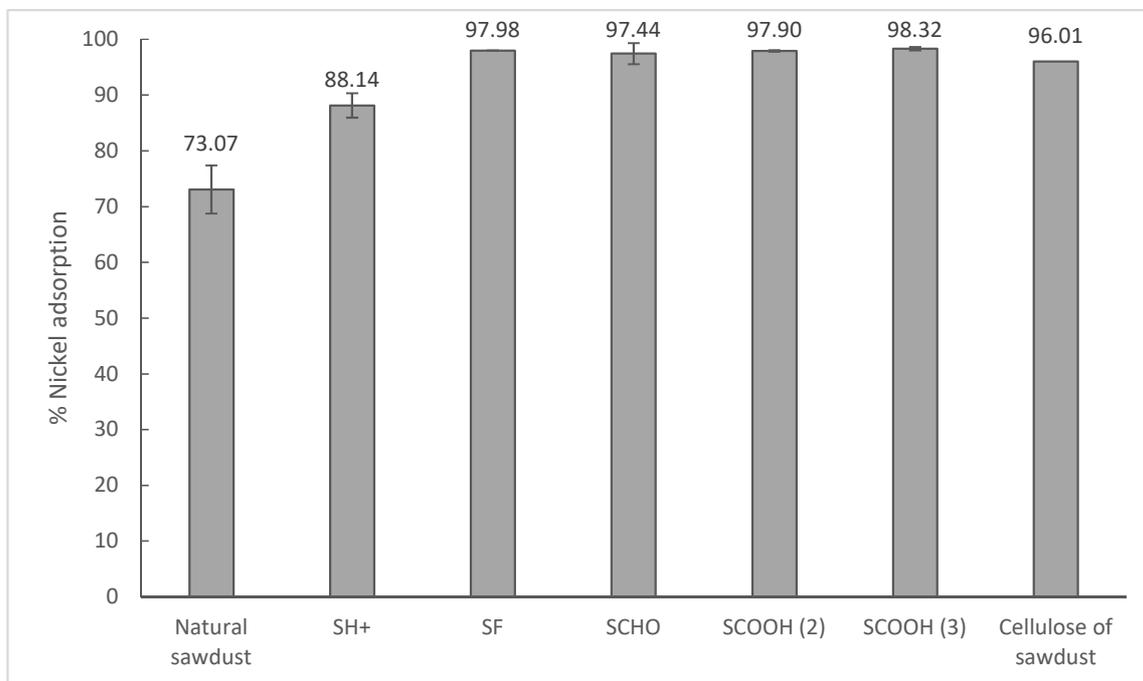
506 3.7. Evaluation of removal capacity of modified sawdust

507

508 Cellulose is the main component of sawdust (73.1%) and better adsorbs Ni²⁺ ions in
509 solution (96.0%) than natural pine sawdust (**Fig. 12**). This result **is** confirmed by the
510 literature, which confirms the high removal capacity of cellulosic polysaccharides and in
511 particular, hydroxyl groups on their surface (Gupta et al., 2015; Basso et al., 2002).

512 Studies of Basso and al. have proved that the presence of cellulose and hemicelluloses in
513 plant biomass improved the biosorption potential (Basso et al., 2002).

514



515

516 **Fig. 12.** Ni²⁺ adsorption on modified sawdust SH⁺ (acidified), SCHO (di-aldehyde), SCOOH (2) (di-
517 carboxylic), SCOOH (3) (tri-carboxylic) compared to natural sawdust and isolated cellulose.

518

519 **As a heterogenous material, sawdust contains** numerous cations like calcium and sodium
520 naturally fixed on the ion exchange sites, which reduce the retention capacities of metal
521 in solution (Hawari et al., 2005). To **overcome** this drawback, this material **was**
522 stabilized through chemical activation, for example by treatment with acid or oxidative
523 degradation. These chemical modifications aim to adding functional groups on the
524 polysaccharide structure or treatments that modifying the physicochemical surface
525 properties. Adsorption results depend on the chemical modification as well as the metal
526 considered. **Compared with natural sawdust according to Fig. 13, all modifications were**
527 **more effective for the Ni²⁺ uptake.** Acid treatment seems to be less effective than
528 oxidized reactions. **Mentioned above, the surface S_H⁺ sawdust seems to be damaged**
529 **compared to smooth surface of oxidized pine sawdust.** All of these modifications are
530 characteristics of increasing surface area making the sites more accessible. The
531 adsorption maximum of 98.3% was observed for tricarboxylic sawdust. This result
532 confirms the proportionality between the number of carboxylic acid functions formed
533 and the amount of ions bounds (Vinícius et al., 2007). The chemical nature and spatial
534 arrangement of binding sites can influence the binding of cations to organic matter.
535 Indeed, carboxylic sites attached to adjacent carbon atoms **and spaced** on a ring, are
536 more selective to multivalent cations (Talibudeen et al. 1981).

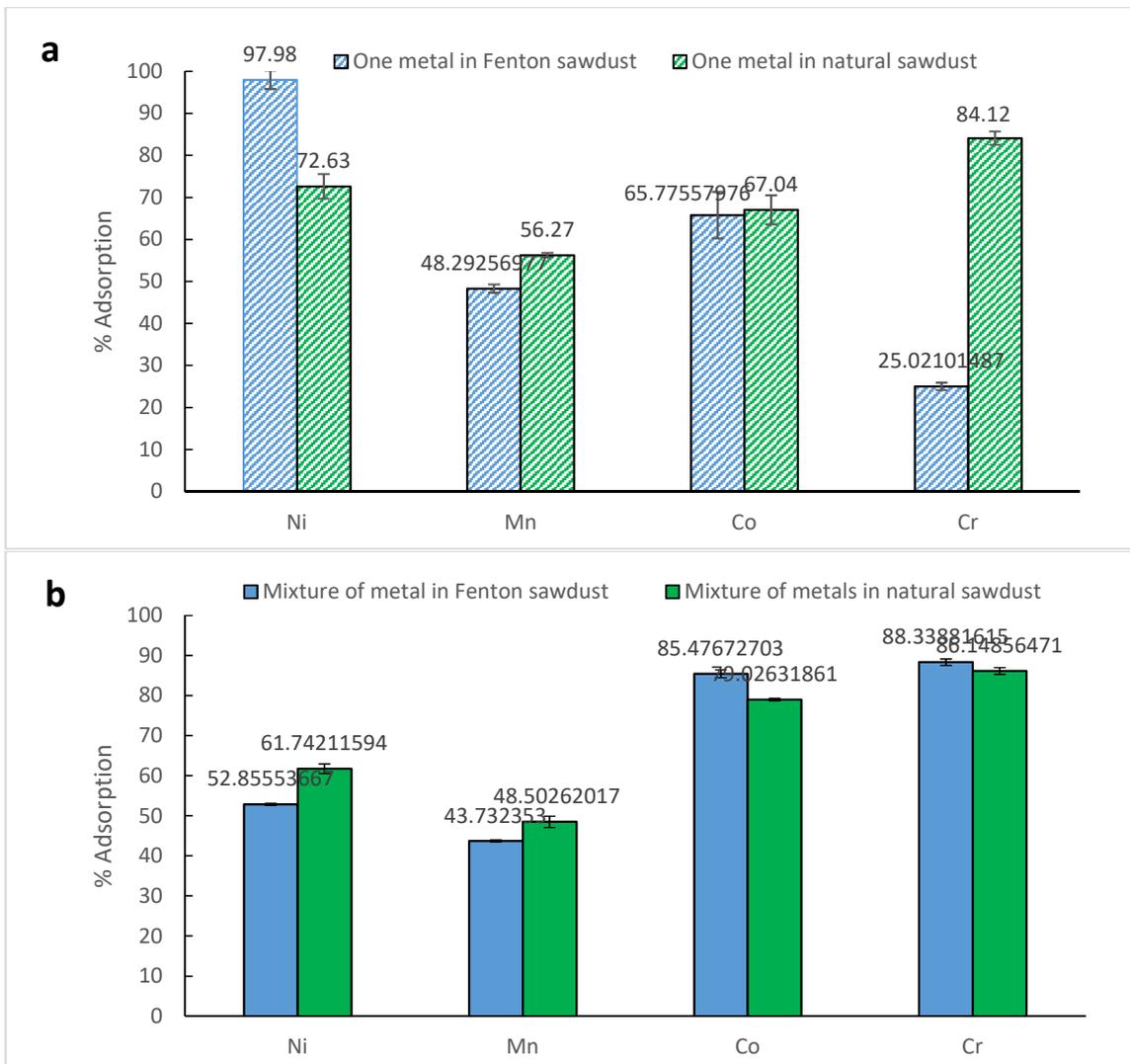
537

538 **3.8. Biosorption of Co²⁺, Cr³⁺ and Mn²⁺ ions by natural and Fenton oxidized**
539 **sawdust**

540

541 As a chemical process for wastewater treatment, oxidation by Fenton's reagents is based
542 on the catalytic decomposition of H_2O_2 in presence of iron salts (Fe^{2+}). As a cost-
543 effective source of hydroxyl radical ($OH\cdot$), this method has many advantages as
544 simplicity of design, safe operation, high efficiency, availability and short reaction time
545 (Neyens et al., 2003). The **Fig. 13** shows that metal adsorption was different as function
546 of active sites and functional groups on the surface of the biosorbent. This behavior is
547 attributed to selectivity of biosorption, which depend on characteristic of metal ions such
548 as electronic charge of the valence layer, the counter ions in solutions, hydration
549 enthalpy, ionic radius, coordination number, electron configuration or electronegativity
550 (Gorgievski et al., 2013; Zeraatkar et al., 2016).

551



552

553

554 **Fig. 13.** Selectivity of metals (Ni^{2+} , Mn^{2+} , Co^{2+} , Cr^{3+}) in natural versus Fenton oxidized sawdust in
555 a mixture of four metals (a) and separately (b) at 5.0 mg/L.

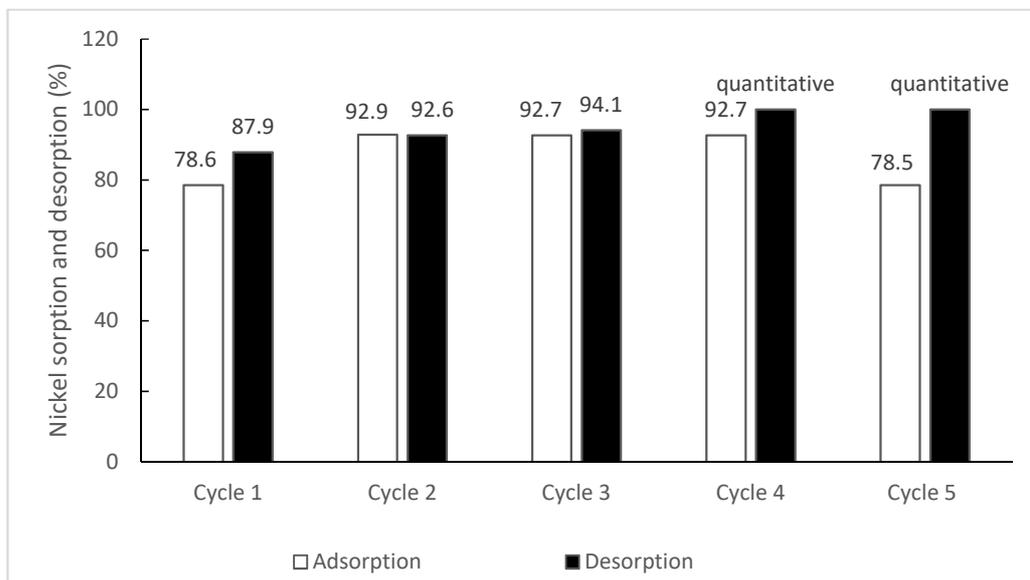
556 For single metal uptake (**Fig. 13,b**), natural pine sawdust showed a greater affinity than
557 for Cr^{3+} (84.1%) followed by Ni^{2+} (72.6%) whereas Fenton oxidized pine sawdust had
558 better adsorption capacity for Ni^{2+} (98.0%) followed by Co^{2+} (65.8%). Oxidation under

559 Fenton conditions was the most favorable treatment for the adsorption of nickel in
 560 solution. As the metals are usually found in mixture in nature, experiments with a
 561 mixture of four metals were conducted (Fig. 13, a). Sawdust is a complex material with
 562 many possible binding sites. In a mixture, metal is competed with another inducing
 563 selectivity according to the available sites on sawdust surface. Results show that in the
 564 presence of a mixture of these four metals, natural sawdust and Fenton oxidized sawdust
 565 had great affinity for Co^{2+} and Cr^{3+} . Affinity of metal ion for biosorbent takes into
 566 consideration all properties of metal ion.

567 3.9. Biomass reusability cycles

568

569 After the first cycle, the biosorption of natural pine sawdust capacity increased then
 570 barely changed before decreasing after the fifth cycle according to Fig. 14.



571

572 **Fig. 14.** Reuse of natural pine sawdust for Ni^{2+} biosorption-desorption cycles (initial Ni^{2+}
 573 concentration = 5.0 mg/L, sawdust concentration = 5.0 g/L, pH = 8, desorption solution: 10 mL
 574 of 0.1 HCl at 16 h).

575 On the contrary, the desorption efficiency slowly increased until quantitative desorption
 576 after the fourth cycle. These results disagree with results obtained in other studies in
 577 which HCl decreases metal adsorption capacity of the biosorbent in successive cycles by
 578 damaging metal binding sites (Mehta et al., 2005). Desorption using HCl solution can
 579 cause a change in sawdust structure as seen in acidic treatment modification, thus
 580 gradually increasing the capacity of biosorption in the first cycles. This structural
 581 modification in acidic conditions can also explain the increase of Ni^{2+} desorbed which
 582 could come from initial ions accumulated into intrapore of the biosorbent during
 583 previous cycles.

584 Conclusion

585 *P. caribaea* sawdust is an ecological, available, inexpensive and effective biosorbent to
586 reduce in aqueous solutions metallic trace elements (Ni^{2+} , Co^{2+} , Cr^{3+} , Mn^{2+}) which are
587 present in rivers and groundwater of New Caledonia. Our work defined the optimal
588 parameters (pH, particle size, biomass and initial concentration) for Ni^{2+} and adsorption
589 rate was reaching equilibrium in short time. From a sustainable development
590 perspective, we proven than *Pinus caribaea* sawdust can be reuse in five cycles after
591 regeneration with a good efficiency. Biomass modifications by acid treatment and
592 oxidative reactions can be accomplished in good yields and improve the metal binding
593 capacities on sawdust. Selectivity of metals on natural sawdust versus Fenton oxidized
594 sawdust is highlighted for Ni^{2+} and Cr^{3+} while variation are observed when metals are in
595 mixture. *P. caribaea* sawdust could thus become an attractive material for the
596 development of water purification techniques by biosorption for depollution installations
597 adapted to the context of tropical islands producing this *Pinus* species in forestry. Many
598 studies focus on the use of biomass to remove heavy metals from water but rarely lead to
599 concrete applications because the treatment of biomass to remove metals require acidic
600 environment and thus generates new waste. Metallurgical extraction techniques have
601 evolved over the last decades with the emergence of hydrometallurgy. This technic
602 currently applied in New Caledonia involve the use of acidic aqueous solutions for the
603 recovery of metals from ores. Our results thus fit in an island context for which a
604 technical solution could be associated with industrial metallurgic complexes to recycle
605 the biomasses used to decontaminate water.

606

607 **CRedit authorship contribution statement**

608 Conceptualization: CS, NL, VS. Methodology: CS, NL. Validation: CS, TG, ML, NL,
609 VS, FB, VC. Formal analysis: CS, TG, VC. Investigation: CS, TG, ML, MM, NL.
610 Resources: MM, NL. Writing - Original Draft: CS. Writing - Review & Editing: MM,
611 FB, NL, VS. Visualization: CS. Supervision: NL. Project administration: NL. Funding
612 acquisition: NL

613

614 **Acknowledgements**

615 The authors are thankful to the research and development institute (IRD) of New
616 Caledonia particularly the LAMA for analysis of metal trace elements. Thank you for
617 the microscopy platform of University of New Caledonia and analysis equipment of
618 PEIRENE Laboratory of University of Limoges.

619

620 **Declaration of Competing Interest**

621 The authors declare no conflict of interest.

622

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