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1 **Competitive and non-competitive zinc, copper and lead**
2 **biosorption from aqueous solutions onto flax fibers**

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36 **Abstract:** Competitive and non-competitive batch experiments were conducted on flax fibers
37 to study Zn^{2+} , Cu^{2+} , and Pb^{2+} ions biosorption performance. Biosorption efficiency was
38 dependent on contact time, pH, and biosorbent concentration. The results under competitive
39 conditions were different from those obtained in non-competitive form. A high affinity of
40 lead, with a selectivity sequence in general of $Pb > Cu > Zn$ was observed. The biosorption
41 data fitted very well the Langmuir model for lead in both types of solutions and for zinc and
42 copper in the monometal form. The fit with the Freundlich model was not as successful,
43 except for copper in the ternary system. Regarding zinc under competitive conditions, the
44 sorption process was quite difficult and thus the equilibrium data could not fit well the
45 adsorption models. The maximum adsorption capacities ($mmol.kg^{-1}$) were respectively
46 112, 122 and 71, for Pb, Cu and Zn in the single metal ion solution and 82, 57 and 8 only in
47 the ternary, showing thus a high competition between metal ions when added simultaneously.
48 Overall, lead could still be efficiently removed in spite of the presence of other ions while
49 zinc would be overcome in the presence of lead and copper.

50 **Keywords:** Heavy metals; Competition; Biosorbent; Biosorption curves; Adsorption models

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61 1. Introduction

62 Water resources contamination is one of the greatest and most current challenges. It is a
63 serious problem which can lead to dangerous risks on human health, flora, wildlife and also
64 environment. Discharge of effluents from industrial runoff, wastewater, agricultural fields and
65 also road runoff are the major sources of water bodies pollution, that release high levels of
66 toxic pollutants (Jern, 2006). These latter include essentially (1) total suspended solids as silts
67 and clays and organic matters, (2) heavy metals such as lead, cadmium, chromium, mercury,
68 zinc, nickel and copper ions, (3) nutrients, mainly phosphate and azote, (4) antibiotics and
69 also (5) polycyclic aromatic hydrocarbons (PAHs) (Jern, 2006; Flanagan et al., 2019). All
70 these pollutants are very persistent in the environment, especially heavy metals, due to their
71 toxicity nature and non-biodegradability (Jern, 2006). Therefore, various technologies have
72 been developed for metal ions removal. Among these, biosorption is one of the most attractive
73 methods, based on metal binding to biological adsorbents. Different types of inexpensive
74 biosorbents have been explored, they include dead biomass like agricultural waste and
75 vegetative fibers, as well as living biomass such as microbial and bacterial organisms. Among
76 these biosorbents, we list wool fibers (Balköse et al., 1992), modified jute fibers (Shukla and
77 Pai, 2005), rice husk (Krishnani et al., 2008), pomegranate peel (El-Ashtoukhy et al., 2008),
78 hazelnut and almond shell (Pehlivan et al., 2009b), pine bark (Cutillas-Barreiro et al., 2014),
79 wheat straw (Coelho et al., 2016) that have been explored for their high capacity of removing
80 heavy metals from contaminated aqueous solutions. The present work focused on the use of
81 flax fibers as biosorbent, in order to remove zinc, copper and lead ions under competitive and
82 non-competitive conditions. The choice of this plant material, is related to its low cost and
83 high availability. The Normandy region is one of the most prolific producers of flax in France
84 and in Europe (Meirhaeghe and Bewa, 2011). Depestele Group, for instance, has developed
85 numerous applications of this natural material in civil engineering. Actually, flax has been
86 extensively used in the manufacture of woven fabrics, insulation materials and non-woven
87 geotextiles (Ouagne et al., 2013).

88 Results of a previous study realized by [Abbar et al., \(2017\)](#) showed a good capacity of flax
89 fibers to remove zinc, copper and lead ions from aqueous solutions in a ternary system at
90 equal massic concentrations. However, numerous questions have been raised after that work,
91 especially regarding concentration effect and adsorption behaviors in non-competitive form
92 for each ion, in order to judge the competition effect which may occur when the three metals
93 are added simultaneously. With regards to heavy metals competition, relatively few studies
94 have considered both single and multi-element systems in biosorption studies. [Park et al.](#)
95 [\(2016\)](#), for instance, evaluated adsorption behaviors of zinc, copper, cadmium, chromium and
96 lead adsorption onto sesame straw biochar and found that multimetal and monometal
97 adsorption behaviors were not similar. Similarly, [Pejic et al. \(2009\)](#) explored the removal of
98 zinc, cadmium and lead ions from aqueous solutions by short hemp fibers and reported that
99 the maximum total uptake capacity for each zinc and cadmium in monometal solutions (78
100 mmol.kg^{-1}) were different from multimetal solution (35 mmol.kg^{-1}), while for lead it was
101 quite the same (78 mmol.kg^{-1} and 74 mmol.kg^{-1} respectively). However, as long as we know,
102 no previous studies have dealt with zinc, copper and lead ions biosorption onto flax fibers in
103 both single and multimetal ion trials. In view of that, a series of biosorption experiments of
104 these three metals were performed in both single and ternary batch systems. The objectives
105 were (i) to compare biosorption capacities of the three metals under competitive and non-
106 competitive forms, and (ii) to evaluate the competition effect on each metal biosorption onto
107 flax fibers when the three metals are added simultaneously. Different conditions, resulting
108 from changing parameters such as contact time, biosorbent concentration and pH, were
109 investigated. Pseudo-first order and pseudo-second order kinetics and intraparticle diffusion
110 models were tested for the adsorption kinetic studies when Langmuir and Freundlich models
111 were used to fit the biosorption data. The goal of this study is to test afterwards a full-scale
112 stormwater device as a biofiltration system, in order to purify industrial and road runoff.

113 **2. Materials and methods**

114 **2.1. Preparation of biosorbent**

115 Flax tows were obtained from Depestele group in Normandy. They were defibrated after
116 retting and scutching processes of linen, which consist of separating the fibers from the
117 straws. Hence, the retrieved biosorbent consisted of flax byproduct. Initially, the tows were
118 rinsed with deionized water to remove dirt, and then dried in the oven for 24 h at 60 °C. The
119 fibers were next cut into small pieces of 0,2 - 2 mm. Scanning electron microscope images
120 and FT-IR spectrum were performed with S-3000N scanning electron microscope and Perkin
121 Elmer spectrum BX FT-IR instrument respectively. The spectrum of flax fibers was measured
122 by a Fourier Transform Infrared Spectrometer within the range 600 - 4000 cm^{-1} in order to
123 determine the vibration frequency in the functional groups before and after adsorption.

124 **2.2. Batch experiments**

125 Adsorption experiments in both competitive and non-competitive forms have been conducted
126 at a temperature of 18°C in order to determine adsorption characteristics of flax fibers for
127 zinc, copper and lead ions. The biosorbent was added to 200 mL of the metallic solution
128 initially prepared from zinc nitrates hexahydrated, ($\text{Zn}(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$), copper nitrates trihydrate
129 ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and lead nitrates ($\text{Pb}(\text{NO}_3)_2$), all purchased from Fisher Scientific (France).
130 The pH was adjusted by adding 1M NaOH or 1M HNO_3 solution, purchased from Sigma
131 Aldrich (France).

132 All solutions were prepared with deionized water and all experiments were run in triplicate.

133 **2.2.1. Kinetics trials in monometal and mulimetal solutions**

134 Single and ternary metal ion experiments were conducted in continuously stirred beakers
135 containing 200 mL of zinc, copper and lead ions solutions at a concentration respectively of
136 0.044 mmol.L^{-1} , 0.042 mmol.L^{-1} and 0.042 mmol.L^{-1} under the ternary form, and 0.045
137 mmol.L^{-1} , 0.045 mmol.L^{-1} and 0.046 mmol.L^{-1} under the single form. The pH was adjusted to
138 6.4 and the amount of biosorbent was 400 mg. The monometal and multimetal solutions were
139 shaken for 5, 15, 30 and 60 min and 2, 4, 6, 8 and 10 h using magnetic agitators, then filtered
140 through a 0.45 μm nylon membrane filter. Samples of 40 mL were retrieved from the filtrated
141 solutions and acidified with 1% of nitric acid, then stored in polyethylene bottles at 4 °C for

142 no more than three days. Zinc, copper and lead ions concentrations were determined in the
143 liquid fractions by means of ICP-AES (Inductively coupled plasma, Atomic emission
144 spectrometry) in COBRA laboratory at INSA-Rouen (France). The ICP-AES spectrometer
145 (ICAP6300, ThermoFisher Scientific, USA) was regularly verified and was calibrated at each
146 time of use.

147 The limits of detection were calculated as three times the standard deviation of the blank
148 matrix and corresponded to $19.2 \mu\text{g.L}^{-1}$ ($2.94 \cdot 10^{-4} \text{ mmol.L}^{-1}$) for Zn, $0.9 \mu\text{g.L}^{-1}$ ($1.42 \cdot 10^{-5}$
149 mmol.L^{-1}) for Cu, and $2.1 \mu\text{g.L}^{-1}$ ($1.01 \cdot 10^{-5} \text{ mmol.L}^{-1}$) for Pb. The limits of quantification were
150 calculated as ten times the standard deviation of the blank matrix and corresponded to 64.0
151 $\mu\text{g.L}^{-1}$ ($9.79 \cdot 10^{-4} \text{ mmol.L}^{-1}$) for Zn, $3.0 \mu\text{g.L}^{-1}$ ($4.72 \cdot 10^{-5} \text{ mmol.L}^{-1}$) for Cu, and $7.0 \mu\text{g.L}^{-1}$ (3.38
152 $\cdot 10^{-5} \text{ mmol.L}^{-1}$) for Pb. The amount of each adsorbed metal (mmol.kg^{-1}) per unit of weight of
153 adsorbent, or adsorption capacity Q_t was calculated as the difference between the
154 concentration added at the start, called also initial concentration C_i (mmol.L^{-1}), and the
155 concentration of the remaining metal C_t (mmol.L^{-1}) in the dissolved fraction after any time t
156 of adsorption, all over solid liquid ratio $\frac{m}{V}$ (kg.L^{-1}) where m is the dried mass of adsorbent and
157 V the volume of the adsorbate solution:

$$158 \quad Q_t = \frac{C_i - C_t}{m} V \quad (1)$$

159 The removal (%) of each heavy metal was calculated as the amount adsorbed (mmol.L^{-1}) over
160 the concentration added at the start:

$$161 \quad \text{Removal}(\%) = \frac{C_i - C_t}{C_i} \cdot 100 \quad (2)$$

162 Kinetic trials describe the biosorption behavior as a function of time, but also helps determine
163 an equilibrium time that will be maintained for next adsorption experiments.

164 To better describe the kinetics of zinc, copper and lead biosorption onto flax fibers, the
165 experimental data was applied to pseudo-first and pseudo-second order kinetic models and
166 intraparticle diffusion model.

167 Introduced by Lagergren (1898), pseudo-first order kinetic model is obtained by integrating
168 the following general equation

169
$$\frac{dQ_t}{dt} = k_n(Q_s - Q_t)^n \quad (3)$$

170 for n = 1:
$$\frac{dQ_t}{dt} = k_1(Q_s - Q_t) \quad (4)$$

171 Eq (4) becomes as follows:

172
$$Q_t = Q_s(1 - e^{-k_1 t}) \quad (5)$$

173 Where Q_s is the adsorption capacity at equilibrium and k_1 (min^{-1}) the rate constant of the
174 pseudo-first order model.

175 The pseudo-second order kinetic model is obtained from equation (3) for n = 2 (Ho and
176 McKay, 1999):

177
$$\frac{dQ_t}{dt} = k_2(Q_s - Q_t)^2 \quad (6)$$

178 Integrating for the boundary conditions $Q_t = 0$ at $t = 0$ and Q_t at time t , and rearranging the
179 equation, we obtain:

180
$$Q_t = \frac{k_2 Q_s^2 t}{1 + k_2 Q_s t} \quad (7)$$

181 where k_2 is the rate constant of pseudo-second order biosorption ($\text{kg} \cdot \text{mmol}^{-1} \cdot \text{min}^{-1}$).

182 According to the theory of Weber and Morris, (1963), the intraparticle diffusion model is
183 expressed by:

184
$$Q_t = k_{pi} t^{\frac{1}{2}} + c_i \quad (8)$$

185 where k_{pi} is the intra-particle diffusion rate constant ($\text{mmol} \cdot \text{kg}^{-1} \cdot \text{min}^{-1/2}$) and c_i is a constant
186 related to the thickness of the boundary layer. The higher is the value of c_i , the greater is the
187 effect of the boundary layer. The adsorption process is completely governed by intra-particle
188 diffusion if the plot of Q_t versus $t^{\frac{1}{2}}$ gives a straight line passing through the origin.

189 2.2.2. The study of pH and biosorbent concentration effects

190 In order to examine the influence of pH on flax biosorption, 400 mg of flax fibers has been
 191 maintained in contact with 200 mL of zinc, copper and lead ions solutions, in both
 192 competitive and non-competitive forms under 60 min of magnetic agitation. The
 193 concentration of heavy metals in all experiments was about 0.045 mmol.L⁻¹, and the pH
 194 values tested were 1.8, 3.0, 4.0 and 6.4. pH was not raised upper to 7.0 in order to avoid the
 195 precipitation of the metal ions (Abbar et al., 2017).

196 The study of biosorbent concentration effect was also carried out at equal molar
 197 concentrations of 0.044 mmol.L⁻¹ in both types of metal ion systems, and the tested
 198 concentrations were 0.5 g.L⁻¹, 1 g.L⁻¹, 2 g.L⁻¹ and 5 g.L⁻¹.

199 2.2.3. Biosorption curves at equilibrium

200 For each batch test, a mass of 400 mg of flax fibers was added within 200 mL of zinc, copper
 201 and/or lead ions solutions, in monometal and ternary metal systems. The solutions were
 202 shaken for 60 min. Parameters values of the adsorption experiments are presented in Table 1.

Table 1. Metal concentration added C (mmol.L⁻¹) and pH values of single and ternary metal batch experiments conducted onto flax fibers at a concentration of biosorbent of 2 g.L⁻¹

| Ternary metal solutions | | | | Monometal solutions | | | | | |
|--------------------------|-------|-------|------|--------------------------------|------|--------------------------|------|--------------------------------|------|
| C(mmol.L ⁻¹) | | | | Zn | | Cu | | Pb | |
| Zn | Cu | Pb | pH | C(mmol.L ⁻¹) 1) | pH | C(mmol.L ⁻¹) | pH | C(mmol.L ⁻¹) 1) | pH |
| 1.258 | 1.231 | 1.213 | 6.38 | 1.195 | 6.43 | 1.243 | 6.28 | 1.237 | 6.38 |
| 0.677 | 0.681 | 0.713 | 6.26 | 0.664 | 6.45 | 0.739 | 6.35 | 0.719 | 6.30 |
| 0.364 | 0.371 | 0.381 | 6.35 | 0.359 | 6.35 | 0.378 | 6.45 | 0.375 | 6.27 |
| 0.167 | 0.175 | 0.191 | 6.46 | 0.178 | 6.50 | 0.176 | 6.45 | 0.187 | 6.48 |
| 0.081 | 0.086 | 0.079 | 6.40 | 0.093 | 6.50 | 0.082 | 6.46 | 0.098 | 6.32 |
| 0.044 | 0.042 | 0.042 | 6.45 | 0.045 | 6.45 | 0.045 | 6.40 | 0.046 | 6.47 |

203 Data obtained from adsorption experiments were adjusted to the Langmuir (Eq. (9)) and
 204 Freundlich (Eq. (10)) models.

$$205 \quad Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (9)$$

$$206 \quad Q_e = K_F C_e^{\frac{1}{n}} \quad (10)$$

207 Where Q_m (mmol.kg⁻¹) is the maximum adsorption capacity, K_L (L.mmol⁻¹) the Langmuir
208 constant related to the adsorption energy, and K_F (L^{1/n}.mmol^(1-1/n).kg⁻¹) and n (dimensionless)
209 are the Freundlich coefficients in Eq. (4).

210 The essential characteristic of Langmuir model, expressed in term of dimensionless separation
211 factor R_L was defined as:

$$212 \quad R_L = \frac{1}{1+K_L C_i} \quad (11)$$

213 This parameter may indicate the nature of adsorption to be either unfavorable ($R_L > 1$), linear
214 ($R_L = 1$), favorable $0 < R_L < 1$, or irreversible ($R_L = 0$).

215 We specify that in all the presented figures ahead, results related to zinc, copper and lead are
216 referred to as Zn_tri, Cu_tri and Pb_tri respectively in the multimetal system, and Zn_mono,
217 Cu_mono and Pb_mono in the monometal system.

218 3. Results and discussion

219 3.1. Characterization of biosorbent: SEM and FT-IR analysis

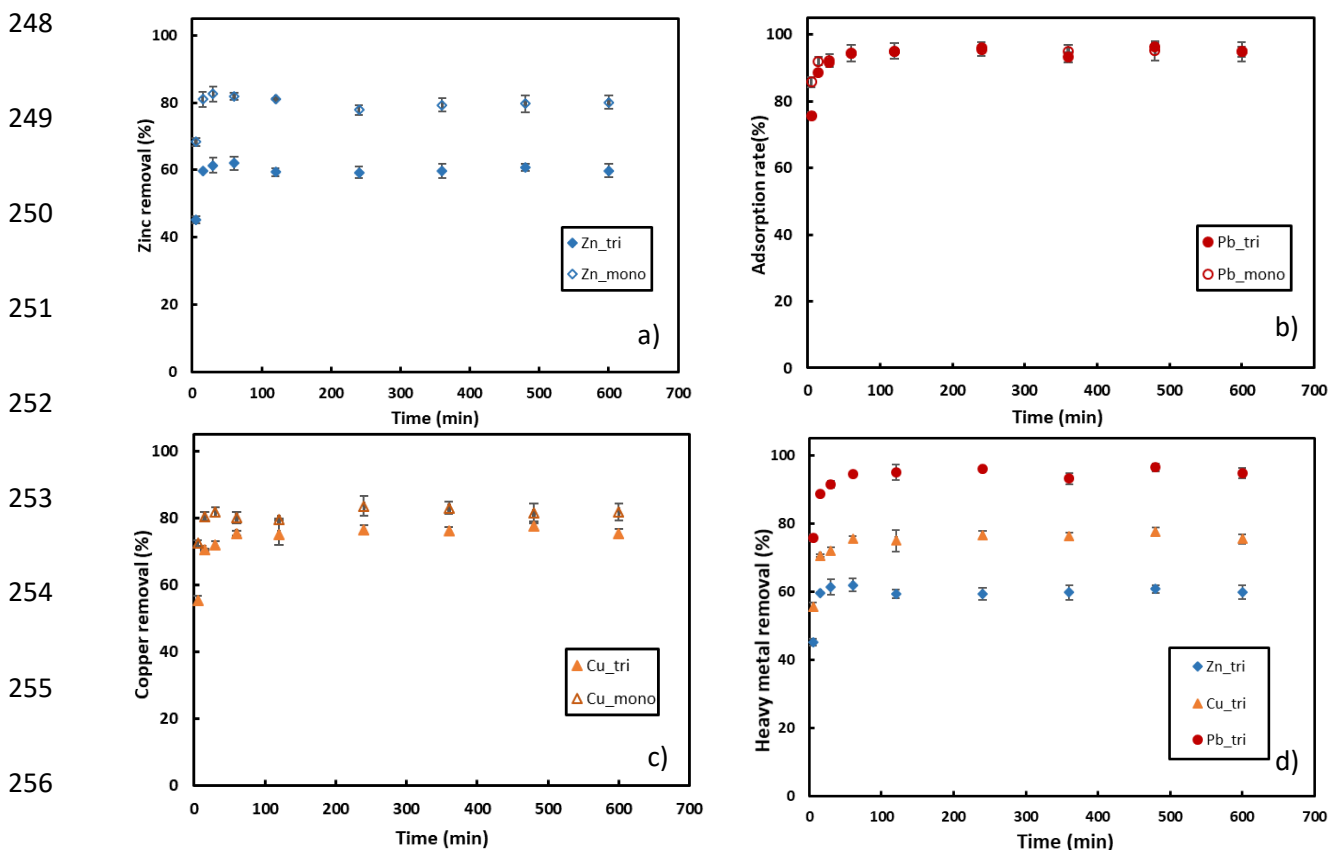
220 SEM images of dried flax fibers were performed, one of these is presented in Fig. S1 (SI)
221 with BSE mode and magnification of 500.

222 The resulted FT-IR spectrum of unloaded flax fibers, presented in the Fig. S2 in SI, indicated
223 the presence of several functional groups for binding metal ions. The band at 3330 suggests
224 the presence of phenolic, alcoholic or acidic hydroxyl groups (O-H), generally present in
225 lignocellulosic materials (López Pasquali and Herrera, 1997). Bands at 1050, 1104 and 1156
226 cm⁻¹ can be related to a C-O stretching of alcohols and carboxylic acids. The peaks at 1638
227 and 1731 can be assigned to the stretching vibrations of C=C, NH-group and C=O (Monier et
228 al., 2010), which indicate the presence of carboxyl groups and amides. The bands at 2916,
229 1314, 1368 and 1426 can be attributed to the C-H group, also found in sisal fibers used for
230 lead and cadmium biosorption (Dos santos et al., 2011), and other biosorbents such as wheat
231 straw (Coelho et al., 2016) and Crambe abyssinica Hochst seeds (Rubio et al., 2013). These
232 functional groups present in lignin, pectin and hemicellulose are reported to be involved in the

233 adsorption mechanism and responsible for metal binding (Lee and Rowell, 2004). The FT-IR
 234 analysis of flax fibers after 60 min adsorption showed no specific difference at the use of
 235 0.044 mmol.L⁻¹ concentration of zinc, copper and lead in the ternary system (Fig. S2), same
 236 bands were observed, which may suggest an abundance of active sites and that only few of
 237 them were engaged in the biosorption process. At the use of higher concentrations, 0.6
 238 mmol.L⁻¹ and 1.2 mmol.L⁻¹, the peaks previously observed at 1638 and 1731 disappeared and
 239 the ones at 1368, 1426 were significantly dissipated (Fig. S2). This finding means that
 240 biosorption process involved chemical reactions between studied metals and existent
 241 functional groups. Also, the transmittance of the curves after adsorption was higher which
 242 confirms less present functional groups on the biosorbent after adsorption.

243 3.2. Biosorption kinetics

244 Each of zinc, copper and lead ions removal by flax fibers was plotted as a function of time
 245 and presented in Fig. 1, for both ternary and single metal ion solutions. Adsorption behavior
 246 was almost the same either in competitive or non-competitive form. Adsorption was very fast
 247 in the first 15 min then attained equilibrium within 60 min.



257 **Fig. 1.** Effect of contact time on Zn, Cu and Pb biosorption in single and ternary metal systems at 0.044 mmol.L⁻¹ metal concentration and biosorbent concentration of 2 g.L⁻¹ and pH of 6.4. 10

258 This result has also been found by other authors, when using waste beer yeast (Han et al.,
259 2006) and seashells powder (Bozbaş and Boz, 2016), and was explained by a quick sites
260 saturation. We also notice that for the three metals, the adsorption is a bit faster in the single
261 metal ion solution (Fig. 1a, b, and c). As regards to the removal rate, it was higher in the
262 single metal form for the three metals. Metal removal was significantly more important in the
263 single ion solution for Zn (62.0% and 81.8% respectively in the ternary and the single metal
264 ion solution), slightly more important for Cu (75.4% and 80.1% respectively in the ternary
265 and single metal ion solutions), and quite the same for lead (94.4%) (Fig. 1a, b, and c). In the
266 ternary metal ion solution (Fig. 1d), the adsorption selectivity was in the order $Pb > Cu > Zn$,
267 which is a similar result as Krishnani et al., (2008), Pehlivan et al., (2009), Coelho et al.,
268 (2016) and Cutillas-Barreiro et al., (2014), found using different biosorbents mentioned in
269 section 1. The difference in metals adsorption percentages as well as adsorption capacities at
270 equilibrium between both types of solutions (Table S1 in SI) highlighted the competition
271 taking place between metals when they are added simultaneously especially for zinc and
272 copper. Besides, lead was still the most favorable removed heavy metal in both forms.

273 To describe zinc, copper and lead biosorption onto flax fibers in single and ternary metal ion
274 solutions, the experimental data were applied to pseudo first order (Figure S3 in SI) and
275 pseudo-second order (Figure S4 in SI) models. Adsorption capacities obtained from the
276 pseudo-first order and pseudo-second order models were very close to the ones observed
277 experimentally (Table S2 in SI). Lead data showed a better fit with the pseudo-second order
278 with high correlation coefficients of 0.97 and 0.98 respectively in the monometal and ternary
279 systems (Table S2 in SI), which assumes a chemisorption reaction due to valency forces
280 through sharing or exchange of electrons between flax fibers and divalent metals, and thus a
281 strong chemical bonding with functional groups. This model has been successfully applied to
282 metal ions adsorption from aqueous solutions onto various materials, mainly vegetative fibers,
283 activated carbons, bacteria and agricultural waste (Ho, 2006). Zinc data, on the contrary,
284 exhibited a better adjustment with the pseudo-first order model in both systems (Table S2 in
285 SI), which may indicate that zinc adsorption was controlled by weak interactions such as van

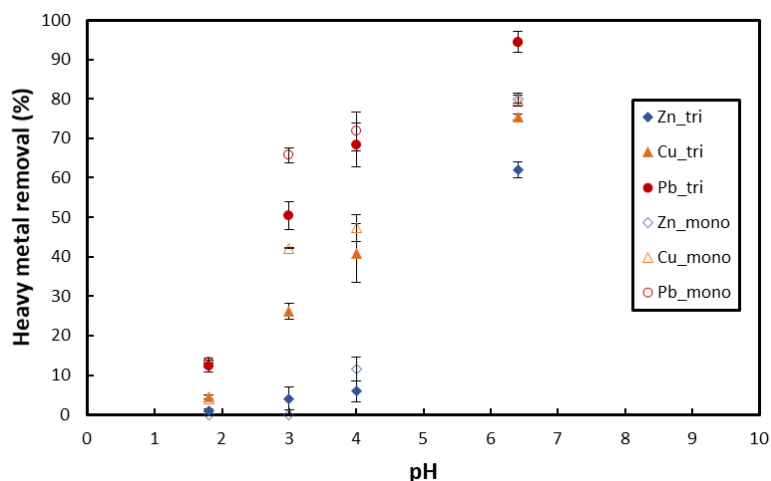
286 der Waals forces between flax and zinc ions, generated by the surface charge density of the
287 adsorbent, explaining thus the weak attachment of zinc to flax fibers compared to lead and
288 copper. Similarly to lead, copper data showed a better fit with the pseudo-second order model
289 in the non-competitive system with a correlation coefficient of 0.98, while in the non-
290 competitive system no specific difference could be observed between both models, which
291 indicated that both physisorption and chemisorption may be involved in the adsorption
292 mechanism when the three metals are simultaneously added.

293 In order to analyze the rate limiting step, the intra-particle diffusion model was also used. The
294 data exhibited multilinear plots in this study for all the investigated metals (Fig. S5);
295 suggesting that more than one step influenced the process of biosorption and that other
296 mechanisms may be involved besides intra-particle diffusion (Duan et al., 2016). The values
297 of k_{pi} and c_i for all stages are listed in Table S3 in SI. It is reported that the first stage
298 describes an instantaneous adsorption where the adsorbate migrates from the aqueous solution
299 towards the external surface of the solid, representing a film diffusion. The second step
300 concerns a gradual adsorption, where adsorbate migrates within the pores of adsorbent. The
301 third and final equilibrium stage, also revealed very rapid, cannot be considered the rate
302 controlling step. Hence, the overall rate is either governed by film diffusion or intra-particle
303 diffusion or both. In addition, the obtained linear lines did not pass through the origin, this
304 deviation can be related to the difference in the mass transfer rate in the initial and final stages
305 of adsorption (Tan et al., 2009).

306 **3.3. Effect of pH**

307 Solution pH is a very essential parameter in adsorption process. It has been very well
308 documented in literature. The effect of pH variation on the removal of metal ions by flax
309 fibers is shown in Fig. 2. Metal biosorption efficiency was very dependent on pH, it decreased
310 along with pH decreasing for the three metals Zn, Cu and Pb. Similarly to Antunes et al.,
311 (2003) and Dang et al., (2009) who investigated brown seaweed and wheat straw biosorption
312 respectively, the results indicated that at lower pH, there might be more competition for the

313 active sites between H^+ and metal ions, resulting in a very low biosorption of metals. This
 314 may also be explained by electrostatic repulsion forces occurring between the surface and the
 315 studied cations once active sites are occupied by the protons H^+ . In addition, it has been
 316 reported in literature that functional groups which act like active sites for metal binding, may
 317 react differently depending on pH. The same sorption selectivity of $Pb > Cu > Zn$, as in
 318 section 3.2, was observed at all pH values tested. Regarding competitive and non-competitive
 319 experiments for the three ions, it was apparent that each metal removal was higher in the non-
 320 competitive form, at all pH values. Overall, biosorption efficiency greatly depended on
 321 solution pH and reached its optimal at 6.4 for the three metals in both mono and multimetal
 322 systems.



331 **Fig. 2.** Effect of pH on Zn, Cu and Pb biosorption onto flax fibers
 332 in single and ternary metal systems at $0.044 \text{ mmol.L}^{-1}$ metal
 333 concentration and biosorbent concentration of 2 g.L^{-1} .

334 3.4- Effect of the amount of biosorbent

335 The effect of biosorbent concentration on zinc, copper and lead ions adsorption was studied in
 336 both single and multimetal forms at the concentration of $0.044 \text{ mmol.L}^{-1}$ and pH around 6.4.
 337 The removal of the three metals was found to increase rapidly with the increase in biosorbent
 338 concentration in all experiments (Fig. 3), showing higher availability of active sites. In
 339 multimetal solution, lead removal was observed to be the highest and zinc removal the least at

340 all biosorbent concentrations. Thus the sequence was still $Pb > Cu > Zn$ as previously shown
341 in sections 3.2 and 3.3. However, zinc ion turned out to be well adsorbed when high amount
342 of biosorbent was utilized, mainly at biosorbent concentration of 5 g.L^{-1} , where no difference
343 was noticed between copper and zinc removal (Fig. 3a), owing to the abundance of
344 exchangeable sites, as similarly found in previous studies as Han et al., (2006), El-Ashtoukhy
345 et al., (2008) and Abbar et al., (2017). Regarding the competition effect, it was very visible
346 for zinc removal in the multimetal solution (Fig. 3b). In competitive experiments, Zn removal
347 increased from 4.0% to 62.0% while in non-competitive experiments it increased from 30.1%
348 to 81.8%, when biosorbent concentration increased from 0.25 g.L^{-1} to 2 g.L^{-1} . The difference
349 of Zn removal between mono and multimetal solutions was though insignificant at the use of
350 5 g.L^{-1} of flax fibers. A similar behavior was shown in copper and lead removal as functions
351 of biosorbent concentration (Fig. 3c, Fig. 3d), but only from 0.25 g.L^{-1} up to 1 g.L^{-1} . Beyond
352 the concentration of 1 g.L^{-1} , a slight decrease of copper and lead removal was shown in the
353 single metal ion solution, which can be explained by particle interaction such as aggregation
354 of biosorbent that may lead to a decrease in total surface area (Shukla et al., 2002; Semerjian,
355 2018). Therefore, the biosorbent concentration of 2 g.L^{-1} was maintained in all subsequent
356 experiments.

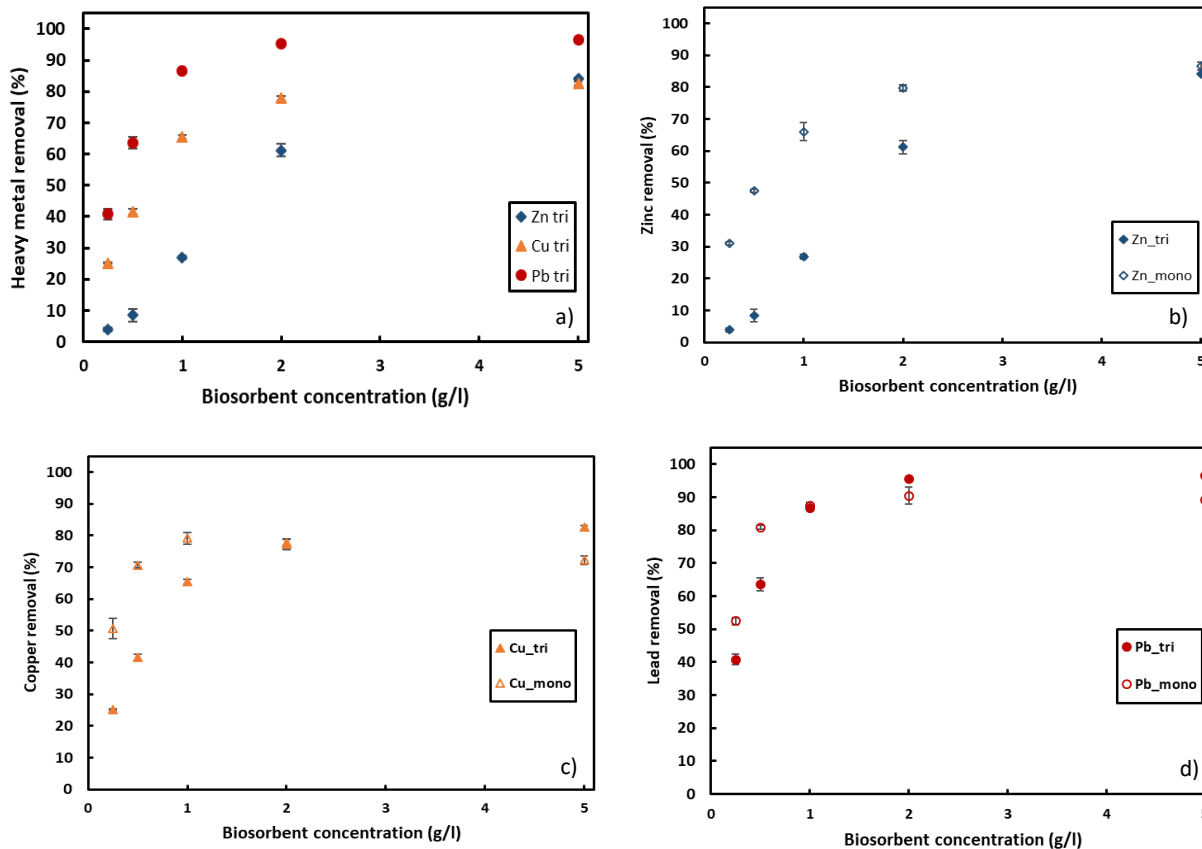


Fig. 3. a) Zn, Cu, and Pb removal in multimetal solution for different biosorbent concentrations (0.25, 0.5, 1, 2, 5 g.L⁻¹). b), c), and d) Comparison of, respectively Zn, Cu, and Pb removal in competitive and non-competitive experiments for the same biosorbent concentrations at 0.044 mmol.L⁻¹ metal concentration and pH of 6.4.

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359 3.5. Effect of initial concentration

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361 To study the effect of initial concentration of heavy metals, metal ion solutions of zinc,
 362 copper and lead were prepared in both single and multimetal forms, with initial concentrations
 363 ranging from 0.04 mmol.L⁻¹ to 1.2 mmol.L⁻¹ (See Table 1). For each adsorption experiment,
 364 400 mg of flax fibers was added to 200 mL of metal ion solution. Figure 4a and Figure 4b
 365 show heavy metal removal and adsorption capacity, respectively, as functions of added
 366 concentrations for the three heavy metals studied, in both types of systems. When initial
 367 concentration increased, heavy metal removal generally decreased for the three metals in both
 368 single and ternary metal solutions (Fig. 4a) while adsorption capacity increased for all metals
 369 except for Zn in the ternary solution (Fig. 4b) where it decreased.

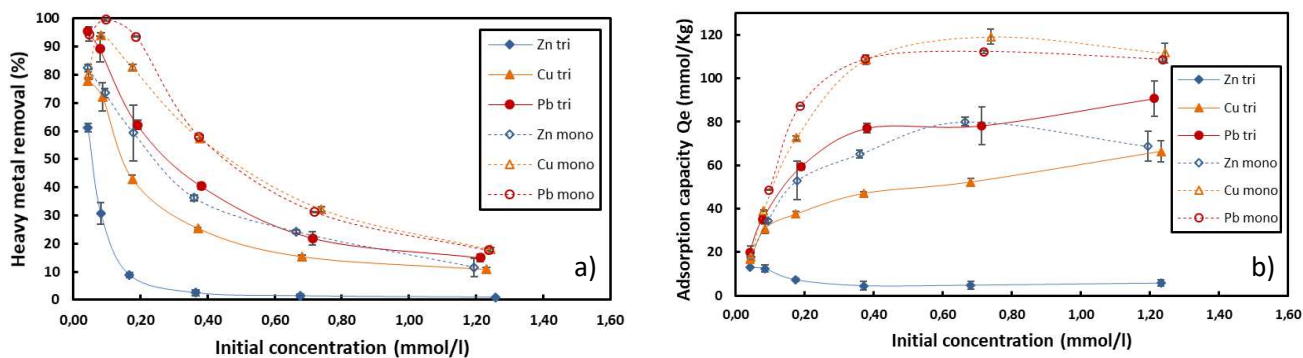
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Fig. 4. a) The removal (%) and b) adsorption capacity (mmol.kg^{-1}) of Zn, Cu and Pb by flax fibers for different initial concentrations (0.04, 0.08, 0.16, 0.36, 0.67 and 1.2 mmol.L^{-1}) in competitive and non-competitive experiments, at biosorbent concentration of 2 g.L^{-1} and pH of 6.4.

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378 In non-competitive experiments, the sorption sequence was in the order $\text{Pb} \approx \text{Cu} > \text{Zn}$ for
379 trials with the lowest molar concentrations (0.04, 0.08, 0.16 and 0.36 mmol.L^{-1}) with optimal
380 adsorption capacity values of 108.76, 108.5 and 65.08 mmol.kg^{-1} respectively (Fig. 4b),
381 corresponding to 58.0%, 57.5% and 36.2% of metal removal (Fig. 4a), obtained at the initial
382 concentration of 0.36 mmol.l^{-1} . Whereas for the highest concentrations (0.67 and 1.2 mmol.L^{-1})
383 1), the selectivity sequence changed to $\text{Cu} \approx \text{Pb} > \text{Zn}$ with maximum adsorption capacity
384 values of 119.2, 112.3 and 80.1 mmol.kg^{-1} respectively, corresponding to 32.3%, 31.3% and
385 24.1% of metal removal, obtained at the initial concentration of 0.67 mmol.L^{-1} . A slight
386 decrease of sorption capacity was shown at 1.2 mmol.L^{-1} for the three ions.

387 On the other hand, the competitive experiments showed the selectivity sequence $\text{Pb} > \text{Cu} \gg$
388 Zn at all times, and also a considerable favorable retention for lead and copper comparing
389 with zinc (Fig. 4a). Lead sorption capacities increased from 19.9 to 90.7 mmol.kg^{-1} , when the
390 initial concentration increased from 0.04 to 1.2 mmol.L^{-1} , although its removal percentage
391 decreased from 94.4% to 15.0%. Similarly, copper sorption capacities increased from 16.1 to
392 66.4 mmol.kg^{-1} with the increase of initial concentration, while its removal percentage
393 decreased from 75.4% to 10.8%. For zinc, the adsorption behavior was different, sorption
394 capacities were very low decreasing from 13.0 to 2.7 mmol.kg^{-1} , and its removal percentage

395 also decreased from 62.0% to 0.9%, when initial concentrations increased from 0.04 to 1.2
396 mmol.L⁻¹. Zinc was thus the less adsorbed ion in all experiments. Comparing competitive and
397 non-competitive experiments, zinc was also the most affected ion by the presence of other
398 ions, its sorption was very considerably higher in the non-competitive trials (from 18.23 to
399 80.1 mmol.kg⁻¹) than in the competitive trials (from 13.0 to 2.7 mmol.kg⁻¹). For copper, the
400 competition effect was also visible. Its sorption was higher in the non-competitive (from 17.9
401 to 119.2 mmol.kg⁻¹) than in the competitive experiments (from 16.1 to 66.4 mmol.kg⁻¹).
402 Concerning lead, the impact of competition was the less important but still quite visible
403 between the non-competitive (21.9 to 112.3 mmol.kg⁻¹) and competitive trials (19.9 to 90.7
404 mmol.kg⁻¹).

405 Therefore, higher affinity with active sites was mainly observed for lead ions, as previously
406 shown by [Al-Asheh and Duvnjak, \(1998\)](#) and [Park et al., \(2016\)](#) at the use of pine bark and
407 sesame straw biochar respectively, which allows faster interaction with functional groups. As
408 evidenced in FT-IR analysis in section 3.1, flax fibers contain negatively charged functional
409 groups that are able to complex metals. The studies developed by [Guo et al., \(2008\)](#) and [Lee
410 and Rowell, \(2004\)](#) have demonstrated that the carboxylic and phenolic groups present in
411 lignin play an important role in adsorption processes. They can induce complexes formation
412 with heavy metals through the coordination bonds. In addition, and according to several
413 researches, it has been suggested that ion exchange is one of the most responsible
414 mechanisms in biosorption process. [Chen et al. \(2010\)](#) demonstrated that biosorption process
415 using *Cinnamomum camphora* leaves powder was dominated by ion-exchange mechanism
416 based on activation energies of the reactions. [Božić et al. \(2009\)](#) showed that heavy metals
417 and protons were substituted by the alkali-earth metals contained in the molecular structure of
418 sawdust of deciduous trees, by investigating the release of Ca²⁺, Mg²⁺, Na⁺, K⁺ and H⁺ from
419 the adsorbent.

420 It is also worthwhile to mention that the sorption capacities for the three metals in both
421 systems followed the same order as their electronegativities Pb (2.33) > Cu (1.90) > Zn (1.65)

422 (McBride, 1994), which is one of the justifications put forward to explain this selectivity
423 order, also found in studies using chitosan and egg shell (Shaheen et al., 2013), pine bark
424 (Cutillas-Barreiro et al., 2014), and sesame straw biochar (Park et al., 2016). This is in
425 particular attributed to the fact that metal ions with higher electronegativities exhibit higher
426 attractions for electrons (Deng et al., 2019). Another explanation is that the hydrated radius of
427 lead (4.01 Å) is smaller than that of copper (4.19 Å) and zinc (4.30 Å), which enables lead to
428 form stronger bonds with most functional groups (Park et al., 2016).

429 Regarding the ionic interaction effect between monometal and multimetal systems, one of the
430 methods consists in evaluating the ratio R of the ion sorption capacity in the multimetal
431 system Q_{e-mult} to the ion sorption capacity in the monometal system Q_{e-mono} (Mohan and
432 Chander, 2001), in a way that for $R > 1$, the ion sorption is promoted in the multimetal
433 system, and for $R < 1$ the ion sorption gets overcome by the presence of other ions, and for R
434 $= 1$ no interaction occurs between ions. In this study, a destructive effect was mainly shown
435 for zinc ions in the ternary metal system as zinc removal got promptly decreasing with the
436 increase of metal initial concentrations. Its sorption capacities were also the lowest and quite
437 constant, unlike zinc behavior in the single metal form, where sorption capacity joined the
438 same behavior as copper and lead sorption capacities. In the ternary system, the ratios $R(Zn)$
439 varied between 0.14 and 0.06 once beyond the initial concentration of 0.08 mmol.L⁻¹, while
440 for copper it was ranged between 0.52 and 0.43, and for lead between 0.84 and 0.68. Other
441 works have reported this destructive effect in multimetal aqueous solutions, such as the work
442 developed by Reynel-Avila et al., (2016), which used flamboyant and bush mango biomasses
443 in binary systems of Pb^{2+} - Ni^{2+} and Pb^{2+} - Cd^{2+} . Monometal experiments showed that
444 cadmium and nickel were considerably affected by the presence of lead whose adsorption
445 capacities in single and binary systems were almost identical ($R(Pb) \approx 1$). A similar behavior
446 was observed in a ternary metal system of Pb^{2+} - Cu^{2+} - Cd^{2+} , using wheat straw as biosorbent
447 (Coelho et al., 2016). Cadmium ions were efficiently removed in the single metal ion
448 experiments (metal removal ranging from 90.6% to 81.5%) but were overcome by the

449 presence of lead and copper especially at the highest concentration of 6.0 mmol.L⁻¹ where
450 only 23.4% of cadmium was removed.

451 3.6. Biosorption curves in competitive and non-competitive experiments

452 Adsorption curves are essential to describe adsorption characteristics at a constant
453 temperature. For that purpose, several adsorption models have been established in literature,
454 the most common used are the Langmuir and Freundlich models. The first assumes a
455 homogeneous surface and that all active sites have equal energies, while the second describes
456 a heterogeneous surface and shows no limit saturation. To study biosorption curves of the
457 three ions by flax fibers, experimental adsorption capacity at equilibrium Q_e was plotted
458 against equilibrium concentration C_e and compared with the Langmuir and Freundlich models
459 for both monometal and multimetal solutions (Fig. 5), except for zinc in the ternary system as
460 zinc adsorption capacity was significantly low and promptly decreased when added
461 concentration increased. Hence, zinc adsorption curve in the ternary system couldn't fit the
462 models and obtained values of K_L and n were meaningless, which confirmed a very difficult
463 adsorption of zinc on active sites. On the other hand, and based on the calculated values
464 (Table 2), it can be inferred that the Langmuir model provides a slightly better fit for flax
465 fibers suggesting thus a monolayer adsorption, besides for copper in the ternary system where
466 the Freundlich showed a better adjustment, indicating a probable multilayer adsorption of
467 copper when other ions are co-existent.

468 The monolayer adsorption capacities Q_{max} (mmol.kg⁻¹) of flax fibers determined using the
469 Langmuir model followed the order Pb (81.61) > Cu (57.48) > Zn (8.03) in the competitive
470 experiments, and changed to Cu (121.57) > Pb (111.68) > Zn (76.40) in the non-competitive
471 experiments. All adsorption capacities were lower in the multimetal solution, as shown in
472 section 3.5. The ratio $\frac{Q_{max\ mono}}{Q_{max\ multi}}$ of each metal where $Q_{max\ mono}$ and $Q_{max\ multi}$ are the
473 maximum sorption capacities in the mono and multimetal systems respectively, indicated that
474 zinc adsorption was 10 times lower in the competitive experiments, while copper and lead

475 adsorption were only 2 and 1.4 times lower respectively. This clearly showed that zinc ions
476 were very affected by competition and easily exchanged by other metals. In addition, the
477 Langmuir constant K_L , related to the affinity of the binding sites was higher in the non-
478 competitive experiments for copper and lead (Table 2), showing a stronger affinity with the
479 adsorbent active sites. Furthermore, the parameter R_L was represented in Fig. S6 in SI for all
480 conducted experiments except for zinc in the multimetal solution. Fig. S6 (SI) indicated a
481 very favorable adsorption for the studied metals in the single form where $0.02 < R_L(\text{Zn}) <$
482 0.41 , $0.01 < R_L(\text{Cu}) < 0.32$ and $0.003 < R_L(\text{Pb}) < 0.09$. In the multimetal system, R_L got
483 higher but was still indicating a good adsorption for copper and lead as $0.02 < R_L(\text{Cu}) < 0.39$
484 and $0.01 < R_L(\text{Pb}) < 0.22$. The competition effect was thus very important for zinc, and less
485 visible for copper and lead. Similarly, in a study conducted by Mahamadi and Nharringo,
486 (2010) on Eichhornia crassipes, it has been shown that cadmium and zinc ions were overcome
487 in the presence of lead. Park et al. (2016) have also found that cadmium and zinc adsorption
488 were respectively 17.2 and 4.85 times lower in the multimetal system of (Cd, Zn, Cu, Cr, Pb)
489 using sesame straw biochar. Liu and Lian (2019) have reported as well that the adsorption of
490 cadmium and nickel ions on biogenic vaterite were reduced by 82.42% and 65.09%
491 respectively in the presence of copper.

492 Compared to other lignocellulosic materials in the scientific literature, flax fibers adsorption
493 capacity was very competitive (see Table S4 in SI). The maximum adsorption capacity of zinc
494 using flax fibers ($76.40 \text{ mmol.kg}^{-1}$) was more important than that of jute fibers (54.30
495 mmol.kg^{-1}) and hemp fibers ($35.00 \text{ mmol.kg}^{-1}$) (Shukla et al., 2005; Pejic et al., 2009). Also,
496 the maximum adsorption capacity of copper ($121.57 \text{ mmol.kg}^{-1}$) was higher than those
497 reported for bornean oil palm shell ($27.63 \text{ mmol.kg}^{-1}$), barley straw ($73.01 \text{ mmol.kg}^{-1}$), jute
498 fibers ($66.56 \text{ mmol.kg}^{-1}$) and sawdust ($28.16 \text{ mmol.kg}^{-1}$) (Chong et al., 2013; Pehlivan et al.,
499 2009a; Shukla et al., 2005; Yu et al., 2001). For lead, flax fibers biosorption (111.68
500 mmol.kg^{-1}) was very high comparing with sisal fibers ($6.47 \text{ mmol.kg}^{-1}$), sawdust (15.40
501 mmol.kg^{-1}), bornean oil palm shell ($16.36 \text{ mmol.kg}^{-1}$), chitosan ($25.62 \text{ mmol.kg}^{-1}$), rice husk

502 (40.11 mmol.kg⁻¹), almond shell (38.99 mmol.kg⁻¹), and hemp fibers (74.00 mmol.kg⁻¹) (Dos
 503 Santos et al., 2011; Yu et al., 2001; Chong et al., 2013; Zulkali et al., 2006; Pehlivan et al.,
 504 2009b; Pejic et al., 2009), very close to that of barley straw (111.96 mmol.kg⁻¹), and slightly
 505 lower than those of hazelnut shell (136.00 mmol.kg⁻¹) and cashew nut shell (138.27 mmol.kg⁻¹)
 506 ¹) (Pehlivan et al., 2009b; Coelho et al., 2014). Based on these results, it has been shown that
 507 flax fibers had a very good adsorption capacity and therefore it is a very efficient material for
 508 water treatment and heavy metals removal.

509 Using the Freundlich model, the Freundlich constant K_F (L^{1/n}.mmol^(1-1/n).kg⁻¹) related to the
 510 adsorption capacity was in the order Pb (92.66) > Cu (63.28) > Zn (8.03) in multimetal
 511 solution and Cu (128.52) > Pb (120.65) > Zn (80.10) in monometal solution (Table 2).

512 Comparing the ratio $\frac{K_{F\text{ mono}}}{K_{F\text{ multi}}}$ for each metal, it followed the order Zn (9.98) > Cu (2.02) > Pb
 513 (1.30) indicating that zinc was very affected by competition while lead and copper were not
 514 very influenced, similarly as demonstrated above with the Langmuir model. Furthermore, the
 515 Freundlich constant n ranging between 2 and 10 (Table 2), attested that the biosorption was
 516 very favorable for all the ions, except again for zinc in the ternary metal system where n value
 517 was meaningless. Therefore, both adsorption models showed the same behavior of ions, even
 518 though a better adjustment was generally shown with the Langmuir rather than the Freundlich
 519 model.

Table 2. Langmuir and Freundlich parameters values⁵²⁰

| Heavy Metal | Adsorption system | Langmuir | | | Freundlich | | |
|-------------|--|--|--|----------------|--|-------------|----------------|
| | | Q _{max} (mmol.kg ⁻¹) | K _L (L.mmol ⁻¹) | R ² | K _F (L ^{1/n} .mmol ^(1-1/n) .kg ⁻¹) | n | R ² |
| Pb | Pb ²⁺ | 111.68 ± 0.3 | 224.10 ± 1.0 | 0.958 | 120.65 ± 0.3 | 7.45 ± 0.03 | 0.737 |
| | Zn ²⁺ , Cu ²⁺ , Pb ²⁺ | 81.61 ± 3.6 | 84.55 ± 8.8 | 0.984 | 92.66 ± 4.4 | 5.03 ± 0.3 | 0.960 |
| Cu | Cu ²⁺ | 121.57 ± 0.1 | 40.00 ± 0.2 | 0.964 | 128.52 ± 3.1 | 4.48 ± 0.04 | 0.789 |
| | Zn ²⁺ , Cu ²⁺ , Pb ²⁺ | 57.48 ± 1.8 | 35.61 ± 4.4 | 0.854 | 63.28 ± 2.0 | 4.25 ± 0.2 | 0.963 |
| Zn | Zn ²⁺ | 76.40 ± 6.0 | 32.36 ± 2.5 | 0.963 | 80.10 ± 5.4 | 4.78 ± 0.7 | 0.824 |
| | Zn ²⁺ , Cu ²⁺ , Pb ²⁺ | 8.03 ± 0.7 | - | - | 8.03 ± 0.7 | - | - |

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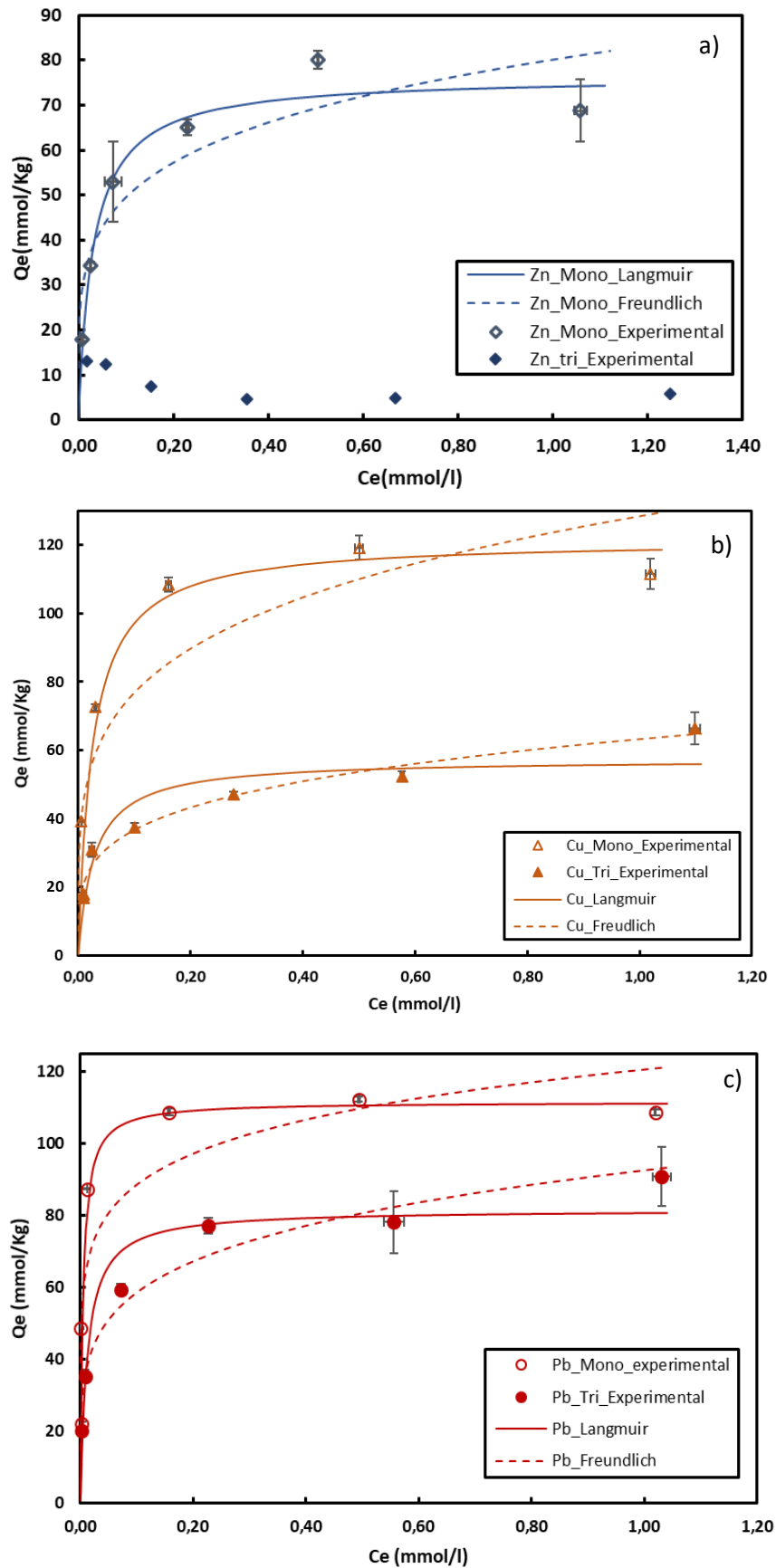


Fig. 5. Experimental data and calculated values from the Langmuir and Freundlich models for a) zinc, b) copper and c) lead in both monometal and ternary metal solutions.

550 Conclusion

551 Flax fibers were used to remove heavy metals from aqueous solutions. A series of batch
552 experiments were performed adding lead, copper and zinc ions, either simultaneously or
553 individually. The aim of the study was to evaluate and compare adsorption behavior of these
554 metals in two conditions. The obtained results under competitive conditions were different
555 from those obtained in non-competitive conditions. The adsorption efficiency of flax fibers
556 related to each heavy metal was higher in the single metal ion solution, and the order of the
557 adsorption selectivity was $Pb \approx Cu > Zn$ and changed to $Pb > Cu \gg Zn$ in the multimetal
558 solution. Lead was the most retained metal in multimetal solution followed by copper, while
559 zinc was very considerably affected by the presence of other ions. Electronegativity, hydrated
560 radius, and ions interactions with functional groups were the main justifications of this
561 finding, in addition to ion exchange which was reported to be the most dominant mechanism
562 in biosorption process. On the other hand, the effectiveness of the ions removal was found to
563 be very dependent on the aqueous solution pH, contact time, initial concentration of metals
564 and biosorbent concentration.

565 Based on the overall results, flax fibers demonstrated a high biosorption capacity of heavy
566 metals in both forms of solutions, except for zinc in the multimetal solution. It is thus an
567 available and efficient low-cost material for water treatment, whose recycling should be
568 promoted. Hence, in order to regenerate flax fibers and judge the reversibility of biosorption,
569 further studies will be conducted to evaluate ions desorption and investigate conditions of
570 ions release.

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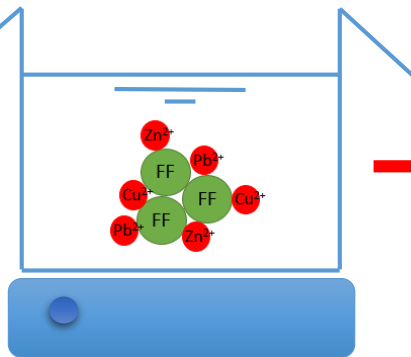
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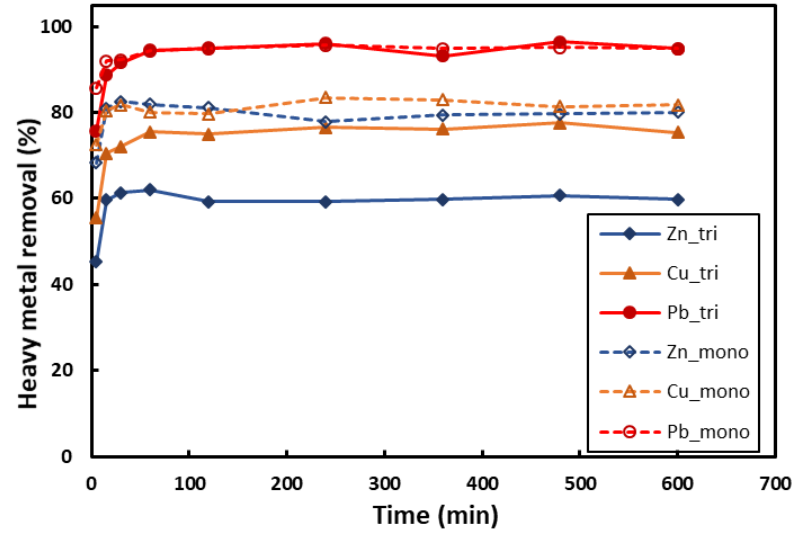
Heavy metals
(Zn^{2+} , Cu^{2+} , Pb^{2+})
+
Flax fibers (FF)



Biosorption under magnetic agitation, using mono and ternary metal systems



Samples analysis by ICP-AES machine



Biosorption performance