3

4   **REUSE POTENTIAL OF RESIDUES OF ARTICHOKE (*Cynara scolymus* L.)**

5   **FROM INDUSTRIAL CANNING PROCESSING AS SORBENT OF HEAVY**

6   **METALS IN MULTIMETALLIC EFFLUENTS**

7   María I. Saavedra, Marta Doval Miñarro, José M. Angosto, José A. Fernández-López*

8   *Technical University of Cartagena (UPCT), Department of Chemical and Environmental*

9   *Engineering, Paseo Alfonso XIII, 52; E-30203 Cartagena (Murcia) SPAIN.*

10   *Corresponding author: telephone: 0034 968325549; email: josea.fernandez@upct.es

11   **Abstract**

12   The suitability of reusing artichoke agrowaste biomass from industrial canning processing as a

13   low-cost and ecofriendly sorbent for the bioremoval of Pb(II), Cd(II) and Cu(II) in multi-metallic

14   aqueous solutions is reported. Understanding the dynamic of heavy metals in the sorption

15   process is critical to assess the removal of these contaminants in aquatic systems. The Taguchi

16   approach was used to design a series of experiments to find the optimum conditions for

17   maximum total sorption capacity, analysing the signal-to-noise (S/N) ratio to assess the

18   experimental responses. Ranks of five controllable factors (the initial concentrations of Pb(II),

19   Cd(II) and Cu(II), sorbent dosage and pH), at three levels each one, in a L27 array were

20   conducted in batch sorption tests. The highest sorption capacity (241 $\mu mol \cdot g^{-1}$) was shown

21   with initial concentrations of 315 $\mu mol \cdot L^{-1}$ Cu(II), 445 $\mu mol \cdot L^{-1}$ Cd(II) and 241 $\mu mol \cdot L^{-1}$ Pb(II), pH

22   5 and 0.5 $g \cdot L^{-1}$ of sorbent dosage. The metal ion predominantly adsorbed was Pb(II).

23   Adsorption kinetics followed a pseudo-second order model. The study of the shares of each

24   metal ion on the total sorption capacity revealed that Cd(II) is actually prone to be adsorbed

25   but the presence of Pb(II) and Cu(II) hinders its adsorption. The valorization of artichoke

26   agrowaste biomass as metal sorbent is considered a way to assist in the promotion of a

27   circular economy.

28   *Keywords*: artichoke, *Cynara scolymus*, agrowaste biomass, competitive adsorption, heavy

29   metals

1. Introduction

Artichoke (*Cynara scolymus* L.) is a vegetable belonging to the Asteraceae family, widely consumed in the Mediterranean countries. The edible part of the plant, is the immature inflorescence called head, which is protected by fleshy leaves known as bracts (Pandino et al., 2013). The artichoke canning industry generates a solid waste consisting mainly of the stems and external bracts of the flowers, which are about 70-80% of the total artichoke flower (Machado et al., 2015), which is not suitable for human consumption. This agrifood residue, a plant biomass of lignocellulosic nature, has been investigated for possible use as source of bioactive compounds (Salem et al., 2015; Zuorro et al., 2016), although mostly it is discarded as green manure or in livestock feed (Meneses et al., 2007). According to the zero-waste programme for Europe of the European Commission (European Commission, 2014), recycling and resource reuse as tools for efficient circular economy is a relevant topic, and particular attention must be paid to providing sustainable strategies for valorization of agrifood residues as a way to assist in the promotion of a circular economy (Peralbo-Molina and Luque de Castro, 2013).

Heavy metals released into the environment, directly from natural sources or indirectly from anthropogenic activities (industrial processes, energy generation plants, improper waste management, etc.) can cause severe deterioration of ecosystems and significant toxic effects on living beings (Oliveira et al., 2011). Even at low concentrations, heavy metals are likely to reach and accumulate in the human body through the food chain, causing a number of severe health diseases (Siswoyo et al., 2014; Daneshfozoun et al., 2017). Therefore, disposal of these contaminants from industrial effluents is of great concern from the perspective of environmental pollution control.

Bioadsorptive removal is accepted as a suitable alternative technology for the treatment of metal-bearing wastewaters (Arief et al., 2008; Wang and Chen, 2009). This is basically a mass

55 transfer process by which metal ions are transferred from the liquid phase to the surface of a

56 solid (sorbent), and become bound by chemical and/or physical interactions (Zhao et al.,

57 2016). It is an eco-friendly process (Rosique et al., 2016) with several advantages over

58 traditional methods for organic and inorganic pollutant removal in wastewater streams such as

59 its simplicity, feasibility, low cost, fast sorption kinetics and reversibility (Petrella et al., 2018).

60 As regards the ability to retain metal ions, the efficiency of a sorbent is related both to their

61 capacity to bind metals, number of metal-binding sites present (binding-site density), and to

62 the bond strength. The sorbent's capacity to bind metals is also dependent on the amount of

63 metal-accessible surface (specific surface area). Plant biomass-based sorbents, particularly

64 agrifood waste, have been extensively investigated as alternative to conventional sorbents,

65 due to their renewable nature, large production and great local availability (Bhatnagar et al.,

66 2015; Escudero-Oñate et al., 2017), being amply proven their potential to remove wastewater

67 pollutants in a cost-effective way (Zhou and Haynes, 2010). Technical applicability and cost-

68 effectiveness are the key factors that play the most important roles in the selection of the

69 most suitable sorbent to bioremove heavy metals from aqueous effluents. Industrial effluents

70 far for being constituted by single-metal species, are complex solutions containing several

71 metals simultaneously. Hence, sorption studies of formerly lesser-known multimetallic systems

72 are quite desirable since a variety of metal ions will compete for the binding sites of the

73 sorbent surface. Depending on the wastewater composition, these competing effects may

74 significantly affect the efficiency of the removal process.

75 In order to promote the circular approach, the focus of this work was to assess the potentiality

76 of lignocellulosic agrowaste biomass from artichoke as a natural cost-effective and sustainable

77 sorbent for the competitive removal of Cd(II), Cu(II) and Pb(II) in multimetallic effluents.

78 Despite the large number of natural residues from the agro-food industry tested as

79 biosorbents to remove heavy metals from wastewater (Lesmana et al., 2009), there are no

80 publications on the use of residues of artichoke industrial processing as metal ion sorbent,

81 being our research group the only one to explore this potential applicability.

82 **2. Materials and methods**

83 *2.1. Plant biomass preparation and characterization*

84 Agrowaste biomass from artichoke (*Cynara scolymus L.*) grown in the Region of Murcia (Spain)

85 was used as sorbent. The raw materials, mainly composed of the external bracts and stems,

86 were repeatedly washed with distilled water to remove dirt particles, cut into small pieces and

87 then were dried at 70 ^{0}C for 24 hours. The dry biomass was milled and sieved using an 18-

88 mesh sieve (1 mm) to obtain artichoke by-products powder. This mechanical comminution is

89 applied in order to reduce particle size, crystallinity and the polymerization degree of present

90 polysaccharides of the lignocellulosic biomass (Kumar et al., 2017).

91 Structural and thermal characterization of agrowaste biomass was performed through

92 scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy,

93 thermogravimetric analysis (TGA) and X-ray powder diffraction (XRD). SEM images were taken

94 with a Hitachi S-3500N model to investigate the surface morphology of the sorbent. FTIR

95 measurements in the region 4000–400 cm^{-1} was used to identify the functional groups present

96 in the surface of the sorbent biomass with a Thermo Nicolet 5700 equipment. The crystallinity

97 of the sorbent was determined by X-ray diffraction (XRD). The diffractogram was recorded

98 using an XRD instrument (XRD Bruker D8 Advance) with Cu Kα radiation, a voltage of 40 kV and

99 a current of 20 mA. The scanning range was from 2θ=5° to 50° at a scan speed of 0.05° s^{-1}. TGA

100 measurements were taken using a TGA/DSC 1 HT instrument (Mettler-Toledo GmbH)

101 operating in nitrogen environment.

102 The zero point of charge (ZPC) of the agrowaste biomass was assessed by the mass titration

103 method (Fiol and Villaescusa, 2009). For this, different masses of sorbent within the dosage

104 range 5-100 g/L were put into contact with a 0.03 M KNO$_3$ solution. These suspensions were

105 stirred for 24 h at 150 rpm until equilibrium pH was reached. The pH at the zero point of

106   charge (pH_{ZPC}) is the pH at which a plateau is achieved when plotting equilibrium pH versus

107   sorbent dosage.

108   The specific surface area and the pore size distribution of the artichoke biomass was

109   determined using N_2 and CO_2 gas sorption and Hg porosimetry. Sorption-desorption isotherms

110   of N_2 at -196 ^{o}C were determined using an Autosorb iQ XR-2 gas sorption analyser

111   (Quantachrome Instruments, Boynton Beach, Florida). Samples were degassed at 100 ^{o}C for 24

112   h prior to gas adsorption measurements. The surface area and pore volume were calculated

113   using the standard Brunauer-Emmett-Teller (BET) procedure. In addition, a surface analysis

114   was also obtained using CO_2 gas as the adsorbate in order to measure narrow micropores (<1

115   nm). Pore size distribution in the raw biomass was also studied with a PoreMaster 60-GT

116   porosimeter (Quantachrome Instruments, Boynton Beach, Florida). Samples were degassed at

117   vacuum at 100 ^{o}C for 24 h prior to the measurements. The density of the sample was

118   determined by helium pycnometry with an UltraPyc gas pycnometer (Quantachrome

119   Instruments, Boynton Beach, Florida).

120   *2.2. Chemical reagents*

121   Stock metal solutions (1000 mg·L^{-1}) of Cu(II), Cd(II) and Pb(II) were prepared by dissolving the

122   respective metal salts ($Cu(NO_3)_2$·3 H_2O, $Cd(NO_3)_2$·4 H_2O, $Pb(NO_3)_2$) in Milli Q water. Nitrates

123   salts were used as it has been shown that this counterion is less interfering in the sorption

124   process than sulfates or chlorides (Hong et al., 2017). Working solutions were obtained by

125   diluting the respective stock solution to the desired concentration of 10, 20 and 50 mg/L of

126   each metal ion. These concentrations were chosen because they are typical values in industrial

127   effluents. Using the molar mass of the corresponding metal ion (Cu, Cd and Pb) the

128   concentrations were converted to those showed in Table 1, expressed as µmol/L. NaOH and/or

129   HCl (0.1 M) solutions were used to adjust the pH to target values. Lead, copper and cadmium

130   concentrations of the working solutions were obtained using an Agilent 720/725 inductively

131   coupled plasma optical emission spectrometer (ICP-OES) system.

132 *2.3. Batch experimental program*

133 Batch experiments were carried out at 25 °C under agitation in a reciprocal shaker by contact of

134 100 mL of the metal working solution at fixed concentration of each cation ($C_{0,i}$) and a known

135 amount of sorbent for 24 hours in a conical flask at a constant agitation speed (150 rpm). The

136 solutions were then filtered and the residual metal concentrations in the solution ($C_{e,i}$) were

137 quantified by ICP-OES.

138 The amounts of metal ions (Pb(II), Cu(II) and Cd(II)) adsorbed at equilibrium (q_e), also known as

139 sorption capacities, (evaluated as µmol metal / g dry biomass) were determined by the mass

140 balance equation (Eq. (1)) on the basis of the concentration of each metal in the liquid solution

141 at the beginning ($C_{0,i}$), and at the end of the test ($C_{e,i}$):

142
$$q_{e,i}\ (\mu mol \cdot g^{-1}) = \frac{\left(C_{0,i} - C_{e,i}\right) \cdot V}{m} \qquad (1)$$

143 where *V* is the solution volume (L) and *m* the sorbent dry weight (g).

144 The total sorption capacity (q_T) was obtained by means of Eq. (2), where *N* is the total number

145 of metal cations in the solution.

146
$$q_T\ (\mu mol \cdot g^{-1}) = \frac{\sum_1^N \left(C_{0,i} - C_{e,i}\right) \cdot V}{m} \qquad (2)$$

147 The efficiency of the process was also quantified as the removal percentage using Eq. (3) and

148 Eq. (4) for the individual ions and the sum of all of them, respectively.

149
$$R_i\ (\%) = \frac{C_{0,i} - C_{e,i}}{C_{0,i}} \cdot 100 \qquad (3)$$

150
$$R_T\ (\%) = \frac{\sum_1^N (C_{0,i} - C_{e,i})}{\sum_1^N C_{0,i}} \cdot 100 \qquad (4)$$

151 The units for initial metal concentration ($C_{0,i}$) and metal concentration at equilibrium ($C_{e,i}$) in

152 Eq. (1-4) were µmol·L^{-1}.

153 *2.4. Design of experiments*

154 The influence of pH, sorbent dosage and initial concentration of Pb(II), Cd(II) and Cu(II) in the

155 competitive removal of metal ions by artichoke agrowaste biomass were studied. A factorial

156 design of experiments was chosen as they are proved to be more efficient than single factor

157 experiments (Montgomery, 2017). Each parameter was studied at 3 levels (Table 1). The

158 selection of these factors and levels was based on the principles of adsorption and previous

159 published works. Initial metal ion concentrations, $C_{o,i}$, and biomass dosage, D, are fundamental

160 variables. Initial metal concentrations used are typical values in industrial effluents. As regards

161 the sorbent dosage, the papers in the literature consulted use sorbent dosages that range from

162 0.1 to 10 g·L^{-1}. We chose sorbent doses of 0.5, 1 and 2 g·L^{-1}, which fit inside this interval. High

163 sorbent dosage increase the availability of active sites and hence favours metal ion uptake.

164 However, at very high sorbent doses, the sorption capacity may show a decremental trend due

165 to the aggregation and overlapping of active sites leading to a decreased surface area and a

166 lower rate of metal ion diffusion into the sorbent matrix (Kumar et al., 2017). According to this,

167 the initial levels of these factors (Table 1) were chosen based on the bibliography (Padilla-Ortega

168 et al., 2013; Srivastava et al., 2007; Wang et al., 2017; Zolfaghari et al., 2011). Moreover, these

169 levels were used in our previous work dealing with single component adsorption (Fernández-

170 López et al., 2019).

171 The pH of aqueous solutions has been proved to be a dominant factor within heavy metal

172 biosorption and this is why this parameter was also chosen. Protonation-deprotonation of the

173 functional groups controlled by the pH of the medium severely affects the adsorption capacity

174 of the sorbents (Kumar et al., 2017). High concentration of H$^+$ (low pH) favours the protonation

175 process that blocks anionic active sites such as $-COO^-$ (Kumar et al., 2017), present on the

176 artichoke biomass. So, therefore, the higher the pH the better. However, pH levels higher than

177 5 gave as a result precipitation of the less soluble metal hydroxide, i.e. $Cu(OH)_2$. Taking all of this

178 into account, pH values ranging from 3 to 5 were chosen.

179   Taguchi design of experiments (DOE) was applied to obtain an L27 orthogonal array which allows

180   to extract the most important process information through only a modest number of

181   experimental runs (Mitra, 2011) and, most interestingly, to detect potential interactions

182   between factors. If a full factorial design had been performed, a [35]-matrix would yield a series

183   of 243 experiments. In this way, Taguchi globally reduces the experimental execution to a

184   practically feasible one whilst making it possible to evaluate each selected parameter separately

185   within the process. In order to achieve this reduction, the principle only focuses on two-factor

186   interactions and main effects whilst higher-order interactions are considered non-existent (Su,

187   2013).

188   According to the Taguchi approach, an analysis of the signal-to-noise (*S/N*) ratio is needed to

189   assess the experimental results. Usually, three types of *S/N* ratio analysis are possible: (1) lower

190   is better (LB), (2) nominal is best (NB), and (3) higher is better (HB) (Zolfaghari et al., 2011). As

191   the target of this investigation is to achieve the highest possible pollutants removal, here, the

192   optimal level of process parameters is the level with the greatest *S/N* ratio, which is given by Eq.

193   (5).

194 $$S/N = -10 \ \log_{10}\left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{1}{y_i}\right)^2\right] \qquad (5)$$

195   where *n* is the number of repetitions under the same experimental conditions (3 in this case),

196   and *y* represents the results of measurements. The analysis of variance (ANOVA) was used to

197   determine the effect of factors on the sorption capacities (Su, 2013). Minitab 17 was the

198   software used to perform the Taguchi approach.

199   *2.5. Uptake kinetic study*

200   Kinetic studies provide useful information about the time required to reach to equilibrium as

201   well as the possible mechanism that describes the sorption process. It is widely accepted that

202   any sorption process requires three steps: (i) the external diffusion of the adsorbate from the

203 bulk solution to the external surface of the adsorbent, (ii) the internal diffusion of the

204 adsorbate to the sorption sites, and (iii) the sorption process itself. Several models based on

205 different assumptions have been proposed in the literature, being some of the most applied

206 those of Lagergren pseudo-first order (Eq.(6)), pseudo-second order (Eq.(7)), Elovich (Eq.(8))

207 and intra-particle diffusion (Eq.(9)) (Sen Gupta and Bhattacharyya, 2011). The first three of

208 them assume that the slowest step in the process is the adsorption itself, whereas the last one

209 considers that the rate limiting step is the second one, that is, the mass transfer into the

210 interior of the particle (Largitte and Pasquier, 2016).

211
$$q_t = q_e[1 - \exp(-k_1 \cdot t)] \tag{6}$$

212
$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{7}$$

213
$$q_t = \frac{1}{\beta} \ln(\alpha \cdot \beta) + \frac{1}{\beta} \ln t \tag{8}$$

214
$$q_t = k_i \cdot t^{1/2} + a \tag{9}$$

215 In Eqs (6-9), q_e and q_t are the sorption capacities at equilibrium and at time t, respectively

216 ($\mu mol \cdot g^{-1}$). Besides, each model has its own parameters: k_1 is the pseudo-first order rate

217 constant (h^{-1}), k_2 is the pseudo-second order rate constant ($g \cdot \mu mol^{-1} \cdot h^{-1}$), α is the initial

218 adsorption rate ($\mu mol \cdot g^{-1} \cdot h^{-1}$), β is the Elovich constant ($g \cdot \mu mol^{-1}$), k_i is the intraparticle

219 diffusion rate constant ($\mu mol \cdot g^{-1} \cdot h^{-1/2}$) and a gives an idea of the thickness of the boundary

220 layer ($\mu mol \cdot g^{-1}$).

221 Several tests were carried out to study the kinetic of the competitive adsorption of Cu(II), Pb(II)

222 and Cd(II) on the artichoke agrowaste biomass. The conditions of these tests were the optimal

223 ones obtained from Taguchi's DOE for maximizing the removal of each metal ion individually

224 and globally; thus, four tests were carried out. The experiments were performed in a 1 L flask

225 with reciprocal agitation. At irregular intervals –more frequently at the beginning of the tests–

226   5 mL of the solution were removed from the flask and filtered through a 0.45 µm nylon

227   Millipore Millex-HN filter. The concentration of the remaining metals in the solution at that

228   time was measured afterwards by ICP-OES.

229   Experimental data were adjusted to Eqs. (6-8) and to Eq. (9) in order to ascertain the kinetic

230   model that best modelled the biosorptive process. A new parameter was proposed, S_i, Eq. (10),

231   in order to study the share of the total sorption capacity (q_T) among the individual sorption

232   capacities ($q_{e,i}$) and was used to determine which metal ion was preferentially adsorbed at

233   different times.

234    $$S_i = \frac{q_{e,i}}{q_T} \cdot 100 \qquad\qquad (10)$$

235   *2.6. Desorption studies*

236   Despite using a low-cost sorbent, the recovery of metals from biomass is important in order to

237   be reused and to minimize the amount of waste produced. In the context of a circular

238   economy it would be a further contribution towards zero waste. Generally, diluted mineral

239   acids and complexing agents are used as desorbents (Oliveira et al., 2011). For desorption of

240   Cu(II), Pb(II) and Cd(II) from artichoke agrowaste biomass (saturated using 50 mg/L of each

241   metal and sorbent dosage of 0.5 g/L) 0.1 M HNO_3 and 0.1 M EDTA were tested as desorbing

242   agents. The desorption efficiencies were determined using loaded-sorbent dosages of 2.0 g/L

243   and stirring contact time of 12 h.

244   **3. Results and discussion**

245   *3.1. Sorbent characterization*

246   The microstructure of the sorbent surface was analyzed by SEM. As can be observed, the

247   filamentous structures composed of fibre cells are aligned longitudinally (Fig. 1). This fibrous

248   structure gives strength and toughness, that together with the microchannels permits the

249   rapid movement of fluids through the fibres increasing the chance of retention of metal ions.

250   The SEM analysis also points to a rough surface and the presence of irregularly shaped and

251   sized cavities, which would enhance the fixation of metal ions (Prodromou and Pashalidis,

252   2013).

253   Fourier−transform infrared spectroscopy (FTIR) was used to obtain information on the nature

254   of functional groups at the surface of the sorbent biomass. The spectra exhibited a broad and

255   intense band around 3273 cm^{-1} corresponding to the stretching vibration of O−H and N−H

256   groups which shifted to 3320 cm^{-1} after the metal sorption. A band around 1603 cm^{-1} was also

257   registered, corresponding to the stretching vibrations of COO^- groups, which was moved to

258   1637 cm^{-1} after the sorption process (Fig. 2). These observations are in line with previously

259   reported works that establish that both hydroxyl and, mostly, carboxylic groups play a crucial

260   role in the binding process of metal ions on lignocellulosic substrates (Velazquez-Jimenez et al.,

261   2013).

262   The cristallinity index (CI) was calculated from the XRD analysis by substracting the minimum

263   intensity of the peak 101 (amorphous band) from the maximum intensity that represents the

264   crystalline portions of the peak 002 and then taking the ratio between the difference and the

265   total intensity (Rambo and Ferreira, 2015). The crystallinity index in the artichoke biomass

266   resulted 42.5% (supplementary data), similar to other agrowaste lignocellulosic residues

267   reported in the bibliography (Rambo and Ferreira, 2015). The thermal stability of the sorbent

268   was determined using TGA under nitrogen environment. Thermal degradation data indicates

269   weight loss and the first derivative (DTG) indicates the corresponding rate of weight loss. The

270   peak of this curve (DTG_{max}) is usually presented as a measure of thermal decomposition and

271   can be used to compare thermal stability characteristics of different sorbents. The thermal

272   decomposition behavior of plant biomass can be divided in several stages: moisture evolution,

273   hemicellulose decomposition, cellulose decomposition and lignin decomposition. The DTG plot

274   (supplementary data) presents three stages of thermal degradation. In the first stage (up to

275   120 ^{o}C) the weight loss is due to humidity and release of the bound water molecules, in the

276   second stage (200-250 °C) the weight loss are due to degradation of hemicellulose and part of

277   cellulose which gives rise to gaseous compounds (CO_2, CO, CH_4, H_2). In the third stage, at

278   higher temperatures (300-400 °C) the degradation is much more evident and is attributed to

279   the cellulose decomposition and a lignin part much more thermostable (Mothé and de

280   Miranda, 2013). The agrowaste biomass of artichoke showed a DTG_{max} at 337 °C

281   (supplementary data). This value is of the same order of those presented by different

282   lignocellulosic biomass resources (328-336 °C) (Watkins et al., 2015).

283   The BET surface area of the artichoke agrowaste biomass turned out to be 0.912 $m^2 \cdot g^{-1}$.

284   Lignocellulosic sorbents are mostly non-porous materials, which is reflected in their low

285   surface area compared to active carbons or biochars. Nevertheless, they are widely studied as

286   potential sorbents as they show capabilities to retain metal ions at low cost while favoring a

287   zero waste approach. It also showed a predominance of macropores and mesopores ranging

288   from 179 µm to 3.59 nm with a total porosity of 47.54%. A small fraction of narrow micropores

289   (0.015 $cm^3 \cdot g^{-1}$) was also observed (supplementary data).

290   The helium density (true density) was found to be 1.3973 $g \cdot mL^{-1}$.

291   The process of sorption involves interactions between a sorbate and a sorbent at the surface-

292   water interface. Hence, surface properties of the sorbent play an important role in the

293   sorption process. The pH at ZPC is the pH value to give a zero net surface charge on a solid,

294   and it informs about the surface functional groups present in the biomass, revealing the

295   predominant acid or basic characteristics at a given pH. The pH_{ZPC} of the agrowaste residue of

296   artichoke was experimentally found to be at pH 4.8 (Fig. 3). At pH higher than pH_{ZPC}, the

297   sorbent surface is negatively charged and such as situation would enhance the electrostatic

298   attraction between the positively charged metal ions and the negatively charged biomass

299   surface, which ultimately would involve an increase in the adsorption of metal ions. At pH

300   values lower than pH_{ZPC} solid surface is positively charged and could interact with negative

301   species. Another aspect to be noted is metal speciation in solution, which is also pH dependent

302 (Fiol and Villaescusa, 2009). For the afore mentioned reasons, pH is a key factor in metal

303 sorption studies by plant biomass and it must be considered as controllable variable to

304 enhance the sorption process.

305 *3.2. Enhancement of the sorption process*

306 Table 2 shows the inputs of the Taguchi analysis and the corresponding results. Total sorption

307 capacity (q_T) and total removal efficiency (R_T) were obtained using Eq. (2) and Eq. (4),

308 respectively. The signal-to-noise (S/N) ratios were calculated by the MINITAB software and

309 they are referred to the total sorption capacity based on the larger-is-better requirement for

310 quality loss.

311 It can be appreciated that, out of all 27 tests performed, the highest sorption capacity (235

312 $\mu mol \cdot g^{-1}$) corresponds to the highest S/N ratio (47.4) and is shown with initial concentrations

313 of 787 $\mu mol \cdot L^{-1}$ Cu(II), 178 $\mu mol \cdot L^{-1}$ Cd(II) and 97 $\mu mol \cdot L^{-1}$ Pb(II), pH 5 and 0.5 $g \cdot L^{-1}$ of sorbent

314 dosage. It is interesting to note that the conditions to obtain the maximum q_T do not coincide

315 with those required to obtain the maximum removal percentage, which seems reasonable

316 given the definitions of both parameters. The highest removal efficiency (57.3 %) was obtained

317 with initial concentrations of 315 $\mu mol \cdot L^{-1}$ Cu(II), 89 $\mu mol \cdot L^{-1}$ Cd(II) and 48 $\mu mol \cdot L^{-1}$ Cu(II), pH 5,

318 and sorbent dosage of 2 $g \cdot L^{-1}$. As expected, a higher sorbent dosage produced a higher overall

319 adsorption percentage –up to certain extent–, as more active sites are available for metal

320 removal, being the initial and final metal concentrations the only variables taken into account

321 in the calculation. Moreover, this dependence was shown to be significant ($p<0.01$). However,

322 in Eq. (2), used to calculate the total sorption capacity, the sorbent dosage is dividing the net

323 adsorption and, therefore, a higher sorbent dosage does not necessarily imply a higher value

324 of q_T. Indeed, this factor (sorbent dosage) did not show a significant effect on the total

325 sorption capacity. Most of the published papers on pollutant adsorption use sorption

326 capacities instead of total removal percentages and, between these two parameters, the

14

327 former is considered a better tool to express and compare the capacities of different biomass

328 types (Rosique et al., 2016). For all these reasons, in this investigation, sorption capacities will

329 be used to perform the subsequent analysis of the results.

330 An overall ranking of the controllable parameters was obtained with Minitab based on delta

331 values (Table 3). This parameter quantifies the size of the effect by taking the difference

332 between the highest and the lowest S/N ratio for each factor and states the relative

333 importance of each of them (Srivastava et al., 2007). Minitab also provides a S/N variance

334 analysis, which is used to evaluate the significance of the main effects on the process based on

335 p-values. The different factors that affect q_T were ranked following the sequence pH>sorbent

336 dosage>[Cd(II)]>[Cu(II)]>[Pb(II)]; however, none of them showed a significant influence

337 ($p<0.05$) (Table 4). This should be seen as a positive fact. From the five factors tested, three of

338 them (initial concentrations of Cu(II), Cd(II) and Pb(II) in a wastewater) are not controllable in

339 an industrial process and, therefore, variations of their values will not significantly affect the

340 performance of the artichoke biomass. Sorbent dosage and pH are controllable parameters.

341 They can be set to the levels that enhance adsorption (pH=5 and sorbent dosage= 0.5 g·L^{-1}) but

342 variations in their values will not significantly alter q_T, giving as a result a robust method.

343 The representation of the general trend of the influence of the factors on the total sorption

344 capacity (q_T) and respective S/N ratios (response curves) are displayed in Fig. 3. The analysis of

345 these experimental results allows us to deduce the optimum levels of each factor to achieve

346 the best S/N response. According to the Taguchi approach, the proposed operational

347 conditions for a maximum total sorption capacity (q_T) were (Table 5): initial Cu(II)

348 concentration at level 2 (315 µmol·L^{-1}), initial Cd(II) concentration at level 3 (445 µmol·L^{-1}),

349 initial Pb(II) concentration at level 3 (241 µmol·L^{-1}), pH at level 3 (5.0) and sorbent dosage at

350 level 1 (0.5 g·L^{-1}).

351   It is interesting to note that the sorption capacity of individual metal ions in the multi-metal

352   system was lower than in the single metal ones. For instance, the highest adsorptions of Pb(II),

353   Cu(II) and Cd(II) achieved in previous works with the same sorbent biomass in single-metal

354   aqueous solutions were respectively 416, 384 and 318 $\mu mol \cdot g^{-1}$ (Fernández-López et al., 2019),

355   whereas in the ternary solutions of this investigation were 135, 127 and 81 $\mu mol \cdot g^{-1}$,

356   respectively (Table 5). Therefore, the maximum metal ion sorption capacity in the multi-metal

357   system was lower than the sum of the single maximum sorption capacities for each metal ion.

358   Metal competition globally hinders the sorption process. This decrease in the total sorption

359   capacity in multi-component systems was also observed previously (Chatterjee et al., 2017;

360   Padilla-Ortega et al., 2013). This inhibitory effect in the multi-metal system may be explained

361   by the competition and differential affinity of metal ions for the reactive sites available onto

362   the sorbent surface (do Carmo Ramos et al., 2015).

363   A comparison of the performance of the artichoke biomass as a sorbent for Pb(II), Cd(II) and

364   Cu(II) in multimetal systems with other lignocellulosic sorbents is shown in Table 6. It is

365   important to note, on the one hand, that this comparison is done only with works that deal

366   with multicomponent solutions, as it was mentioned before the presence of different metals

367   hinders the global adsorption; and, on the other hand, that it is not exhaustive, as this paper is

368   not a review. The comparison shows a good performance of the artichoke agrowaste biomass,

369   with removal efficiencies similar and even higher than other sorbents reported in the

370   literature.

371   *3.3 Analysis of the competitive sorption in the multi-metal system*

372   The results confirmed that the degree of metal sorption was not similar for all metals and

373   there was a manifest competitive effect among them when they were fixed by the biomass.

374   Fig. 4 shows the percentage of times that each metal ion was preferredly adsorbed as a

375   function of the predominant metal in solution. It is noticeable that when Pb(II) was the metal

376   ion predominant in solution, Pb(II) was always adsorbed in a higher proportion. When the

377   metal ion predominant was Cu(II), this was the metal ion that was adsorbed in higher

378   proportion in the 82% of the experiments, whereas Pb(II) was preferably adsorbed in 18% of

379   the tests. When the highest initial concentration was that of Cd(II), in 48% of the cases Pb(II)

380   was adsorbed in a higher proportion than Cu(II) (32% of the cases) and Cd(II) (20% of the

381   cases). Therefore, the metal ion that exhibited the greatest affinity for the artichoke agrowaste

382   biomass was Pb(II), whereas Cd(II) showed the lowest affinity. This behavior has also been

383   observed with other sorbent materials (Wang et al., 2017) and it is usually explained examining

384   the ionic radius, the hydrated ionic radius and the electronegativity of the metals investigated.

385   Pb(II) has the largest ionic radius, which increases the probability of collision with the biomass

386   active sites (Bayo, 2012). Additionally, a larger ionic radius means that the hydration layer of

387   Pb(II) is weaker than those of Cu(II) and Cd(II) (Berber-Mendoza et al., 2018). In this way, Pb(II)

388   has the lowest hydrated ionic radius (4.01 Å) among the metals studied (Chen et al., 2010). As

389   a result, these ions encounter the least resistance whilst migrating through the solution and

390   are therefore more likely to reach the biomass surface faster in comparison with the other

391   metal ions present. This resistance increases for Cu(II) with a hydrated ionic radius of 4.19 Å,

392   and it is the strongest for Cd(II) ions which have a radius of 4.26 Å (Chen et al., 2010).

393   Electronegativity is also thought to play a crucial role in determining adsorption affinities. In

394   this sense, the more electronegative the ions, the more strongly they are attracted to the

395   sorbent surface (Bayo, 2012; McKay and Porter, 1997). Pb(II) has also the highest value of

396   electronegativity of the three elements considered in this work, so these three factors all

397   enhance its preferential sorption over Cu(II) and Cd(II).

398   These results are very interesting in order to plan a wastewater treatment plant for the

399   elimination of metal ions based on bioremoval with agrifood wastes. Indeed, Cd(II) is the most

400   toxic metal among the three studied but its adsorption is very limited due to the presence of

401   Pb(II). Therefore, more than one adsorption stage will be needed in order to increase the

402   sorption efficiency of this harmful metal ion. In this way, the concentration of Pb(II) will be

403   substantially decreased in the first stage, allowing a more effective removal of Cd(II) and Cu(II)

404   in the following ones.

405   *3.4. Kinetic studies*

406   In batch systems, the sorption kinetics was described by a number of models with different

407   levels of complexity such as pseudo-first-order, pseudo-second-order, Elovich and intraparticle

408   diffusion kinetic model.

409   Table 7 shows the results of nonlinear regression analysis of kinetic data. The tests were

410   conducted at the optimal conditions of q_T (Cu(II) at level 2, Cd(II) at level 1, Pb(II) at level 3, pH

411   at level 3 and sorbent dosage at level 1). The representation of the results and the correlation

412   coefficient of each adjustment reveal that for both, each metal ion and the sum of all of them,

413   the pseudo-second order model is the model that better explains the experimental results.

414   This process was also performed at the optimum factor levels for the removal of each

415   individual metal ion. In all cases, the pseudo-second order model better described the

416   experimental results (Table 8). This model returns two parameters, q_e and k_2, which are used

417   to ascertain the extent and speed of the sorption process. The comparison of the q_e values

418   gives information about the metal ion adsorbed in a higher proportion at equilibrium

419   conditions, whilst k_2 reports the rate sorption of each metal ion. Interestingly enough, Cd(II)

420   was shown to have the highest value of k_2 in all tests (Table 8), meaning that the sorption of

421   this element was favored energetically over that of Cu(II) and Pb(II), at least at the first stages

422   of the process. This was also observed when adjusting the results of the three tests conducted

423   at the respective optimum conditions to enhance the removal of each individual metal ion to

424   the pseudo-second order model.

425   In order to look further into the characterization of the sorption process, the share of each

426   metal ion (S_i), calculated according to Eq. (10), was obtained during all the time monitored in

427 the kinetic assay (Table 9). Some interesting conclusions can be inferred from the analysis of

428 these results. First of all, for the three tests at the conditions to optimise the removal of the

429 individual metal ions, the metal mainly adsorbed is the one that is present at higher

430 concentration, independently of its nature. This would mean that the concentration gradient

431 determines the metal ion that will be preferentially bound to the sorbent. At the end of these

432 three tests, the metal ion with a higher share on q_T at equilibrium keeps being the one initially

433 at higher concentration, although a competitive effect among the metal ions can be observed.

434 For instance, in the experiment at the conditions to optimize Cd(II) removal, S_{Cd} is going down

435 as the test progresses, whereas S_{Cu} and S_{Pb} increase. In this way, although Cd(II) is still the

436 metal ion mostly adsorbed it is progressively displaced by Cu(II) and Pb(II). Something similar

437 happened in the experiment at the conditions to optimise Pb(II) removal. Whereas S_{Pb} keeps

438 more or less constant throughout the test, S_{Cd} is higher than S_{Cu} at the beginning but becomes

439 lower at the equilibrium conditions. Thus, Cd(II) is again being displaced by Cu(II). This also

440 happens to a certain extent in the test to optimise Cu(II). Moreover, one should note, that at

441 the global optimal conditions (optimization of q_T), with initial concentrations of Cd(II) and Pb(II)

442 of 445 and 241 $\mu mol \cdot L^{-1}$, respectively, initially S_{Cd} was higher than S_{Pb}, meaning that at the

443 beginning of the test, Cd(II) is quickly adsorbed, but as the test goes on S_{Cd} decreases in favour

444 of S_{Pb}. This would indicate that Cd(II) has certainly high affinity for the artichoke agrowaste

445 biomass but it is displaced when Pb(II) and Cu(II) are also in solution.

446 *3.5. Desorption studies*

447 In the context of a circular economy, desorption of metal ions from the spent sorbent was

448 effectively performed for the recovery and reuse of the biomass and for the possible

449 reintroduction of the desorbed metals in the industrial chain and looking to go "zero waste".

450 The literature reports different types of eluent agents, mainly organic and inorganic acids

451 solutions and complexing agents (Hashim et al., 2000). Nitric acid (HNO$_3$ 0.1 M) and EDTA 0.1

452 M were tested for the desorption of the metal ions investigated. The best recovery was carried

453 out by HNO_3 0.1 M (93%), whilst EDTA 0.1 M yielded lower desorption (78%). This result gives

454 an idea that the mechanism involved in the sorption process is mostly ion-exchange, so acid

455 washing yields better results in the desorption process, based on the ion-exchange between

456 the protons in solution and the metal ions adsorbed to the biomass.

457 *3.6. Importance and sustainability of valorizing artichoke residues as low-cost sorbent*

458 Among the different techniques used to remove heavy metals from wastewater, adsorption is

459 generally preferred as it is one of the most effective. The widest used adsorbent is activated

460 charcoal; however, its high treatment cost has turned focus on searching low-cost, natural,

461 effective adsorbents (Anna et al., 2015). Currently, the residues of artichoke from the canning

462 industry are disposed of in landfills or, as best, used to prepare cattle feed. The possibility of

463 using it as a heavy metal sorbent opens a gate to a low-cost valorization of this waste, as it

464 uses a residue as a raw material without any previous treatment, apart from drying at 70 °C

465 and milling. It is worth reminding that the mass of artichoke agro-waste amounts to

466 approximately 70% of the entire plant (Machado et al., 2015).

467 Sustainability of the process is guaranteed in several ways. First of all, it is a natural product

468 and its use as a sorbent does not compete with food resources as only the waste parts are

469 used. In this way, it contributes to diminish the amount of residues generated. Moreover, it is

470 reusable as checked in our desorption tests. Secondly, used as a sorbent, it can remove metals

471 from wastewater streams, contributing to the potential reuse of treated water in places of

472 water scarcity. Thirdly, the energy consumption of the batch process is low. The energy cost of

473 a continuous process is higher because of the pumping of the water stream through the

474 scrubbers but still not as energy demanding as other processes that require, for instance, high

475 temperatures to operate. Finally, the adsorption process is environmentally friendly (there are

476 no emissions of gaseous pollutants or use of any toxic substances).

477 The utilization of residues of artichoke from industrial canning processing as sorbent for the

478 removal of heavy metal ions from aqueous media in addition to ensuring treatment in

479   accordance with the principles of sustainable development is also helpful in the environment

480   bioremediation processes.

481

482   **Conclusions**

483   The search of efficient and environmental friendly sorbents has positioned the lignocellulosic

484   biomass resources as attractive and low-cost alternatives instead of synthetic sorbents. This

485   paper illustrates the efficiency of artichoke agrowaste biomass as sorbent of metal ions in a

486   multimetal study.

487   The analysis of experimental data led to the following conclusions:

488   I.   Residues of artichoke from industrial canning processing show a great potential as

489   sorbent of Pb(II), Cd(II) and Cu(II) in multi-metallic solutions.

490   II.   The Taguchi approach facilitated understanding of the interaction of the factors

491   investigated with a reduced number of experiments, suggesting optimal operating

492   conditions to achieve a maximum sorption capacity.

493   III. Pb(II) was the metal ion predominantly adsorbed at equilibrium, followed by Cd(II)

494   and, lastly, Cu(II).

495   IV.   The kinetic study of the process reveals that it follows a pseudo-second order model.

496   The highest value of the rate constant, k_2, was always that of Cd(II).

497   V.   The share of each metal ion on the total sorption capacity (S_i) was found to be a good

498   parameter to explain these results. Indeed, Cd(II) is actually rapidly adsorbed at the

499   beginning of the tests but often displaced by Cu(II) and Pb(II) as the sorption process

500   progresses.

501   VI.   The concentration gradient of each metal ion was found to be the major driving force

502   in the sorption process.

503   VII. In sum, artichoke agrowaste biomass could effectively be used to reduce the amount

504   of metal ions in multi-metallic aqueous effluents in order to attain a zero waste

505   economy and a valorization of this agrifood waste. This project would be a perfect

506   example of a circular economy applied to the agricultural and food sector.

507

513

514

515   **References**

516   Anna, B., Kleopas, M., Constantine, S., Anestis, F., Maria, B., 2015. Adsorption of Cd(II), Cu(II), Ni(II) and

517   Pb(II) onto natural bentonite: study in mono- and multi-metal systems. Environ. Earth Sci. 73,

518   5435–5444. https://doi.org/10.1007/s12665-014-3798-0

519   Arief, V.O., Trilestari, K., Sunarso, J., Indraswati, N., Ismadji, S., 2008. Recent progress on biosorption of

520   heavy metals from liquids using low cost biosorbents: Characterization, biosorption parameters and

521   mechanism studies. Clean-Soil, Air, Water 36, 937–962. https://doi.org/10.1002/clen.200800167.

522   Bayo, J., 2012. Kinetic studies for Cd(II) biosorption from treated urban effluents by native grapefruit

523   biomass (*Citrus paradisi* L.): The competitive effect of Pb(II), Cu(II) and Ni(II). Chem. Eng. J. 191,

524   278–287. https://doi.org/10.1016/j.cej.2012.03.016

525   Berber-Mendoza, M.S., Martínez-Costa, J.I., Leyva-Ramos, R., Javier, H., Garcia, A., 2018. Competitive

526   adsorption of heavy metals from aqueous solution onto oxidized activated carbon fiber. Water Air

527   Soil Pollut. 229, 257. https://doi.org/10.1007/s11270-018-3906-y

528   Bhatnagar, A., Sillanpää, M., Witek-Krowiak, A., 2015. Agricultural waste peels as versatile biomass for

529   water purification–a review. Chem. Eng. J. 270, 244–271. https://doi.org/10.1016/j.cej.2015.01.135

530   Chatterjee, S., Sivareddy, I., De, S., 2017. Adsorptive removal of potentially toxic metals (cadmium,

531   copper, nickel and zinc) by chemically treated laterite: Single and multicomponent batch and

532   column study. J. Environ. Chem. Eng. 5, 3273–3289. https://doi.org/10.1016/j.jece.2017.06.029

533   Chen, S.B., Ma, Y.B., Chen, L., Xian, K., 2010. Adsorption of aqueous Cd^{2+}, Pb^{2+}, Cu^{2+} ions by nano-

534   hydroxyapatite: Single-and multi-metal competitive adsorption study. Geochem. J. 44, 233–239.

535   https://doi.org/10.2343/geochemj.1.0065

536 Daneshfozoun, S., Abdullah, M.A., Abdullah, B., 2017. Preparation and characterization of magnetic
537   biosorbent based on oil palm empty fruit bunch fibers, cellulose and *Ceiba pentandra* for heavy
538   metal ions removal. Ind. Crops Prod. 105, 93–103. https://doi.org/10.1016/j.indcrop.2017.05.011

539 do Carmo Ramos, S.N., Xavier, A.L.P., Teodoro, F.S., Elías, M.M.C., Gonçalves, F.J., Gil, L.F., de Freitas,
540   R.P., Gurgel, L.V.A., 2015. Modeling mono-and multi-component adsorption of cobalt (II), copper
541   (II), and nickel (II) metal ions from aqueous solution onto a new carboxylated sugarcane bagasse.
542   Part I: Batch adsorption study. Ind. Crops Prod. 74, 357–371.
543   https://doi.org/10.1016/j.indcrop.2015.05.022

544 Escudero-Oñate, C., Fiol, N., Poch, J., Villaescusa, I., 2017. Valorisation of lignocellulosic biomass wastes
545   for the removal of metal ions from aqueous streams: a review. In: Tumuluru J.S. (Eds.), Biomass
546   Volume Estimation and Valorization for Energy. In Tech Pub., Rijeka, pp. 381–407.
547   http://dx.doi.org/10.5772/65958

548 European Commission, 2014. COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN
549   PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE
550   COMMITTEE OF THE REGIONS, Towards a circular economy: A zero waste programme for Europe.

551 Fernández-López, J.A., Angosto, J.M., Roca, M.J., Miñarro, M.D., 2019. Taguchi design-based
552   enhancement of heavy metals bioremoval by agroindustrial waste biomass from artichoke. Sci. Tot.
553   Environ. 653, 55–63. https://doi.org/10.1016/j.scitotenv.2018.10.343

554 Fiol, N., Villaescusa, I., 2009. Determination of sorbent point zero charge: usefulness in sorption studies.
555   Environm. Chem. Lett. 7, 79–84. https://doi.org/10.1007/s10311-008-0139-0

556 Hashim, M.A., Tan, H.N., Chu, K.H., 2000. Immobilized marine algal biomass for multiple cycles of copper
557   adsorption and desorption. Sep. Purif. Technol. 19, 39–42. https://doi.org/10.1016/S1383-
558   5866(99)00076-3

559 Hong, X., Fang, C., Hui, K.S., Hui, K.N., Zhuang, H., Liu, W., Shan, S., 2017. Influence of interfering anions
560   on Cu^{2+} and Zn^{2+} removal on chestnut outer shell-derived hydrochars in aqueous solution. RSC Adv.
561   7, 51199–51205. https://doi.org/10.1039/c7ra10384k

562 Hossain, M.A., Ngo, H.H., Guo, W.S., Nghiem, L.D., Hai, F.I., Vigneswaran, S., Nguyen, T. V., 2014.
563   Competitive adsorption of metals on cabbage waste from multi-metal solutions. Bioresour.
564   Technol. 160, 79–88. https://doi.org/10.1016/j.biortech.2013.12.107

565 Kumar, R., Sharma, R.K., Singh, A.P., 2017. Cellulose based grafted biosorbents - Journey from
566   lignocellulose biomass to toxic metal ions sorption applications - A review. J. Mol. Liq. 232, 62–93.
567   https://doi.org/10.1016/j.molliq.2017.02.050

568 Largitte, L., Pasquier, R., 2016. A review of the kinetics adsorption models and their application to the
569   adsorption of lead by an activated carbon. Chem. Eng. Res. Des. 109, 495–504.
570   https://doi.org/10.1016/j.cherd.2016.02.006

571 Lesmana, S.O., Febriana, N., Soetaredjo, F.E., Sunarso, J., Ismadji, S., 2009. Studies on potential
572   applications of biomass for the separation of heavy metals from water and wastewater. Biochem.
573   Eng. J. 44, 19–41. https://doi.org/10.1016/j.bej.2008.12.009

574 Machado, M.T., Eça, K.S., Vieira, G.S., Menegalli, F.C., Martínez, J., Hubinger, M.D., 2015. Prebiotic

575   oligosaccharides from artichoke industrial waste: evaluation of different extraction methods. Ind.

576   Crops Prod. 76, 141–148. https://doi.org/10.1016/j.indcrop.2015.06.047

577 McKay, G., Porter, J.F., 1997. Equilibrium parameters for the sorption of copper, cadmium and zinc ions

578   onto peat. J. Chem. Technol. Biotechnol. 69, 309–320. https://doi.org/10.1002/(SICI)1097-

579   4660(199707)69:3<309::AID-JCTB724>3.0.CO;2-W

580 Medellin-Castillo, N.A., Padilla-Ortega, E., Regules-Martínez, M.C., Leyva-Ramos, R., Ocampo-Pérez, R.,

581   Carranza-Alvarez, C., 2017. Single and competitive adsorption of Cd(II) and Pb(II) ions from aqueous

582   solutions onto industrial chili seeds (*Capsicum annuum*) waste. Sustain. Environ. Res. 27, 61–69.

583   https://doi.org/10.1016/j.serj.2017.01.004

584 Meneses, M., Megías, M. D., Madrid, J., Martínez-Teruel, A., Hernández, F., Oliva, J., 2007. Evaluation of

585   the phytosanitary, fermentative and nutritive characteristics of the silage made from crude

586   artichoke (*Cynara scolymus* L.) by-product feeding for ruminants. Small Ruminant Res. 70, 292–296.

587   https://doi.org/10.1016/j.smallrumres.2006.05.008

588 Mitra, A., 2011. The Taguchi method. Wiley Interdiscip. Rev. Comput. Stat. 3, 472–480.

589   https://doi.org/10.1002/wics.169

590 Montgomery, D.C., 2017. Design and analysis of experiments, 9th ed. John Wiley & Sons, Inc., Hoboken,

591   NJ.

592 Mothé, C. G., de Miranda, I. C. 2013. Study of kinetic parameters of thermal decomposition of bagasse

593   and sugarcane straw using Friedman and Ozawa–Flynn–Wall isoconversional methods. J. Therm.

594   Anal. Calorim. 2, 497–505. https://doi.org/10.1007/s10973-013-3163-7

595 Neris, J.B., Luzardo, F.H.M., Santos, P.F., De Almeida, O.N., Velasco, F.G., 2019. Evaluation of single and

596   tri-element adsorption of Pb^{2+}, Ni^{2+} and Zn^{2+} ions in aqueous solution on modified water hyacinth

597   (*Eichhornia crassipes*) fibers. J. Environ. Chem. Eng. 7, 102885.

598   https://doi.org/10.1016/j.jece.2019.102885

599 Oliveira, R., Palmieri, M., García Jr. O., 2011. Biosorption of metals: State of the art, general features,

600   and potential applications for environmental and technological processes. Shaukat, S. (Eds.),

601   Progress in Biomass and Bioenergy Production. In Tech Pub. Rijeka, pp. 151–176.

602   http://dx.doi.org/10.5772/17802

603 Padilla-Ortega, E., Leyva-Ramos, R., Flores-Cano, J.V., 2013. Binary adsorption of heavy metals from

604   aqueous solution onto natural clays. Chem. Eng. J. 225, 536–546.

605   https://doi.org/10.1016/j.cej.2013.04.011

606 Pandino, G., Lombardo, S., Lo Monaco, A., Mauromicale, G., 2013. Choice of time of harvest influences

607   the polyphenol profile of globe artichoke. J. Funct. Foods, 5, 1822–1828.

608   https://doi.org/10.1016/j.jff.2013.09.001

609 Peralbo-Molina, A., Luque de Castro, M.D., 2013. Potential of residues from the Mediterranean

610   agriculture and agrifood industry. Trends Food Sci. Technol. 32, 16–24.

611   https://doi.org/10.1016/j.tifs.2013.03.007

612 Petrella, A., Spasiano, D., Rizzi, V., Cosma, P., Race, M., De Vietro, N., 2018. Lead ion sorption by perlite
613   and reuse of the exhausted material in the construction field. Appl. Sci. 8, 1882.
614   https://doi.org/10.3390/app8101882

615 Prodromou, M., Pashalidis, I., 2013. Copper (II) removal from aqueous solutions by adsorption on non-
616   treated and chemically modified cactus fibres. Water Sci. Technol. 68, 2497–2504.
617   https://doi.org/10.2166/wst.2013.535

618 Reynel-Avila, H.E., Mendoza-Castillo, D.I., Olumide, A.A., Bonilla-Petriciolet, A., 2016. A survey of multi-
619   component sorption models for the competitive removal of heavy metal ions using bush mango
620   and flamboyant biomasses. J. Mol. Liq. 224, 1041–1054.
621   https://doi.org/10.1016/j.molliq.2016.10.061

622 Rosique, M., Angosto, J.M., Guibal, E., Roca, M.J., Fernández-López, J.A., 2016. Factorial design
623   methodological approach for enhanced cadmium ions bioremoval by *Opuntia* biomass. Clean–Soil,
624   Air, Water, 44, 959–966. https://doi.org/10.1002/clen.20150036

625 Salem, M.B., Affes, H., Ksouda, K., Dhouibi, R., Sahnoun, Z., Hammami, S., Zeghal, K.M., 2015.
626   Pharmacological studies of artichoke leaf extract and their health benefits. Plant Foods Hum. Nutr.
627   70, 441–453. https://doi.org/10.1007/s11130-015-0503-8

628 Sellaoui, L., Mendoza-Castillo, D.I., Reynel-Ávila, H.E., Ávila-Camacho, B.A., Díaz-Muñoz, L.L., Ghalla, H.,
629   Bonilla-Petriciolet, A., Lamine, A. Ben, 2019. Understanding the adsorption of Pb^{2+}, Hg^{2+} and Zn^{2+}
630   from aqueous solution on a lignocellulosic biomass char using advanced statistical physics models
631   and density functional theory simulations. Chem. Eng. J. 365, 305–316.
632   https://doi.org/10.1016/J.CEJ.2019.02.052

633 Sen Gupta, S., Bhattacharyya, K.G., 2011. Kinetics of adsorption of metal ions on inorganic materials: A
634   review. Adv. Colloid Interf. Sci. 162, 39–58. https://doi.org/10.1016/j.cis.2010.12.004.

635 Siswoyo, E., Endo, N., Mihara, Y., Tanaka, S., 2014. Agar-encapsulated adsorbent based on leaf of
636   platanus sp. to adsorb cadmium ion in water. Water Sci. Technol. 70, 89–94.
637   https://doi.org/10.2166/wst.2014.190

638 Srivastava, V.C., Mall, I.D., Mishra, I.M., 2007. Multicomponent adsorption study of metal ions onto
639   bagasse fly ash using Taguchi's design of experimental methodology. Industrial Eng. Chem. Res. 46,
640   5697–5706. https://doi.org/10.1021/ie0609822

641 Su, C.T., 2013. Quality Engineering: Off-line Methods and Applications. CRC Press, Boca Ratón.

642 Velázquez-Jiménez, L.H., Pavlick, A., Rangel-Méndez, J.R., 2013. Chemical characterization of raw and
643   treated agave bagasse and its potential as adsorbent of metal cations from water. Ind. Crops Prod.
644   43, 200–206. https://doi.org/10.1016/j.indcrop.2012.06.049

645 Wang, J., Chen, C., 2009. Biosorbents for heavy metals removal and their future. Biotechnol. Adv., 27,
646   195–226. https://doi.org/10.1016/j.biotechadv.2008.11.002

647 Wang, S., Vincent, T., Faur, C., Guibal, E., 2017. Modelling competitive sorption of lead and copper ions
648   onto alginate and greenly prepared algal-based beads. Bioresour. Technol. 231, 26–35.
649   https://doi.org/10.1016/j.biortech.2017.01.066

650 Zhao, M., Xu, Y., Zhang, C., Rong, H., Zeng, G., 2016. New trends in removing heavy metals from

651   wastewater. Appl. Microbiol. Biotechnol. 100, 6509–6518. https://doi.org/10.1007/s00253-016-

652   7646-x

653 Zhou, Y.F., Haynes, R.J., 2010. Sorption of heavy metals by inorganic and organic components of solid

654   wastes: significance to use of wastes as low-cost adsorbents and immobilizing agents. Crit. Rev.

655   Environm. Sci. Technol. 40, 909–977. https://doi.org/10.1080/10643380802586857

656 Zolfaghari, G., Esmaili-Sari, A., Anbia, M., Younesi, H., Amirmahmoodi, S., Ghafari-Nazari, A., 2011.

657   Taguchi optimization approach for Pb(II) and Hg(II) removal from aqueous solutions using modified

658   mesoporous carbon. J. Hazard. Mater. 192, 1046–1055.

659   https://doi.org/10.1016/j.jhazmat.2011.06.006

660 Zuorro, A., Maffei, G., Lavecchia, R., 2016. Reuse potential of artichoke (*Cynara scolymus* L.) waste for

661   the recovery of phenolic compounds and bioenergy. J. Clean. Product. 111, 279–284.

662   https://doi.org/10.1016/j.jclepro.2015.06.011
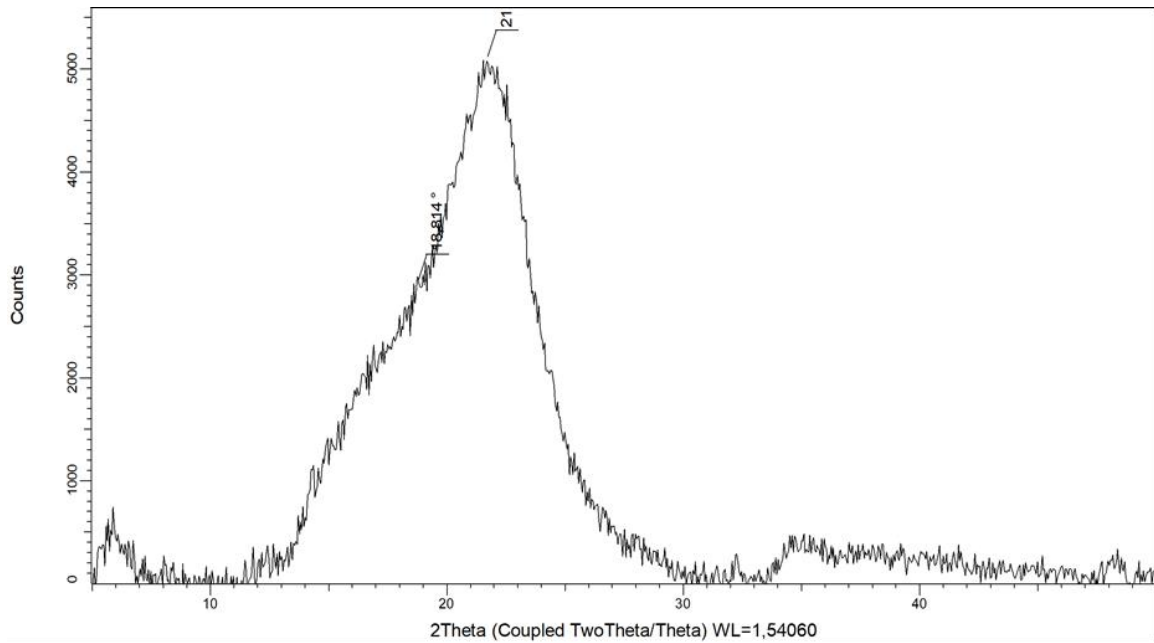
663

SUPPLEMENTARY MATERIAL

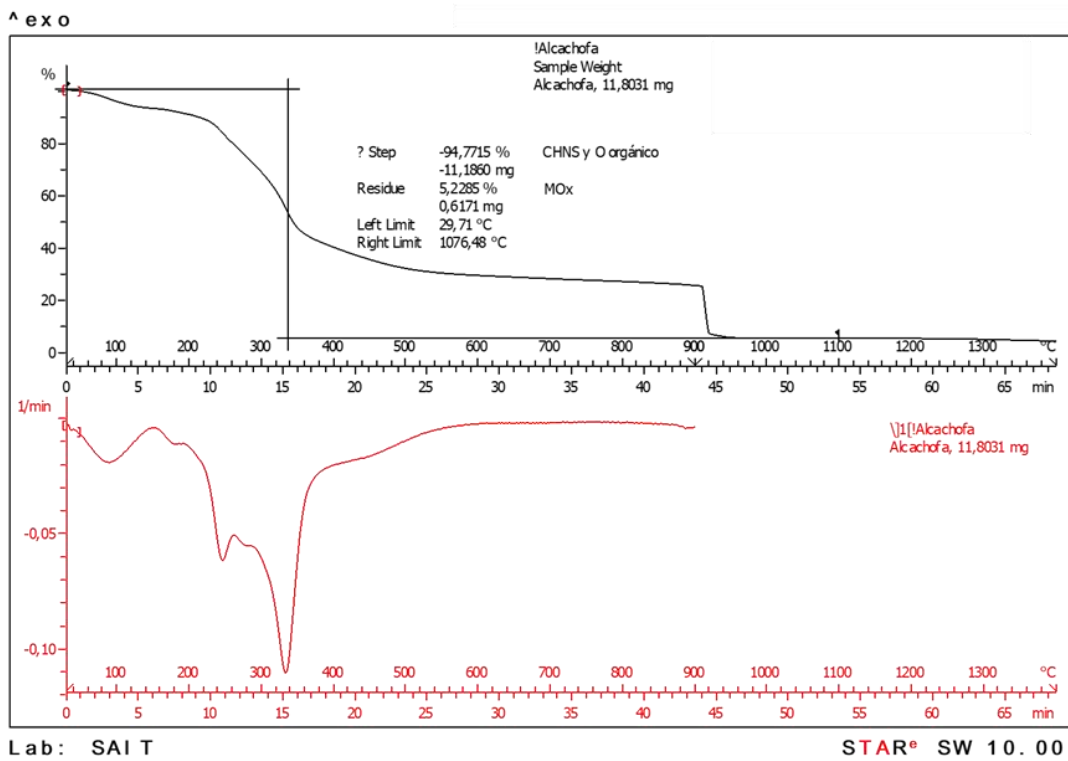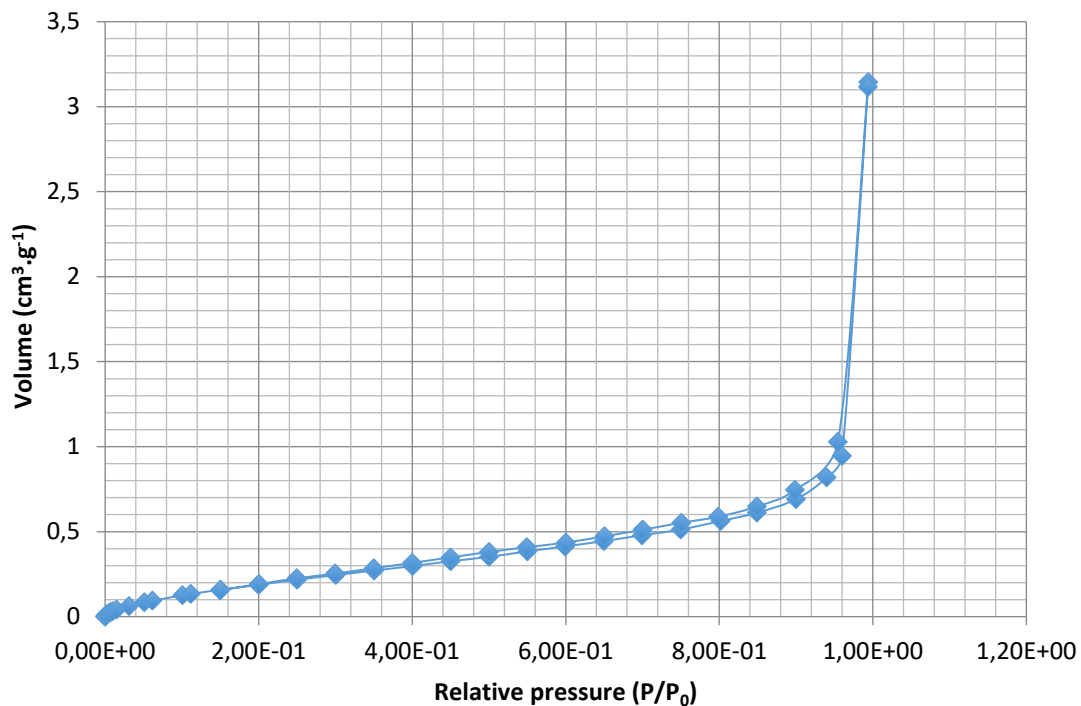Fig. S1. XRD pattern of the artichoke agrowaste biomass used to calculate the cristallinity index

Fig. S2. Thermogravimetric analysis (TGA) curve of the artichoke agrowaste biomass recorded in nitrogen atmosphere
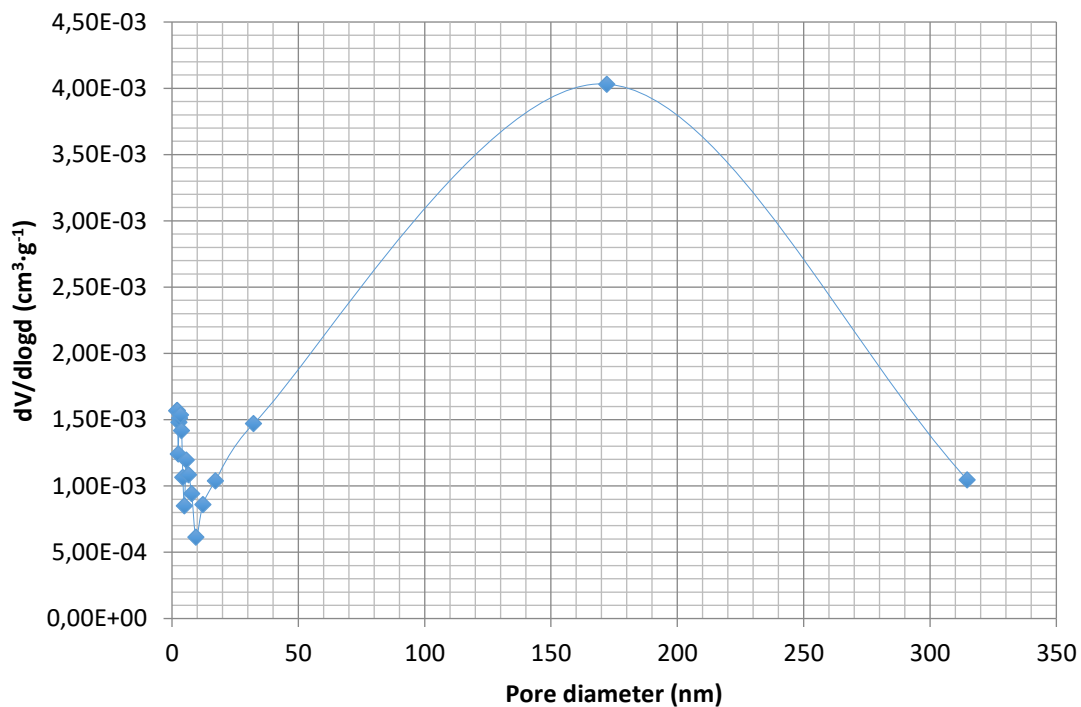
665

666

Fig. S3. Plot of N$_2$ adsorption-desorption volume *vs* pressure applied (P/Po).

668

669

Fig. S4. BJH pore size distribution for mesopores and micropores of artichoke agrowaste biomass.