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1 **Wheat and ryegrass biomass ashes as effective sorbents for** 2 **metallic and organic pollutants from contaminated water** 3 **in lab-engineered cartridge filtration system**

4
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17
18 **Keywords:** sorption; metal and emerging organic **contaminant**; numerical modelling, miscanthus
19 biochar; ryegrass; wheat straw; cartridge filtration technology.

20 21 **Abstract**

22 Three plant biomasses (**miscanthus, ryegrass and wheat**) have been considered for the preparation of
23 five different sorbents evaluated for their potential to sorb cadmium and lead and four emergent
24 organic compounds (diclofenac, sulfamethoxazole, 17 α -ethynylestradiol and triclosan) **from**
25 **artificially contaminated water. Lab-created cartridges were filled with each sorbent and all**

26 experiments were systematically compared to activated charcoal Norit®. Results from activated
27 charcoal, wheat straw and acidified wheat straw were supported by the Langmuir and Freundlich
28 models. Wheat straw ashes were an excellent metal extractor that exceeded the potential of well-
29 known activated charcoal. Acidified sorbents (wheat and ryegrass) were very effective in eliminating
30 the selected emerging organic contaminants displaying equipotent or superior activity compared to
31 activated charcoal. These results open the way for further *in natura* studies by proposing new
32 biosource materials as new effective tools in the fight against water pollution.

33

34 Introduction

35 Chemical pollution has a major contribution in degrading water quality and so, a negative impact on
36 human and environmental health. Human activities (*e.g. industries, care institutions, animal farming*)
37 generate metal trace elements (MTE) and emerging organic contaminants (EOCs) which are spilled
38 into natural water stream. This pollution is very problematic since pollutants accumulate rapidly and
39 reach toxic concentrations for the environment and humans. Cadmium (Cd) and lead (Pb) are the most
40 common toxic MTE since they are both carcinogenic, mutagenic and reprotoxic. EOCs are also a real
41 concern (Lapworth et al., 2012). They include a wide array of different categories such as
42 pharmaceutical compounds, pesticides or food additives. They have undesirable impacts on the
43 environment and induce human health damages (Jean et al., 2012). They also generate microbial drug
44 resistance (Andersson et al., 2012). Despite their lower concentration compared to MTE, they have a
45 longer half-time life and persist in the environments in which they are found. Nowadays, the sewage
46 treatment plants are not sufficiently effective to completely purify these contaminated waters. It is
47 therefore crucial to find low-cost, sustainable and effective solutions to manage these pollutants and to
48 clean water.

49 Research and technology have led to the discovery of diversified techniques for the removal of
50 pollutants (Rodriguez-Narvaez et al., 2017). Among them, sorption is one of the most preferred mainly
51 because it is economically viable whereas the other practices are much more expensive (Sophia et al.,
52 2018). This technique consists in the use of materials which are able to sorb inorganic and organic
53 pollutants in order to remove them from water. Activated charcoal (AC) is the most widely used

54 sorbent due to its efficiency and availability (Burakov et al., 2018). However, its cost remains a
55 limiting factor for a large-scale applications. To overcome this main drawback, sorbents like zeolites,
56 mineral clays, industrial solid wastes and nanostructured materials have been developed (Burakov et
57 al., 2018) and new sorbents have recently been identified from crude or modified biomass (e.g.
58 biochar, coffee grounds, biopolymers, agricultural waste) (Bhatnagar et al., 2015; Zhou et al., 2016;
59 Janus et al., 2017; Ahsan et al., 2018; Luo et al., 2018; Naga Babu et al., 2018; Tursi et al., 2018;
60 Żółtowska-Aksamitowska et al., 2018; Fernández-López et al., 2019; Fu et al., 2020 ;).

61 Since the end of the 20th century, several studies have been carried out on ash-based sorbents. Ashes
62 are secondary products generated in very large quantities by industries and they are often considered
63 as a waste. From an ecological and economical point of view, they may constitute sorbents of choice.
64 In this context, Gupta and coworkers (2000, 2002, 2003) tested the efficiency of bagasse fly ashes in
65 the removal of dyes, lindane, malathion, Cd and copper from contaminated water (Gupta and Ali,
66 2000). More recently, research efforts have been focused on ash-based sorbents from *Citrullus*
67 *colocynthis* (Qasemi et al., 2018), coir pith (Bahar et al., 2018) or Jamun (*Syzygium cumini*) leaves
68 (Tirkey et al., 2018) in order to respectively remove phenol, arsenic and fluoride from contaminated
69 water.

70 To tackle the complex problem of contaminated water, new low-cost and sustainable sorbents were
71 developed from two different biomass ashes (*Lolium perenne* L. and *Triticum aestivum* L.) with or
72 without acidification. Because MTE contamination and EOCs are both extremely problematic, the
73 retention performance of representative molecules selected from the two classes of pollutants was
74 evaluated on acidified and non-acidified ashes. The sorption tests reported herein covered the use
75 Cd, Pb and four poorly studied EOCs: a nonsteroidal anti-inflammatory drug (diclofenac, DCF;
76 Bonnefille et al., 2018), an antibiotic (sulfamethoxazole, SFX; Wang et al., 2018), a female hormone
77 (17 α -ethinylestradiol, EE2; Jackson et al., 2019) and an endocrine disruptor (triclosan, TCL; Thomaidi
78 et al., 2017; Zaltauskaite et al., 2018). The chemical structure, selected chemical and physical
79 properties as well as pictograms of these compounds are described in Table 1.

80

81 **Materials and Methods**

82

83 *Organic and inorganic pollutants*

84 All chemicals and reagents used were of analytical grade. Sulfamethoxazole (SFX), triclosan (TCL)
85 and 17 α -ethynylestradiol (EE2) were obtained from Sigma Aldrich and diclofenac (DCF) from TCI
86 Chemicals. These organic pollutants were dissolved in a mixture of ultra-pure water (18 M Ω -cm at 25
87 $^{\circ}$ C) and absolute ethanol (purchased from Carlo Erba Reagents) as follows: 50/50 EtOH/H₂O for EE2,
88 40/60 EtOH/H₂O for DCF, 30/70 EtOH/H₂O for TCL and 100 H₂O for SFX. The Cd and Pb metal
89 stock solutions at 1000 mg L⁻¹ in 2% HNO₃ (Chemical Products for Analysis, Association Corporation
90 Standard Distribution, C.P.A. groupe A.C.S.D., Voisins le Bretonneux, France) were used for the
91 preparation of diluted metal solutions with ultra-pure water.

92

93 *Solid support*

94 Activated Charcoal (AC) Norit SA-2 from Acros Organics was chosen as the reference sorbent. The
95 properties of this material are given hereafter: iodine number: 850; specific surface area: 950 m² g⁻¹;
96 apparent density: 460 kg m⁻³; particle size D₁₀ (μ m): 3; particle size D₅₀ (μ m): 20; particle size D₉₀
97 (μ m): 140; ash content (% mass): 9. The first investigated sorbent was a miscanthus biochar (MB),
98 described in detail in Janus et al. (2017). Four additional sorbents were produced for the current study
99 using shoots of ryegrass (*Lolium perenne* L.) and wheat straw (*Triticum aestivum* L.). Two sorbents
100 were obtained from crude ashes of ryegrass (R) and wheat straw (WS) and the others resulted from an
101 acidic treatment of the respective crude ashes, named AR and AWS, respectively. The shoots of
102 ryegrass were harvested in a private lawn without specificity. They were transformed into ashes in a
103 muffle furnace (Nabertherm P330, Lilienthal, Germany) under air flow using the following
104 temperature program: (i) 20 to 250 $^{\circ}$ C in 30 min, (ii) 250 $^{\circ}$ C for 1 hour, (iii) 250 to 500 $^{\circ}$ C in 2 hours
105 and (iv) 500 $^{\circ}$ C for 8 hours. The wheat straw ashes were obtained from a spirulina powder producer
106 (La Spiruline de Marc, Saint-Léger-lès-Authie, France). The acidification of ashes was conducted
107 using a 2M HCl aqueous solution with a weight ratio ashes/HCl: 1/10. The mixture was stirred at 70
108 $^{\circ}$ C for 2 hours and then, filtered. The resulting solid was then dried at 105 $^{\circ}$ C for 16 hours.

109

110 *Mineralisation*

111 300 mg of ashes (R, WS, AR and AWS) were added to a mixture of 37% HCl (4.5mL) and 70%
112 HNO₃ (1.5 mL). The resulting suspension was heated at 120 °C for 90 min in a digester (HotBlock™
113 Environmental Express®SC100, Charleston, USA). Ultra-pure water was then added until reaching a
114 total volume of 25 mL and was then filtered over an acetate Millipore membrane (0.45 µm porosity).
115 The concentrations of Cd and Pb were measured by flame atomic absorption spectrometry (FAAS;
116 AA-6800 Shimadzu, Tokyo, Japan) following the recommendation described in the literature
117 (Waterlot and Douay, 2009; Savio et al., 2010). The limits of detection (LD) of Cd and Pb were 2.1 µg
118 L⁻¹ and 41 µg L⁻¹, respectively (Waterlot and Hechelski, 2019). It is worth mentioning that the
119 concentrations of Cd and Pb in R, WS, AR and AWS were below the limit of detection.

120

121 *Sorption experiments*

122 With the aim of getting as close as possible to an industrially exploitable process, the adsorption
123 experiments were carried out by eluting the contaminated solutions on lab-made cartridges (Redisep
124 Rf column with a diameter of 1.5 cm from Teledyne Technologies Inc.) filled with ashes from the
125 selected solid supports (AC, MB, R, WS, AR or AWS; Figure 1). All experiments were conducted
126 under normal temperature and pressure (NTP) conditions (20 °C; 1 atm). After adding and packing
127 200 mg of cotton, 1000 mg of sorbent were introduced in the column. Then, 25 mL of artificially
128 contaminated water (20 mg pollutant L⁻¹) were added into the column. After the filtration (30 min
129 were necessary for the complete elution), the resulting solutions were analysed in order to select
130 sorbents with the best retention capacity. This capacity was then defined using solutions of different
131 concentrations (from 10 mg L⁻¹ to 1000 mg L⁻¹) on 250 mg of sorbent by means of Freundlich and
132 Langmuir models. The concentrations of Cd and Pb in the contaminated water samples before and
133 after filtration were measured by FAAS.

134

135 *EOCs and PAHs analyses*

136 EOCs (TCL, SFX, EE2 and DCL) were analysed on a Shimadzu UFLC system (Prominence,
137 Shimadzu, Tokyo, Japan) equipped with a LC-20AD quaternary pump, an automatic refrigerated

138 sample injector (SIL-20AC), a thermostatted column compartment (CTO-20AC), a five-channel
139 online degasser (DGU-20A5R) and a diode array detector (SPD-M20A). All material was linked
140 through a CBM-20 controller monitored by the LabSolutions® software (Shimadzu) to acquire and
141 process the chromatograms. The column used in the current study was a Kinetex®-C18 column (250
142 mm x 4.6 mm) packed with 5 µm core-shell particles (Phenomenex, Le Pecq, France). The calibration
143 curves were obtained using solutions of single organic pollutant (SFX, EE2, TCL or DCL) at the
144 following concentrations: 0.1, 0.2, 0.5, 0.8, 1, 2, 5, 8, 10, 15 and 20 mg L⁻¹. The limits of detection
145 (LD) and quantification (LQ) were determined from the ratios signal-to-noise of 3 and 10, respectively
146 (Sun et al., 1998; Santos et al., 2007). A list of selected parameters was given in Table 2.

147 Due to the potential release of polycyclic aromatic hydrocarbons (PAHs) from the biochar to the
148 purified solutions (Janus et al., 2017), naphthalene, fluorene, acenaphthene, phenanthrene, anthracene,
149 fluoranthene, pyrene, chrysene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene,
150 benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*g,h,i*]perylene, and indeno[1,2,3-*c,d*]pyrenes were
151 analysed in filtrates according to the procedure described in previous studies (Goulas et al., 2015;
152 Waterlot and Goulas, 2016). The chromatographic system was fitted with an FLD (RF-20A) set at
153 varying excitation and emission wavelengths. A standard solution (EPA-610 OekanalR; Sigma-
154 Aldrich, Saint-Quentin Fallavier, France) of these 15 EPA PAHs was diluted to a concentration of 500
155 g L⁻¹ with acetonitrile (HPLC quality, purity >99.9%, ChromasolvR; Sigma–Aldrich) as working
156 solution.

157

158 **Results and discussion**

159

160 *Preliminary results obtained with miscanthus biochar, shoots of ryegrass and wheat straw*

161 *Miscanthus biochar (MB)*

162 Janus et al. (2017) showed that MB (0.5 g) was able to sorb Cb (78-96%) and Pb (98-99%) from
163 solution at 0.06 mg Cd kg⁻¹ and at 4 mg Pb kg⁻¹ in batch conditions. These results have been recently
164 confirmed by Boni et al (2018, 2020). As indicated in Table 3, MB was efficient to sorb Pb (99.7%)
165 from the stock solution at 20 mg L⁻¹ (25 mL) using the newly engineered cartridge filtration system

166 (Figure 1). In contrast, Cd sorption was very low (15.3%). This means that only 76.5 mg of Cd were
167 adsorbed per g of MB support. As shown in Table 3, this support was not effective either in the
168 retention of EE2, SFX and DCF (respectively 5%, 0% and 0%). Contrariwise, 87.7% of the initial
169 TCL concentration was retained on the MB support, which was produced at 600 °C (Janus et al.,
170 2017). In their review, Tomczyk et al. (2020) reported the retention of compounds like phenolic acid
171 and carboxyl functions when biochars were produced up to 480 °C. Above this temperature, the
172 authors revealed a decrease of the cation exchange capacity (CEC) and the formation of aromatic
173 carbon, improving π - π interactions with aromatic pollutants. These both phenomena could explain
174 why TCL was the only retained compound among the organic pollutants studied. Drawbacks in using
175 biochars as sorbents were related to the release of PAHs as described in literature (Liu et al., 2019;
176 Wang et al., 2019). In the current study, fluorene, acenaphthene, phenanthrene and anthracene were
177 detected in solutions after their filtration on biochars. Concentrations of these PAHs were 28.35 ± 1.15
178 $\mu\text{g L}^{-1}$, $17.25 \pm 8.56 \mu\text{g L}^{-1}$, $6.01 \pm 2.08 \mu\text{g L}^{-1}$, $4.00 \pm 1.29 \mu\text{g L}^{-1}$, respectively.

179 Shoots of ryegrass and wheat straw

180 Ashes from ryegrass (R) and wheat straw (WS) were used as sorbents as well as their respective
181 acidified forms (AR, AWS). These supports were compared to the activated charcoal (AC) support,
182 used as reference. The first experiments were conducted with pollutants in solution at 20 mg L^{-1} using
183 1 g of sorbent. As shown in Table 4, the MTE concentrations measured in the filtrates were below
184 0.05 mg L^{-1} meaning that AC has retained 99.96% and 99.75% of Cd and Pb from the initial solution.
185 Similar results were obtained with ashes from ryegrass (R) and wheat straw (WS) since the retention
186 of Cd was 99.71% and 99.99%, respectively and 99.50% and 99.92%, respectively for Pb. In contrast,
187 the efficiency of these two supports after their acidification (AR, AWS) dramatically decreased,
188 making it impossible to use them for the intended purpose.

189 Reference support (AC), non-acidified and acidified supports from biomass were also used in the
190 retention of organic pollutants. 25 mL of each solution (TCL, SFX, EE2 and DCF at 20 mg L^{-1}) were
191 passed through the studied sorbents (1 g; Figure 1) and the resulting filtrates were analysed.
192 Depending on the organic pollutants, the retention varied from 97.45% to 99.99% by using activated
193 charcoal (Table 5). This result is not surprising since activated charcoal was described as an effective

194 support for the removal of emerging pollutants like pesticides, pharmaceuticals, endocrine disrupting
195 chemicals due to the presence of various mechanisms (π - π interactions, hydrogen bonds and electron
196 donor-acceptor complex formation) and chemical functions (Jeirani et al., 2017). Ashes from ryegrass
197 didn't retain any of the studied organic pollutants and the retention of these pollutants using ashes
198 from WS was very low, ranging from 0% to 30.43%. Acidified supports were more appropriate to the
199 retention of TCL, SFX and DCF since the percentages of retention were in the range of 86.55% to
200 99.99%. The best results were obtained with ashes AWS since the concentration of TCL, SFX and
201 DCF in filtrates were below the limits of detection. Regarding EE2, this support is less effective than
202 AC since the achieved retention was only 43.83% versus 97.46% (Table 5). As shown in Table 1, the
203 chemical composition, molecular structure, functional groups, dipole moment and lipophilicity of EE2
204 are very different from those of TCL, SFX and DCF. On the other hand, the hydrophobic property of
205 EE2 is higher than that of the three other compounds. Consequently, the hydrophobicity partitioning
206 does not seem to be the main sorption mechanism in this case. This result correlated well with the
207 studies conducted by several authors which highlighted that this mechanism was dominant on biochar,
208 activated charcoal, sediment and soil (Sun et al., 2012; Li et al., 2013; Guo et al., 2013; Trigo et al.,
209 2014).

210

211 *Sorption Isotherms and modelling*

212 The sorption capacity was evaluated for the reference support (AC) and the best biomass supports
213 (WS and AWS) using Cd and TCL as metal and organic pollutants. Experiments were conducted in
214 three independent experiments using the system described in Figure 1 in which 250 mg of solid
215 support were preliminary added to the addition of contaminated water (25 mL).

216 Cd isotherms were presented in Figure 2A. Excellent linearity was obtained up to 350 mg L⁻¹ using
217 WS (R² = 0.999) and 200 mg L⁻¹ for CA (R² = 0.996). In the current experimental conditions, the two
218 sorption curves clearly highlighted a best capacity of Cd sorption of ashes from wheat straw since (i)
219 the slope of the curve obtained for AC is the lowest and (ii) Q_e value is lower than that obtained with
220 WS.

221 Sorption isotherms of TCL using AC and acidified ashes from wheat straw (AWS) are presented in
222 [Figure 2B](#). Although AWS support was more efficient in the retention of TCL between 10 mg L⁻¹ and
223 60 mg L⁻¹ than AC, the sorption capacity of both supports was quite similar at 80 mg L⁻¹ (Q_e = 5.04
224 mg g⁻¹ for AC and Q_e = 4.76 mg g⁻¹ for AWS). It is worth noting that the maximum sorption capacity
225 of AC was at 100 mg TCL L⁻¹.

226 [Langmuir and Freundlich models were used for modeling adsorption data \(Hamdaoui and](#)
227 [Naffrechoux., 2007\)](#).

228 Langmuir model

229 Langmuir isotherm model suggests that sorption occurs as monolayer exposure on homogeneous
230 surface comprising energetically equivalent sites without any steric hindrance and lateral interactions
231 between sorbed molecules. The energy of sorption is constant and is independent on the degree of
232 occupation of the sorbent active centers. [One of the linear expressions of the Langmuir isotherm is](#)
233 [given by the equation \(1\)](#).

$$234 \quad 1/q_e = 1/C_e b q_m + 1/q_m, \quad (1)$$

235 where q_e is the amount of pollutant adsorbed per g of support (mg g⁻¹), C_e represents the equilibrium
236 concentration of the adsorbate material (mg L⁻¹), q_m is the maximum adsorption capacity (mg g⁻¹) and
237 b is a constant associated to the free energy of adsorption (L mg⁻¹).

238 Langmuir isotherms of Cd and TCL were plotted in [Figures 3A and 3B](#), respectively. Very good
239 correlation coefficients were obtained for each modality, ranging from 0.975 to 0.996 ([Table 6](#)). From
240 the linear equation, the Langmuir constants (b and q_m) were calculated ([Table 6](#)). The maximal
241 sorption capacities of SW/ASW were 2.6 and 3.6-fold higher than those of AC. On the other hand, for
242 the two pollutants, b values for AC were slightly higher than those obtained for SW/ASW. These
243 results indicated that the affinity of Cd and TCL for AC were slightly higher than for SW/ASW
244 ([Blázquez et al., 2012](#)). This constant is very interesting since it can be expressed as a function of the
245 Gibbs free energy according to the equation (2) ([Djelloul 2014](#)).

$$246 \quad \text{Ln}(1/b) = \Delta G^\circ/RT \quad (2)$$

247 where ΔG° is the Gibbs free energy of the sorption reaction (J mol^{-1}), b is a constant associated to the
248 free energy of adsorption (L mol^{-1}), T is the temperature (K) and R the universal gas constant (J mol^{-1}
249 K^{-1}).

250 This Gibbs free energy is expressed by the equation (3).

$$251 \quad \Delta G^\circ = -RT \ln b \quad (3)$$

252 Numerical values of ΔG° were negative for both Cd and TCL on AC ($-10.72 \text{ KJ mol}^{-1}$ and -20.70 KJ
253 mol^{-1} , respectively) as well as on WAS/AWS ($-7.42 \text{ KJ mol}^{-1}$ and $-18. \text{KJ mol}^{-1}$). In this regard, the
254 adsorption processes onto AC and WS/AWS supports were found to be spontaneous.

255 As described by Hamdaoui and Naffrechoux (2007), the equilibrium parameter R_L was calculated
256 following the equation (4).

$$257 \quad R_L = 1/(1 + b \cdot C_0) \quad (4)$$

258 where C_0 is the initial concentration of the adsorbate in solution (mg L^{-1}) and b is a constant associated
259 to the free energy of adsorption (L mg^{-1}). Depending of the value of the Hall parameter (R_L), the
260 sorption can be defined as irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or
261 unfavourable ($R_L > 1$).

262 Figure 4 shows the variation of the Hall parameter of Cd (Fig. 4A) and TCL (Fig. 4B) using the two
263 supports studied. Whatever the initial concentration was, the R_L value ranged from 0.4 to 1, reflecting
264 that the sorption was favourable. As shown in Figure 5, the hall parameters decreased when the initial
265 concentrations increased. These results mean that the sorption was the most favourable at high initial
266 concentration. On the other hand, the lowest values of the Hall parameters for the activated charcoal
267 correlated well with the lowest values of the free Gibbs energy, indicating that the sorption of Cd and
268 TCL on AC was more spontaneous and less reversible than the sorption process on WS and AWS.

269 Freundlich model

270 Freundlich isotherm model can be used for non-ideal sorption on heterogeneous surfaces and
271 multilayer adsorption. This model is the earliest known empirical model which is shown to be stable
272 with exponential distribution of active sites, characteristic of heterogeneous surfaces. The linear form
273 of the Freundlich model is given by the following equation (5).

$$274 \quad \ln(q_e) = \ln K_f + 1/n \ln(C_e), \quad (5)$$

275 where q_e is the amount of pollutant adsorbed per g of support (mg g^{-1}), C_e represents the equilibrium
276 concentration of the adsorbate material (mg L^{-1}). K_f and n are both the Freundlich constants. K_f is
277 related to the relative adsorption capacity of the sorbent when the equilibrium concentration equals 1
278 mg L^{-1} and is a characteristic of the sorption system (adsorbent and adsorbate) ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$)
279 (Mallek et al., 2018) whereas n gives information about adsorption intensity (dimensionless).

280 Freundlich isotherms of Cd and TCL were presented in Figures 5A and 5B, respectively. Very good
281 correlation coefficients were obtained for each modality, ranging from 0.969 to 0.996 (Table 6).
282 Freundlich constants, K_f and n , were assessed from the origin intercept and the slope of the curves
283 (Fig. 5A and 5B) as indicated by the linearized equation (5). As shown in Table 6, the relative sorption
284 capacity of Cd on AC ($K_f = 0.08$) was lower than that on WS ($K_f = 0.16$) suggesting that AC is less
285 efficient than WS to sorb Cd when the concentration of initial solution is 1 mg L^{-1} . This result needs to
286 be considered with caution since Asuquo et al. (2017) demonstrated that the Langmuir isotherm is a
287 better isotherm for the description of Cd on AC than the Freundlich isotherm. For TCL, this constant
288 was equal ($K_f = 0.17$), suggesting the same efficacy of AC and AWS supports in the sorption of TCL
289 at 1 mg L^{-1} . According to the study of Mallek et al. (2018), the n constant provides information about
290 the intensity of the sorption. It can be considered as favourable ($2 < n < 10$), moderate ($1 < n < 2$) or
291 difficult ($0 < n < 1$). In the current study, n was in the range 1 – 2, indicating that the intensity of the
292 sorption of Cd and TCL on AC and WS/AWS was moderate (Table 6). Nevertheless, it is worth
293 mentioning that the sorption intensity on the two studied supports seemed to be better for TCL than
294 Cd.

295

296 **Conclusion**

297 Among the three sorbents studied, MB had the inconvenient of releasing intrinsic PAHs in filtrates.
298 For ashes from R and WS, modeling isotherms revealed that: i) WS ashes were an excellent MTE
299 extractor that exceeded the potential of well-known AC and ii) AR and AWS ashes were very
300 effective in eliminating the selected EOCs displaying equipotent or superior activity compared to AC.
301 Acidification of the sorbents allowed to modulate their affinity for targeted MTE or EOCs. Additional

302 efforts are now needed to study the retention capacity of combos of pollutants on these supports and to
303 test the technology *in natura*.

304

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310

311 **Declaration of competing interest**

312 The authors declare that they have no known competing financial interests or personal relationships
313 that could have appeared to influence the work reported in this paper.

314

315 **References**

316 Ahsan, M.A., Islam, M.T., Imam, M.A., Hyder, A.H.M.G., Jabbari, V., Dominguez, N., Noveron, J.C.,
317 2018. Biosorption of bisphenol A and sulfamethoxazole from water using sulfonated coffee waste:
318 Isotherm, kinetic and thermodynamic studies. *J. Environ. Chem. Eng.* 6, 6602–6611.

319 Andersson, D.I., Hughes, D., 2012. Evolution of antibiotic resistance at non-lethal drug
320 concentrations. *Drug Resist. Updates* 15, 162–172.

321 Asuquo, E., Martin, A., Nzerem, P., Siperstein, F., Fan X., 2017. Adsorption of Cd(II) and Pb(II) ions
322 from aqueous solutions using mesoporous activated carbon adsorbent: Equilibrium, kinetics and
323 characterization studies. *J. Environ. Chem. Eng.* 5, 679–698.

324 Bahar, M.M., Mahbub, K.R., Naidu, R., Megharaj, M., 2018. As(V) removal from aqueous solution
325 using a low-cost adsorbent coir pith ash: Equilibrium and kinetic study. *Environ. Technol. Innov.* 9,
326 198–209.

327 Bhatnagar, A., Sillanpää, M., Witek-Krowiak, A., 2015. Agricultural waste peels as versatile biomass
328 for water purification – A review. *Chem. Eng. J.* 270, 244–271.

329 Blázquez, G., Martín-Lara, M.A., Dionisio-Ruiz, E., Tenorio, G., Calero, M. 2012. **Copper biosorption**
330 **by pine cone shell and thermal decomposition study of the exhausted biosorbent.** J. Ind. Eng. Chem.
331 18, 1741–1750.

332 Boni, M.R., Chiavola, A, Marzedu, S. 2018. Application of biochar to the remediation of Pb-
333 contaminated solutions. Sustainability 10, 4440–1750.

334 Boni, M.R., Chiavola, A, Marzedu, S. 2020. Remediation of lead-contaminated water by virgin
335 coniferous wood biochar adsorbent: batch and column application. Water Air Soil Pollut. 231, 171–
336 187. Bonnefille, B., Gomez, E., Courant, F., Escande, A., Fenet, H., 2018. Diclofenac in the marine
337 environment: A review of its occurrence and effects. Mar. Pollut. Bull. 131, 496–506.

338 Burakov, A.E., Galunin, E.V., Burakova, I.V., Kucherova, A.E., Agarwal, S., Tkachev, A.G., Gupta,
339 V.K., 2018. Adsorption of heavy metals on conventional and nanostructured materials for wastewater
340 treatment purposes: A review. Ecotox. Environ. Safe. 148, 702–712.

341 Djelloul, K, 2014. Experimentation, modélisation et optimization de l'adsorption des effluents textiles.
342 Thesis, University Mohamed Khider De Briska, 116 pp.

343 Fernández-López, J.A., Angosto, J.M., Roca, M.J., Doval Miñarro, M., 2019. Taguchi design-based
344 enhancement of heavy metals bioremoval by agroindustrial waste biomass from artichoke. Sci. Total
345 Environ. 653, 55–63.

346 Fu, C., Zhang, H., Xia, M., Lei W., Wang, F., 2020. The single/co-adsorption characteristics and
347 microscopic adsorption mechanism of biochar-montmorillonite composite adsorbent for
348 pharmaceutical emerging organic contaminant atenolol and lead ions. Ecotox. Environ. Safe. 187,
349 109763.

350 Goulas, A., Louvel, B., Waterlot, C. 2015. Analytical method for determining polycyclic aromatic
351 hydrocarbon pollutants using ultra-fast liquid chromatography with fluorescence detection and the
352 new column packed with 5 µm Kinetex-C18 core-shell particles. Can. J. Chem. 93, 564–571.

353 Guo, X., Tian, B., Xin, L., (2013). Adsorption removal process and mechanism of diclofenac. Chinese
354 Journal of Environmental Engineering, 7(10), 3779–3784.

355 Gupta, V.K., Ali, I., 2000. Utilisation of bagasse fly ash (a sugar industry waste) for the removal of
356 copper and zinc from wastewater. Sep. Purif. Technol. 18, 131–140.

357 Gupta, V.K., Jain, C.K., Ali, I., Chandra, S., Agarwal, S., 2002. Removal of lindane and malathion
358 from wastewater using bagasse fly ash—a sugar industry waste. *Water Res.* 36, 2483-2490.

359 Gupta, V.K., Jain, C.K., Ali, I., Sharma, M., Saini, V.K., 2003. Removal of cadmium and nickel from
360 wastewater using bagasse fly ash—a sugar industry waste. *Water Res.* 37, 4038–4044.

361 Gupta, V.K., Mohan, D., Sharma, S., Sharma, M., 2000. Removal of Basic Dyes (Rhodamine B and
362 Methylene Blue) from Aqueous Solutions Using Bagasse Fly Ash. *Sep. Sci. Technol.* 35, 2097–2113.

363 Hamdaoui, O., Naffrechoux, E., 2007. Modeling of adsorption isotherms of phenol and chlorophenols
364 onto granular activated carbon Part I. Two-parameter models and equations allowing determination of
365 thermodynamic parameters. *J. Hazard. Mater.* 147, 381–394

366 Jackson, L.M., Felgenhauer, B.E., Klerks, P.L., 2019. Feminization, altered gonadal development, and
367 liver damage in least killifish (*Heterandria formosa*) exposed to sublethal concentrations of 17 α -
368 ethinylestradiol. *Ecotox. Environ. Safe.* 170, 331–337.

369 Janus, A., Pelfrène, A., Sahmer, K., Heymans, S., Deboffe, C., Douay, F., Waterlot, C., 2017. Value of
370 biochars from *Miscanthus x giganteus* cultivated on contaminated soils to decrease the availability of
371 metals in multicontaminated aqueous solutions. *Environ. Sci. Pollut. Res.* 24, 18204–18217.

372 Jean, J., Perrodin, Y., Pivot, C., Trepo, D., Perraud, M., Droguet, J., Tissot-Guerraz, F., Locher, F.,
373 2012. Identification and prioritization of bioaccumulable pharmaceutical substances discharged in
374 hospital effluents. *J. Environ. Manage.* 103, 113–121.

375 Jeirani, Z., Hui Niu, C., Soltan, J., 2017. Adsorption of emerging pollutants on activated carbon. *Rev.*
376 *Chem. Eng.* 33, 491–522.

377 Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S., 2012. Emerging organic contaminants in
378 groundwater: A review of sources, fate and occurrence. *Environ. Pollut.* 163, 287–303.

379 Li, J., Jiang, L., Xiang, X., Xu, S., Wen, R., Liu, X., 2013. Competitive sorption between 17 α -ethinyl
380 estradiol and bisphenol A /4-n-nonylphenol by soils. *J. Environ. Sci.* 25, 1154–1163.

381 Liu, X., Ji, R., Shi, Y., Wang, F., Chen W., 2019. Release of polycyclic aromatic hydrocarbons from
382 biochar fine particles in simulated lung fluids: Implications for bioavailability and risks of airborne
383 aromatics. *Sci. Total. Environ.* 655, 1159–1168.

384 Luo, M., Lin, H., Li, B., Dong, Y., He, Y., Wang, L., 2018. A novel modification of lignin on
385 corncob-based biochar to enhance removal of cadmium from water. *Biores. Technol.* 259, 312–318.

386 Naga Babu, A., Reddy, D.S., Kumar, G.S., Ravindhranath, K., Krishna Mohan, G.V., 2018. Removal
387 of lead and fluoride from contaminated water using exhausted coffee grounds based bio-sorbent. *J.*
388 *Environ. Manage.* 218, 602–612.

389 Mallek, M., Chtourou, M., Portillo, M., Monclús, H., Walha, K., Salah, A. ben, Salvadó, V., 2018.
390 Granulated cork as biosorbent for the removal of phenol derivatives and emerging contaminants. *J.*
391 *Environ. Manage.* 223, 576–585.

392 Qasemi, M., Afsharnia, M., Zarei, A., Najafpoor, A.A., Salari, S., Shams, M., 2018. Phenol removal
393 from aqueous solution using *Citrullus colocynthis* waste ash. *Data in Brief* 18, 620–628.

394 Rodriguez-Narvaez, O.M., Peralta-Hernandez, J.M., Goonetilleke, A., Bandala, E.R., 2017. Treatment
395 technologies for emerging contaminants in water: A review. *Chem. Eng. J.* 323, 361–380.

396 Santos, J.L., Aparicio, I., Alonso, E., 2007. A new method for the routine analysis of LAS and PAH in
397 sewage sludge by simultaneous sonication-assisted extraction prior to liquid chromatographic
398 determination. *Anal. Chim. Acta.* 605, 102–107.

399 Savio, M., Cerutti, S., Martinez, L.D., Smichowski, P., Gil, R.A., 2010. Study of matrix and spectral
400 interferences in the determination of lead in sediments, sludges and soils by SR-ETAAS using slurry
401 sampling. *Talanta* 82, 523–527.

402 Sophia, A.C., Lima, E.C., 2018. Removal of emerging contaminants from the environment by
403 adsorption. *Ecotox. Environ. Safe.* 150, 1–17.

404 Sun F., Littlejohn, D., Gibson, M.D., 1998. Ultrasonication extraction and solid phase extraction
405 clean-up for determination of US EPA 16 priority pollutant polycyclic aromatic hydrocarbons in soils
406 by reversed-phase liquid chromatography with ultraviolet absorption detection. *Anal. Chim. Acta.* 364,
407 1–11.

408 Sun K., Jin, J., Gao, B., Zhang, Z.-Y., Wang, Z., Pan, Z.-Z., Xu, D., Zhao, Y., 2012. Sorption of 17 α -
409 ethinyl estradiol, bisphenol A and phenanthrene to different size fractions of soil and sediment.
410 *Chemosphere* 88, 577–583.

411 Thomaidi, V.S., Matsoukas, C., Stasinakis, A.S., 2017. Risk assessment of triclosan released from
412 sewage treatment plants in European rivers using a combination of risk quotient methodology and
413 Monte Carlo simulation. *Sci. Total Environ.* 603–604, 487–494.

414 Tirkey, P., Bhattacharya, T., Chakraborty, S., 2018. Optimization of fluoride removal from aqueous
415 solution using Jamun (*Syzygium cumini*) leaf ash. *Process Safe. Environ. Protect.* 115, 125–138.

416 Tomczyk, A., Sokolowska, Z., Boguta, P., 2020. Biochar Physicochemical properties: pyrolysis
417 temperature and feedstock kind effects. *Rev. Environ. Sci. Bio.* 19, 191–225.

418 Trigo, C., Spokas, K. A., Cox, L., & Koskinen, W. C., 2014. Influence of soil biochar aging on
419 sorption of the herbicides MCPA, nicosulfuron, terbuthylazine, indaziflam, and
420 fluoroethyldiaminotriazine. *J. Agri. Food. Chem.* 62, 10855–10860.

421 Tursi, A., Beneduci, A., Chidichimo, F., De Vietro, N., Chidichimo, G., 2018. Remediation of
422 hydrocarbons polluted water by hydrophobic functionalized cellulose. *Chemosphere* 201, 530–539.

423 Wang, C., Liang, S., Zhang, Y., 2018. The ecological competition and grazing reverse the effects of
424 sulfamethoxazole on plankton: a case study on characterizing community-level effect. *Environ. Sci.*
425 *Pollut. Res.* 25, 17283–17288.

426 Wang, C., Odinga, E.S., Zhang, W., Zhou, X., Yang, B., Waigi, M.G., Gao, Y., 2019. Polyaromatic
427 hydrocarbons in biochars and human health risks of food crops grown in biochar-amended soils: A
428 synthesis study. *Environ. Int.* 130, 104899.

429 Waterlot, C., Bidar, G., Pruvot, C., Douay F., 2011. Analysis of cadmium in water extracts from
430 contaminated soils with high arsenic and iron concentration levels. *J. Environ. Sci. Eng.* 5, 271–280.

431 Waterlot, C., Douay, F., 2009. The problem of arsenic interference in the analysis of Cd to evaluate its
432 extractability in soils contaminated by arsenic. *Talanta* 80, 716–722.

433 Waterlot, C., Goulas, A., 2016. Temperature effects on retention and separation of PAHs in reversed-
434 phase liquid chromatography using columns packed with fully porous and core-shell particles. *J.*
435 *Chem-ny* 12 pages.

436 Waterlot, C., Hechelski, M., 2019. Benefits of ryegrass on multicontaminated soils. Part 1: Effects of
437 fertilizers on bioavailability and accumulation of metals. *Sustainability* 11, 5093-6013.

438 Zaltauskaite, J., Miskelyte, D., 2018. Biochemical and life cycle effects of triclosan chronic toxicity to
439 earthworm *Eisenia fetida*. *Environ. Sci. Pollut. Res.* 25, 18938–18946.

440 Zhou, J., Chen, H., Huang, W., Arocena, J.M., Ge, S., 2016. Sorption of atrazine, 17- α -estradiol, and
441 phenanthrene on wheat straw and peanut shell biochars. *Water Air Soil Pollut.* 227, 1–13.

442 Żółtowska-Aksamitowska, S., Bartczak, P., Zembrzuska, J., Jesionowski, T., 2018. Removal of
443 hazardous non-steroidal anti-inflammatory drugs from aqueous solutions by biosorbent based on chitin
444 and lignin. *Sci. Total Environ.* 612, 1223–1233.

445

446 **Table 1.** Structure, physicochemical properties and pictograms of the studied MTE and EOCs
 447 pollutants

448

	Chemical Structure	MW ^a (g mol ⁻¹)	Water solubility (mg L ⁻¹)	Log K _{ow} ^b	Pictogram
DCF		296.15	2.37	4.51	
SFX		253.28	610	0.89	
EE2		296.41	11.3	3.67	
TCL		289.54	10	4.76	
Cd	-	112.41	-	-	
Pb	-	207.20	-	-	

449 DCF: diclofenac; SFX: sulfamethoxazole; EE2: 17 α -ethinylestradiol; TCL: triclosan; Cd: cadmium;

450 Pb: lead.

451 ^a Molecular weight;

452 ^b Log octanol-water partition coefficient.

453

454 **Table 2:** UFLC analyses: composition of the mobile phase, λ_{\max} , retention time, limits of detection and
455 quantification for each organic pollutant

456

		CH ₃ CN/H ₂ O (%)	Flow rate (mL min ⁻¹)	λ_{\max} (nm)	Retention time (min)	LD ^a (mg L ⁻¹)	LQ ^b (mg L ⁻¹)
457							
458							
459	SFX	30/70	0.8	267	3.070	0.0026	0.0079
460	TCL	20/80	0.8	280	5.561	0.0448	0.1345
461	EE2	20/80	0.8	282	3.664	0.3181	0.9542
462	DCL	10/90	0.8	277	3.594	n.d	n.d

463 ^a limit of detection; ^b limit of quantification ; n.d.: no determined

464

465 **Table 3:** Concentration of metals in solution after filtration of artificially contaminated water
466 ([metal] or [organic pollutant] = 20 mg L⁻¹, V = 25 mL, mass of support = 1 g) on miscanthus biochar
467 (MB)
468

[Cd] (mg L ⁻¹)	[Pb] (μg L ⁻¹)	[TCL] (mg L ⁻¹)	[EE2] (mg L ⁻¹)	[SFX] (mg L ⁻¹)	[DCF] (mg L ⁻¹)
16.95	52.7	2.47	19.5	20	20

469
470 Indicated values are the mean of two independent experiments.
471

472 **Table 4:** Residual concentration of filtrates after filtration of contaminated solutions (at 20 mg L⁻¹)
473 using 1 g of solid support

Support	[Cd] mg L ⁻¹	[Pb] mg L ⁻¹
AC	0.00420	0.0492
R	0.00525	0.101
WS	<LD*	0.0362
AR	4.29	12.60
AWS	17.60	6.88

474

475 * LD = 0.0021 µg L⁻¹

476 AC=activated charcoal Norit® SA-2; R=ryegrass ashes; WS= wheat straw ashes; AR=acidified
477 ryegrass ashes; ACS=acidified wheat straw ashes.

478 Indicated values are the mean of two independent experiments.

479

480 **Table 5:** Residual concentration in solutions after their filtration using 1 g of solid support

Support	EE2 (mg L ⁻¹)	TCL (mg L ⁻¹)	SFX (mg L ⁻¹)	DCF (mg L ⁻¹)
AC	0.508	0.073	0.016	<LD
R	20	20	<LD	20
WS	17	13.915	15.65	20
AR	18.135	2.690	1.835	<LD
AWS	11.235	<LD	<LD	<LD

481 AC=activated charcoal Norit® SA-2; R=ryegrass ashes; WS= wheat straw ashes; AR=acidified

482 ryegrass ashes; ACS=acidified wheat straw ashes.

483 Indicated values are the mean of two independent experiments.

484

485 **Table 6:** Langmuir and Freundlich constants of Cd and TCL sorption on AC and WS/AWS

Pollutant	Support	Langmuir constants			Freundlich constants		
		q_m ($mg\ g^{-1}$)	b ($L\ mg^{-1}$)	R^2	K_f^*	n	R^2
Cd	AC	145.5	7.23E-04	0.993	0.08	1.01	0.983
	WS	529.1	1.87E-04	0.996	0.16	1.09	0.996
TCL	AC	6.36	1.81E-02	0.975	0.17	1.35	0.975
	AWS	16.6	6.44E-03	0.996	0.17	1.26	0.969

486

487 * Unit of K_f is $mg^{1-(1/n)} L^{1/n} g^{-1}$

488 AC=activated charcoal Norit® SA-2; WS= wheat straw ashes; ACS=acidified wheat straw ashes.

489

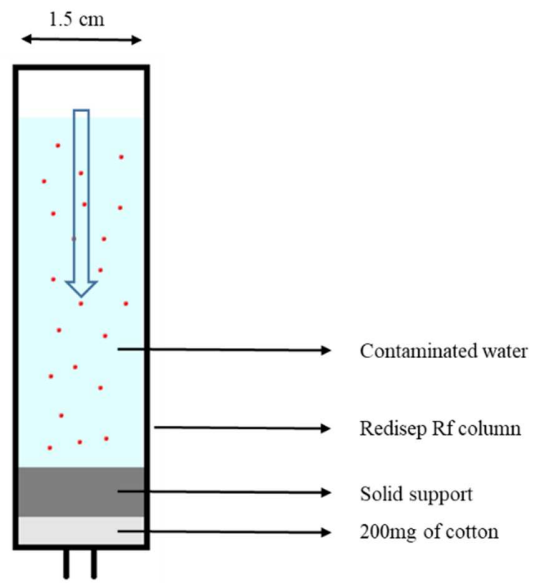


Figure 1: Lab-engineered cartridge filtration system

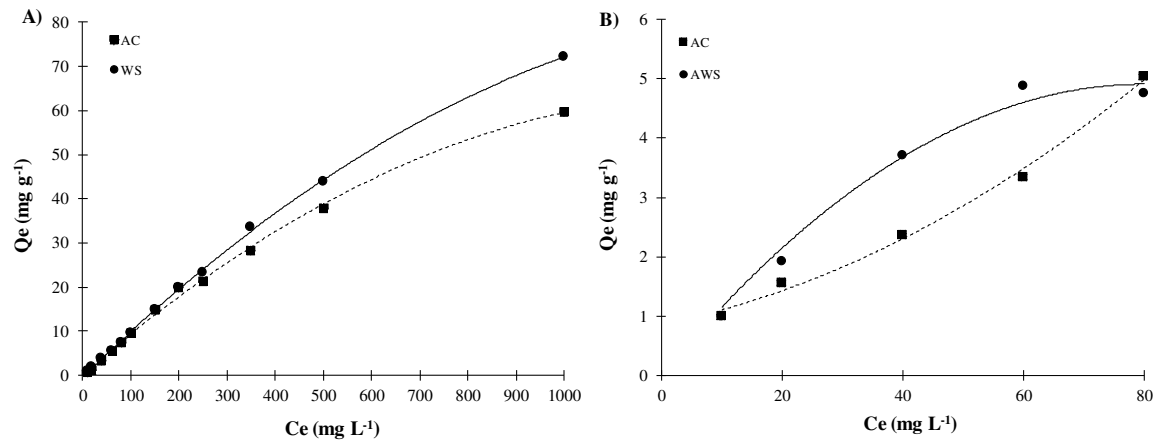


Figure 2: Sorption isotherm of Cd (A) and TCL (B) on AC and WS/AWS

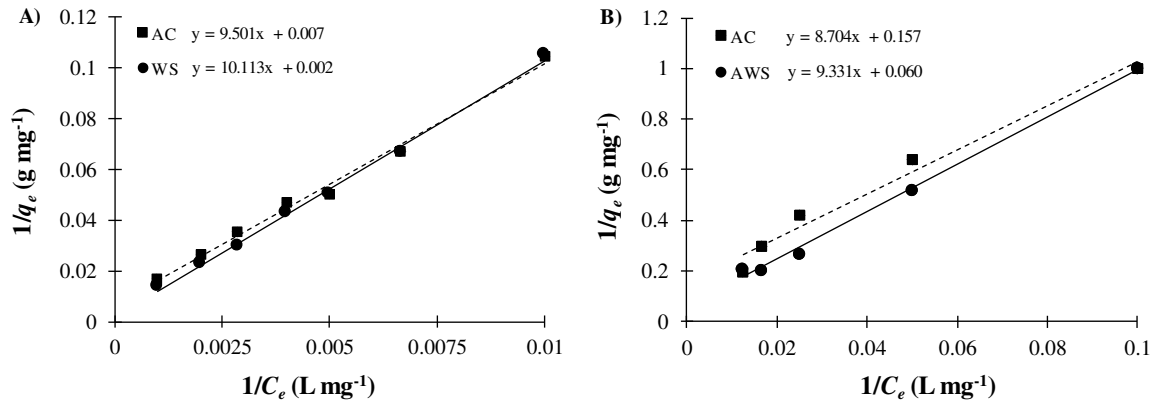


Figure 3: Langmuir isotherm on AC and WS/AWS; A) Cd and B) TCL

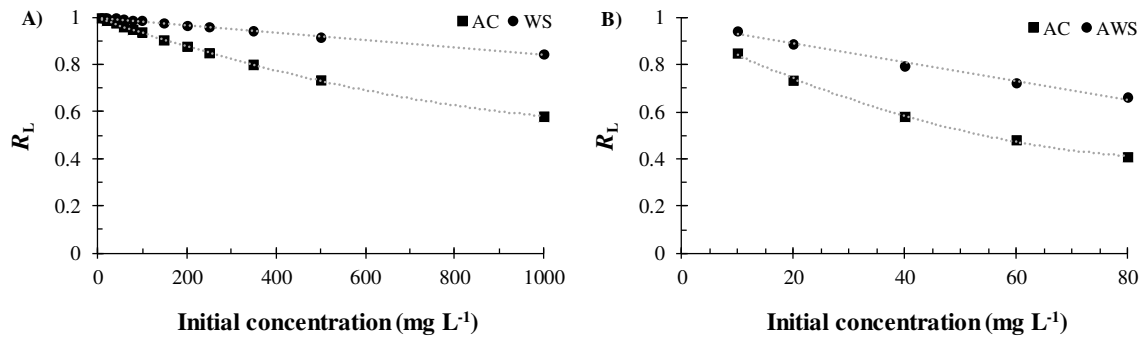


Figure 4: Variation of the Hall parameter; A) Cd and B) TCL

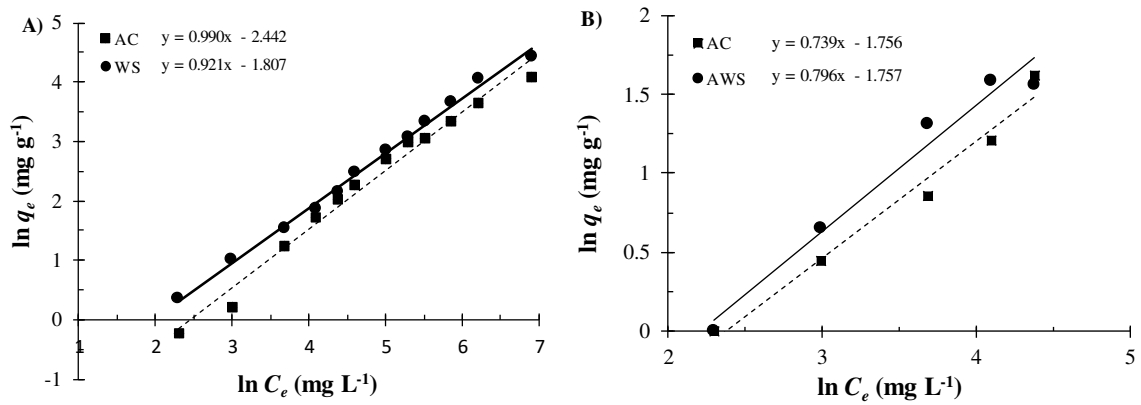


Figure 5: Freundlich isotherm on AC and WS/AWS; A) Cd and B) TCL

