

1 **Development and evaluation of a new multi-metal binding biosorbent**

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14

15 **Abstract**

16 A novel multi-metal binding biosorbent (MMBB) was developed by combining a group
17 of three from the selective natural lignocellulosic agro-industrial wastes for effectively
18 eliminating lead, cadmium, copper and zinc from aqueous solutions. Four MMBBs with
19 different combinations (MMBB1: tea waste, corncob, sugarcane bagasse; MMBB2: tea
20 waste, corncob and sawdust; MMBB3: tea waste, corncob and apple peel; MMBB4: tea
21 waste, corncob and grape stalk) were evaluated. FTIR analysis for characterizing the
22 MMBB2 explored that the MMBB2 contains more functional groups available for
23 multi-metals binding. Comparing among the MMBBs as well as the single group
24 biosorbents, MMBB2 was the best biosorbent with the maximum biosorption capacities
25 of 41.48, 39.48, 94.00 and 27.23 mg/g for Cd(II), Cu(II), Pb(II) and Zn(II), respectively.
26 After 5 times of desorption with CaCl₂, CH₃COOH and NaCl as eluent, the MMBB2
27 still remained excellent biosorptive capacity, so as it could be well regenerated for reuse
28 and possible recovery of metals.

29 **Keywords:** Agro industrial waste; Biosorption; Heavy metal; Isotherm; Kinetic study

30 **1 Introduction**

31 Typical heavy metals such as lead, cadmium, copper and zinc in water and wastewater
32 cause severe disasters in environment and subsequently serious types of acute and
33 chronic diseases in human. The common techniques used for metal removal from water
34 and wastewater includes chemical precipitation, membrane, filtration, ion exchange,
35 carbon adsorption and co-precipitation/adsorption which involve high capital and
36 operational costs and may have secondary wastes after processes (Bilal et al., 2013;
37 Bulut and Tez, 2007).

38 In recent years, biosorption has been considered as cost effective alternatives for
39 removing metals (Bulut and Tez, 2007; Gupta et al., 2009; Gadd, 2009a; Gadd, 2009b,
40 Volesky, 2007). Generally, biosorption process can reduce capital costs by 20%,
41 operational costs by 36% and total treatment costs by 28% compared with the
42 conventional systems (Loukidou et al., 2004). Thus, the interest in utilization of cheap
43 alternatives has been significantly increased. Many attempts have therefore been made
44 by many researchers on feasibility of biosorption potential of lignocellulosic materials
45 as economic and eco-friendly options, both natural substances and agro-industrial
46 wastes and by-products. These adsorbents may be classified either on basis of their
47 availability (natural materials and industrial/agro-industrial/domestic wastes or by-
48 products and synthesized ones) or depending on their nature (organic and inorganic
49 materials) (Gupta et al., 2009). Among inexpensive biosorbents, most of the studies
50 have been engrossed in lignocellulosic wastes (as naturally intact or chemically
51 modified) such as sawdust, weed and wood waste (Asadi et al., 2008; Bulut and Tez,

52 2007; Pereira et al., 2010), sugarcane bagasse (Homagai et al., 2010; Martín-Lara et al.,
53 2010; Pereira et al., 2010), fruit rind, pulp and seeds (Feng et al., 2011; Liu et al., 2012;
54 Martín-Lara et al., 2010; Torab-Mostaedi et al., 2013), wheat or barley straw (Pehlivan
55 et al., 2012), rice husk, hull and straw (Asadi et al., 2008; Kazemipour et al., 2008),
56 olive pomace and stone (Blázquez et al., 2009; Martín-Lara et al., 2012), etc . The
57 heavy metal bio-recovery can be affected by physico-chemical parameters of the
58 solution such as pH, ion strength, initial metal concentration, temperature and by other
59 characteristics of the adsorbent like concentration, presence of organic and inorganic
60 functional groups and chemical modification (Gupta et al., 2009; Montazer-Rahmati et
61 al., 2011; Pehlivan et al., 2012; Tan and Xiao, 2009; Tan et al., 2010; Velazquez-
62 Jimenez et al., 2013).

63 The present work is a preliminary study on developing a new multi-metal binding
64 biosorbent (MMBB) by combining a group of high biosorptive capability natural
65 lignocellulosic agro-industrial wastes (e.g. tea waste, corncob, sugarcane bagasse, grape
66 stalk, sawdust, apple peel) to remove cadmium, copper, lead and zinc ions from aqueous
67 solution. These wastes were selected because of the good results reported in other
68 literatures for heavy metal removal. Besides, tea waste, sugarcane, sawdust, apple peel
69 and grape stalk are properly available in Australia and also all over the world.

70 The effect of pH, contact time, biosorbent dosage and also elution efficiency (sorption
71 and adsorptions cycles) on adsorption capacity were then studied. Finally, the
72 appropriate isotherm and kinetic models were established.

73 **2 Materials and methods**

74 **2.1 Preparation of adsorbents and heavy-metal-containing effluent**

75 The stock solution containing Cd, Cu, Pb and Zn were prepared by dissolving cadmium,
76 copper, lead and zinc nitrate salt, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}_3(\text{NO})_2 \cdot 3\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and
77 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in Milli-Q water. All the reagents used for analysis were of analytical
78 reagent grade from Scharlau (Spain) and Chem-Supply Pty Ltd (Australia). For remove
79 any inaccuracies in metal concentration, all stock solutions were analyzed by AAS
80 (Contra® AA 300, Analytikjena, Germany) to correct their concentration to use in
81 experiments with required amounts.

82 All biosorbent were bought or collected from local market in Sydney area and after
83 using the useful parts were washed by tap water and distilled water to remove any dirt,
84 color or any impurity and then dried in oven (Labec Laboratory Equipment Pty Ltd.,
85 Australia) at 105°C over night. Having ground and sieved (RETSCH AS-200, Germany)
86 to a particle size of 75-150 μm , the natural biosorbents were kept in desiccator prior to
87 use.

88 **2.2 Biosorption studies in batch system**

89 The tests were performed with synthetic multi-metal solution with concentration of
90 3000 mg/L for each metal by dilution in Milli-Q water for predetermined metal
91 concentration. The pH of suspensions was adjusted by appropriate amount of HCl and
92 NaOH with concentrations of 0.1 and 1 M.

93 A known weight of adsorbent (5 g/L) was added to a series of 100 mL Erlenmeyer
94 flasks containing 40 mL of metal solution on a shaker (Ratek, Australia) at room
95 temperature and 150 rpm for 3 hr. After equilibration, to separate the biomasses from
96 solutions, the solutions were filtered and final concentration of metal was measured
97 using AAS.

98 2.3 Desorption studies in batch system

99 Desorption of metal-loaded biosorbent was studied with four types of eluting agents
100 including 0.1 M NaCl, 0.1 M CaCl₂, 0.1 M CH₃COOH and milli-Q water. These salts and
101 organic acid were selected for eluting the used biosorbent due to prevent any damages to
102 biosorbent structure. Following biosorption cycle with contact time of 3 hr, metal-
103 loaded biosorbent was filtered and then added in 100 ml of above solutions and shaken
104 at 150 rpm for 3 h. After desorption, adsorbent was washed repeatedly with milli-Q
105 water to remove any residual eluting solution and used for the next biosorption cycle.

106 2.4 Calculations

107 The amount of heavy metal ion adsorbed, q (mg/g) was calculated from the following
108 Equation 1:

$$109 \quad q = \frac{v(C_i - C_f)}{m}$$

110 (1)

111 where, C_f and C_i (mg/L) are the initial and equilibrium metal concentrations in the
112 solution, respectively. v (L) the solution volume and m (g) is the mass of biosorbent. All
113 the experiments were carried out in duplicates and the deviation within 5%.

114 3 Results and discussion

115 3.1 Selection of adsorbents

116 6 individual biosorbents, namely, sawdust (SD), sugarcane (SC), corncob (CC) and tea
117 waste (TW), apple peel (AP) and also grape stalk (GS), individually (biosorbent dose: 5

118 gr/L, 50 ppm initial metal Conc. at room temperature and pH of 5.0-5.5, rotary speed of
119 150 rpm for 24 hr) were evaluated and compared in terms of biosorption capacity
120 (Figure 1). As can be seen in Figure 1, TW showed the best in removing all tested heavy
121 metal ions (cadmium, copper, lead and zinc) while SC, SD and CC had quite less
122 biosorptive capacity in comparison with GS and TW. AP for Pb, Zn, Cd and Cu
123 removals was very dissatisfactory. Among four MMBBs with different combinations,
124 MMBB2 had highest adsorption capacity of Pb, Cu and Zn (8.08 and 5.49 mg/g, 1.66
125 mg/g, respectively). However, MMBB2 was not as good as MMBB1 and MMBB3 in
126 terms of Cd removal. Overall, MMBB2 (TW-CC-SD combination) with ratio of 1:1:1
127 was selected to apply for further experiments. The pH, moisture content (%), loss of
128 mass and bulk density g/cm^3) of MMBB2 were 5.16, 18.63, 0.92 and 0.23, respectively.

129 **3.2 Characterization of adsorbents by FTIR**

130 To determine the functional groups involved in biosorption of Cd(II), Cu(II), Pb(II) and
131 Zn(II) onto MMBB2, a comparison between the FTIR spectra before and after metal
132 loading was done using SHIMADZU FTIR 8400S (Kyoto, Japan). The FTIR spectrum
133 of MMBB2 exhibited a large number of absorption peaks, indicating the complexity in
134 nature of this adsorbent. It also confirmed changes in functional groups and surface
135 properties of MMBB2. The shift of some functional groups bands and their intensity
136 changed because of heavy metal biosorption (Table 2). These shifts may be attributed to
137 carboxylic (C=O) and hydroxylic (O-H) groups on the MMBB2's surface. They were
138 dominantly active groups in Cd(II), Cu(II), Pb(II) and Zn(II) biosorption process,
139 suggesting that acidic groups, carboxyl and hydroxyl, are main contributors in the
140 complexation of metal cations and ion exchange processes. Amine and amide groups

141 were found between medium intensity peaks in the frequency range of 3400-3250 with
142 4.9 cm^{-1} shift after biosorption process. The strong peaks detected in spectra were lied
143 between $1320\text{-}1000\text{ cm}^{-1}$ and $1820\text{-}1680\text{ cm}^{-1}$ which are related to C–O stretch (COOH)
144 and C=O stretch in amides, ketones, aldehydes, carboxylic acids and esters, respectively
145 (Feng et al., 2011; Hossain et al., 2012).

146 Moreover, a big change occurred on the biosorbent after metal loading which is
147 reflected in the strong and broad band present between $3500\text{-}3200\text{ cm}^{-1}$. This may be
148 assigned to complexation of metal ions with the ionized O–H groups of polymeric
149 compounds such as alcohols, phenols and carboxylic acids of cellulose and lignin of
150 lignocellulosic materials (Feng et al., 2011; Hossain et al., 2012).

151 The changes of peaks in the range of $3000\text{-}2850\text{ cm}^{-1}$ and $1470\text{-}1450\text{ cm}^{-1}$ indicated the
152 involvement of H-C-H asymmetric and symmetric stretch and C-H stretch of alkanes,
153 respectively which can be found in the molecular structure of MMBB2.

154 **3.3 Effect of different physico-chemical parameters**

155 **3.3.1 Influence of pH**

156 The adsorption of cadmium, copper, lead and zinc was studied as a function of pH
157 altering in the range of $2.0\text{-}5.5\pm 0.1$. At initial pH values of 6.0, lead and copper
158 hydroxide precipitation occurred. Thus, the experiments were not conducted beyond pH
159 5.5 to avoid any precipitation. Figure 2 shows that the adsorption capacity of metals
160 increased with increasing in pH values in all cases. However, the changes of Cu and Pb
161 adsorption was much more obvious than that of Zn and Cd (e.g. Cu; 1.07 to 5.70 mg/g,
162 Pb: 2.50 to 8.53 mg/g, Zn: 0.29 to 1.83 and Cd: 1.30 to 1.72 mg/g).

163 In addition some metal ions have better affinity towards biosorbents than other ions and
164 this fact ascertains the selectivity potential of functional group (Šćiban et al., 2007).
165 This phenomenon can be confirmed later by calculating the Langmuir parameter of b_L
166 representing this attraction.

167 **3.3.2 Influence of contact time**

168 A series of contact time experiments for cadmium, copper, lead and zinc adsorption on
169 MMBB2 from 0-24 hr were carried out at 50 mg/L initial concentration and room
170 temperature. It is evident from the Figure 3 that the rate of metal uptake was very fast
171 within first 30 min as a result of exuberant number of available active sites on adsorbent
172 surface and the process reached the equilibrium state within approximately 180 min of
173 contact time for all cases.

174 **3.3.3 Influence of adsorbent dose**

175 As shown in Figure 4, there is a hike in removal efficiency of all heavy metal ions on
176 MMBB2 when adsorbent dose increased and after 5 g/L of adsorbent dose. As it
177 plateaued, the optimum amount of adsorbent for future study would be 5 g/L whose
178 highest removal efficiencies were about 68 %, 75 %, 85 % and 55 % for Cd, Cu, Pb and
179 Zn, respectively.

180 **3.3.4 Sorption and desorption experiments**

181 The ability of biosorbent regeneration and batch sorption and desorption studies were
182 conducted using four eluting agents (0.1 M NaCl, 0.1 M CaCl₂, 0.1 M CH₃COOH and
183 Milli-Q water). The biosorption capacity of eluted biosorbent was tested in five repeated
184 cycles at optimum pH 5.5 ± 0.1 and 50 mg/L initial metal concentrations. The contact

185 time was 3 hours for sorption and desorption in each cycle. The biosorption capacity of
186 MMBB2 for Cd(II), Cu(II), Pb(II) and Zn(II) removal in the five cycles are indicated in
187 Figure 5. To evaluate level of significance in the sorption and desorption cycles on the
188 biosorption capacity, SPSS software was used for statistical testing of the model in the
189 form of analysis of variance (ANOVA) and the one-sample t-test were done. For a 5%
190 level of significance, the ANOVA data are given in Table 3. From this table for all
191 metals, P value is less than 0.05 and also the values of F are higher than the critical F.
192 Therefore, the type of eluent affects the sorption capacity and there is significant
193 difference between the four desorbing agents in Cd(II), Cu(II), Pb(II) and Zn(II)
194 removal. In this case, a P value less than 0.05 would result in the rejection of the null
195 hypothesis at the 5% (significance) level.

196 For a 5% level of significance T values for NaCl, CH₃COOH and CaCl₂, for all Zn(II)
197 and Cd(II), the P value is higher than 0.05 and also the values of T are lower than the
198 critical T (2.13). In other word, it is obvious from the t-tests that for these eluents, the
199 number of elution times does not affect the biosorption process. However, biosorption
200 results show that the effect of CaCl₂ and NaCl on the biosorbent is significant and
201 causes higher increase in the sorption capacity in comparison with CH₃COOH and
202 Milli-Q water. Hence, these two chemicals are recommended as elution agents and
203 desorption of cadmium, copper, lead and zinc from the biosorbent. Of course the much
204 lower cost of NaCl should also be taken into consideration.

205 3.4 SEM Analysis

206 Scanning Electron Microscopy (SEM) of the free and loaded biomass of TMM and
207 MMBB2 was performed on ZEISS EVOILS15 (Germany) at an accelerating voltage of

208 10 kV and with the working distance of 10-100 μ m for MMBB2 to elucidate the porous
 209 properties of the biosorbents. SEM images exhibited the morphological changes on the
 210 biosorbent surface before and after metal biosorption as well as 5 cycle of sorption and
 211 desorption. The surface of natural MMBB2 was found to be more porous and rougher
 212 than that of metal-loaded biosorbent. It was also observed that after 5 cycles of sorption
 213 and desorption, the surface of MMBB2 remained as rough as that of biosorbent after
 214 only one sorption process.

215 3.5 Adsorption kinetics

216 In batch systems, the adsorption kinetics was described by a number of models with
 217 varying degrees of complexity such as pseudo-first-order, pseudo-second-order and
 218 intra-particle diffusion kinetic model. The pseudo-first-order kinetic model known as
 219 the Lagergren equation and takes the form as Febrianto et al., 2009:

$$220 \quad q_t = q_e [1 - \exp(-K_1 t)] \quad (2)$$

221 where, q_t and q_e are the metal adsorbed at time t and equilibrium, respectively, and K_1
 222 (min^{-1}) is the first-order reaction rate equilibrium constant.

223 The pseudo-second-order kinetic model considered in this study is as follows::

$$224 \quad \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

$$225 \quad (3)$$

226 where, K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the second-order reaction rate equilibrium constant.

227 The intra-particle diffusion model follows:

$$228 \quad q_t = K_p t^{\frac{1}{2}} + C \quad (4)$$

229 The experimental data and obtained parameters of these models were measured by

230 MATLAB[®] and shown in Table 4. The results indicate that pseudo-second-order kinetic

231 model can describe experimental data better than the two other kinetic models ($R^2=$
 232 0.99), suggesting that chemical reaction would be presumably the rate limiting step of
 233 Cd, Cu, Pb and Zn biosorption on MMBB2. The calculated value of q_e for pseudo-
 234 second-order kinetic model (1.92, 5.88, 8.06 and 1.60 mg/g for Cd(II), Cu(II), Pb(II)
 235 and Zn(II), respectively) are also close to the experimental values (1.89, 5.57, 8.04 and
 236 1.60 mg/g).

237 3.6 Adsorption isotherm

238 To optimize the design of biosorption process, it is necessary to acquire the appropriate
 239 correlation for equilibrium curve. In this study, the metal biosorption capacity as a
 240 function of metal concentration (1-500 mg/g) at equilibrium state has been described by
 241 very common two-parameter models of Langmuir, Freundlich, Dubinin–Radushkevich
 242 and Temkin and three-parameter models of Sips, Redlich-Peterson and Radke-Prausnitz
 243 adsorption isotherms. All the model parameters were evaluated by non-linear regression
 244 using MATLAB[®] software. Furthermore, residual root mean square error (RMSE), error
 245 sum of square (SSE) and coefficient of determination (R^2) were used to measure the
 246 goodness of fitting along with model parameters.

247 Langmuir isotherm model is as follows:

$$248 \quad q_e = \frac{q_{m,L} b_L C_e}{1 + b_L C_e} \quad (5)$$

249 where, $q_{m,L}$ is the maximum metal biosorption and b_L (L/mg) the Langmuir constant.

250 These constants related to monolayer adsorption capacity and energy of adsorption
 251 respectively [27]. Maximum monolayer adsorption capacities ($q_{m,L}$) were 41.48, 39.48,
 252 94.00 and 27.23 mg/g for Cd(II), Cu(II), Pb(II) and Zn(II) sorption, respectively. The b

254 values of Cd(II), Cu(II), Pb(II) and Zn(II) biosorption which were estimated from this
 255 isotherm are 0.001, 0.004, 0.007 and 0.002 L/mg, respectively and shows the steepest
 256 initial isotherm slope (the highest b_L) is for Pb(II) as can be expected.

257 Freundlich isotherm model is an empirical equation presented as follows (Montazer-
 258 Rahmati et al., 2011):

$$259 \quad q_s = K_F C_s^{\frac{1}{n}} \quad (6)$$

260

261 where K_F (L/g) is Freundlich constant and n the Freundlich exponent. It is assumed that
 262 the stronger binding sites on a heterogeneous surface are occupied first and binding
 263 strength decreases with increasing degree of site occupation.

264 From Table 5 (a), it is apparent that equilibrium data of Cd(II), Cu(II) and Pb(II)
 265 biosorption fitted well by the Freundlich isotherm ($R^2=0.99$) and for Zn(II) the
 266 Langmuir isotherm was quite better fitted than Freundlich isotherm according to the
 267 values of R^2 of Langmuir isotherm model (0.97) being higher than that of Freundlich
 268 isotherm (0.95) as well as values of RMSE and SSE which are quite less than those of
 269 the other three models. Besides, it was understood that the Langmuir isotherm
 270 corresponded to a dominant ion exchange mechanism while the Freundlich isotherm
 271 showed adsorption-complexation reactions taking place in the adsorption process
 272 (Asadi et al., 2008).

273 The Dubinin-Radushkevich (D-R) equation is generally expressed as follows:

$$274 \quad q_s = q_{D-R} \exp(-B_{D-R} \varepsilon_{D-R}^2) \quad (7)$$

$$275 \quad \varepsilon_{D-R} = RT \ln \left[\left(1 + \frac{1}{C_s} \right) \right]$$

276 (8)

277 Where ε_{D-R} , the Polanyi potential, is a constant related to the biosorption energy, R is the
 278 gas constant (8.314 kJ/mol) and T is the absolute temperature (K). q_{D-R} and B_{D-R} are the
 279 D-R isotherm constants in mg/g and mol^2/kJ^2 , respectively. Moreover, the mean free

280 energy of adsorption ($E = \frac{1}{\sqrt{2B_{D-R}}}$) calculated from Dubinin–Radushkevich isotherm
 281 which is applied to evaluate sorption properties and indicates if main mechanism is
 282 chemical reaction dominated by ion exchange or physical adsorption. Based on
 283 hypothesis of D–R isotherm, E values between 8 and 12 kJ/mol mean chemical
 284 adsorption by ion exchange process whereas E values less than 8 kJ/mol means physical
 285 adsorption. Hence, according to calculated B_{D-R} for Cd, Cu, Pb and Zn, E values show
 286 physical adsorption for cadmium and zinc removal (7.81 and 5.27 kJ/mol, for Cd and
 287 Zn, respectively) and ion-exchange process for lead and copper biosorption (9.45
 288 kJ/mol for Cu and 10.54 kJ/mol for Pb).

289 According to Temkin isotherm, interactions between adsorbate and adsorbent make
 290 linear decrease in adsorption energy and heat of adsorption. The model is
 291 mathematically represented as Febrianto et al., 2009:

$$292 \quad q_s = \frac{RT}{b_{Te}} \ln(K_{Te} C_s) \quad (9)$$

293 where b_{Te} (kJ/mol) and K_{Te} (L/g) are Temkin model constants which are 0.77, 0.55, 0.31
 294 and 0.77 kJ/mol and 0.15, 0.21, 1.16 and 0.08 L/g, for Cd(II), Cu(II), Pb(II) and
 295 Zn(II), respectively. This model is not a proper correlation for examined heavy metals
 296 according to R^2 , RMSE and SSE values.

297 Radke-Prasnitz isotherm can be represented as Montazer-Rahmati et al., 2011:

$$q_e = \frac{a_{R-P} \Gamma_{R-P} C_e^{\beta_{R-P}}}{a_{R-P} + \Gamma_{R-P} C_e^{\beta_{R-P}-1}} \quad (10)$$

298
299

300 where a_{R-P} and Γ_{R-P} are Radke-Prausnitz model constants and β_{R-P} the Radke-Prausnitz
301 model exponent. Radke-Prausnitz isotherm constants, a_{R-P} and Γ_{R-P} for Cd(II), Cu(II),
302 Pb(II) and Zn(II) were calculated as 5.10, 9.24, 3.25 and 4.10 L/mg, 0.21, 0.63, 2.57 and
303 0.18 L/g, respectively.

304

305 As the results in Table 5 (a) and (b), among two-parameter isotherms, both Freundlich
306 and Langmuir models agreed very well with experimental data rather than the other
307 two-parameter isotherm models and these are confirmed by small values of RMSE and
308 SSE and R^2 amounts closed to 1.0, too. This result indicates the formation of monolayer
309 coverage of metal ions at the outer heterogeneous surface of the sorbent.

310 The Sips isotherm is a combination of the Langmuir and Freundlich isotherm models
311 and is expected to describe heterogeneous surfaces much better. At high sorbate
312 concentrations it predicts a monolayer adsorption capacity characteristic of the
313 Langmuir isotherm whereas at low sorbate concentrations it reduces to the Freundlich
314 isotherm. It is given as (Febrianto et al., 2009):

$$q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}}$$

315

316 (11)

317 where K_S and a_S are the Sips model constants in L/g and L/mg, respectively and β_S is
318 the Sips model exponent. Cd(II), Cu(II) and Zn(II) biosorption data was

319 As the results given by Sips model, the experimental results of Cd(II), Cu(II) and Zn(II)
320 biosorption are well fitted by all Sips better than Redlich-Peterson and Radke-Prausnitz
321 models due to small RMSE and SSE as well as high R^2 close to 1.0.

322 Unlike Sips model, the Redlich–Peterson isotherm behaves like the Freundlich isotherm
 323 at high adsorbate concentrations and comes close the Henry’s law at low amounts of
 324 concentration. The model can be presented as (Febrianto et al., 2009; Montazer-Rahmati
 325 et al., 2011):

$$326 \quad q_e = \frac{K_{RP}C_e}{1 + a_{RP}C_e^{\beta_{RP}}}$$

327 (12)

328 where K_{RP} and a_{RP} are the Redlich–Peterson model constants in L/g and L/mg,
 329 respectively and β_{RP} is the Redlich–Peterson model exponent which lies between 0 and
 330 1 (0.27, 0.60, 0.19 and 0.56 for Cd(II), Cu(II), Pb(II) and Zn(II), respectively). Pb(II)
 331 biosorption data is best correlated by the Redlich–Peterson as confirmed by the smallest
 332 values of RMSE, SSE and R^2 values very close to 1.0 (0.999).

333 The foregoing analysis of isotherm models show that the best fit for Cd(II), Cu(II),
 334 Pb(II) and Zn(II) biosorption is produced by three-parameter isotherm models than two-
 335 parameter isotherm models.

336 Comparison between maximum adsorptive capacities of some adsorbents investigated
 337 by other researchers is shown in Table 6. This study results are compatible with other
 338 adsorbents by higher or at least equal sorptive potential for heavy metal removal from
 339 aqueous solutions. Besides, combination of several types of low-cost agro-industrial
 340 waste provides more selectivity as a result of increase in different effective functional
 341 groups involved in metal binding. Hence, this kind of adsorbent will be recommended
 342 for its significant advantages.

343 4 Conclusion

344 The new biosorbent containing tea waste, corncob and sawdust was found to be an
345 effective and low-cost alternative for detoxifying of heavy metals contaminated aqueous
346 solutions. The pH, contact time, adsorbent dose and initial metal concentrations of the
347 adsorbate significantly governed the overall process of cadmium, copper, lead and zinc
348 cations adsorption. The sorption equilibrium time was reached within 3 h and pseudo-
349 second-order kinetic model well fitted the experimental data. NaCl was successfully
350 used as eluent without affecting its sorption capability after five cycles of sorption and
351 desorption.

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446 **Figure Caption**

447 Figure 1 Comparison between different single and multi-metal binding biosorbent for
448 Cd(II), Cu(II), Pb(II) and Zn(II) adsorption(initial pH 5.5 ± 0.1 ; room temperature, 22 ± 2
449 $^{\circ}\text{C}$; contact time: 24 hr; initial metal conc.: 50 mg/L; biosorbent dose: 5g/L; rotary
450 speed: 150 rpm, particle size: 75-150 μm)

451 SC: Sugarcane, SD: Sawdust, CC: Corncob, TW: Tea Waste, GS: Grape Stalk and AP:
452 Apple Peels

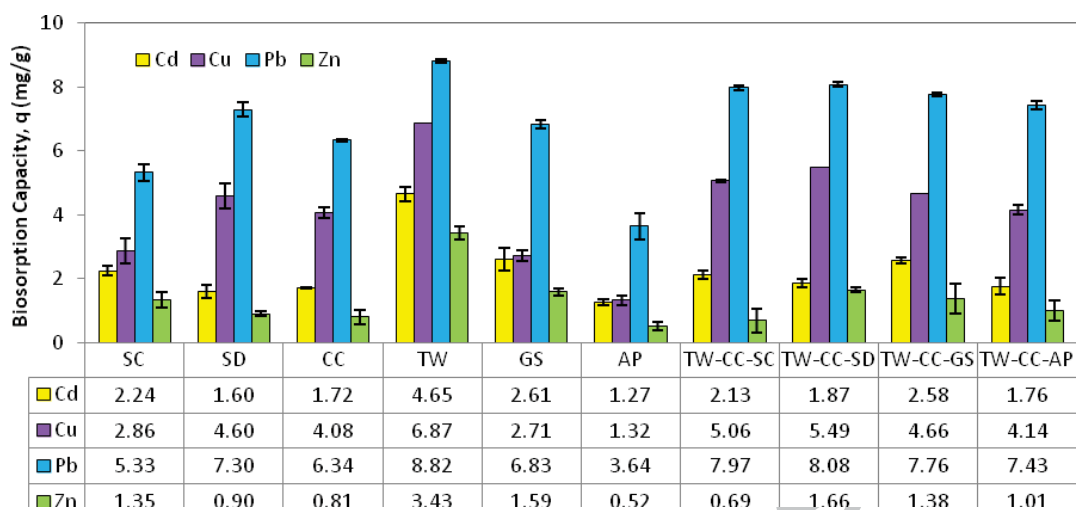
453 Figure 2 Effect of initial pH of solution on Cd(II), Cu(II), Pb(II) and Zn(II) adsorption
454 (room temperature, 22 ± 2 $^{\circ}\text{C}$; contact time: 24 hr; initial metal conc.: 50 mg/L;
455 biosorbent dose: 5g/L; rotary speed: 150 rpm, particle size: 75-150 μm)

456 Figure 3 Effect of contact time on Cd(II), Cu(II), Pb(II) and Zn(II) adsorption (pH
457 5.5 ± 0.1 ; room temperature, 22 ± 2 $^{\circ}\text{C}$; initial metal conc.: 50 mg/L; biosorbent dose:
458 5g/L; rotary speed: 150 rpm, particle size: 75-150 μm)

459 Figure 4 Effect of biosorbent dose on Cd(II), Cu(II), Pb(II) and Zn(II) adsorption (initial
460 pH 5.5 ± 0.1 , room temperature, initial metal conc.: 50 mg/L, contact time: 3 hr, rotary
461 speed: 150 rpm, particle size: 75-150 μm)

462 Figure 5 Biosorption capacity of Cd(II), Cu(II), Pb(II) and Zn(II) onto MMBB2 washed
463 by four eluting agents (optimum pH 5.5 ± 0.1 ; room temperature: 22 ± 2 $^{\circ}\text{C}$; sorption time:
464 3 hr ; desorption time: 3 hr; 5 cycles; initial metal conc.: 50 mg/L)

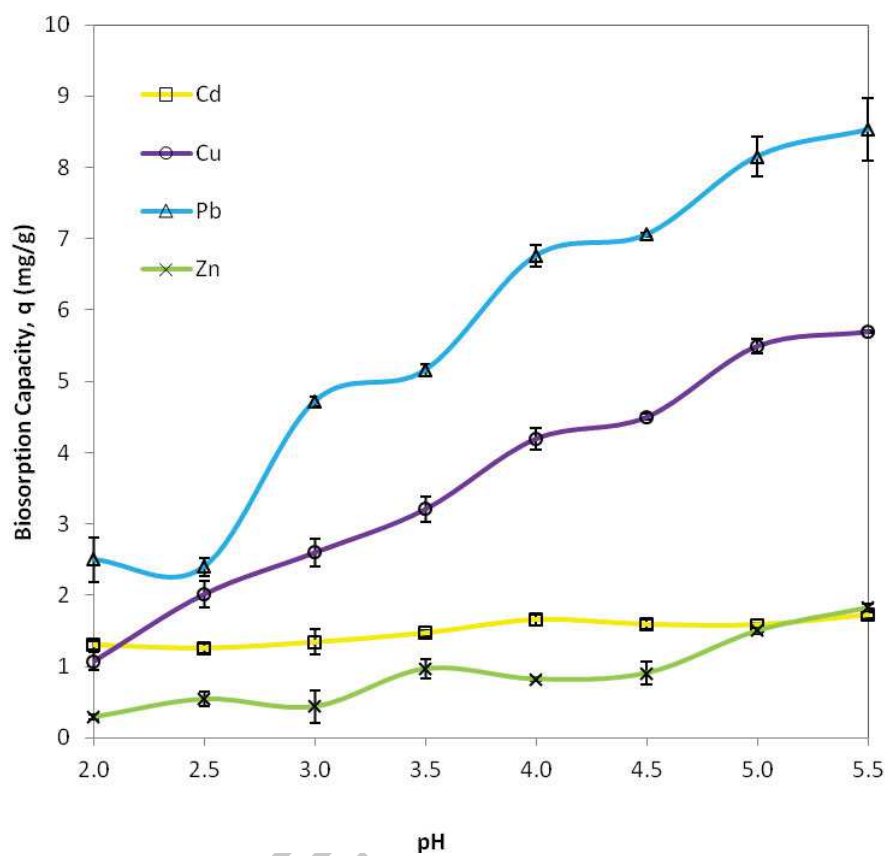
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467 **Figure 1**

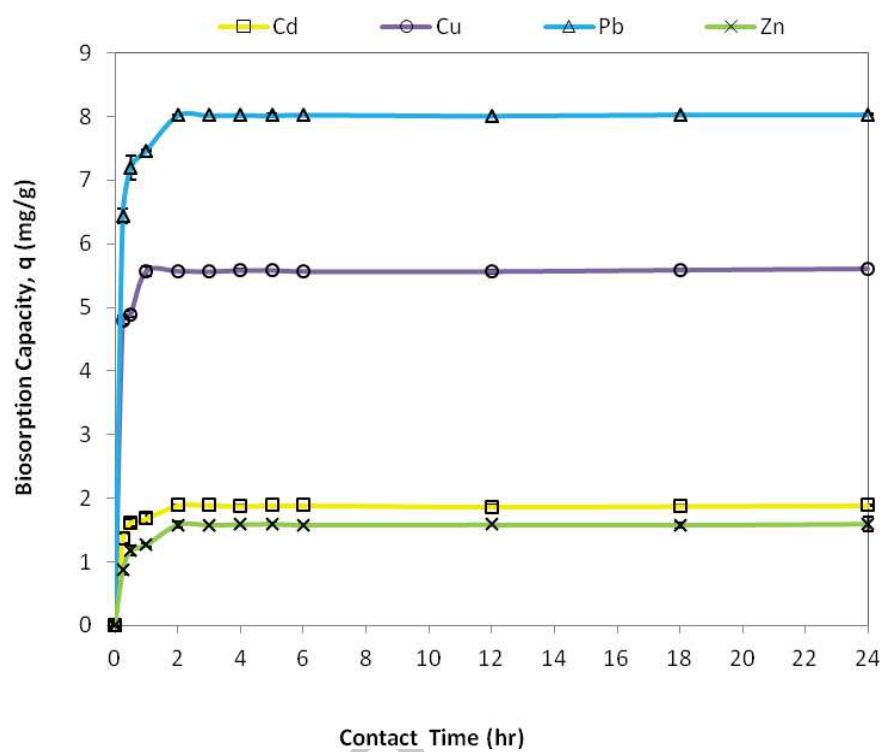
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470 **Figure 2**

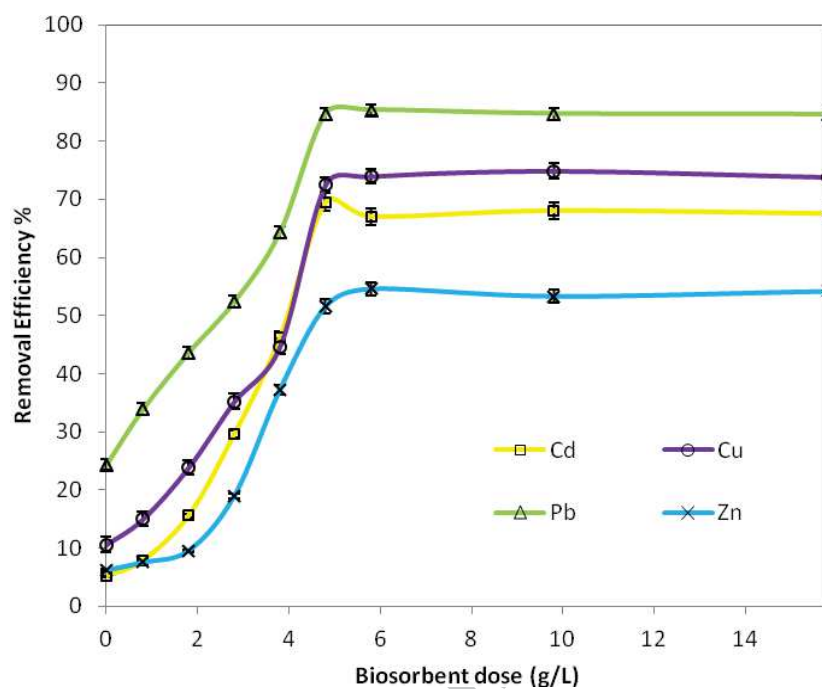
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473 **Figure 3**

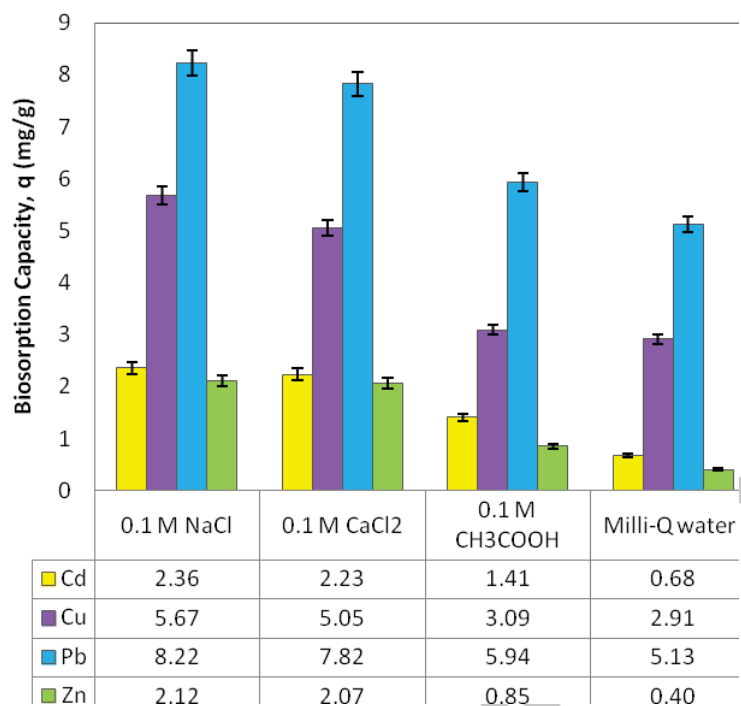
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476 **Figure 4**

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479 **Figure 5**

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481 **Table Caption**

482 Table 1 FTIR spectra of unloaded and metal loaded- biosorbents

483 Table 2 ANOVA and One sample t-test data for sorption and desorption experiments of

484 Cd(II), Cu(II), Pb(II) and Zn(II) biosorption onto MMBB2 (optimum pH 5.5 ± 0.1 ; room485 temperature: 22 ± 2 °C; sorption time: 3 hr ; desorption time: 3 hr; 5 cycles; initial metal

486 conc.: 50 mg/L)

487 Table 3 Comparison between adsorption rate constants, the estimated q_e and the

488 coefficients of determination associated with the Lagergren pseudo-first-order, the

489 pseudo-second order and intra-particle diffusion kinetic models (pH 5.5 ± 0.1 ; room490 temperature, 22 ± 2 °C; initial metal conc.: 50 mg/L; biosorbent dose: 5g/L; rotary speed:491 150 rpm, particle size: 75-150 μ m)

492 Table 4 Isotherm constants of (a)two-parameter and (b) three-parameter models for

493 Cd(II), Cu(II), Pb(II) and Zn(II) adsorption(initial pH 5.5 ± 0.1 , initial metal Conc.: 1-

494 500 mg/L, contact time: 3 hr, rotary speed: 150 rpm, biosorbent dose: 5 g/L, particle

495 size: 75-150 μ m)

496 Table 5 Biosorption capacities of various biosorbent

Table 1 FTIR spectra of unloaded and metal loaded- biosorbents

Wavelength range (cm ⁻¹)		Transmittance (%)			Bond/Functional group
Frequency	Difference	Unloaded	Loaded	Difference	
3500-3200	-8.3	71.8	64.4	-7.4	O-H stretch/Alcohols and phenols
3400-3250	-4.9	64.5	53.5	-11.0	N-H band/1° and 2° amines and amides
3000-2850	-10.4	73.2	65.7	-7.5	H-C-H asymmetric and symmetric stretch/Alkanes
1820-1680	-9.1	69.3	64.3	-5.0	C=O stretch/Amides, ketones, aldehydes, carboxylic acids and esters
1470-1450	-3.6	62.7	61.1	-1.7	C-H band/Alkanes
1550-1475	+6.0	72.3	65.5	-6.8	N-O asymmetric stretch/Nitro compounds
1320-1000	-9.3	79.1	68.5	-10.6	C-O stretch (COOH)/Alcohol, carboxylic acid, esters and ethers

Table 2 ANOVA and One sample t-test data for sorption and desorption experiments of Cd(II), Cu(II), Pb(II) and Zn(II) biosorption onto MMBB2 (optimum pH 5.5 ± 0.1 ; room temperature: 22 ± 2 °C; sorption time: 3 hr ; desorption time: 3 hr; 5 cycles; initial metal conc.: 50 mg/L)

Statistical Analysis Method	Metal			
	Cd	Cu	Pb	Zn
One-way ANOVA for NaCl, CaCl ₂ , CH ₃ COOH and Milli-Q water				
F factor	12.23	4.66	4.86	4.59
F _{critical} factor	3.23	3.23	3.23	3.23
P value	0.0002	0.0158	0.0136	0.0166
One-sample T for NaCl				
T factor	2.31	4.08	4.66	0.02
T _{critical} factor	2.13	2.13	2.13	2.13
P	0.04	0.007	0.004	0.49
One-sample T for CaCl ₂				
T factor	0.64	4.92	4.47	1.19
T _{critical} factor	2.13	2.13	2.13	2.13
P	0.27	0.004	0.005	0.15
One-sample T for CH ₃ COOH				
T factor	1.93	7.16	5.19	2.81
T _{critical} factor	2.13	2.13	2.13	2.13
P	0.06	0.001	0.003	0.02
One-sample T for Milli-Q water				
T factor	5.00	5.60	4.76	5.48
T _{critical} factor	2.13	2.13	2.13	2.13
P	0.003	0.02	0.004	0.005

Table 3 Comparison between adsorption rate constants, the estimated q_e and the coefficients of determination associated with the Lagergren pseudo-first-order, the pseudo-second order and intra-particle diffusion kinetic models (pH 5.5±0.1; room temperature, 22±2 °C; initial metal conc.: 50 mg/L; biosorbent dose: 5g/L; rotary speed: 150 rpm, particle size: 75-150µm)

Model	Parameter	Metal			
		Cd	Cu	Pb	Zn
Experimental	$q_{e,exp}$ (mg/g)	1.89	5.57	8.04	1.60
1 st -order kinetic model $q_t = q_e [1 - \exp(-K_1 t)]$	K_1 (min ⁻¹)	0.03	0.10	0.07	0.02
	$q_{e,cal}$ (mg/g)	1.19	5.98	8.39	1.21
	R^2	0.79	0.95	0.94	0.85
2 nd -order kinetic model $\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$	$K_2 \times 10^3$ (gmg ⁻¹ min ⁻¹)	0.17	0.08	0.06	0.09
	$q_{e,cal}$ (mg/g)	1.92	5.88	8.06	1.60
	R^2	0.99	0.99	0.99	0.99
Intra-particle diffusion model $q_t = K_p t^{0.5} + C$	K_p (mg g ⁻¹ min ^{-0.5})	0.07	1.12	0.15	0.07
	C	1.16	4.35	6.19	0.68
	R^2	0.93	0.81	0.88	0.90

Table 4 Isotherm constants of (a) two-parameter and (b) three-parameter models for Cd(II), Cu(II), Pb(II) and Zn(II) adsorption (initial pH 5.5 ± 0.1 , initial metal Conc.: 1-500 mg/L, contact time: 3 hr, rotary speed: 150 rpm, biosorbent dose: 5 g/L, particle size: 75-150 μ m)

(a)				
Two-parameter models	Metal			
	Cadmium	Copper	Lead	Zinc
Langmuir	$q_s = \frac{q_{m,L} b_L C_s}{1 + b_L C_s}$			
$q_{m,L}$ (mg/g)	41.48	39.48	94.00	27.23
b_L (L/mg)	0.001	0.004	0.007	0.002
SSE	2.24	4.52	65.03	3.89
R^2	0.99	0.99	0.97	0.97
RMSE	0.75	1.06	4.03	0.98
Freundlich	$q_s = K_F C_s^{\frac{1}{n}}$			
K_F	0.21	0.63	2.57	0.18
n	1.37	1.63	1.74	1.42
SSE	1.83	0.27	12.71	6.65
R^2	0.99	0.99	0.99	0.95
RMSE	0.67	0.25	1.78	1.29
Dubinin- Radushkevich	$q_s = q_{D-R} \exp(-B_{D-R} C_s^2)$			
q_{D-R} (mg/g)	18.00	21.68	47.99	14.56
B_{D-R}	0.008	0.005	0.004	0.018
SSE	18.54	59.54	40.60	6.50
R^2	0.91	0.83	0.81	0.96
RMSE	2.15	3.85	10.07	1.27
Temkin	$q_s = \frac{RT}{b_{Tc}} \ln(K_{Tc} C_s)$			
K_{Tc} (L/g)	0.15	0.21	1.16	0.08
b_{Tc} (kJ/mol)	0.77	0.55	0.31	0.77
SSE	50.17	56.4	42.34	26.89
R^2	0.75	0.84	0.80	0.82
RMSE	3.54	3.75	10.29	2.59
(b)				
Three-parameter models	Metal			
	Cadmium	Copper	Lead	Zinc
Radke-Prausnitz	$q_s = \frac{\alpha_{R-P} \gamma_{R-P} C_s^{\beta_{R-P}}}{\alpha_{R-P} + \gamma_{R-P} C_s^{\beta_{R-P}-1}}$			

Three-parameter models	Metal			
	Cadmium	Copper	Lead	Zinc
a_{R-P} (L/g)	5.10	9.24	3.25	4.10
β_{R-P}	0.68	0.61	0.57	0.70
r_{R-P} (L/mg)	0.21	0.63	2.57	0.18
SSE	1.33	0.26	12.71	6.65
R^2	0.99	0.99	0.99	0.95
RMSE	1.52	0.99	2.05	1.48
	$q_s = \frac{K_{RP} C_s}{1 + a_{RP} C_s^{\beta_{RP}}}$			
Redlich-Peterson				
a_{RP} (L/mg)	1.25	0.10	2.09	5.39
β_{RP}	0.27	0.60	0.19	0.56
K_{RP} (L/g)	5.65	0.89	1.00	0.05
SSE	1.83	6.77	0.23	2.87
R^2	0.99	0.99	0.99	0.98
RMSE	0.78	4.75	0.27	0.97
	$q_s = \frac{K_S C_s^{\beta_S}}{1 + a_S C_s^{\beta_S}}$			
Sips				
a_S (L/mg)	0.001	0.004	0.063	0.001
β_S	0.83	0.59	0.38	1.72
K_S (L/g)	0.20	0.66	3.68	0.002
SSE	1.52	0.25	2.92	1.89
R^2	0.99	0.99	0.99	0.98
RMSE	0.23	0.29	0.98	0.79

1 **Table 5** Biosorption capacities of various biosorbent

Adsorbent	Matal	q_{\max} (mg/g)	Reference
MMBB2	Cd(II)	41.48	Present study
	Zn (II)	27.23	
	Pb(II)	94.00	
	Cu (II)	39.48	
Sugarcane bagasse	Cd(II)	69.06	(Garg et al., 2008)
	Cu(II)	6.88	(Šćiban et al., 2007)
Sawdust	Zn(II)	0.96	
	Cd(II)	0.15	
Rice straw	Cd(II)	13.89	(Ding et al., 2012)
Olive stone	Pb(II)	92.6	(Fiol et al., 2006)
	Cd(II)	77.3	
Orange peel	Ni(II)	21.3	(Feng et al., 2011)
	Cu(II)	20.2	
	Pb(II)	113.5	
	Cd(II)	63.35	
Cashew nut shell	Ni(II)	9.82	(Kumar et al., 2012)
	Zn(II)	24.98	
Tea waste	Cu(II)	48	(Amarasinghe and Williams, 2007)
	Pb(II)	65	

2

3

4 **Highlights**

5

6 ▶ The effectiveness of a novel multi-metal binding biosorbent was studied.

7 ▶ The biosorption of Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} on MMBBs was investigated.

8 ▶ Equilibrium data were presented and the best fitting models were introduced.

9 ▶ The pseudo-second order model best describe the biosorption kinetics.

10 ▶ The obtained results recommend this MMBB as potentially low-cost biosorbent.

11 31.

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