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1 **Tea waste-supported hydrated manganese dioxide (HMO) for enhanced**

2 **removal of typical toxic metal ions from water**

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20 **Abstract**

21 Tea waste (TW) was modified by depositing hydrated manganese oxide (HMO) onto it

22 through *in situ* precipitation and a novel hybrid bio-adsorbent, namely HMO-TW, was

23 obtained. The successful deposition of HMO in/on tea waste was confirmed by transmission

24 electron microscope (TEM) and Fourier transform infrared spectroscopy (FT-IR) analysis.

25 The removal of four typical heavy metals (i.e., Pb(II), Cd(II), Cu(II), Zn(II)) by HMO-TW

26 was pH-dependent, and higher pH favored the sorption at tested pHs of 2-7. HMO-TW

27 showed excellent sorption selectivity toward all four metal ions, and the removal efficiency of

28 target metal ions sustained at 30%~90% even in the presence of 50 times higher competing

29 Ca(II) and Mg(II) ions. Sorption isotherms of four metal ions by HMO-TW are all well

30 represented by the Freundlich model, and the maximum experimental sorption capacities of

31 Pb(II), Cd(II), Cu(II), Zn(II) were 174.3, 78.38, 54.38 and 37.5 mg g^{-1}, respectively.

32 Compared to the unmodified tea waste, the sorption capacities and selectivity of Pb(II), Cd(II)

33 and Cu(II) onto HMO-TW improved significantly. The sorption process reached equilibrium

34 within 200 min, and the kinetics could be well fitted by a pseudo-second order model.

35 Fixed-bed column sorption results further showed that bed volume (BV) of C_e/C_0 reaching 0.5

36 for Pb(II), Cd(II), Cu(II), Zn(II) were 1170, 1130, 820 and 1450 BV, respectively. In addition,

37 the exhausted HMO-TW can be effectively regenerated using a 0.5 M HCl solution. All

38 results reported herein validate that HMO-TW is a promising sorbent for practical treatment

39 of heavy metal contaminated water.

40 **Introduction**

41 Heavy metal contamination has attracted increasing attention due to their high toxicity,

42 widespread presence in many kinds of environmental medium and potential bio-accumulation

43 in food chain.[1] Even at extremely low concentrations, heavy metals can cause many harmful

44 effects towards public health and aquatic life. [2] Unfortunately, heavy metals are inevitable

45 by-products of rapid economic development. Owing to high perniciousness of heavy metals,

46 stringent regulations have been set up to control their maximum residual concentrations in all

47 industrial effluents of China. For example, Chinese government has set the maximum residual

48 concentrations of Pb(II), Cd(II), Cu(II) and Zn(II) in effluents as 1.0, 0.1, 0.5, and 2.0 mg L^{-1},

49 respectively. [3] Therefore, it is of great importance and urgency to develop efficient and

50 cost-effective technologies for toxic heavy metals removal from wastewater.

51

52 The primary methods for removing heavy metals from water/wastewater include chemical

53 precipitation, adsorption, coagulation, and membrane filtration.[4,5] Among above-mentioned

54 technologies, adsorption has been generally regarded as one of the most promising

55 technologies.[6] The development of adsorbent is the key for adsorption technology, and

56 numerous new types of adsorbents like polymer, chelates, and composite have been

57 constantly developed in recent years.[7-10] Meanwhile, many ordinary and original

58 bio-adsorbents have gradually come into the vision of researchers because of their salient

59 advantages such as easy availability, cheapness and low pollution. For example, wastes like

60 walnut shells,[11] tea leaves,[12] rice hulls,[13] bamboo,[14] corn cobs[15] and eggshell membrane[16-18]

61 with reasonable numbers of carboxyl, phenolic hydroxyl and amine groups that can bind to

62 metal ions have been used for toxic metal capture, and some relatively satisfactory results

3

63   were obtained. Unfortunately, a lot of fatal defects such as low sorption capacity and poor

64   sorption selectivity have seriously limited their further application. The sorption behavior of

65   Pb(II), Cd(II), Cu(II) onto original tea waste (TW) was systematically investigated in our

66   previous research,[19] and the sorption capacities and selectivity of these metals were not very

67   satisfactory. Therefore, it is very imperative to improve the performance of tea waste through

68   some modifications in order to promote its practical application.

69

70   Hydrous manganese oxides (HMO) have always been considered to be one of the most

71   efficacious adsorbents for heavy metal removal due to its specific and strong binding to target

72   metal ion.[20,21] However, HMO is still far from practical application in fixed-bed and

73   flow-through systems because of excessive pressure drop and difficulty of solid-liquid

74   separation caused by its fine or ultrafine particle size. Some host materials such as activated

75   carbon,[20,22] zeolite,[23] and porous polymer[24] have been selected to synthesize various hybrid

76   adsorbents to overcome this technical barrier and these hybrid sorbents usually have good

77   performance toward heavy metal removal. However, the high cost of these supporting

78   materials makes their application in real world wastewater treatment unaffordable. Therefore,

79   efficient and low-cost supporting materials are still in great demand to facilitate the

80   application of HMO in wastewater treatment.

81

82   In this study, we prepared a novel composite sorbent (HMO-TW) by depositing HMO onto

83   TW to maximally utilize the benefits of both adsorbents for heavy metal removal. We

84   anticipate that TW would be an effective and cost-efficient support for highly dispersed HMO.

85   HMO, on the other hand, provides the composite good selectivity for heavy metal ions against

86   competing cations commonly existing in water (e.g., Ca(II) and Mg(II)). Sorption behaviors

87   of four typical toxic metal ions, Pb(II), Cd(II), Cu(II) and Zn(II), from aqueous solution were

88   investigated by evaluating the influence of solution pH, coexist competing ions, temperature

89   and contact time. Column experiments were performed to simulate the real situation treatment

90   process. In addition, the regeneration of HMO-TW was also evaluated.

91

92   **Experimental**

93   **1. Chemicals**

94   All chemicals used in the current study are analytical grade (AR) or better and were purchased

95   from Guoyao Reagent Station (Anhui, China). Stock solutions containing 1 g L^{-1} of the target

96   heavy metals were prepared by dissolving their corresponding nitrates with ultrapure water

97   (resistivity > 18.2 MΩ cm^{-1}), which were further diluted prior to use.

98

99   **2. Preparation of HMO-TW**

100   The TW was collected from tea plants located in Green tea region in Huangshan, China. The

101   pretreatment of TW had been described in our previous research.[19] HMO-TW was prepared

102   by in-situ precipitation and the procedures are as following: Firstly, 10.0 g TW after

103   pretreatment was added into 1 mol L^{-1} $MnSO_4 \cdot H_2O$ solution and stirred continuously at 303 K

104   for 24 h. Secondly, the Mn(II)-loaded tea waste was filtered from solution and then dried

105   under vacuum at 333 K for 2 h. After this, the solid was added into a binary NaClO-NaOH

106   solution with alkalinity of 10% and active chlorine of 13%, and stirred continuously at 303 K

107   for 24 h to oxidize Mn(II) to Mn(IV) and precipitate.[24] Finally, the obtained hybrid materials

108   were washed with 0.1 M HCl and ultrapure water until neutral pH and followed by

5

109   desiccation under vacuum at 333 K till reaching a constant weight. The final products were

110   stored in sealed glass bottles for future use.

111

112   **3.   Batch sorption experiments**

113   Batch sorption experiments were carried out using traditional bottle-point method in 250 mL

114   Erlenmeyer flasks. The detailed experimental information is described in following sections.

115

116   3.1 Effect of solution pH on heavy metal adsorption

117   20.0 mg of HMO-TW particles were dispersed into 100-mL Erlenmeyer flasks containing 50

118   mL solution of either Pb(II) (40 mg L^{-1}), Cd(II) (20 mg L^{-1}) , Cu(II) (10 mg L^{-1}) or Zn(II) (10

119   mg L^{-1}). A 1.0 M HCl or NaOH solution was used to adjust the desired solution pH to 2-7

120   throughout the experiments. A thermostatic orbit incubator shaker (New Brunswick Scientific

121   Co. Inc.) was used to shake the stoppered flasks at 120 rpm and 303 K for 24 h, which was

122   sufficient to reach adsorption equilibrium according to preliminary kinetic tests. Finally, the

123   supernatant was sampled and analyzed for equilibrium solution pH and concentration of target

124   metal ions. The amount of adsorbed heavy metals onto HMO-TW was calculated based on

125   mass balance between initial and finial metal ion concentrations.

126

127   3.2 Competitive sorption test

128   For the competitive sorption tests, the initial concentrations of heavy metals were 40 mg L^{-1}

129   for Pb(II), 20 mg L^{-1} for Cd(II), 10 mg L^{-1} for Cu(II) and 5 mg L^{-1} of Zn(II), respectively.

130   Other conditions were basically same as the above-mentioned pH effect experiments except

131   certain amount of representative competitive ions (Ca(II) and Mg(II)) were introduced into

132   the test solution.

133

134   3.3 Sorption isotherm

135   For sorption isotherms tests, 20 mg HMO-TW was dispersed into 100 mL flasks containing

136   50 mL solution of various contents of metal ions. The experiment temperature was set at 298

137   K. Langmuir and Freundlich equations [25] were applied to fit the sorption data from the

138   isotherm tests：

$$q_e = \frac{K_L q_m C_e}{K_L C_e + 1} \qquad (1)$$

139

$$q_e = K_f C_e^{\frac{1}{n}} \qquad (2)$$

140

141   where q_e is the amount of adsorbed metal at equilibrium (mg g^{-1}); C_e is the concentration of

142   the metal ion in solution at equilibrium (mg L^{-1}); q_m is the maximum adsorption capacity of

143   metal on HMO-TW (mg g^{-1}); and K_L (L mg^{-1}) is a binding constant, and both K_f and n are the

144   Freundlich constants.

145

146   3.4 Adsorption kinetics

147   For kinetic tests, 200 mg HMO-TW was added into 1000-mL Erlenmeyer flasks containing

148   500 mL solution of either 70 mg L^{-1} of Pb(II), 25 mg L^{-1} of Cd(II), 30 mg L^{-1} of Cu(II) or 10

149   mg L^{-1} of Zn(II). Aliquots of 0.5 mL were sampled at various time intervals, e.g., every 5 min

150   for 0~30 min, every 10 min for 30~150 min, every 20 min for 150~210 min and every 30 min

151   for 210~360 min. The sorption capacities of heavy metals versus time constituted the kinetic

152   curve.

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154   The pseudo-second-order equation [26] was used to fit the kinetic data:

155

$$q_t = \frac{k_2 q_e^{2} t}{t k_2 q_e + 1} \tag{3}$$

156   Where q_e and q_t are sorption capacities of heavy metal (mg g^{-1}) at equilibrium and at time t,

157   respectively and k_2 is second-order sorption rate constant.

158

159   **4. Fixed-bed column sorption and desorption**

160   In column experiments, a 5-mL aliquot of wet HMO-TW particles was filled into a

161   polyethylene column (12 mm diameter and 130 mm length) equipped with a water bath to

162   maintain a desired temperature. A Lange-580 pump (Baoding, China) was used to ensure a

163   constant flow rate. Simulated wastewater containing given concentration of target metal ions

164   was supplied as influent. A 0.5 M HCl solution was used to regenerate the exhausted

165   HMO-TW after sorption. Detailed operation conditions (e.g., superficial liquid velocity (SLV)

166   and empty bed contact time (EBCT)) are depicted in the related figure captions.

167

168   **5. Analyses**

169   Metal ion concentration in aqueous phase was determined using a TAS-990 flame atom

170   adsorption spectrophotometer (Persee inc., China), and the absorbance of all samples was

171   tested in triplicate. An atom fluorescence spectrophotometer (AF-640) (Ruili Co., Ltd) was

172   also used to determine metal ion content，if lower than 1 mg L^{-1}. The amount of loaded HMO

173   in/on tea waste was calculated using Mn content in aqueous phase after HNO_3-$HClO_4$

174   digestion process. FT-IR spectra of HMO-TW before and after metal sorption were obtained

175   using a Nicolet 380 FT-IR spectrometer (USA) with a pellet of powered potassium bromide

176   and adsorbent in the range of 400–4000 cm^{-1}. Speciation of HMO-TW was determined by

177   means of X-ray diffraction analysis with a step size of 0.02^{o} (D8 ADVANCE, Germany). The

178   surface morphology of the host tea waste and HMO-TW was observed using a scanning

179   electron microscope (S-3400N, Japan) and a transmission electron microscopy

180   (JEM-2000EX). The zeta potential of HMO-TW was measured using a Malvern Zetasizer

181   Nano ZS90. N_2 adsorption-desorption tests onto HMO-TW particles were carried out at 77K

182   to obtain specific surface area based on BET model and pore size distribution based on BJH

183   model using a Micromeritics ASAP2020 (USA).

184

185   **Results and discussion**

186   **1. Characterization of the adsorbents**

187   The successful deposition of nano-sized HMO particles on the surface of tea waste is clearly

188   shown in a TEM image of HMO-TW (Fig.1a). The sizes of the highly dispersed HMO

189   particles are typically less than 5 nm. The surface morphology of TW was obviously different

190   before and after HMO loading according to SEM images of TW and HMO-TW depicted in

191   Fig.S1. Specifically, the pores located in host tea waste surface were wide and sparse, while

192   the pores became tiny and dense after HMO particles loading. FT-IR spectra of the original

193   tea waste and HMO-TW are depicted in Fig.1b. Obvious sorption peaks of 1623, 915 cm^{-1}

194   assigned to Mn-OH group [27,28] are observed in the FT-IR spectra of HMO-TW but not TW,

195   which indicates that HMO particles had been successfully loaded onto TW. The zeta potential

196   of HMO-TW (Fig.1c) was always negative in the tested pH range of 2-10, indicating

197   HMO-TW can strongly attract cations. The broad and weak diffraction peaks in X-ray

198   diffraction pattern of HMO-TW (Fig.S2) are similar to those of δ-MnO_2,[29] which suggests

199   that most of the loaded HMO is amorphous in nature. Some major physicochemical properties

200   of the host TW and HMO-TW are listed in Table 1. The loaded HMO amount on TW was

201   4.82(w/w)% in Mn mass, while no Mn was detected in the supporting TW. The larger BET

202   specific surface area of HMO-TW (5.92 m^2 g^{-1}) compared to that of host TW（0.86 m^2 g^{-1}）

203   should result from the large surface area of HMO, which was reported to be 100.5 m^2 g^{-1} [28]

204   (Note that the HMO content is only 4.86% as Mn in HMO-TW).

205

206   2. **Effect of Solution pH**

207   Solution pH is a significant environmental factor that usually influences the sorption process

208   by altering surface properties of the sorbent and the speciation of the sorbate. Therefore,

209   removal of Pb(II), Cd(II), Cu(II) and Zn(II) by HMO-TW at different solution pH was

210   conducted, and the effect curves are shown in Fig. 2. The removal efficiency of heavy metals

211   increased with the increase of solution pH. More specifically, the removal of heavy metals

212   almost linearly increased at acidic pH range 2-5, and became more gradual at the near neutral

213   pH range 5-7. The above pH effect results are consistent to sorption of many heavy metals

214   onto other adsorbents,[15,28,30] which can be explained by the exchange of H in functional

215   groups of sorbent with target metal ions. In our previous research, we elucidated the ion

216   exchange process between the functional groups, e.g. carboxyl and phenolic hydroxyl groups,

217   on TW and the target metal ions.[19] For the as-prepared HMO-TW, the loaded HMO would

218   result in the same pH effect by forming inner-sphere complexes with metal ions as [31,32]

219                    $-Mn\text{-}OH\text{-} + M^{2+} \quad -Mn\text{-}O\text{-}M^{+} + H^{+}$ （1）

220                    $-Mn\text{-}(OH)_2\text{-} + M^{2+} \quad -Mn\text{-}O\text{-}M + 2H^{+}$ （2）
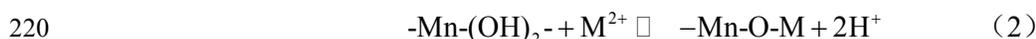
221   Obviously, more H^{+}, namely, lower solution pH, is unfavorable for heavy metals sorption

222 onto loaded HMO, while higher pH promotes the above reactions. The inner-sphere

223 complexes between Mn-OH and heavy metals had been extensively researched previously

224 using EXAFS.[33,34] The combined effects of HMO and host TW lead to the pH–dependent

225 plots depicted in Fig. 2. Besides, the contents of Mn released into solution after Pb(II)

226 adsorption at different pHs (2-7) were analyzed, and no Mn leaching was detected (data not

227 shown). Thus, HMO-TW could be an ideal sorbent for heavy metals removal from slightly

228 acidic wastewater (e.g., pH 4-7) in terms of both material stability and removal performance.

229

230 **3. Effect of coexisting ions**

231 The effects of co-existing alkali and alkaline-earth metal cations on Pb(II), Cd(II), Cu(II) and

232 Zn(II) adsorption by HMO-TW were conducted, and the results are shown in Fig.3. Here, two

233 divalent cations with low hydration energy, Ca(II) (-1656 KJ mol^{-1}) and Mg(II) (-2049 KJ

234 mol^{-1}),[35] were selected as representative co-ions because of their stronger competition for

235 heavy metal adsorption than Na(I) or K(I). The addition of Ca(II) and Mg(II) resulted in

236 decline of the sorption of four heavy metals onto HMO-TW to various degrees. Specifically,

237 only slight drop of removal efficiency (< 25%) (i.e., good selectivity) was observed for

238 Pb(II) and Cu(II) in the presence of co-ions with 0 to 50 times higher concentrations.

239 However, greater impacts with drop of removal efficiency up to 60% were observed for Cd(II)

240 and Zn(II).

241

242 The sorption selectivity order of Pb(II)>Cd(II)>Zn(II) can be explained using two

243 mechanisms, ion exchange with the host TW and inner-sphere complexes with the loaded

244 HMO. Generally, the hydration energy of metal ions is related to their ion exchange ability,

11

245 and lower hydration energy favors ion exchange.[36] Thus, Pb(II) with lower hydration energy

246 (-1504 KJ mol^{-1}) compared to that of Cd(II) (-1708 KJ mol^{-1}) and Zn(II) (-1992 KJ mol^{-1}) [35]

247 had the most ion exchange with TW. As for the inner-sphere complexes with HMO, it can be

248 illustrated by the hard and soft acids and bases (HSAB) principle.[37] Here, the target heavy

249 metal ions act as Lewis acids while HMO as a Lewis base. We note that the softness of Pb(II)

250 is higher than that of Cd(II) and Zn(II) as a result of their different ionic radius (0.118 nm for

251 Pb(II), 0.095 nm for Cd(II) and 0.075 nm for Zn(II)). Since high softness favors Lewis

252 acid-base interaction, the adsorption of Pb(II) to HMO was the strongest (i.e., best

253 selectivity).

254

255 The stronger adsorption selectivity of Cu(II) than Cd(II) and Zn(II) is somewhat unexpected

256 since Cu(II) has the highest hydration energy (-2030 KJ mol^{-1}) and the smallest ionic radius

257 (0.073 nm), which suggest the lowest ion exchange and weakest HMO-Cu(II) interaction. The

258 results can be attributed to the amine groups on host TW, which form strong, specific

259 coordination with Cu(II).[38, 39] This also explains that the sorption of Cu(II) onto TW was

260 higher than Cd(II) although Cu(II) has much higher hydration energy in our previous study.[19]

261

262 Since TW does not have satisfactory selectivity for metal ion adsorption, the good sorption

263 selectivity of HMO-TW is mainly from the HMO on TW, which is known to have strong

264 sorption specificity for heavy metals. Nonetheless, the functional group rich TW can facilitate

265 the sorption selectivity through the Donnan membrane effect [40] caused by the attraction of

266 positively charge metal ions by non-diffusible, negatively charged carboxyl groups on TW.

267 The Donnan membrane effect is illustrated in Fig.S3. The Ca(II) had greater influence than

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268   Mg(II) on sorption of all four heavy metals by HMO-TW as expected due to its lower Gibbs

269   free energy of hydration.[36]

270

271   The distribution coefficient K_d (L g^{-1}) is also introduced to quantify the sorption selectivity of

272   four metal ions onto HMO-TW [41]

273    $$K_d = \frac{Co - Ce}{Ce} \times \frac{V}{m} \qquad (3)$$

274   Where C_o (mg L^{-1}) is the aqueous initial heavy metal ion concentration, C_e is the aqueous

275   heavy metal ion concentration at equilibrium (mg L^{-1}), V (mL) is the volume of the solution,

276   and m (g) is the mass of the adsorbent. Table 2 summarized the K_d values for four heavy metal

277   ions in the presence of different levels of Ca(II) and Mg(II). The trend of K_d value variation is

278   in good agreement with the curves in Fig. 3.

279

280   **Sorption Isotherms and Kinetic**

281   The sorption isotherms of Pb(II), Cd(II), Cu(II) and Zn(II) by HMO-TW were investigated at

282   298K, and the results are illustrated in Fig. 4. The sorption capacities of four metal ions all

283   increased with the increase of C_e as well as C_o (Fig.S4). Subsequently, the four isotherms are

284   fitted using both the Freundlich and Langmuir models. Generally, the Langmuir model refers

285   to a monolayer adsorption onto homogeneous surface with no interactions between the

286   adsorbed molecules, and the Freundlich model is an empirical equation usually used to

287   describe chemisorption on heterogeneous surface sorption.[42] The detailed fitted parameters are

288   listed in Table 3. As shown, the sorption isotherms of four heavy metals can be better fitted

289   by the Freundlich model than the Langmuir one, with related coefficients R^2 larger than 0.962.

290   The better fitting of Freundlich model indicates a chemisorption process, and the effective

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291   binding sites on HMO-TW surface for four metal ions are heterogeneous. The strong

292   interaction (e.g., inner-sphere complexes) between heavy metal ions and HMO clearly

293   contributes to the heterogeneous chemisorption process. The experimental sorption capacities

294   for Pb(II), Cd(II), Cu(II) and Zn(II) were 174.3, 78.38, 54.38 and 37.5 mg g^{-1}, respectively.

295   The capacities for Pb(II), Cd(II) and Cu(II) are much higher than the calculated q_m values of

296   the host TW, which were 26.98 mg g^{-1} for Pb(II), 15.04 mg g^{-1} for Cd(II) and 18.54 mg g^{-1} for

297   Cu(II).[19]

298

299   It is worth noting that the utilization efficiency of unit mass Mn is improved for around 5

300   times by loading HMO onto tea waste. The Pb(II), Cd(II) and Zn(II) sorption capacities of

301   unit mass Mn for HMO-TW were 3616.2, 1626.1 and 778 mg g^{-1}, respectively, and for pure

302   HMO were 710.1 , 304.1 and 117.7 mg g^{-1}, respectively.[28] The improvement of Mn utilization

303   efficiency can be attributed to the dispersion of HMO nanoparticles (< 5nm based on TEM)

304   on TW increased accessible binding sites of HMO. In addition, the sorption capacities of

305   Pb(II), Cd(II), Cu(II) and Zn(II) by HMO-TW and other previously reported materials are

306   compared in Table 5. The sorption capacities of four heavy metals onto HMO-TW are better

307   than most previously reported sorbents with low-cost merits. It is also noteworthy that

308   HMO-TW is more applicable for heavy metal removal from lightly polluted water base on the

309   results depicted in Fig.S4. The removal efficiency of four toxic metals decreased with the

310   increase of initial metal ion concentration, which can be explained by the diminished

311   opportunities of target metal ions binding to sorption sites on HMO-TW at higher initial

312   concentrations.

313

14

314 The sorption kinetics of the four heavy metal ions onto HMO-TW was also investigated (Fig.

315 5). The sorption process was very quick by HMO-TW in the initial 100 min then slowed

316 down to approach sorption equilibrium within 200 min. The kinetic data of all heavy metal

317 ions were well fitted by the pseudo-second-order model, and the fitting parameters are listed

318 in Table 4. The calculated q_e values based on pseudo-second-order model (110.3 mg g^{-1} for

319 Pb(II), 37.7 mg g^{-1} for Cd(II), 28.2 mg g^{-1} for Cu(II), 17.3 mg g^{-1} for Zn(II)) are close to the

320 experimental data (119.28 mg g^{-1} for Pb(II), 38.45 mg g^{-1} for Cd(II), 29.35 mg g^{-1} for Cu(II)，

321 18.03 mg g^{-1} for Zn(II)). The sorption of heavy metal ions by HMO-TW was relatively slow

322 compared to host TW, which may be caused by the pore blockage effect as a result of HMO

323 loading.

324

325 **Fix-bed Column Sorption and regeneration**

326 Fix-bed column sorption trail is an essential step for evaluating the engineering application

327 potential of a given sorbent. The column sorption tests of HMO-TW were conducted, and the

328 complete effluent history is described in Fig. 6. The bed volume (BV) of C_e/C_0 reaching 0.5

329 for Pb(II), Cd(II), Cu(II) and Zn(II) are around 1170, 1130, 820 and 1450 BV, respectively.

330 Note that almost no target heavy metal ions was detected in the effluent until a sudden

331 increase after 830 BV for Pb(II), 400 BV for Cd(II), 650 BV for Cu(II) and 950 BV for Zn(II).

332 The excellent results of all four heavy metal adsorption by HMO-TW in the column tests,

333 especially in the early stage, imply that HMO-TW has great potential for practical wastewater

334 treatment in flow-through systems.

335

336 The exhausted HMO-TW was able to be regenerated using a 0.5 M HCl solution at 298 K as

337   shown in Fig. 7. The adsorbed heavy metals were completely regenerated after only 6-BV of

338   HCl solution flushing, and the regeneration efficiency was larger than 95%. In addition, only

339   negligible Mn was detected in the regeneration solution.

340

341   **Conclusions**

342   A novel bio-adsorbent HMO-TW was successfully prepared by impregnating hydrated

343   manganese oxide (HMO) onto tea waste. Sorption of Pb(II), Cd(II), Cu(II) and Zn(II) onto

344   HMO-TW was observed to be pH-dependent due to a combined effect induced by the

345   ion-exchange with the host TW and the inner-sphere complexation with impregnated HMO.

346   Even in the presence of competing ions with 50 times higher concentration, HMO-TW

347   maintained excellent sorption selectivity toward four heavy metal ions due to the specific

348   binding between heavy metal ions and the loaded HMO and Donnan membrane effect.

349   Besides, the sorption of four metal ions onto HMO-TW can be well fitted by the Freundlich

350   model and a pseudo-second-order model. Satisfactory results of column sorption and

351   regeneration tests further show that HMO-TW is a promising sorbent for removing heavy

352   metals from contaminated water in engineering settings.

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433

434   Table 1 Major physicochemical properties of the host tea waste and HMO-TW

Designation	Tea waste	HMO-TW
Functional group	-COOH, -NH$_2$,-OH	-COOH, -NH$_2$,-OH and HMO
Particles size (mm)	0.25~0.88	0.25~0.88
BET surface area (m^2 g^{-1})	0.86	5.92
Average pore diameter (nm)	3.62	1.03
Mn content (%)	0	4.82

435

436   Table 2 Distribution coefficients (K_d) of Pb(II), Cd(II), Cu(II) and Zn(II) for HMO-TW in the
437   presence of different levels of Ca(II) and Mg(II)

438

Competing ions	Heavy metals	K_d (mL g^{-1}) at different initial Ca(II)or Mg(II)/M(II) ratios in solution (mol/mol)				
		5	10	15	20	50
Ca(II)	Pb(II)	23644	25048	16105	15967	12260
	Cd(II)	4799	3263	2589	2024	1224
	Cu(II)	15681	14167	8968	8661	5325
	Zn(II)	4238	2935	2336	1737	1400
Mg(II)	Pb(II)	30126	24418	18959	15013	73039
	Cd(II)	11105	4122	3616	2628	1468
	Cu(II)	26740	18333	12293	12652	8736
	Zn(II)	13028	6241	6091	5751	3221

439

440

441 Table 3 Isotherm constants for uptakes of Pb(II), Cd(II), Cu(II) and Zn(II) onto HMO-TW
442 at 298K

Heavy metals	Freundlich model			Langmuir model		
	K_f (mg^{1-n}L^n g^{-1})	n	R^2	K_L (L mg^{-1})	q_m (mg g^{-1})	R^2
Pb(II)	101.18	0.17	0.974	0.99	172.50	0.882
Cd(II)	47.19	0.13	0.979	1.55	72.88	0.807
Cu(II)	28.15	0.19	0.962	1.08	52.70	0.887
Zn(II)	19.92	0.16	0.988	3.27	32.37	0.756

443

444
445 Table 4 Kinetic parameters of Pb(II), Cd(II), Cu(II) and Zn(II) removal by HMO-TW at 298
K

Heavy metals	Pseudo-second-order			Experimental values
	k_2, 10^{-2} min^{-1}	q_e, mg g^{-1}	R^2	q_e, mg g^{-1}
Pb(II)	1.80	110.3	0.957	118.9
Cd(II)	1.41	37.7	0.994	38.4
Cu(II)	2.38	28.2	0.991	29.0
Zn(II)	1.00	17.3	0.993	18.0

446
447

448   Table 5 Comparison of the sorption capacities for Pb(II), Cd(II), Cu(II) and Zn(II) onto
449   various adsorbents

Sorbent	Metal ions	Conditions		Sorption capacity (mg g^{-1})	Refs.
HMO-TW	Pb(II)	pH 5.5	298 K	174.3	Present study
The host tea waste	Pb(II)	pH 5.0	298 K	33.49	19
Wheat bran	Pb(II)	NA		63.9	43
SD-SNTs	Pb(II)	pH 7.0	303 K	112.36	44
HMO-D001	Pb(II)	pH4.4	298 K	395	24
Manganese oxide-coated carbon nanotubes	Pb(II)	pH 5.0	323 K	78.74	45
manganese oxide coated sand	Pb(II)	pH 4.0	318 K	1.9	46
HMO-TW	Pb(II)	pH 5.5	298 K	78.38	Present study
The host tea waste	Cd(II)	pH 5.5	298 K	15.04	19
Wheat bran	Cd(II)	NA		24.2	43
Lewatit CNP 80	Cd(II)	pH 8	298 K	4.48	47
Graphene oxide membranes	Cd(II)	pH 5.8	303 K	83.8	48
Moss	Cd(II)	pH 5.0	303 K	29.0	49
Phosphorylated PAN-based nanofiber	Cd(II)	NA		37.3	50
HMO-TW	Cd(II)	pH 5.5	298 K	54.38	Present study
The host tea waste	Cu(II)	pH 5.0	298 K	18.54	19
Wheat bran	Cu(II)	NA		14.5	43
Graphene oxide membranes	Cu(II)	pH 5.8	303 K	72.6	48
manganese oxide coated sand	Cu(II)	pH 4.0	318 K	0.48	46
Lewatit CNP 80	Cu(II)	pH 8	298 K	10.24	47
HMO-TW	Zn(II)	pH 5.5	298 K	37.5	Present study
Moss	Zn(II)	pH 5.0	303 K	15.0	49
Lewatit CNP 80	Zn(II)	pH 8	298 K	20.15	47
Tree fern	Zn(II)	NA		7.58	51

450   NA: not available
451

452 Fig.1 Physical characterization of TW and HMO-TW: (a) TEM of HMO-TW; (b) FT-IR
453 spectrum of TW and HMO-TW; and (c) Zeta potential of HMO-TW at 298 K.

454

(a)

(b)

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461   (c)

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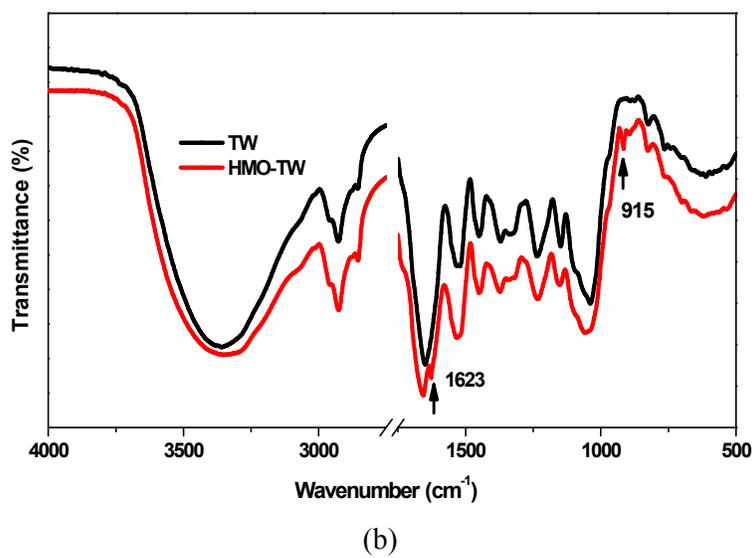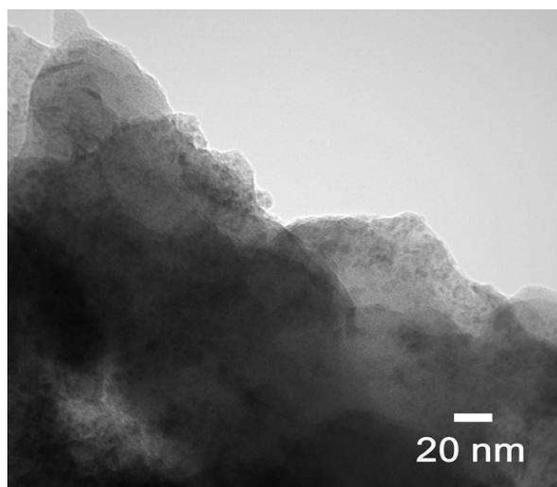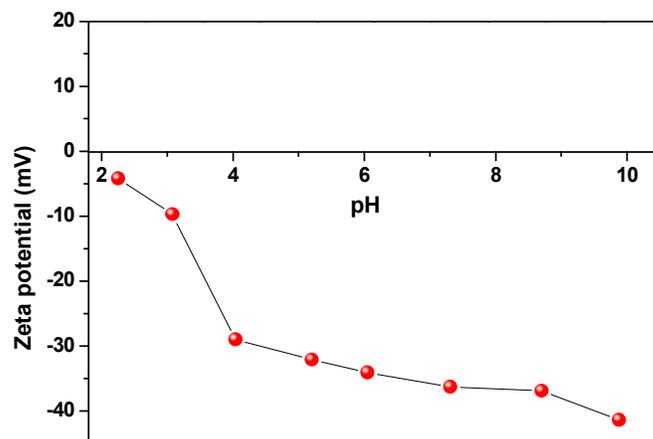
463   Fig.2 Influence of pH on sorption of Pb(II), Cd(II), Cu(II) and Zn(II) by HMO-TW.
464   Conditions: C_0 (Pb(II)) = 40 mg L^{-1}; C_0 (Cd(II)) = 20 mg L^{-1}; C_0 (Cu(II)) = 10 mg L^{-1}; C_0
465   (Zn(II)) = 10 mg L^{-1}; sorbent dose = 0.4 g L^{-1}; Temperature = 298 K.
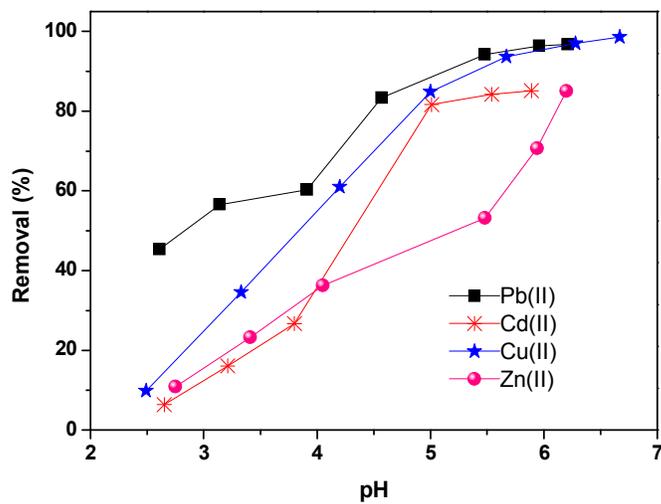
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469   Fig. 3 Influence of Ca(II) (a) and Mg(II) (b) on sorption of Pb(II), Cd(II), Cu(II) and Zn(II) by

470   HMO-TW. Conditions: C_0 (Pb(II)) = 40 mg L^{-1}; C_0 (Cd(II)) = 20 mg L^{-1}; C_0 (Cu(II)) = 10 mg

471   L^{-1}; C_0 (Zn(II)) = 5 mg L^{-1}; sorbent dose = 0.4 g L^{-1}; pH = 5.5±0.2; Temperature = 298 K.

472

473   (a)

474

475

476   (b)
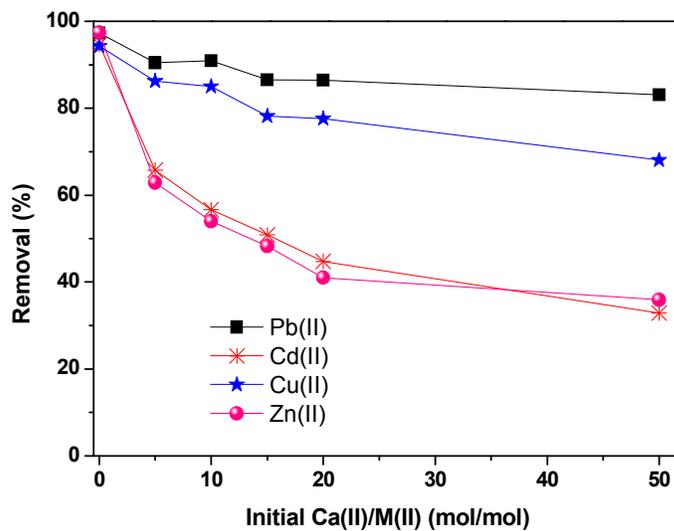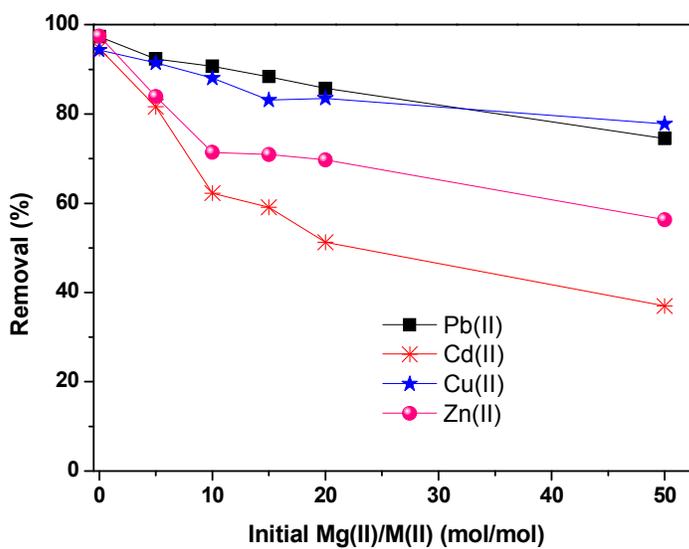
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480   Fig. 4 Sorption isotherms of Pb(II), Cd(II), Cu(II) and Zn(II) onto HMO-TW. Conditions:

481   Sorbent dose = 0.4 g L^{-1}; pH = 5.5±0.2; Temperature = 298 K.

482
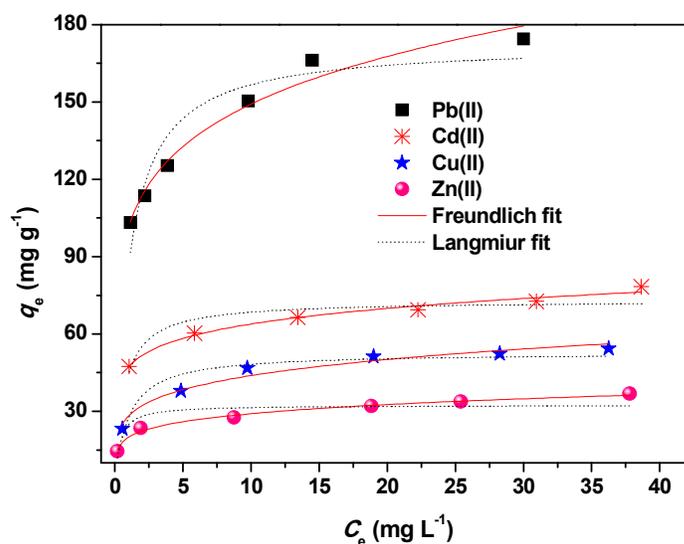
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485   Fig.5 Sorption kinetics of Pb(II), Cd(II), Cu(II) and Zn(II) onto HMO-TW. Conditions: C_0

486   (Pb(II)) = 70 mg L^{-1}; C_0 (Cd(II)) = 25 mg L^{-1}; C_0 (Cu(II)) = 30 mg L^{-1}; C_0 (Zn(II)) = 10 mg

487   L^{-1}; sorbent dose = 0.4 g L^{-1}; pH = 5.5±0.2; Temperature = 298 K.
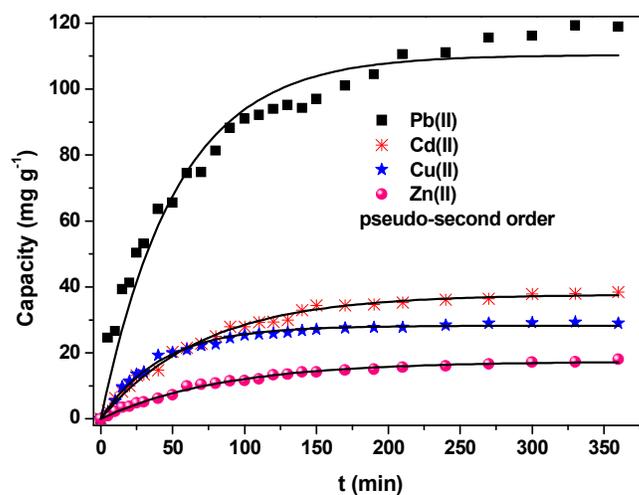
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490   Fig. 6 Breakthrough curves of Pb(II), Cd(II), Cu(II) and Zn(II) in a column system filled with
491   5 mL wet HMO-TW. Conditions: Influent concentration (C_{in}) of Pb(II) = 9.0 mg L^{-1}; C_{in}
492   (Cd(II)) = 1.5 mg L^{-1}; C_{in} (Cu(II)) = 2.7 mg L^{-1}; C_{in} (Zn(II)) = 1.1 mg L^{-1}.
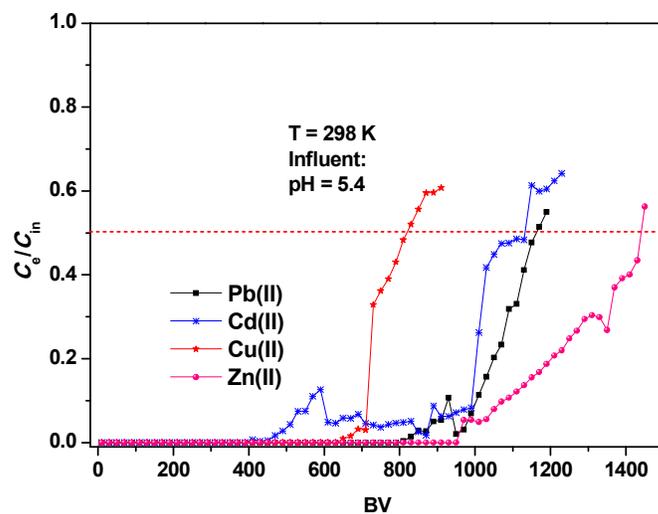
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495 Fig. 7 The cumulative desorption curves of the exhausted HMO-TW in column flushed with
496 0.5 M HCl.

497