

Removal of Various Heavy Metals by Sewage Sludge Immobilized Onto Rod-type Chitosan Biosorbent

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Removal of various heavy metals by sewage sludge immobilized onto rod-type chitosan biosorbent

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22 **Abstract**

23 The potential use of wastewater sludge as a biosorbent for removing various metals and
24 metalloids from aqueous solutions was examined. The sludge was immobilized by chitosan
25 into rods to enhance the sorption capacity and solid-liquid separation ability. An optimum
26 condition of rod-type chitosan-immobilized sludge (RCS) was selected from possibility of
27 produced biosorbent and the removal efficiency of As(V). The optimal sludge and chitosan
28 content and RCS thickness was 6.0%, 4.0% and 0.2-0.3 mm, respectively. The experiments
29 targeted cations(Cd(II)) and anions(As(V), Cr(VI), and Mn(VII)). Pseudo-first-order and
30 pseudo-second-order models adequately described kinetics models and Langmuir and
31 Freundlich models described isotherm models for RCS, which showed higher adsorption
32 ability for anionic metals over cationic metals. The results indicate that electrostatic attraction
33 or ion exchange is the most important mechanism for metal/metalloid adsorption, except in
34 the case of Mn(VII), for which an adsorption-coupled reduction mechanism is suggested.

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38 *Keywords:* sludge; biosorption; chitosan; arsenic; mechanism;

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41 **1. Introduction**

42 During the development of industry, the presence of toxic heavy metal contamination of
43 the environment is a source of serious concern. Due to their harmful effects on human health,
44 finding methods to remove heavy metals is of great importance. Chemical precipitation, ion
45 exchange, evaporation, electroplating and membrane processes are common commercial
46 methods for removing excessive concentrations of heavy metals from aqueous solutions [1,
47 2]. However, these methods can be expensive and inefficient and generate chemical sludge.
48 New environmentally friendly technologies for removing heavy metal ions from wastewater
49 are urgently needed.

50 Recently, biosorption has been suggested as a possible alternative to conventional
51 methods of heavy metal removal [3]. The main advantages of biosorption are reusability, low
52 operating costs, and no production of toxic secondary compounds. Biosorbents, the
53 adsorbents used in biosorption, are prepared from various biomasses such as algae, aquatic
54 plants, moss, and bacteria, all of which can be difficult to produce in large quantities. Many
55 researches have been carried out to produce biosorbent using wastewater sludge which has no
56 limitation on the production amount [4-7]. The use of wastewater sludge for biosorbent
57 offered not the naturally abundant but also no requirement of nutrients, and easy availability.
58 Even though it has merits, it often suffers several drawbacks using raw wastewater sludge.
59 The most important limitations include solid-liquid separation problems, possible biomass
60 swelling and inability to regenerate/reuse [3, 8]. To overcome this drawback, wastewater
61 sludge therefore needs to be immobilized. Chitosan, sodium alginate, polysulfone,
62 polyacrylamide, and polyurethane have been used as matrix materials for immobilization of
63 biosorbents [9, 10]. Special attention has been given to polysaccharides and natural polymers
64 such as chitosan, which is an emerging matrix materials for immobilizing biomass [11].

65 In this study, sewage-sludge waste was used as a raw material for the manufacture of

66 biosorbents for the removal of heavy metals from aqueous solutions by batch biosorption
67 experiments. To facilitate solid-liquid separation, sludge was immobilized by chitosan, which
68 is known as a common, inexpensive, and environmentally friendly matrix material. Fourier-
69 transform infrared spectroscopy (FTIR) analysis and total organic carbon (TOC)
70 measurements were taken to confirm immobilization strength and characteristics. Kinetic and
71 isotherm experiments were conducted to evaluate biosorption rates and the capacity of the
72 biosorbent to remove various metals.

73

74

75 **2. Materials**

76

77 ***2.1. Preparation of the rod-type biosorbent***

78 The raw material used in the experiments was a biochemical sludge from a biological
79 wastewater treatment plant in Yonsei University, Korea. Average sludge comprised $15 \pm 5\%$
80 total solids and $70 \pm 5\%$ volatile solids/total solids. The immobilization process began with
81 2–6% (w/v) activated sludge (ignoring moisture) stirred in distilled water. After mixing, a 3–
82 6% (w/v) solution of chitosan and 5% acetic acid (v/v) was added by continuous stirring with
83 a mechanical stirrer at 160 rpm for 24 h. The mixture was extruded through syringes (0.2–0.3
84 mm, 0.5–0.6 mm, 0.8–0.9 mm and 1.0–1.2 mm diameter) into 2 M sodium hydroxide. The
85 resultant rod-type biosorbent was kept in a polymerizing medium for 4 h. To compare
86 biosorbent types, we also produced bead-type biosorbents with the same process. Biosorbents
87 were washed in distilled and deionized water to leach out excess solvents and then freeze-
88 dried. The dried biosorbent rods were stored in a desiccator until used in the experiments.

89

90 ***2.2. Reagents***

91 Chitosan (75–85% acetylation degree, molecular weight: 200–800 kDa) was supplied by
92 Sigma-Aldrich (USA). Acetic acid (purity > 99%) was purchased from Duksan (Korea). Pure
93 analytical grade As(V), Cd(II), Cr(VI), and Mn(VII) solutions were prepared by dissolving
94 solid $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich, USA), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich, USA),
95 $\text{K}_2\text{Cr}_2\text{O}_7$ (Junsei, Japan), and KMnO_4 (Samchun, Korea) in distilled water. All chemicals
96 used in this study were of analytical grade. The pH of the solutions was adjusted by adding
97 sodium hydroxide (Samchun, Korea) or hydrogen chloride (Samchun, Korea) solutions.

98

99 **2.3. Batch adsorption studies**

100 The kinetics and isothermal removal of As(V), Cd(II), Cr(VI), and Mn(VII) from
101 aqueous solutions by biosorbent rods was observed in 230 mL plastic bottles. The
102 equilibration (shaking) time was 6 h in contact with 200 mL of the wastewater. The bottles
103 were agitated in a shaker at 200 rpm at room temperature. In the kinetics experiment, 2.0 g/L
104 of each biosorbent was put into contact with 50 mg/L of each metal or metalloid solution. All
105 solutions were adjusted to pH 5.5. Isotherm experiments were carried out at various metal
106 concentrations, ranging from 50 mg/L to 1500 mg/L. In all batch experiments, the solution
107 pH was maintained at the desired value using 1 M HCl and 1 M NaOH solutions. The amount
108 of metal or metalloid adsorbed on the biosorbent, q (mg/g), was calculated using the mass
109 balance equation

110

$$111 \quad q \text{ (mg/g)} = \frac{(C_0 - C_e)V}{m} \quad (1)$$

112

113 where C_0 and C_e are the initial and equilibrium concentrations (mg/L), respectively, V is the
114 working volume (L), and m is the weight of the biomass (g). All biosorption experiments

115 were performed in triplicate, with an error rate of less than 5%. Mean values were used for
116 kinetic and isotherm experimental data.

117

118 **2.5. Analytical methods**

119 TOC of the solution was measured using a TOC analyzer (TOC-VCPH/CPN,
120 SHIMADZU, Japan). Total nitrogen (TN) and total phosphorous (TP) were determined using
121 a test kit (C-MAC. Co., Korea). An infrared spectrum of the biosorbent with an FTIR
122 spectrometer (Vertex 70, Bruker, USA). An inductively coupled plasma-optical emission
123 spectrometer (ICP/IRIS, Thermo Jarrell Ash Co., USA) was used to analyze total metals after
124 being filtered through a 0.20 μm membrane. The Cr(VI) concentration was determined by
125 spectrophotometric analysis at 540 nm according to a standard method using 1,5-
126 diphenylcarbazide. The pink color of Mn(VII) was analyzed at 525 nm to measure its
127 concentration.

128

129

130 **3. Results and discussion**

131 **3.1. Characteristics of chitosan-immobilized biosorbent**

132 Because the activated sludge was composed of bacteria and protozoa, a biosorbent made
133 directly from the sludge may unintentionally contaminate a water system [12]. An
134 immobilization technique can address this problem. In this study, biosorbents were prepared
135 by an immobilization technique using chitosan. While much research in recent years has
136 focused on immobilization using chitosan, few studies have attempted to evaluate
137 immobilization performance. We tested the performance of immobilization through analysis
138 of TOC released from the biosorbent during pretreatment with deionized and distilled water.
139 TOC released from immobilized biosorbents was much lower than TOC released from raw

140 biosorbent. In addition, TN and TP, which are indicators of pollution, were also found to be
141 less eluted (Table 1), suggesting that immobilization can alter the properties of a biosorbent,
142 including surface functional groups. In particular, a functional groups on the surface often
143 changes after immobilization. To determine the nature of functional group change, raw
144 biosorbents and chitosan-immobilized biosorbents were examined using FTIR analysis (SI
145 Fig. 1). The spectra of the raw biosorbent and chitosan-immobilized biosorbents displayed
146 many absorption peaks. A broad and strong band in the 3600–3200 cm^{-1} region was
147 associated with N-H and O-H stretching vibrations in amine and hydroxyl groups [13]. Two
148 spectra also displayed absorption peaks at 1650 cm^{-1} and 1750 cm^{-1} relevant to the stretching
149 band of the carboxyl double bond in the carboxyl functional group [14]. The phosphate group
150 also observed everything (1150 cm^{-1} [=O stretching] and 1050 cm^{-1} [POH stretching and/or
151 POC stretching]) [15]. After the chitosan immobilized the biomass, the FTIR spectrum
152 showed some peak changes (SI Fig. 1). The band at 3378 cm^{-1} broadened because of the
153 large number of amine groups in chitosan. Amine group biosorption sites played the most
154 significant role in anionic metal removal [16]. The FTIR results show that chitosan-
155 immobilized biomass was expected to remove anionic metal more effectively than raw
156 biomass [17].

157

158 ***3.2. Optimization of rod-type biosorbent modification conditions***

159 The biosorbent shape, sludge content, chitosan content, and diameter of the biosorbent
160 were manipulated to optimize biosorbent preparation.

161

162 ***3.2.1 Effect of biosorbent shape***

163 A kinetics study was conducted to determine the effect of immobilization and biosorbent
164 shape on adsorption. Experiments using raw sludge (RS), bead-type of chitosan-immobilized

165 sludge (BCS), and rod-type chitosan-immobilized sludge (RCS) were performed to evaluate
166 the contact time required to reach equilibrium. Chitosan is a biopolymer with a high nitrogen
167 content that confers an adsorption ability for anionic metal ions. As(V) was used to evaluate
168 the performance of each biosorbent. Figure 1(a) exhibits the As(V) removal of RS, BCS, and
169 RCS as a function of contact time at a pH of 5.5. BCS and RCS delivered an As(V) removal
170 efficiency that was 2–3 times higher than that of RS. This result can be attributed to the
171 presence of amine groups on the biosorbent [18].

172

173 **3.2.2 Effect of material content in biosorbent**

174 The amounts of sludge and chitosan were important variables affecting sorption
175 performance. Figure 1(b) shows the effects of sludge on As(V) removal onto RCS. The
176 sludge content influenced the biomass surface, affecting the capacity of the biomass for
177 As(V) biosorption. For finer details, we compared adsorption results through pseudo-first-
178 order and pseudo-second-order kinetics modeling. These models were employed to
179 investigate the adsorption dynamics of pollutants onto the biosorbents in relation to time and
180 to estimate the rate of the process. They can also shed light on biosorption mechanisms and
181 potential rate-controlling steps, which may include mass transport and chemical reaction
182 processes [19]. The pseudo-first-order equation is:

183

$$184 \quad q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

185

186 where q_e is the amount of adsorbate adsorbed (mg/g) at equilibrium, q_t is the amount of
187 adsorbate adsorbed (mg/g) at time t (min) and k_1 (min^{-1}) is the rate constant.

188 The pseudo-second-order equation is usually associated with the situation in which the
189 rate of direct adsorption or desorption controls the overall sorption kinetics, and typically

190 describes the removal behavior of metals [20, 21]. An integrated form of the pseudo-second-
191 order equation can be expressed as:

192

$$193 \quad \frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (3)$$

194 or

$$195 \quad \frac{q_t}{t} = \frac{h}{1+k_2 q_e t} \quad (4)$$

196

197 where h (g/mg·h) is the initial sorption rate and k_2 (g/mg·h) is the rate constant. From the
198 equations of the different obtained the equilibrium metal sorption, values for the rate constant,
199 initial sorption rate, and coefficients were calculated and are presented in Table 2. In the case
200 of equilibrium uptake, q_e , removal increases with increasing sludge ratio in RCS. When
201 comparing the rate constant and initial sorption rate, RCS with 4.0% sludge shows the fastest
202 rate. From these results, it can be seen that 4.0% was satisfied in terms of speed, but 6.0%
203 was the optimal adsorption amount. To increase adsorption, we attempted to produce an
204 adsorbent containing more than 6.0% sludge. However, producing the biosorbent in this
205 manner proved problematic. We therefore set the optimum sludge content at 6.0% of RCS,
206 which showed the maximum amount and has the benefit environmental load.

207 The effect of the chitosan content in RCS on biosorption of As(V) is shown in Fig. 1(c).
208 The data used in Equations 2–4 are presented in Table 2. A chitosan content of 6.0% in RCS
209 showed higher removal of As(V) compared with other RCS. The higher removal may be due
210 to the effect of As(V) on the chitosan amine group in RCS. Comparing correlation
211 coefficients (R^2), the pseudo-second-order kinetic model was a better fit in describing the
212 biosorption kinetics of studied heavy metals onto RCS. It was assumed that the As(V)
213 adsorption process was chemisorption involving valency forces through sharing or the

214 exchange of electrons between the RCS and As(V) as covalent forces [22]. This facilitated
215 the electrostatic attraction of As(V) ions toward RCS, leading to an increase in biosorption.
216 However, when the equilibrium uptake, rate constant, and initial sorption rate values of As(V)
217 were examined, the effect of chitosan in RCS was not as dramatic, considering the
218 economical manufacture of biosorbent focuses on RCS with sludge and chitosan contents of
219 6.0% and 4.0%, respectively.

220

221 **3.2.3 Effect of biosorbent size**

222 Biosorbent diameter size is an important controlling parameter of the biosorption
223 process. The effect of RCS diameter size on As(V) biosorption was studied using samples of
224 four biosorbents with average diameters of 0.2–0.3, 0.5–0.6, 0.8–0.9 and 1.0–1.2 mm, and
225 sludge and chitosan contents of 6.0% and 4.0%. The results are presented in Fig. 1(d).
226 Equilibrium uptake values showed similar values (Table 2). However, the rate constant and
227 initial sorption rate decreased when the biosorbent diameter increased from 0.2–0.3 to 1.0–
228 1.2 mm. The higher biosorption with smaller RCS diameters may be attributed to the fact that
229 RCS with smaller diameter has greater surface area. Therefore, an RCS diameter size of 0.2–
230 0.3 mm was selected for experimental purposes.

231

232 **3.3. Adsorption study**

233 **3.3.1 Kinetics**

234 Figure 2 shows the kinetics of metalloid/metal adsorption onto RCS by batch contact
235 time. Equilibrium times were different among the metalloids/metals. For Cd(II) ions,
236 equilibrium states were reached after 1 h. The As(V) and Cr(VI) sorptions were achieved
237 after 3 and hours of contact time, respectively. The Mn(VII) sorptions were finished after 6 h.
238 Table 3 shows that the pseudo-second-order equation, which agrees that chemisorption is the

239 rate-controlling mechanism, was able to better describe the adsorption of As(V), Cd(II),
240 Cr(VI) and Mn(VII) onto RCS. By comparing the amount of metals adsorbed at equilibrium,
241 the following order was obtained: Mn(VII) > Cr(VI) > As(V) > Cd(II). While Mn(VII) was
242 completely removed, sorption of Mn(VII) did not fit the kinetics models. The Mn(VII)
243 removal mechanism is recognized to differ from that of other metals. To examine the
244 Mn(VII) removal characteristics of RCS, total Mn concentrations were investigated (SI Fig.
245 2). After complete Mn(VII) removal, Mn remained in the aqueous phase. It can therefore be
246 concluded that the Mn(VII) removed from aqueous phase was reduced to other species of Mn
247 [23]. Despite the fact that Cd(II) ions, as representative metal cations, were more weakly
248 adsorbed than the other metals, their removal showed the fastest kinetics. It appears that
249 Cd(II) reacted strongly with other functional groups. In general, it is known that the carboxyl
250 group is involved in the adsorption of Cd (II) [24, 25]. The adsorption of Cd (II) was weakly
251 adsorbed because it was decreased carboxyl group in the RCS compared the raw sludge (SI
252 Fig. 1).

253

254 **3.3.2 Isotherms**

255 Biosorption isotherms can represent the interaction between a biosorbate and biosorbent,
256 and provide information about the distribution of the biosorbate between the liquid and solid
257 phases at several equilibrium concentrations. Isotherm modeling is therefore important for
258 biosorption data interpretation and prediction [7, 26]. In this study, isotherm models of
259 Freundlich and Langmuir were used to evaluate biosorption equilibrium data. Freundlich and
260 Langmuir isotherm equations are in the forms of:

261

$$262 \quad q_e = K_F C_e^{1/n} \quad (5)$$

263 and

264
$$q_e = \frac{q_{max}bC_e}{1+bC_e} \tag{6}$$

265

266 where K_f and n are constants incorporating all parameters affecting the biosorption process in
267 the Freundlich equation and b is the constant related to affinity of the binding sites in the
268 Langmuir equation. In the Freundlich equation, K_F (L/mg)^{1/n} and n (dimensionless) are
269 constants. On average, a favorable adsorption tends to have a n between 1 and 10. In the
270 Langmuir equation, q_{max} is the maximum adsorption capacity (mg/g) and b (L/g) is the
271 isotherm constant.

272 Langmuir and Freundlich isotherm models were used to interpret the experimental
273 isotherm data of RCS. Model parameters and R^2 values are summarized in Table 3. The
274 sorption experimental data and respective Langmuir and Freundlich isotherms are plotted
275 in Fig. 3(a), (b), (c) and (d) respectively. A linear regression of the experimental results for
276 As(V) and Cr(VI) proved a better fit in Langmuir isotherms. This result can be attributed to
277 the fact that As(V) and Cr(VI) biosorption of RCS was assumed by sorbate, and the equation
278 describing the reaction rate allows for simultaneous adsorption and desorption [27]. When
279 comparing Langmuir parameters values obtained for As(V) and Cr(VI), q_{max} was
280 approximately 42.25 mg As(V) or 70.79 mg Cr(VI) per g of RCS. The values for As(V) from
281 the present study are comparable or considerably greater than other reported sludge sorbents
282 (Table 4). The other metals, Cd(II) and Mn(VII), were well described by the Freundlich
283 equation based on R^2 . This difference may be explained by the presence of an operating
284 mechanism other than basic ion exchange, such as specific adsorption-complexation reactions
285 taking place in the adsorption process [28]. As mentioned above, the biosorption mechanism
286 of Mn(VII) was suggested by an adsorption-coupled reduction mechanism.

287

288 **4. Conclusions**

289 The aim of the present study was to develop a high-performance biosorbent of non-
290 living activated sludge. The incorporation of immobilizing chitosan, which was confirmed by
291 the release of TOC, TN, and TP from the biosorbent during pretreatment with deionized-
292 distilled water wash, may offer an effective method of decreasing metal and metalloid
293 concentrations in wastewater. Comparing experiments for adsorption of As(V), the optimal
294 conditions for biosorption were a rod shape, 4.0% chitosan, and a biosorbent diameter of 0.2–
295 0.3 mm, in contact with 6.0% dried sludge. An investigation of the removal rates of various
296 cationic and anionic heavy metals found that RCS had adsorbed anionic metals more
297 effectively than cationic metals. The maximum biosorption capacities of RCS were
298 determined to be 42.25 mg/g for As(V), 28.69 mg/g for Cd(II), 70.79 mg/g for Cr(VI), and
299 284.11 mg/g for Mn(VII). The model-fitting results indicate that adsorption-coupled
300 reduction and ion exchange must be involved in the adsorption of the Mn(VII), while ion
301 exchange or electrostatic attraction is the most important mechanism for other metals and
302 metalloids.

303

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308

309

310 **Author contributions**

311 Ji Hae Seo: Methodology, Experiment

312 Namgyu Kim: Conceptualization, Writing-Original draft preparation

313 Munsik Park: Investigation, Methodology

314 Donghee Park: Project administration, Writing-Review & Editing

315

316

317

318 **Competing interests statement**

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

321

322

323 **References**

- 324 1. Fu, F., Wang, Q. Removal of heavy metal ions from wastewaters: A review. *J. Environ.*
325 *Manage.* **92**, 407-418 (2011).
- 326 2. Yaqub, M., Lee, S. H. Heavy metals removal from aqueous solution through micellar
327 enhanced ultrafiltration: A review. *Environ. Eng. Res.* **24**, 363-375 (2019).
- 328 3. Park, D., Yun, Y. S., Park, J. M. The past, present, and future trends of biosorption.
329 *Biotechnol. Bioprocess Eng.* **15**, 86-102 (2010).
- 330 4. Al-Qodah, Z. Biosorption of heavy metal ions from aqueous solutions by activated sludge.
331 *Desalination* **196**, 164-176 (2006).
- 332 5. Maderova, Z., Baldikova, E., Pospiskova, K., Safarik, I., Safarikova, M. Removal of dyes
333 by adsorption on magnetically modified activated sludge. *Int. J. Environ. Sci. Technol.* **13**,
334 1653-1664 (2016).
- 335 6. Ozdemir, S., Turp, S. M., Oz, N. Simultaneous dry-sorption of heavy metals by porous
336 adsorbents during sludge composting. *Environ. Eng. Res.* **25**, 258-265 (2020).
- 337 7. Seo, J. H., Kim, N., Park, M., Lee, S., Yeon, S., Park, D. Evaluation of metal removal
338 performance of rod-type biosorbent prepared from sewage-sludge. *Environ. Eng. Res.* **25**,
339 700-706 (2020).
- 340 8. Dai, Y., Zhang, N., Xing, C., Cui, Q., Sun, Q. The adsorption, regeneration and
341 engineering applications of biochar for removal organic pollutants: A review.
342 *Chemosphere* **223**, 12-27 (2019).
- 343 9. Lin, X., Wang, L., Jiang, S., Cui, L., Wu, G. Iron-doped chitosan microsphere for As(III)
344 adsorption in aqueous solution: Kinetic, isotherm and thermodynamics studies. *Korean J.*
345 *Chem. Eng.* **36**, 1102-1114 (2019).
- 346 10. Vijayaraghavan, K., Yun, Y. -S. Bacterial biosorbents and biosorption. *Biotechnol. Adv.*
347 **26**, 266-291 (2008).

- 348 11. Gerente, C., Lee, V. K. C. , Le Cloirec, P., McKay, G. Application of chitosan for the
349 removal of metals from wastewaters by adsorption - Mechanisms and models review. *Crit.*
350 *Rev. Environ. Sci. Technol.* **37**, 41-127 (2007).
- 351 12. Amrullah, A., Paksung, N., Matsumura, Y. Cell structure destruction and its kinetics
352 during hydrothermal treatment of sewage sludge. *Korean J. Chem. Eng.* **36**, 433-438
353 (2019).
- 354 13. Altun, T., Ecevit, H. Cr(VI) removal using Fe₂O₃-chitosan-cherry kernel shell pyrolytic
355 charcoal composite beads. *Environ. Eng. Res.* **25**, 426-438 (2000).
- 356 14. Chen, Q., Zheng, J., Wen, L., Yang, C., Zhang, L. A multi-functional-group modified
357 cellulose for enhanced heavy metal cadmium adsorption: Performance and quantum
358 chemical mechanism. *Chemosphere* **224**, 509-518 (2019).
- 359 15. Ramrakhiani, L., Majumder, R., Khowala, S. Removal of hexavalent chromium by heat
360 inactivated fungal biomass of *Termitomyces clypeatus*: Surface characterization and
361 mechanism of biosorption. *Chem. Eng. J.* **171**, 1060-1068 (2011).
- 362 16. Kim, N., Park, M., Yun, Y.-S., Park, D. Removal of anionic arsenate by a bacterial
363 biosorbent prepared from fermentation biowaste. *Chemosphere* **226**, 67-74 (2019).
- 364 17. Lipatova, I. M., Makarova, L. I., Yusova, A. A. Adsorption removal of anionic dyes from
365 aqueous solutions by chitosan nanoparticles deposited on the fibrous carrier.
366 *Chemosphere* **212**, 1155-1162 (2018).
- 367 18. Deng, S., Ting, Y.P. Polyethylenimine-modified fungal biomass as a high-capacity
368 biosorbent for Cr(VI) anions: Sorption capacity and uptake mechanisms. *Environ. Sci.*
369 *Technol.* **39**, 8490-8496 (2005).
- 370 19. Ho, Y. S. Review of second-order models for adsorption systems. *J. Hazard. Mater.* **136**,
371 681-689 (2006).
- 372 20. Ho, Y. S., McKay, G. Pseudo-second order model for sorption processes. *Process*

- 373 *Biochem.* **34**, 451-465 (1999).
- 374 21. Tran, H. N., You, S. -J., Hosseini-Bandegharai, A., Chao, H. -P. Mistakes and
375 inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical
376 review. *Water Res.* **120**, 88-116 (2017).
- 377 22. Graillet, A., Bouyer, D., Monge, S., Robin, J. J., Loison, P., Faur, C. Sorption properties
378 of a new thermosensitive copolymeric sorbent bearing phosphonic acid moieties in multi-
379 component solution of cationic species. *J. Hazard. Mater.* **260**, 425-433 (2013).
- 380 23. Dash, S., Patel, S., Mishra, B. K. Oxidation by permanganate: synthetic and mechanistic
381 aspects. *Tetrahedron* **65**, 707-739 (2009).
- 382 24. Kim, N., Park, M., Park, D. A new efficient forest biowaste as biosorbent for removal of
383 cationic heavy metals. *Bioresource Technol.* **175**, 629-632 (2015).
- 384 25. Su, J., Gao, C., Huang, T., Gao, Y., Bai, X., He, L. Characterization and mechanism of
385 the Cd(II) removal by anaerobic denitrification bacterium *Pseudomonas* sp. H117.
386 *Chemosphere* **222**, 970-979 (2019).
- 387 26. Ren, Z., Chen, F., Wang, B., Song, Z., Zhou, Z., Ren, D. Magnetic biochar from alkali-
388 activated rice straw for removal of rhodamine B from aqueous solution. *Environ. Eng.*
389 *Res.* **25**, 536-544 (2020).
- 390 27. Saeed, A., Iqbal, M., Akhtar, M. W. Removal and recovery of lead(II) from single and
391 multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). *J. Hazard.*
392 *Mater.* **117**, 65-73 (2005).
- 393 28. Liu, H., Yang, F., Zheng, Y., Kang, J., Qu, J., Chen, J. P. Improvement of metal
394 adsorption onto chitosan/*Sargassum* sp. composite sorbent by an innovative ion-imprint
395 technology. *Water Res.* **45**, 145-154 (2011).
- 396 29. Tavares, D. S., Lopes, C. B., Coelho, J. P., Sánchez, M. E., Garcia, A. I., Duarte, A. C.,
397 Otero, M., Pereira, E. Removal of arsenic from aqueous solutions by sorption onto

- 398 sewage sludge-based sorbent. *Water Air Soil Pollut.* **223**, 2311-2321 (2012).
- 399 30. Agrafioti, E., Kalderis, D., Diamadopoulos, E. Arsenic and chromium removal from
400 water using biochars derived from rice husk, organic solid wastes and sewage sludge. *J.*
401 *Environ. Manage.* **133**, 309-314 (2014).
- 402 31. Yang, J. S., Kim, Y. S., Park, S. M., Baek, K. Removal of As(III) and As(V) using iron-
403 rich sludge produced from coal mine drainage treatment plant. *Environ. Sci. Pollut. Res.*
404 **21**, 10878-10889 (2014).
- 405 32. Lee, H., Kim, D., Kim, J., Ji, M. K., Han, Y. S., Park, Y. T., Yun, H. S., Choi, J. As(III)
406 and As(V) removal from the aqueous phase via adsorption onto acid mine drainage
407 sludge (AMDS) alginate beads and goethite alginate beads. *J. Hazard. Mater.* **292**, 146-
408 154 (2015).
- 409 33. Wang, L., Wang, J. M., Zhang, R., Liu, X. G., Song, G. X., Chen, X. F., Wang, Y., Kong,
410 J. L. Highly efficient As(V)/Sb(V) removal by magnetic sludge composite: synthesis,
411 characterization, equilibrium, and mechanism studies. *RSC Adv.* **6**, 42876-42884 (2016).
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414

415 **Figure legends**

416

417 **Figure 1.** Effect of (a) biosorbent shape, (b) chitosan content, (c) sludge content and (d)
418 biosorbent size on adsorption of As(V) on the sludge chitosan (biosorbent dosage = 2 g/L,
419 agitation rate = 200 rpm, contact time = 6 h, temperature = 25 °C, Vw = 200mL, pH non
420 shift(pH 5.5)).

421

422 **Figure 2.** Kinetics of metalloid/metal adsorption (As(V), Cd(II), Cr(VI), and Mn(VII)) onto
423 the sludge chitosan. (biomass dosage = 2 g/L, agitation rate = 200 rpm, contact time = 6 h,
424 temperature = 25 °C, Vw = 200mL, pH non shift(pH 5.5)).

425

426 **Figure 3.** Adsorption isotherms of (a) As(V), (b) Cd(II), (c) Cr(VI) and (d) Mn(VII) by the
427 rod-type biosorbent. The continuous lines were predicted by the Langmuir model; the dotted
428 lines were produced by the Freundlich model. (biomass dosage = 2 g/L, agitation rate = 200
429 rpm, temperature = 25 °C, Vw = 200mL, pH non shift(pH 5.5))

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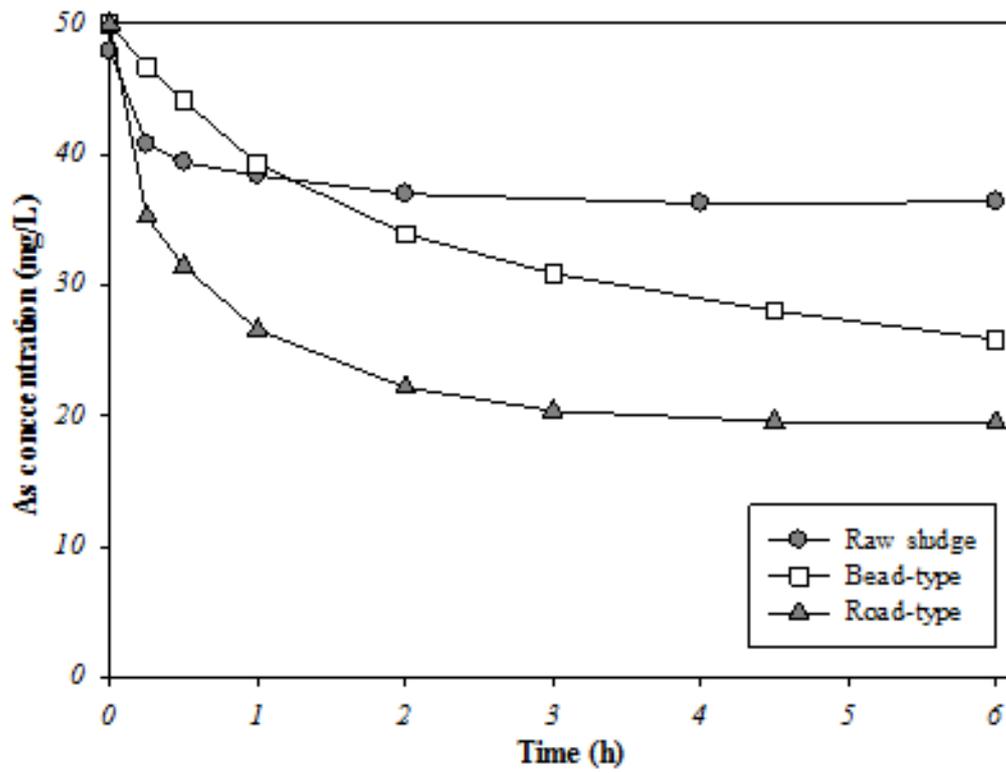
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Figure 1 (a)

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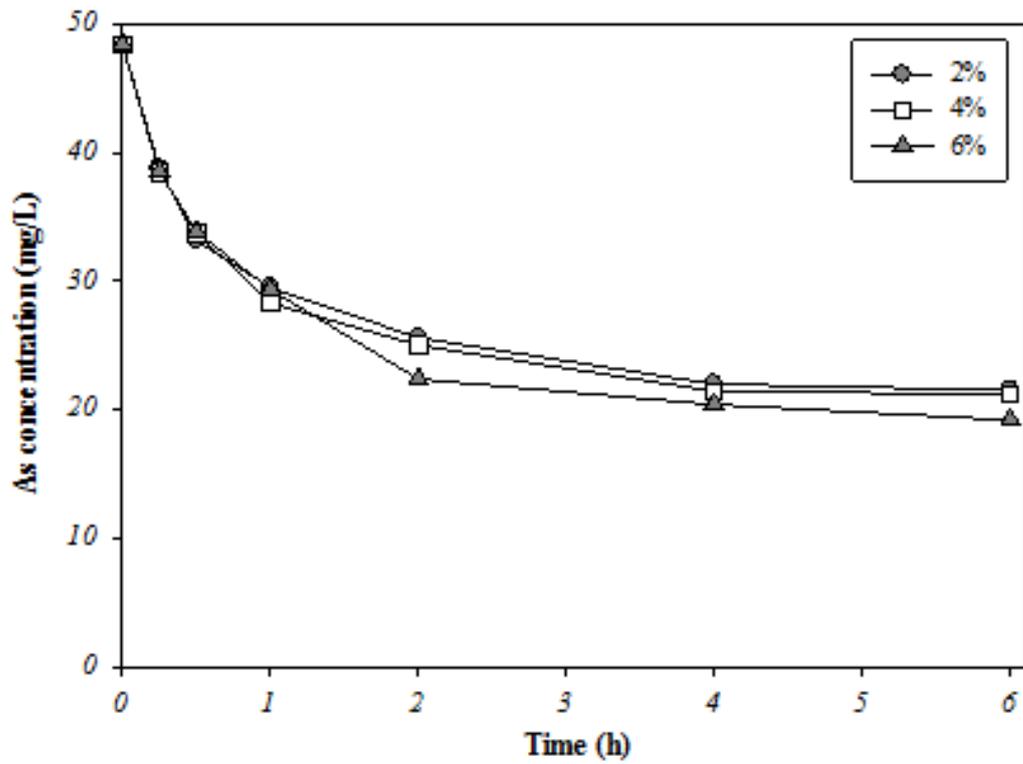
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Figure 1 (b)

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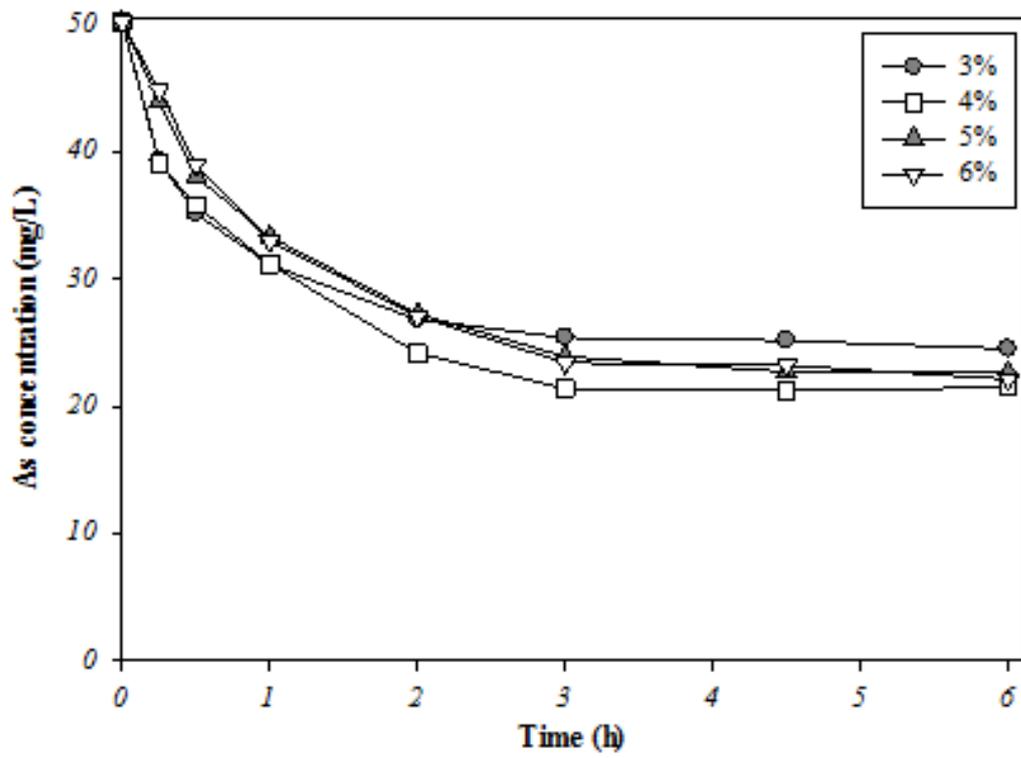
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Figure 1 (c)

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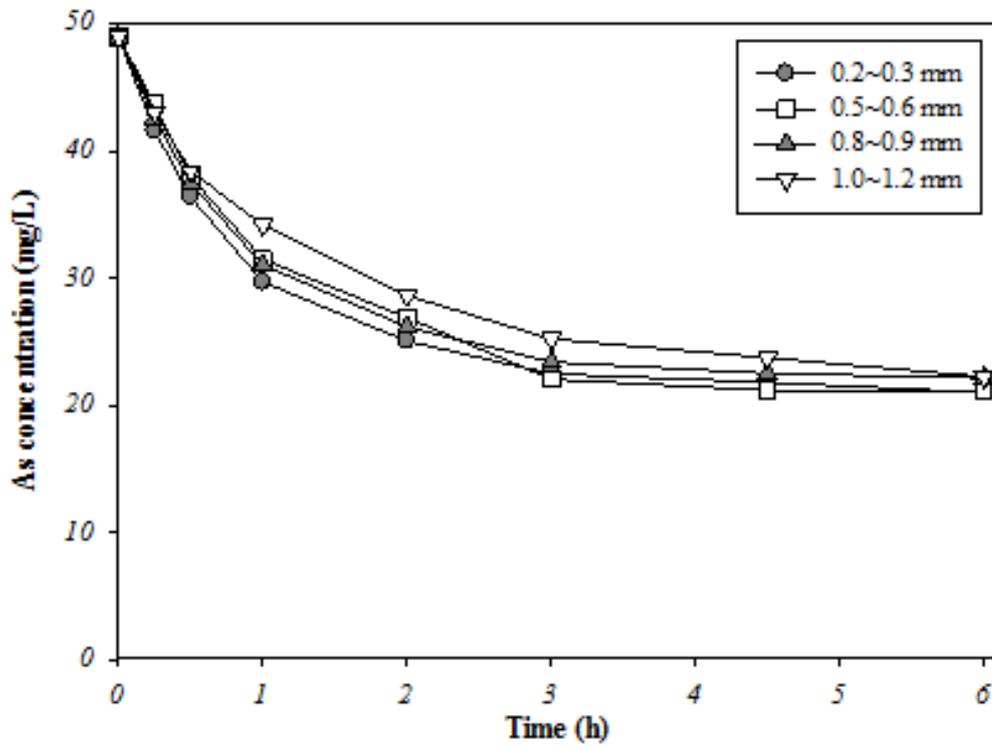
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Figure 1 (d)

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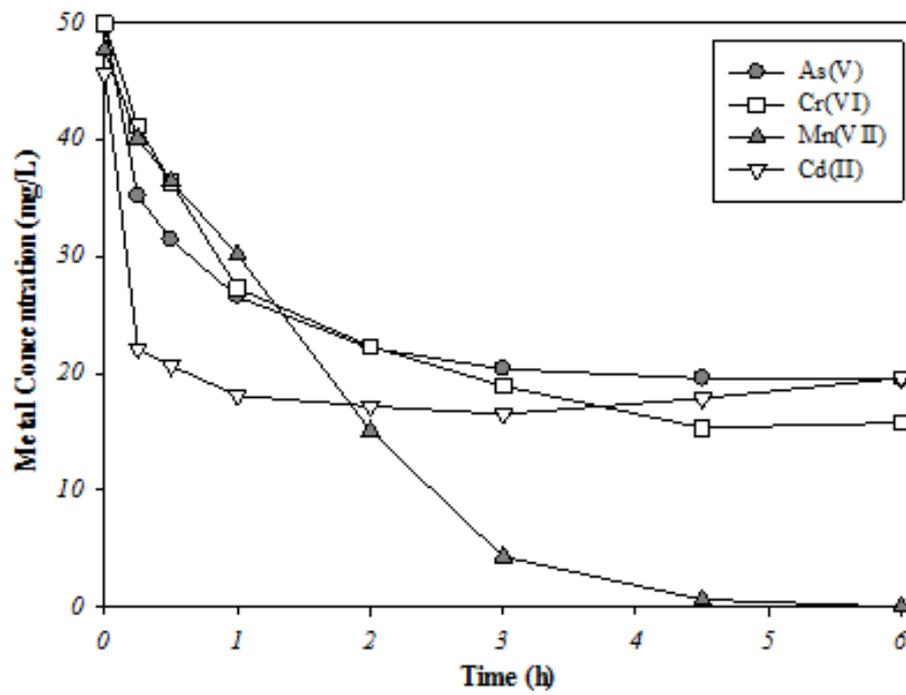
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Figure 2

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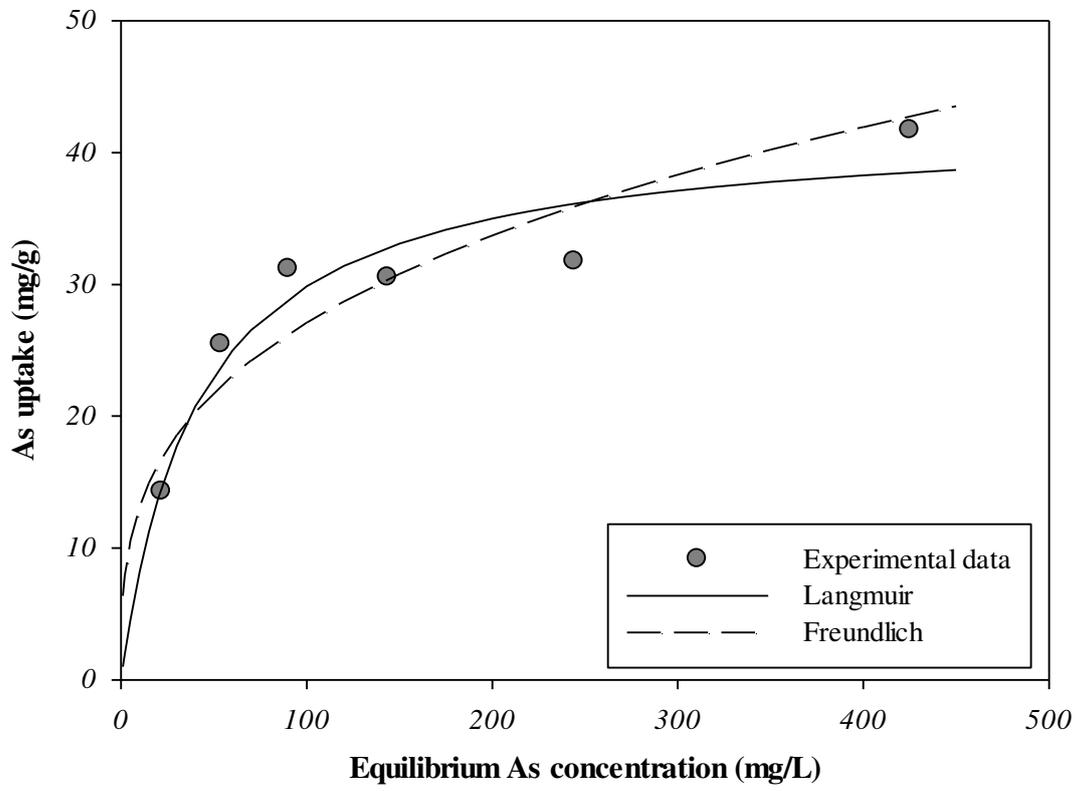
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Figure 3 (a)

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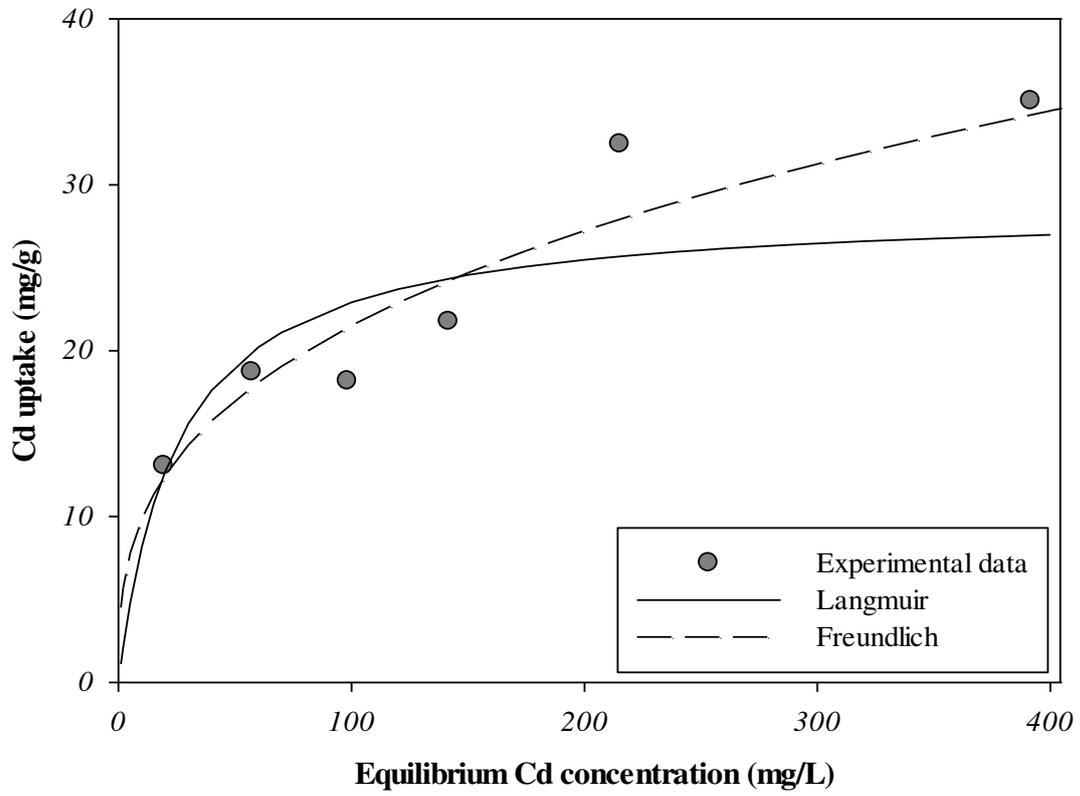
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Figure 3 (b)

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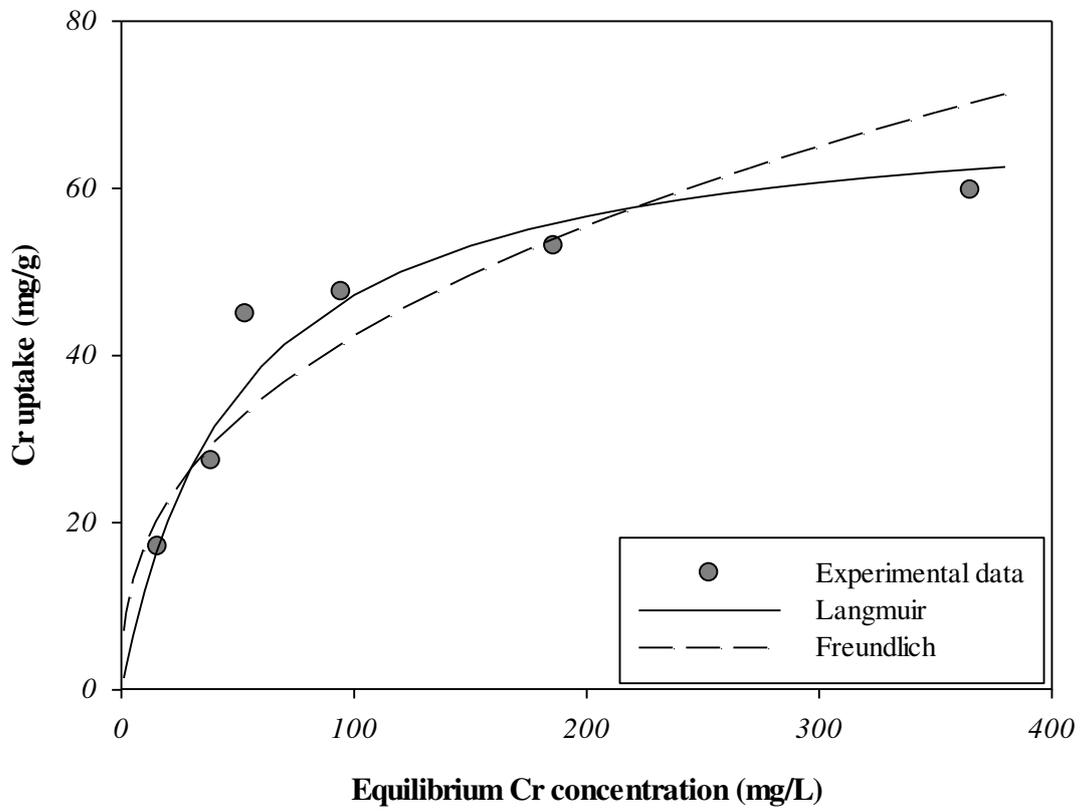
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Figure 3 (c)

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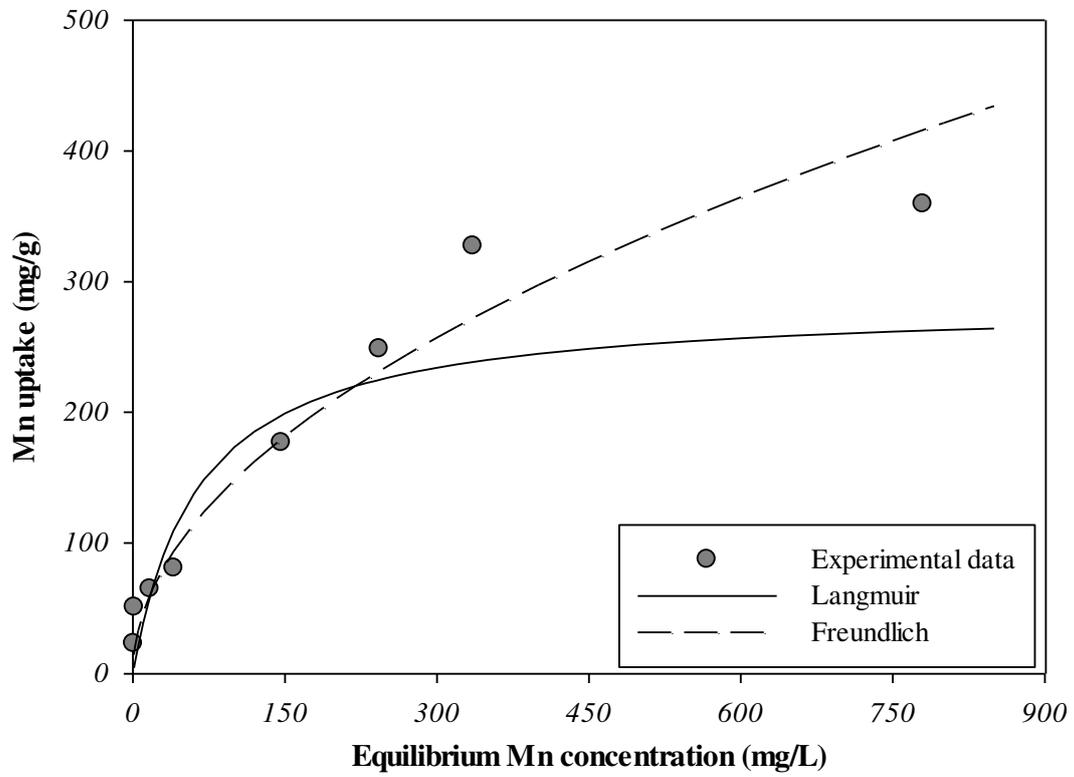
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Figure 3 (d)

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481 **Table 1.** Values of TN, TP, TOC and TC released from raw sludge and sludge chitosan.

482

	Biosorbent type	
	Raw sludge	Sludge Chitosan
TN (mg-N/L)	30.46	3.60
TP (mg-P/L)	11.63	1.28
TOC (mg-C/L)	26.66	5.02
TC (mg-C/L)	43.77	6.72

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487 **Table 2.** Comparison of Pseudo-first-order model and Pseudo-second-order model parameter

488 values for different sludge, chitosan content and diameter of the biosorbent

489

Sludge content (%)	Chitosan content (%)	Diameter (mm)	Pseudo first order			Pseudo second order			
			K_1 (1/h)	q_e (mg/g)	R^2 (-)	K_2 (g/mg·h)	q_e (mg/g)	R^2 (-)	h (mg/g·h)
2.0	4.0	0.2–0.3	0.96	0.09	0.9889	0.13	14.64	0.9995	28.65
4.0	4.0	0.2–0.3	1.13	0.08	0.9855	0.14	14.84	0.9995	29.94
6.0	4.0	0.2–0.3	0.79	0.09	0.9636	0.11	16.08	0.9990	27.33
6.0	3.0	0.2–0.3	0.84	0.12	0.9395	0.19	13.69	0.9996	35.55
6.0	4.0	0.2–0.3	1.58	0.06	0.9422	0.10	16.66	0.9956	27.63
6.0	5.0	0.2–0.3	1.28	0.06	0.9628	0.07	16.16	0.9963	18.48
6.0	6.0	0.2–0.3	0.78	0.08	0.9475	0.06	16.69	0.9931	16.55
6.0	4.0	0.2–0.3	0.81	0.09	0.9759	0.09	15.78	0.9984	22.42
6.0	4.0	0.5–0.6	1.63	0.04	0.9192	0.06	16.82	0.9916	16.13
6.0	4.0	0.8–0.9	0.95	0.08	0.9969	0.08	15.47	0.9971	19.47
6.0	4.0	1.0–1.2	0.64	0.08	0.9911	0.06	15.70	0.9992	14.84

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493 **Table 3.** Kinetic and isotherm constants for the biosorption of As(V), Cd(II), Cr(VI) and

494 Mn(VII) by RCA

495

	Metals	Pseudo first order			Pseudo second order			
		K_1 (1/h)	q_e (mg/g)	R^2 (-)	K_2 (g/mg·h)	q_e (mg/g)	R^2 (-)	h (mg/g·h)
Kinetic	As(V)	0.85	8.64	0.9924	0.18	16.21	0.9996	47.68
	Cd(II)	0.51	2.91	0.8452	0.80	14.96	0.9999	178.06
	Cr(VI)	1.33	38.27	0.9840	0.06	19.94	0.9974	23.06
	Mn(VII)	1.02	34.94	0.9642	0.01	34.75	0.9645	14.66
	Metals	Langmuir			Freundlich			
		Q_{max} (mg/g)	b (L/mg)	R^2 (-)	K_F (mg/g)	n	R^2 (-)	
Isotherm	As(V)	42.25	0.0241	0.9711	6.3703	3.18	0.8643	
	Cd(II)	28.69	0.0398	0.8030	4.5064	2.94	0.9048	
	Cr(VI)	70.79	0.0201	0.9648	7.0609	2.57	0.8447	
	Mn(VII)	275.43	0.0163	0.8948	14.1749	1.98	0.9766	

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499 **Table 4.** Maximum uptakes of As(V) by various biosorbents manufactured from sludge

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Sorbent type	Uptake (mg/g)	Experimental condition	Reference
Pyrolysed sludge (Insustry)	0.07	pH 3.0-3.5, 48 h	[29]
Biochar sewage sludge (Domestic)	13.42	pH 6.7-7, 24 h	[30]
Acid mine drainage sludge (Industry)	21.50	pH 7, 24 h	[31]
Acid mine drainage sludge alginate bead (Industry)	21.79	pH 5, 96 h	[32]
Magnetic sludge composite (Domestic)	21.3	pH 2.6, 5 h	[33]
Sludge Chitosan (Domestic)	42.25	pH 5.5, 6 h	This study

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Figures

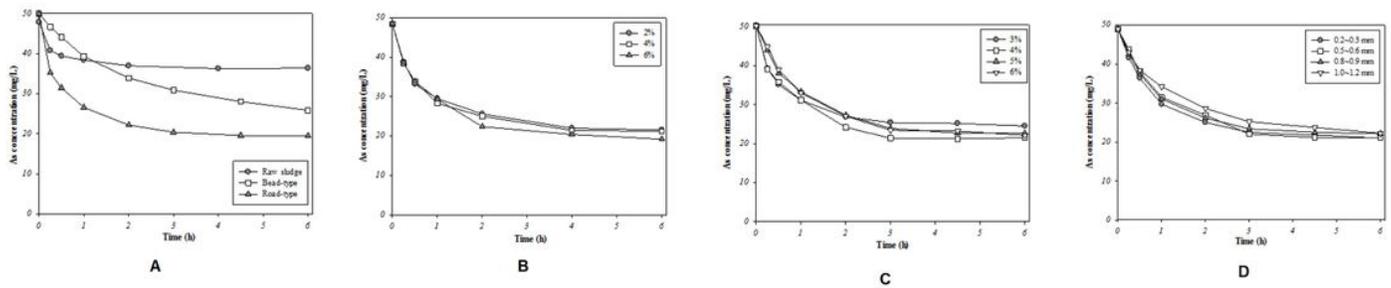


Figure 1

Effect of (a) biosorbent shape, (b) chitosan content, (c) sludge content and (d) biosorbent size on adsorption of As(V) on the sludge chitosan (biosorbent dosage = 2 g/L, agitation rate = 200 rpm, contact time = 6 h, temperature = 25 °C, Vw = 200mL, pH non shift(pH 5.5)).

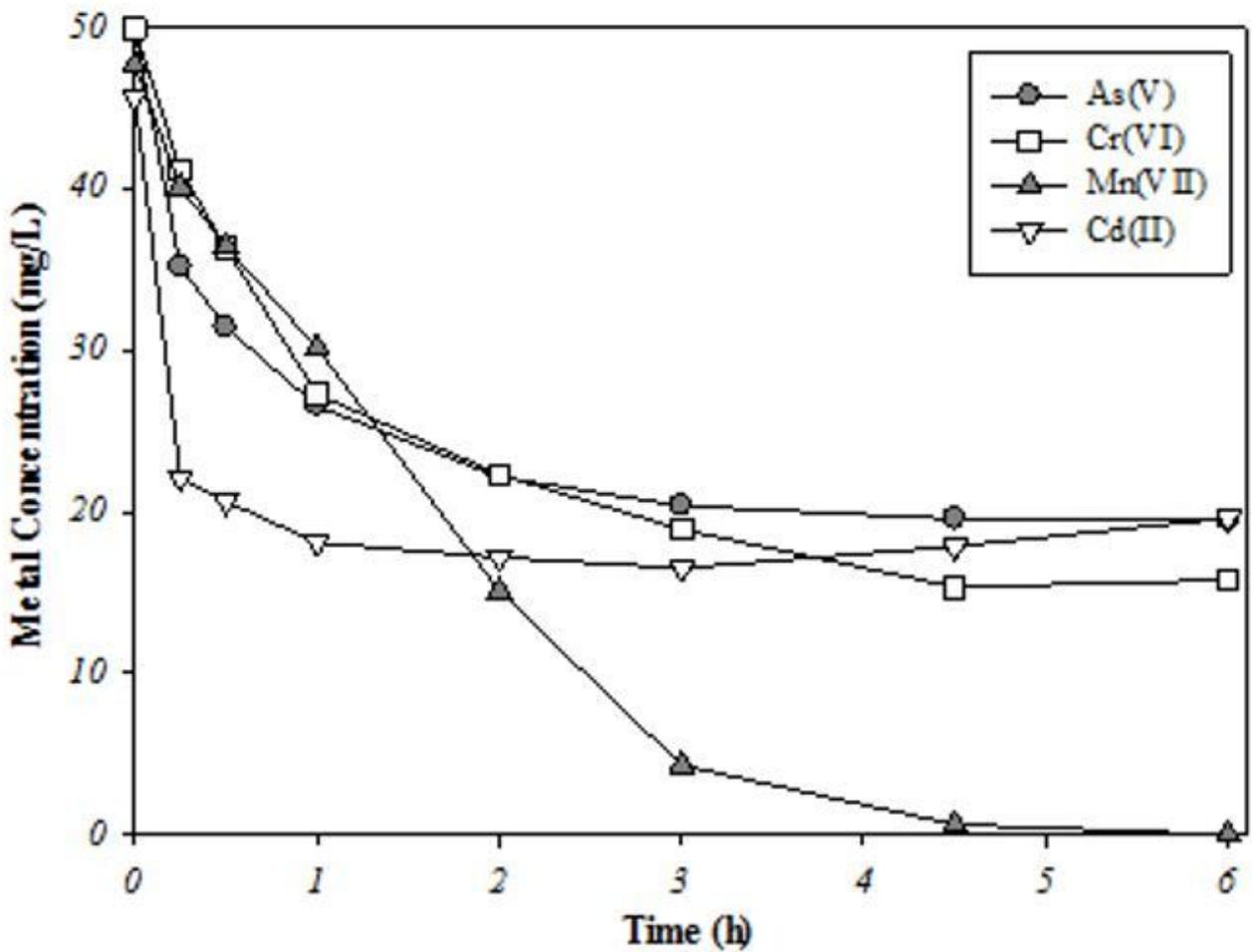


Figure 2

Kinetics of metalloids/metal adsorption (As(V), Cd(II), Cr(VI), and Mn(VII)) onto the sludge chitosan. (biomass dosage = 2 g/L, agitation rate = 200 rpm, contact time = 6 h, temperature = 25 °C, Vw = 200mL, pH non shift(pH 5.5)).

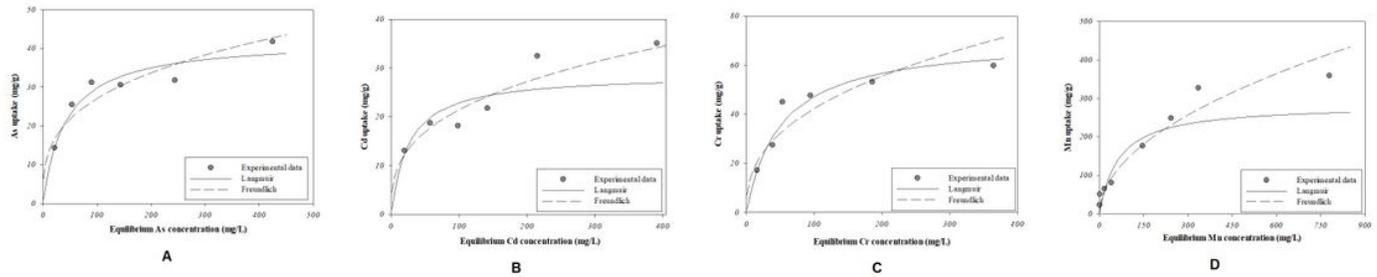


Figure 3

Adsorption isotherms of (a) As(V), (b) Cd(II), (c) Cr(VI) and (d) Mn(VII) by the rod-type biosorbent. The continuous lines were predicted by the Langmuir model; the dotted lines were produced by the Freundlich model. (biomass dosage = 2 g/L, agitation rate = 200 rpm, temperature = 25 °C, Vw = 200mL, pH non shift(pH 5.5))

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