

Efficient Lithium Extraction from Shale Gas Wastewater Using Sodium Alginate/H1.33Mn1.67O4
Composite Granular Adsorbents

Original

Efficient Lithium Extraction from Shale Gas Wastewater Using Sodium Alginate/H1.33Mn1.67O4 Composite Granular Adsorbents / Tian, L; Yang, Ys; Chen, Gj; Tiraferri, A; Liu, Bc. - In: ACS ES&T ENGINEERING. - ISSN 2690-0645. - 3:11(2023), pp. 1676-1685. [10.1021/acsestengg.3c00167]

Availability:

This version is available at: 11583/2983860 since: 2023-11-15T11:03:30Z

Publisher:

AMER CHEMICAL SOC

Published

DOI:10.1021/acsestengg.3c00167

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1 Efficient lithium extraction from shale gas
2 wastewater using sodium alginate/H_{1.33}Mn_{1.67}O₄
3 composite granular adsorbents

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14 **ABSTRACT:**

15 Dual carbon policies have spurred a rapid growth in the electric vehicle and energy
16 storage industry, leading to a surge in demand for lithium batteries. To help meeting this
17 demand sustainably, the natural polymer sodium alginate (SA) was crosslinked with
18 Ca^{2+} , and the SA/HMO composite granular adsorbent was successfully prepared by
19 crosslinking method. The aim is to extract lithium from shale gas wastewater in the
20 Sichuan Basin, China. The produced microporous composite granular adsorbents have
21 an average pore size of 20 nm and excellent hydrophilicity, with a swelling ratio of
22 roughly 15 g/g at a mass concentration of 3.5 wt% alginate and 2 wt% HMO. When
23 deployed with a real wastewater, this material achieved a lithium adsorption capacity
24 of 4.3 mg/g. In laboratory-scale fixed bed filtration experiments, the optimal adsorbent
25 material was saturated after approximately 700 minutes at an approach velocity
26 (hydraulic load) of 0.47 cm/min and using total bed volume of 15 cm³ containing
27 approximately 0.55 g of adsorbent. In the subsequent recovery step of the adsorbed
28 lithium through desorption, a lithium solution with concentration of 113 mg/L was
29 achieved. The results suggest that this novel composite granular adsorbent has
30 promising adsorption capacity and that an optimization of adsorption and desorption
31 cycles and an engineering of the separation system deploying this material would allow
32 high-efficiency lithium adsorption.

33 **KEYWORDS:** Lithium recovery; Composite granular adsorbent; Shale gas
34 wastewater (SGW); Sodium alginate (SA); Hydrogen manganese oxide ($\text{H}_{1.33}\text{Mn}_{1.67}\text{O}_4$)

35 **SYNOPSIS:** The SA/HMO composite granular adsorbent prepared by crosslinking
36 method is promising for efficient lithium recovery from shale gas wastewater.

37 INTRODUCTION

38 Lithium and its compounds possess exceptional physical and chemical properties,
39 making them indispensable in a wide range of materials and applications, such as
40 batteries, ceramics and glass, lubricants, air treatment, polymer processing, nuclear
41 industry, medical, aerospace, metallurgy.¹⁻⁴ Consequently, lithium has been dubbed as
42 “energy metal for promoting world progress” and “the white oil of the future”.^{5, 6} With
43 the targets of “dual carbon” driving the rapid development of electric vehicles and
44 energy storage industries, the demand for batteries has surged, and lithium batteries
45 have specifically become the first choice owing to their high energy density, long
46 service life, and relative environmental friendliness.^{7, 8} It is estimated that global annual
47 sales of electric vehicles will reach 56 million by 2040, and energy storage development
48 will exceed 1,095 GW.⁹ Therefore, it is imperative to increase the supply of lithium
49 resources. At present, lithium resources are mainly distributed in ores, seawater and
50 brines, such as oilfield brines, continental brines and geothermal brines.¹⁰ Extraction of
51 lithium from ore is complicated and will pollute the environment.^{11, 12} The concentration
52 of lithium in seawater is too low (0.17 mg/L) to be economical. Oilfield wastewater is
53 a potential resource for recovering lithium resources.¹³

54 Shale gas is an unconventional natural gas resource that predominantly comprises
55 methane. China has the world’s largest reserves of shale gas, with technically
56 recoverable resources reaching $31.6 \times 10^{12} \text{ m}^3$.¹⁴ However, the process of extracting
57 shale gas using horizontal drilling and hydraulic fracturing techniques generates

58 enormous amounts of shale gas wastewater (SGW).^{15, 16} The composition of SGW is
59 complex, with high concentrations of salt, heavy metals, various organic compounds,
60 naturally occurring radioactive materials (NORM), and many other potentially
61 hazardous substances, posing environmental threats and technological challenges
62 related to its treatment.¹⁶⁻¹⁸ Consequently, new approaches have been proposed for
63 SGW management that also enable the recovery of valuable elements, such as rare earth
64 elements, uranium, and lithium, which could not only provide revenue to offset the cost
65 of SGW treatment, but also augment the supply of strategic resources.^{13, 19-21} The
66 median concentration of lithium in SGW in the Sichuan Basin and in the Marcellus
67 Basin is 33 mg/L and 95 mg/L,^{22, 23} respectively, indicating the potential of SGW as a
68 lithium resource. Despite these numbers, SGW remains an untapped lithium resource,
69 and it is highly consequential to develop appropriate technology for extracting lithium
70 from SGW.

71 Based on the water quality characteristics of SGW, the advantages, disadvantages
72 and applicability of various solution lithium extraction techniques were compared. The
73 assessed techniques include precipitation,²⁴ adsorption,^{25, 26} electrochemical methods,^{27,}
74 ²⁸ membrane-based methods,^{29, 30} and extraction.^{31, 32} Adsorption method was thus
75 considered the most appropriate technique and selected to extract lithium from SGW.
76 In our previous studies,³³ we synthesized hydrogen manganese oxide (HMO) powder
77 adsorbents and applied them to SGW, which showed high adsorption capacity and
78 excellent selectivity for Li⁺. However, powder cohesiveness may result in poor

79 flowability and difficulty in fluidization.³⁴ When the ratio of Mg/Li is high, Mg²⁺ in the
80 brine is easily hydrolyzed, increasing the viscosity of the brine and reducing its pH.³⁵
81 These phenomena reduce the diffusion rate and the adsorption capacity of the adsorbent
82 in solution.³⁶ In addition, during a filtration process, the powder adsorbent will lead to
83 a large pressure drop and consequent increase in energy consumption, while the
84 difficulty in recovering the powder adsorbent will lead to the loss of part of the powder
85 itself.²⁶ The above factors limit the industrial application of powder adsorbents. In order
86 to overcome such limitations, a number of alternative powder adsorbent forming
87 methods have been proposed, including granulation, film forming, nanofiber, foaming.
88 Among these, granulation is a forming method with mature technology and simple
89 operation.

90 Sodium alginate (SA) is a biopolymer mainly derived from seaweed, which
91 consists of β -D-mannuronic acid (M) and α -L-gulonic acid (G) linked by 1 \rightarrow 4 bonds.³⁷
92 SA is rich in carboxyl and hydroxyl groups, rendering it highly hydrophilicity, non-
93 toxic, environmentally friendly, and readily available. Thus, it is widely used as a gel
94 agent in various industries.^{38, 39} The carboxyl group in SA has an affinity for metal
95 cations. For example, SA solutions containing divalent or multivalent metal ions may
96 become insoluble due to the interaction of adjacent carboxyl groups with one metal ion.
97 By using Ca²⁺ as a cross-linking agent, the SA solution can be converted into insoluble
98 gels, described by the “egg box model”.³⁹ In addition, the water permeability and
99 hydrophilicity of SA have advantages when used as binder materials, because a more

100 permeable binder materials can reduce the overall volume of actual adsorbent that does
101 not come into contact with SGW within the granule (vice versa, binders of poor
102 permeability hinder the interaction of water with the adsorbent, as the latter becomes
103 inaccessible to water due to a low-permeability isolating binder layer). Therefore, the
104 Li^+ adsorption capacity of HMO powder adsorbent is not significantly impaired by
105 granulation when high-permeability binders are used.⁴⁰ Therefore, SA was chosen as
106 the crosslinking agent for the granulation of HMO powder adsorbent.

107 In this study, the preparation of SA/HMO composite granular adsorbent by
108 crosslinking method is presented, and the adsorption behavior and the optimal ratio of
109 SA and HMO powder adsorbents are discussed using adsorption kinetics and adsorption
110 isotherms data. Under the condition of the optimal ratio of SA to HMO powder
111 adsorbents, results of fixed bed experiments filled with SA/HMO composite granular
112 adsorbents are evaluated, with the goal of facilitating the industrial application of
113 lithium extraction from SGW. To better understand the physicochemical properties and
114 adsorption behavior of the materials, we also present the outcome of a detailed material
115 characterization, including the swelling ratio, and data obtained with SEM, XRD, and
116 FT-IR analyses.

117 **MATERIALS AND METHODS**

118 **MATERIALS.** The SGW used in the experiments was from a shale gas well in
119 the Lower Silurian Longmaxi Formation in Gongxian, Sichuan Basin, China, and
120 collected in 2020.¹⁹ The SGW samples collected prior to the experiments were stored

121 in plastic drums under dark conditions. Lithium carbonate (Li_2CO_3), manganese
122 carbonate (MnCO_3), hydrochloric acid (HCl), and anhydrous calcium chloride (CaCl_2)
123 were obtained from Kelong Chemical (Chengdu, China) and were all analytical grade.
124 Sodium alginate (SA, Lot# MKBL7997V) were obtained from MilliporeSigma (St.
125 Louis, MO, USA).

126 **Preparation of the SA/HMO composite granular adsorbents.** HMO powder
127 adsorbent was first synthesized by solid phase reaction method as described in detail in
128 our previous study.³³ Briefly, Li_2CO_3 and MnCO_3 were mixed in a molar ratio of
129 1.33:1.67, calcined at 500 °C for 4 hours, fully pickled with 0.5 mol/L HCl, and then
130 rinsed and dried several times with ultrapure water to obtain HMO powder adsorbent.
131 The HMO powder adsorbent was added into an SA solution of different concentrations
132 and stirred until evenly dispersed to form a slurry mixture. The mixture was rapidly
133 injected into 96-well enzyme labeled plates with a syringe, frozen at -20°C for 24 hours,
134 and then freeze-dried (-50°C , < 20 Pa) for 24 hours to obtain cylindrical granules. The
135 granules were placed in 3 wt% CaCl_2 solution for 12 hours to complete the cross-linking
136 and rinsed 3 times with ultrapure water to remove excess CaCl_2 from the surface. The
137 wet adsorbent was again frozen and freeze-dried as mentioned above to obtain the final
138 dried adsorbents, which were stored in a plastic bottle for subsequent experiments. The
139 obtained composite granular adsorbents were named 3.5SA0H, 3SA2H, 3.5SA2H,
140 4SA2H according to the concentration of SA and HMO powder (**Table 1**).

141

142 **Table 1.** Composition of SA/HMO composite granular adsorbents.

	SA (wt%)	HMO (wt%)
3.5SA0H	3.5	0
3SA2H	3	2
3.5SA2H	3.5	2
4SA2H	4	2

143

144 **Characterization of SA/HMO composite granular adsorbents.** Power X-ray
145 diffraction (XRD) patterns were recorded with a DX-2700 instrument (Dandong
146 Haoyuan, China) equipped with Cu K α radiation ($k = 0.15418$ nm). The adopted
147 method was a stepwise measurement with each step angle equal to 0.05° , starting at an
148 angle of 10° and ending at an angle of 80° . The sampling time was 0.5 s, the tube voltage
149 and tube current were 40 kV and 30 mA, respectively. The chemical moieties of the
150 adsorbent was analyzed with FT-IR (Spectrum Two, Perkinelmer, USA). A field-
151 emission scanning electron microscopy (FE-SEM) (Regulus-8230, Hitachi, Japan) was
152 used to measure the surface morphology of adsorbents. The ASAP 2460 N₂ analyzer
153 (Micromeritics, USA) was used to determine the distribution of pore size and specific
154 surface area of the adsorbents. The samples were degassed at 120°C for 24 hours prior
155 to the assay, and the sample tubes were placed in a liquid N₂ (77K) environment during
156 the assay. The specific surface area was calculated using the Brunauer-Emmett-Teller
157 (BET) method based on the nitrogen adsorption data, and the Barrett-Joyner-Halenda
158 (BJH) method was used to calculate the pore size and distribution, as well as the
159 cumulative pore volume/pore area based on nitrogen desorption data.

160 The swelling properties of SA/HMO composite granular adsorbent were

161 characterized by determining the swelling ratio. Two pieces SA/HMO composite
162 granular adsorbent samples were immersed in 50 mL ultrapure water and left in the
163 solution at room temperature for 24 hours. The weight of SA/HMO composite granular
164 adsorbent before and after immersion was measured as m_d (g) and m_s (g), respectively.
165 The swelling ratio, S , was calculated according to Eq. (1) :

$$166 \quad S = \frac{m_d - m_s}{m_d} \quad (1)$$

167 **Adsorption experiments.** To understand whether the adsorption of lithium on the
168 adsorbents is governed by equilibrium mechanisms and to gain insight on the adsorption
169 capacity of the composite granular adsorbents, adsorption isotherm experiments were
170 performed by mixing 2, 4, 7, 9, 11, or 13 pieces SA/HMO composite granular
171 adsorbents with 30 mL of SGW. The mixture was gently stirred (200 rpm) in a shaking
172 incubator at 25°C for 48 h to reach equilibrium. Then, the supernatant was filtered with
173 a PES microporous membrane characterized by a pore size of 0.45 μm (Jinteng, Tianjin,
174 China), and the concentration of lithium was measured with a PinAAcle 900T
175 (Perkinelmer, USA). The equilibrium adsorption capacity of Li^+ was calculated
176 according to Eq. (2).

$$177 \quad q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

178 where q_e (mg/g) is equilibrium adsorption capacity, V (L) is the volume of the solution,
179 m (g) is the weight of SA/HMO composite granular adsorbents immerse in the solution,
180 C_0 and C_e are the initial and equilibrium Li^+ concentrations in solution (mg/L),

181 respectively. To explore the adsorption mechanism, the Langmuir model (Eq. (3)), the
182 Freundlich model (Eq. (4)), and the Temkin model (Eq. (5)) were applied, and the
183 details are described in Text S1 (SI).

$$184 \quad q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$185 \quad q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

$$186 \quad q_e = B \ln(K_T \cdot C_e) \quad (5)$$

187 Where q_e (mg/g) and q_m (mg/g) are the equilibrium adsorption capacity and the
188 maximum adsorption capacity, respectively. K_L (L/mg), K_F ($\text{mg}^{1-1/n} \cdot \text{L}^{1/n}/\text{g}$) and K_T
189 (L/mg) are constants representing the affinity between adsorbents and pollutants. C_e
190 (mg/L) is the equilibrium concentration of Li^+ and n values represents the degree of
191 nonlinearity between solution concentration and adsorption. B is the constant related to
192 gas constant, equilibrium binding constant, adsorption heat and absolute temperature in
193 the Temkin model.

194 The dimensionless equilibrium parameter (R_L) can be calculated based on the
195 Langmuir model according to Eq. (6). R_L is related to the adsorption characteristics,
196 specifically, when R_L is greater than 0 and smaller than 1, the adsorption is a favorable
197 process; when R_L is equal to 1, the adsorption is linear; when R_L is greater than 1, the
198 adsorption is unfavorable; when R_L is equal to 0, the adsorption process is irreversible
199 and not governed by equilibrium mechanisms^{41, 42}.

$$200 \quad R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

201 Adsorption kinetics experiments were performed by mixing 7 pieces SA/HMO
 202 composite granular adsorbents with 30 mL of SGW; then, the mixture was kept gently
 203 stirred (200 rpm) in a shaking incubator at 25 °C for different times ($t = 1, 3, 6, 9, 12,$
 204 $24, 36, 48, 60, 72$ hours). The supernatant was filtered with a PES microporous
 205 membrane characterized by a pore size of 0.45 μm (Jinteng, Tianjin, China), and the
 206 concentration of lithium was measured with a PinAAcle 900T (Perkinelmer, USA). The
 207 adsorption capacity of lithium at different times was calculated as follows:

$$208 \quad q_t = \frac{(C_0 - C_t)V}{m} \quad (7)$$

209 where q_t (mg/g) and C_t (mg/L) represent the adsorbed amount and the Li^+
 210 concentration in solution at time t , respectively. There, V (L) is the volume of the
 211 solution, m (g) is the weight of adsorbent and C_0 is the initial lithium concentration in
 212 solution. A pseudo-first-order kinetic model (Eq. (8)), a pseudo-second-order kinetic
 213 model (Eq. (9)), and the Elovich model (Eq. (10)) were used to investigate the
 214 adsorption kinetic behaviors; the details of the models can be found in Text S2 of the
 215 Supporting Information (SI).

$$216 \quad q_t = q_e \times (1 - \exp(-k_1 \cdot t)) \quad (8)$$

$$217 \quad q_t = \frac{k_2 \times q_e^2 \times t}{1 + q_e \times k_2 \times t} \quad (9)$$

$$218 \quad q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (10)$$

219 where t (h) is the adsorption time, q_e (mg/g) and q_t (mg/g) represent the equilibrium
 220 adsorption capacity and the adsorption capacity at time t , respectively. k_1 (h^{-1}) and k_2

221 ($\text{g}\cdot\text{mg}^{-1}\text{h}^{-1}$) are the adsorption rate constant of the pseudo-first-order kinetic model and
 222 the pseudo-second-order kinetic model, respectively. α ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) and β ($\text{g}\cdot\text{mg}^{-1}$)
 223 represent the initial adsorption rate and the Elovich model adsorption constant.

224 An adsorption selectivity test was performed by mixing 7 pieces SA/HMO
 225 composite granular adsorbents with 30 mL of SGW and the mixture was gently stirred
 226 (200 rpm) in a shaking incubator at 25°C for 48 hours. The supernatant was filtered
 227 with a PES microporous membrane characterized by pore size of 0.45 μm (Jinteng,
 228 Tianjin, China) to measure the metal ion concentration using a Dionex Integriion HPIC
 229 (Thermo Fisher, USA). The partition coefficient (K_d , Eq. (11)), concentration factor
 230 (CF, Eq. (12)), and separation factors (α_{Me}^{Li} , Eq. (13)) were calculated to investigate the
 231 adsorption selectivity of SA/HMO adsorbents, as follows:

$$232 \quad K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (11)$$

$$233 \quad CF = \frac{q_e(Me)}{C_0(Me)} \quad (12)$$

$$234 \quad \alpha_{Me}^{Li} = \frac{K_d(Li)}{K_d(Me)} \quad (13)$$

235 where Me refer to a metal ion, namely, Li^+ , Na^+ , K^+ , Mg^{2+} , Ba^{2+} , Sr^{2+} . In the equations
 236 above, $q_e(Me)$ (mg/g) represents the equilibrium adsorption capacity, C_0 and C_e
 237 are the initial and equilibrium Me concentrations in solution (mg/L), respectively, V (L)
 238 is the volume of the solution, and m (g) is the weight of SA/HMO composite granular
 239 adsorbents.

240 **Fixed bed filtration experiments.** The fixed bed adsorption experimental device

241 is shown in **Figure S1** of the SI. The adsorbent bed was obtained by filling a glass sand
 242 core chromatography column with 3.5SA2H composite granular adsorbents. An
 243 appropriate amount of glass beads of suitable size was placed above the adsorbent to
 244 prevent the adsorbent from floating. The continuous water inlet and continuous water
 245 outlet were adopted with the upward flow direction under fully saturated conditions.
 246 The specific operating parameters of the bed filtration are summarized in **Table 2**. After
 247 different running times, the concentration of Li^+ in the effluent of the bed was measured
 248 with a PinAAcle 900T (Perkinelmer, USA).

249 **Table 2.** Fixed bed filtration operating parameters.

Pump speed (r/min)	Flow rate (mL/min)	EBCT (min)	Adsorbent weight (g)	Fixed bed diameter (cm)	Fixed bed length (cm)	Empty bed volume (cm ³)	Approach velocity (cm/min)
0.5	0.269	55	0.547	1	19	14.92	0.34
0.7	0.366	40	0.5432	1	19	14.92	0.47
1	0.545	27	0.5385	1	19	14.92	0.70

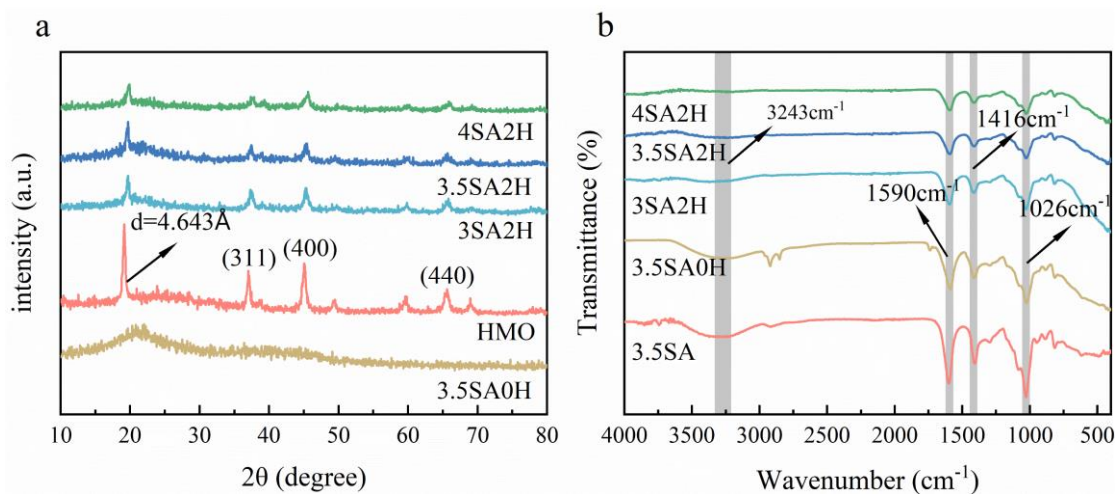
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251 RESULTS AND DISCUSSION

252 Physico-chemical characteristics of SA/HMO composite granular adsorbents.

253 **Figure 1a** shows representative XRD patterns of HMO alone, 3.5SA0H (only sodium
 254 alginate), 3SA2H, 3.5SA2H, 4SA2H. Two broad peaks of low intensity can be seen for
 255 the alginate material, 3.5SA0H, near $2\theta=20^\circ$ and 40° . The three main characteristic
 256 peaks of the HMO powder are instead 19.1° , 37° , 45.05° , and the corresponding crystal
 257 face distances are 4.643 Å, 2.428 Å, 2.011 Å, respectively. The three main characteristic
 258 peaks of the XRD patterns of the composite materials, namely, 3SA2H, 3.5SA2H and

259 4SA2H, are around 19.7° , 37.45° and 45.3° , and the corresponding crystal face
 260 distances are 4.503 \AA , 2.399 \AA and 2.000 \AA , respectively, indicating that HMO powder
 261 was successfully loaded within the alginate matrix. Compared with pure HMO powder,
 262 the peak positions of SA/HMO composite granular adsorbents shifted to larger angle
 263 and this shift increased with higher sodium alginate content. Also, the presence of
 264 sodium alginate also corresponded to a reduction of the peak intensity, which was
 265 associated with the two wide peaks characterizing the pure alginate sample, 3.5SA0H.
 266 **Figure 1b** presents representative FT-IR spectra of 3.5SA (not cross-linked pure SA),
 267 3.5SA0H, 3SA2H, 3.5SA2H, and 4SA2H. There are four typical absorption bands at
 268 3243 , 1590 , 1416 , and 1026 cm^{-1} , corresponding to the functional groups O-H, C=O,
 269 C-OH, and OC-OH.³⁹ Compared with 3.5SA, 3.5SA0H showed a new absorption band
 270 at 2852 cm^{-1} , which may be related to the C-H stretch vibration caused by the reaction
 271 of SA polymerization chain with Ca^{2+} , thus suggesting appropriate cross-linking of the
 272 sample.³⁸



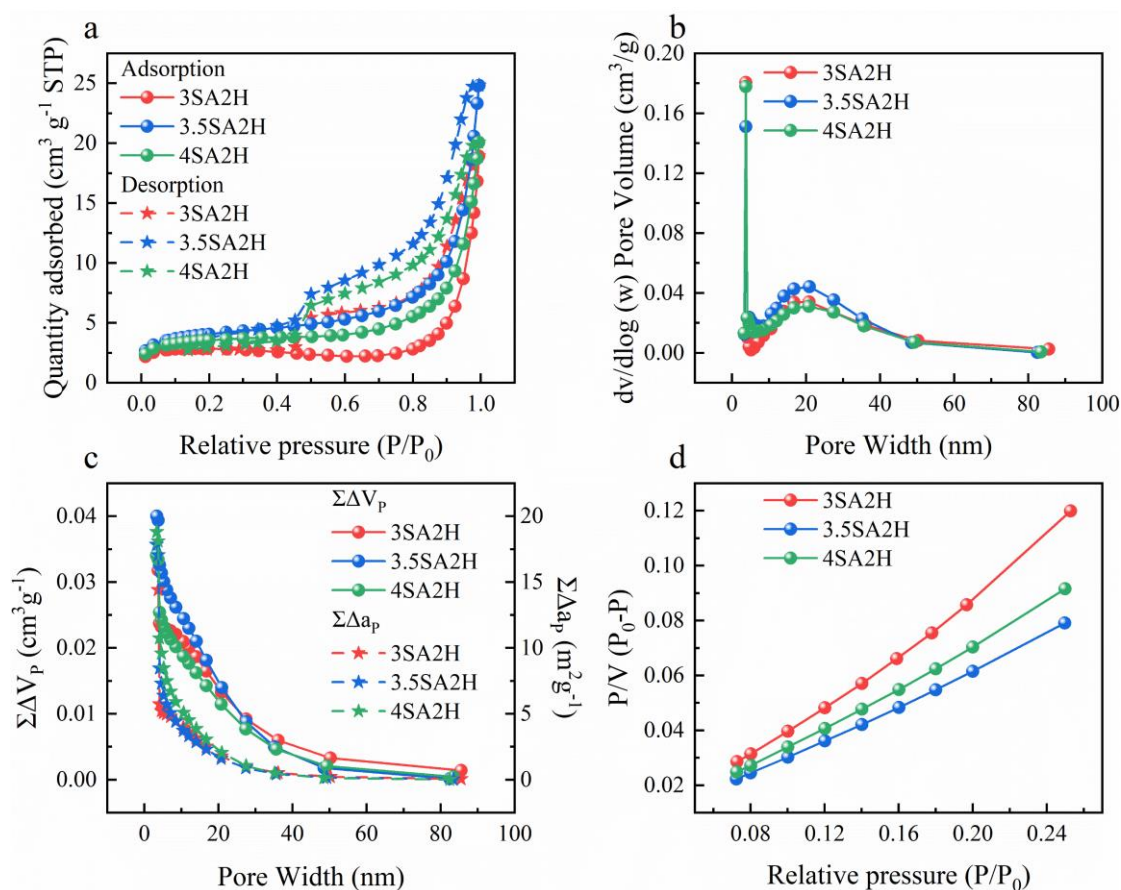
273
 274 **Figure 1.** (a) XRD patterns of various samples, including cross-linked alginate

275 (3.5SA0H), pure adsorbent powder (HMO), composite granular adsorbent (3SA2H,
276 3.5SA2H, 4SA2H). (b) FT-IR spectra of not cross-linked alginate (3.5SA) and the same
277 samples analyzed with XRD.

278

279 **Figure S2** (SI) presents representative SEM micrographs of 3.5SA2H composite
280 granular adsorbent before and after its use for adsorption. The SA/HMO composite
281 granular adsorbent had a three-dimensional porous structure, which is conducive to
282 swelling and diffusion of Li^+ into the gel.⁴³ **Figure 2a** shows the nitrogen adsorption-
283 desorption isotherms of 3SA2H, 3.5SA2H, and 4SA2H composite granular adsorbents,
284 all of which are typical type IV isotherms with H3 hysteresis loop.⁴⁴ This behavior is
285 similar to the nitrogen adsorption-desorption isotherm of the HMO powder,³³ again
286 corroborating the conclusion that the HMO powder was successfully loaded into the
287 granule. Specifically, the nitrogen adsorption capacities of 3SA2H, 3.5SA2H, and
288 4SA2H were 18.9, 24.8, and 20.1 cm^3/g (STP), respectively. The BJH method was
289 applied to calculate the pore size distribution of desorption branches of nitrogen
290 adsorption-desorption isotherm, and the results are shown in **Figure 2b**. The average
291 pore diameter of the three adsorbents was about 20 nm. **Figure 2c** is the superposition
292 diagram of the cumulative pore volume and pore area as a function of pore size: the
293 cumulative pore volume of 3SA2H, 3.5SA2H, and 4SA2H was 0.032, 0.04, 0.034
294 cm^3/g , respectively, and the cumulative pore area was 14.4, 18.8, 17.8 m^2/g , respectively.
295 Finally, **Figure 2d** shows the BET surface area plot drawn as a function of relative

296 pressure of the isothermal adsorption branch with values in the range 0.07-0.26: the
 297 resulting BET surface area of 3SA2H, 3.5SA2H, and 4SA2H was estimated as 8.95,
 298 13.79 and 11.82 m²/g, respectively. Overall, the nitrogen adsorption capacity and
 299 surface areas were the highest for the 3.5SA2H adsorbent.



300

301 **Figure 2.** (a) Nitrogen adsorption-desorption isotherm diagram of three SA/HMO

302 composite granular adsorbents. (b) Pore size distribution diagram. (c) Cumulative

303 pore volume and pore area distribution. (d) BET specific surface area diagram.

304

305 **Swelling behavior of SA/HMO composite granular adsorbents.** Swelling is a

306 physicochemical phenomenon that has been studied to explain the behavior and

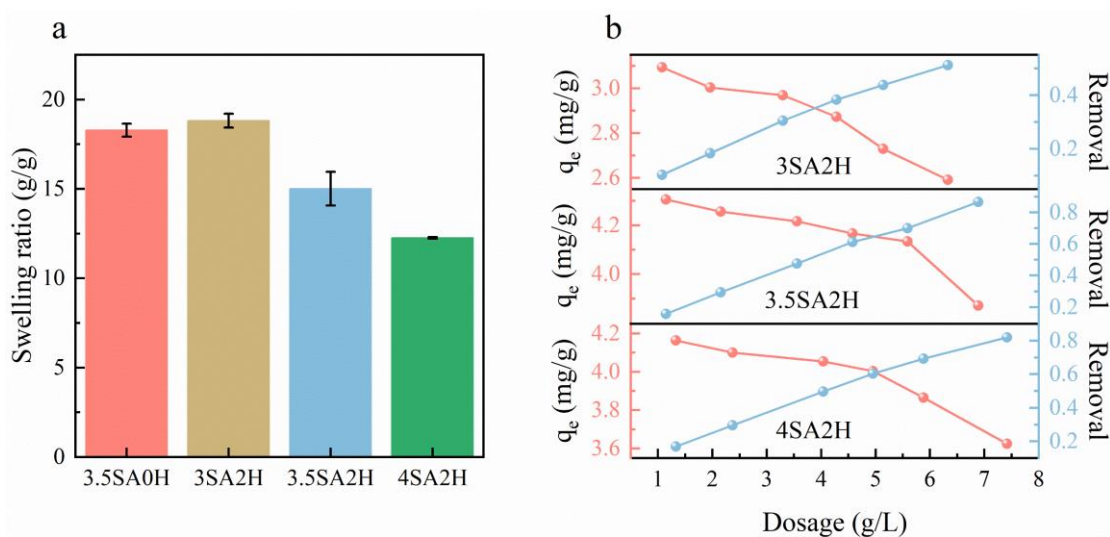
307 properties of hydrogels.⁴⁵ Excellent swelling behavior is typically conducive to the

308 adsorption of heavy metal ions.⁴³ The SA/HMO composite granular adsorbents possess
309 remarkable water-clearing properties, swiftly absorbing water molecules and causing
310 them to swell. The alteration in the water contact angle, reflecting the super hydrophilic
311 nature of 3.5SA2H, is depicted in **Movie S1**. The calculated swelling ratios of the
312 SA/HMO composite granular adsorbents are shown in **Figure 3a**. The ratio obtained
313 for 3SA2H was as high as 18.8 g/g, indicating its excellent swelling property, which is
314 attributed to its three-dimensional pore structure and the abundant hydrophilic groups
315 on the sodium alginate polymer chain. Note that the swelling ratio of alginate-only
316 3.5SA0H was greater than that of the composite 3.5SA2H sample, due in part to the
317 increase of dry weight caused by the addition of HMO powder adsorbent and in part to
318 the fact that the water absorption performance of HMO powder adsorbent itself is much
319 lower than that of sodium alginate. Interestingly, when comparing 3SA2H, 3.5SA2H,
320 and 4SA2H samples under normalized mass concentration of HMO powder adsorbent,
321 the swelling ratio slightly decreased with the increase of sodium alginate amount. This
322 fact is attributed to the fact that the pore size of the composite granular adsorbent was
323 smaller with increased alginate, and to the fact that the dry weight increased. However,
324 the swelling ratio of 4SA2H was 12.3 g/g, indicating that the composite granular
325 adsorbents prepared by the method described above had excellent swelling performance
326 regardless of the amount of alginate, providing valuable conditions for interactions with
327 water, and consequently high potential for adsorption of lithium.

328

329 **Effect of adsorbent dose on Li⁺ adsorption.** The extraction of lithium from SGW
330 with different adsorbent dosages was investigated, and the results are summarized in
331 **Figure 3b**. Indeed, the dosage had a significant impact on the lithium recovery rate and
332 adsorption capacity. Specifically, the recovery rate gradually increased with dosage, but
333 the adsorption capacity gradually decreased. Taking 3.5SA2H as an example, when the
334 dosage increased from 1.1 g/L to 6.9 g/L, the recovery rate of lithium increased from
335 15.7% to 86.7%, while the adsorption capacity decreased from 4.31 mg/g to 3.87 mg/g.
336 The increase in recovery rate is associated with an increase in total adsorption sites that
337 can capture more Li⁺. The high lithium recovery rate achieved under the condition of
338 relatively low dosage of adsorbent indicates that the adsorbent has excellent affinity for
339 lithium extraction.⁴⁶ The adsorption capacity decreased with increasing adsorbent
340 dosage likely due overdosing of the adsorbent, which translates into a smaller amount
341 of lithium adsorbed per unit mass of adsorbent and to the lower kinetics of adsorption
342 during the process, as more lithium passed into solid phase (and less remained in
343 solution) compared to the case at lower adsorbent dosage. Therefore, although the
344 removal rate was higher at higher dosage, the actual utilization of adsorbent was less
345 efficient, because of underconsumption of available adsorption site, pointing to the fact
346 that there is an engineering trade-off that needs consideration to simultaneously
347 maximize absolute lithium adsorption while minimizing the amount of required
348 adsorbent. Simply comparing the various composite granular adsorbents at the same
349 dosage, one can conclude that the adsorption capacity and recovery rate of 3.5SA2H

350 was the largest, and that of 3SA2H was the smallest.



351

352 **Figure 3.** (a) Swelling ratio of composite granular adsorbents prepared with different

353 sodium alginate amount. (b) Influence of the dosage on the adsorption capacity and

354 removal rate of lithium in SGW with three composite granular adsorbents.

355

356 **Adsorption isotherms of lithium onto SA/HMO composite granular adsorbents.**

357 Adsorption isotherm and the respective fitting models are presented in **Figure 4a-c**. The

358 data suggests that a saturation condition existed for the adsorbents, as the adsorption

359 capacity was only slightly higher when in equilibrium with larger liquid concentration

360 above a certain value. The maximum adsorption capacities obtained in the experiments

361 for 3SA2H, 3.5SA2H, and 4SA2H were 3.09 mg/g, 4.31 mg/g, and 4.16 mg/g

362 respectively, which can be converted to 7.73 mg/g HMO, 11.85 mg/g HMO and 12.48

363 mg/g HMO respectively. Compared with the adsorption capacity of HMO powder

364 adsorbents for lithium (13.27 mg/g) in shale gas wastewater, the adsorption efficiency

365 of 3SA2H, 3.5SA2H and 4SA2H composite granular adsorbents is 58.2%, 89.3%,

366 94.0%, respectively, which is superior to the literature adsorbents presented in Table S1.

367 This order was consistent with the results of nitrogen adsorption, indicating that a higher

368 BET surface area was correlated to a better adsorption of Li^+ . The value of fitting

369 coefficient, R^2 , was highest for the Langmuir model, corroborating the observation of a

370 saturation condition and suggesting that the adsorption of Li^+ was akin to that of a

371 monolayer chemisorption process that occurs at specific homogeneous sites on the

372 surface of SA/HMO.⁴⁷ Also, the data suggests that there was no obvious competition

373 between solvent and sorbate to occupy the adsorption sites.⁴⁸ This result was analogous

374 to the adsorption behavior of pure HMO powder adsorbent, indicating that granulation

375 by polymer sodium alginate did not significantly change the adsorption mechanism.

376 The separation factor R_L calculated with the equilibrium coefficient K_L of the Langmuir

377 model was 0.207, 0.027 and 0.034, respectively, for 3SA2H, 3.5SA2H and 4SA2H

378 samples. Being between 0 and 1, adsorption can be described as favorable, also

379 suggested by the n parameters of the Freundlich model being greater than 1.⁴⁹ Note that

380 the fact that the parameter was relatively close to 0 possibly suggests that the adsorption

381 was not entirely, or quickly, reversible, and that equilibrium models may not be

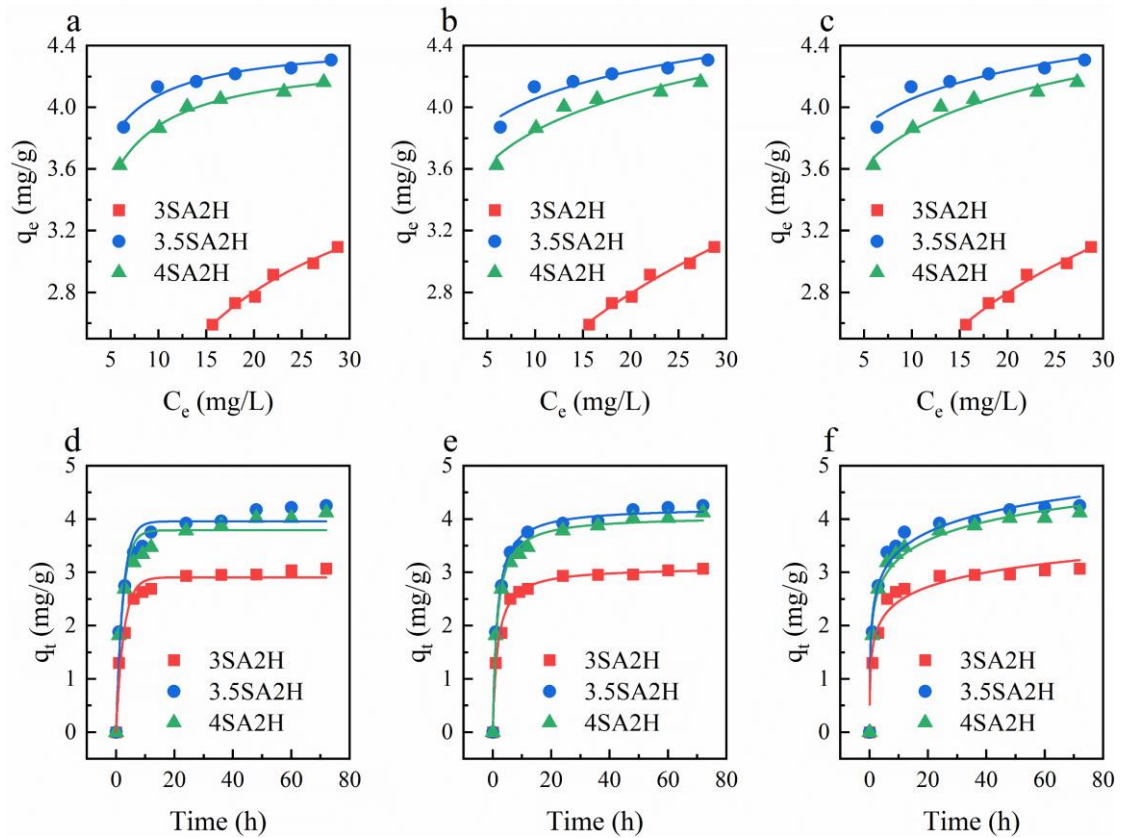
382 completely adequate to describe the adsorption/desorption phenomena and /or that

383 desorption kinetics are significantly slower than adsorption kinetics. This fact would

384 pose a challenge when attempting to extract and recover (load and unload) lithium with

385 the adsorbents, further suggesting the need for an engineering optimization of a

386 potential system deploying these materials.



387

388 **Figure 4.** Adsorption isotherms of lithium with three different composite granular
 389 adsorbents fitted with the (a) Langmuir model, (b) Freundlich model, and (c) Temkin
 390 model. Adsorption kinetics fitted with a (d) pseudo-first-order kinetic model, (e)
 391 pseudo-second-order kinetic model, and (f) Elovich model.

392

393 **Table 3.** Fitting parameters from adsorption isotherm models.

	Parameters	3SA2H	3.5SA2H	4SA2H
Langmuir	Q_m (mg/g)	3.98	4.43	4.33
	K_L (L/mg)	0.120	1.16	0.863
	R^2	0.980	0.960	0.992
Freundlich	K_F ($\text{mg}^{1-1/n} \cdot \text{L}^{1/n}/\text{g}$)	1.25	3.51	3.16
	n	3.56	16.0	11.6
	R^2	0.977	0.888	0.940
Temkin	B	0.802	0.260	0.341
	K_T (L/mg)	1.64	608	792
	R^2	0.979	0.895	0.949

394 **Adsorption kinetics of lithium onto SA/HMO** composite granular adsorbents.

395 Kinetics data and model results are shown in **Figure 4d-f**, while the resulting fitting

396 parameters are summarized in **Table 4**. Generally, the adsorption was faster during the

397 first 6 hours of the tests, then the rate decreased and ceased after roughly 48 hours. The

398 main reason is that the number of readily available adsorption sites on the SA/HMO

399 surface decreased with time. In later stages of the test, the adsorption of Li^+ is controlled

400 by diffusion into the smaller pores of the adsorbent, significantly reducing the kinetics,

401 until all the available adsorption sites within the timescale of the experiments were

402 consumed.⁴⁹ The adsorption capacity calculated from the kinetics data by the pseudo-

403 second-order kinetic model was in better agreement with the experimental results with

404 respect to other models, and was also consistent with the isotherms data. Additionally,

405 the correlation coefficient R^2 for the pseudo-second-order kinetic model was also the

406 largest among the three models, which suggests that chemisorption is the rate limiting

407 step for Li^+ adsorption.⁵⁰ This conclusion is the same as observed in the adsorption

408 process with pure HMO, once again indicating that granulation did not change the

409 adsorption mechanism or capability of the powder.

410

411 **Table 4.** Parameters from data fitting with kinetics models.

	Parameters	3SA2H	3.5SA2H	4SA2H
Pseudo-first	$q_{e,cal}$ (mg/g)	2.91	3.96	3.79
	k_1 (min^{-1})	0.383	0.434	0.443
	R^2	0.969	0.957	0.949
Pseudo-second	$q_{e,cal}$ (mg/g)	3.10	4.22	4.05
	k_2 (g/(mg.h))	0.201	0.162	0.168
	R^2	0.995	0.994	0.993
Elovich	α (mg/g/min)	20.3	35.2	32.2
	β (g/mg)	2.55	1.92	1.98
	R^2	0.969	0.981	0.987

412

413 **Adsorption selectivity of lithium by 3.5SA2H adsorbent in SGW.** SGW

414 contains substantial amounts of Na^+ , K^+ , Mg^{2+} , Ba^{2+} , Sr^{2+} , which are the main

415 competition ions potentially limiting lithium extraction. The 3.5SA2H composite

416 granular adsorbent had a high selectivity for Li^+ , and the results of selectivity

417 experiments are summarized in **Table 5**. The partition coefficients of the cations were

418 ordered as $\text{Li}^+ > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$. In addition, the separation factors

419 estimated for Li^+ , namely, 1.21, 3.84, 23.85, 24.86, 27.52 for Ba^{2+} , Sr^{2+} , Mg^{2+} , K^+ , and

420 Na^+ , respectively, corroborated that Li^+ was preferentially adsorbed onto 3.5SA2H⁵¹

421 and that Ba^{2+} is the cation posing the larger potential competition to adsorption. The

422 adsorption capacity of the SA/HMO composite granular adsorbent for Li^+ is mainly

423 determined by the HMO component. The high selectivity for Li^+ is rationalized with

424 the ion sieve effect of HMO: the spinel structure size is suitable for Li^+ , and suitable

425 ion exchange occurs between H^+ and Li^+ . According to this rationalization, other metal

426 ions can only be adsorbed on the surface by van der Waals force because their ionic

427 radius is larger than the adsorption site/cavity size and/or because the free energy of
 428 hydration is larger than Li^+ , which prevents their entry into the HMO cavity site.^{52, 53}

429

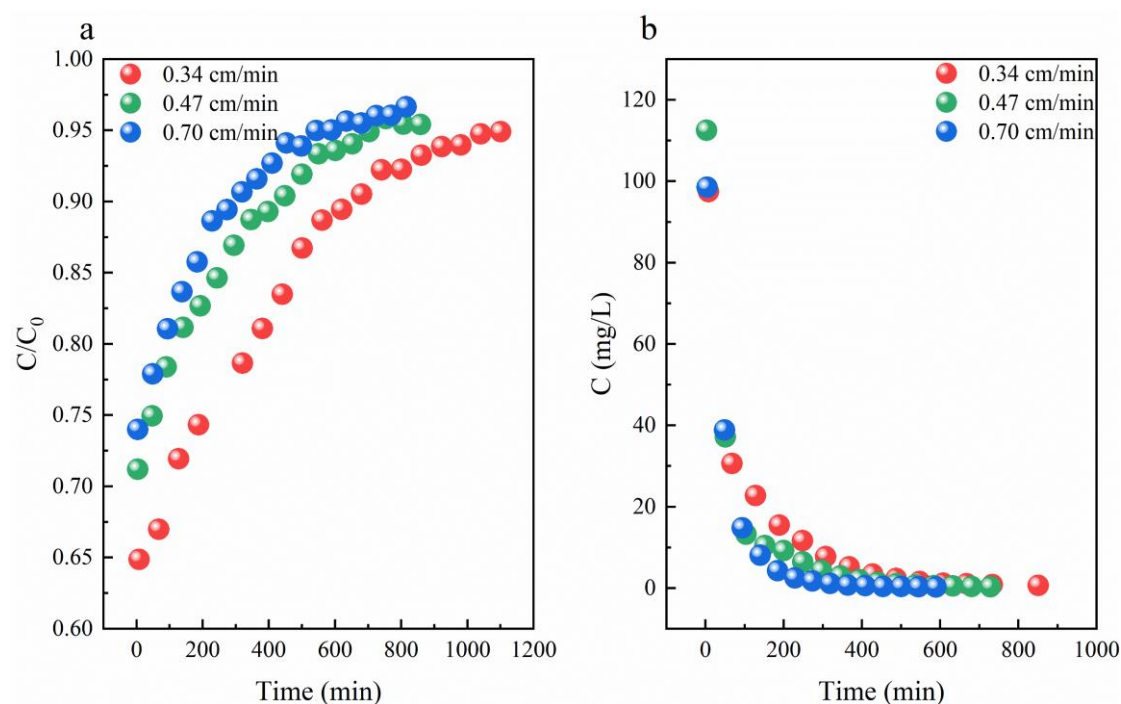
430 **Table 5.** Adsorption selectivity of lithium by 3.5SA2H sample in the SGW

	C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)	K_d (ml/g)	CF (ml/g)	α_{Me}^{Li}
Li^+	32.9	17.6	4.05	231	123	1.00
Na^+	11000	10700	89.2	8.38	8.08	27.5
K^+	266	257	2.38	9.28	8.97	24.9
Ba^{2+}	110	64.2	16.5	190	150	1.21
Sr^{2+}	105	85.8	5.15	60.0	49.0	3.84
Mg^{2+}	74.9	72.2	0.700	9.67	9.33	23.9

431

432 **Results of lithium extraction and recovery in preliminary depth filtration**
 433 **experiments.** The empty bed contact time (EBCT) is an important parameter related to
 434 the reactor volume size or to the flow rate processable in a system and should be as
 435 small as possible to ensure economy of the process. Indeed, decreasing EBCT may
 436 reduce the efficacy of lithium extraction if the timescales of solution flow in the
 437 granular bed are too high with respect to the kinetics of partition between the liquid and
 438 the solid phase (adsorption). In this study, various EBCT values were investigated in
 439 preliminary filtration tests. **Figure 5a** presents the performance of lithium recovery
 440 observed for the 3.5SA2H composite granular adsorbent in SGW. The adsorbent
 441 depletion time ($C/C_0=0.95$) was 1100, 703, and 543 minutes for different and increasing
 442 flow rates. The initial effluent (recovered) lithium concentration was high regardless of
 443 the flow rate, and then rapidly decreased approaching 0. Specifically, the initial effluent

444 lithium concentration was as high as 113 mg/L at an approach velocity of roughly 0.7
445 cm/min, indicating that reasonable control of the desorption time can achieve a lithium-
446 rich solution. Indeed, the optimization of the filtration conditions is outside the scope
447 of this study, but it is crucial to optimize adsorbent utilization as well as lithium
448 extraction and recovery.



449
450 **Figure 5.** (a) Changes of residual lithium ratio in effluent with time under adsorption
451 at different approach velocity values through a fixed bed. (b) Changes of lithium
452 concentration in the effluent with time under different approach velocity conditions.

453

454 CONCLUSION

455 To overcome the practical limitations of the use of HMO powder adsorbents for
456 lithium extraction, SA/HMO composite granular adsorbents with three-dimensional
457 network structure were proposed, prepared by crosslinking method using SA as

458 crosslinking agent, and evaluated for lithium adsorption in SGW. The SA/HMO was a
459 mesoporous material with an average pore size of 20 nm and had excellent
460 hydrophilicity with a swelling ratio of up to 15 g/g for a specific optimal combination
461 of sodium alginate and HMO powder amounts, namely, for sample referred to as
462 3.5SA2H. When the dosage of 3.5SA2H was 6.9 g/L, the recovery rate of lithium was
463 86.7%, and the adsorption capacity was 3.87 mg/g. The adsorption kinetics and
464 adsorption isotherm experiments suggested that the adsorption process of SA/HMO in
465 SGW could be adequately described by a pseudo-second-order kinetic model and by a
466 Langmuir saturation model, suggesting that the adsorption process was akin to a
467 monolayer chemisorption and that the adsorption rate was likely controlled by the
468 chemisorption step. Consequentially, the composite granular adsorbent had high
469 selectivity for lithium and its behavior was analogous to that of a pure HMO powder,
470 indicating that the incorporation of HMO within a sodium alginate granule did not
471 reduce the capability of the adsorbent material and that the granule configuration is
472 therefore superior to the pure powder, as the former provides significant gains toward
473 the practical implementation of the technology. The results of preliminary fixed-bed
474 filtration experiments consisting of SGW flowing through a column filled with
475 3.5SA2H suggested that this material has high potential for use in the extraction and
476 recovery of lithium from complex aqueous matrices. In particular, the recovered lithium
477 concentration during the desorption step reached 112.5 mg/L: further engineering of the
478 system would significantly increase the efficacy of lithium recovery and the utilization

479 efficiency of the adsorbent. This study demonstrates that SA/HMO composite granular
480 adsorbent has practical application value in extracting lithium from SGW.

481 **ASSOCIATED CONTENT**

482 **Supporting Information**

483 The Supporting Information is available free of charge online.

484 Adsorption isotherm models (Text S1); Adsorption kinetic models (Text S2);
485 Fixed bed experimental setup diagram (Figure S1); SEM micrographs (Figure S2);
486 Water contact angle of 3.5SA2H (Movie S1) and comparison of Li⁺ uptake properties
487 (Table S1).

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515 **ACKNOWLEDGMENTS**

516 This work was supported by the National Natural Science Foundation of China
517 (52270075, 52070134), Litree Purifying Technology Co., Ltd. Project (2021H012), and
518 Sichuan University and Yibin City People's Government strategic cooperation project
519 (2020CDYB-2). A.T. acknowledges the MICS (Made in Italy – Circular and
520 Sustainable) Extended Partnership and funding from the European Union Next-

521 GenerationEU (Piano Nazionale di Ripresa e Resilienza (PNRR) – Missione 4
522 Componente 2, Investimento 1.3 – D.D. 1551.11-10-2022, PE00000004). This
523 manuscript reflects only the authors’ views and opinions, none of the funding agencies
524 can be considered responsible for them.
525

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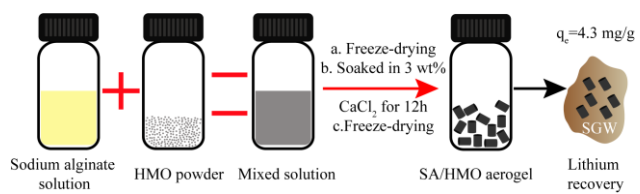
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694 **For Table of Contents Use Only.** SA/HMO composite granular adsorbent was

695 prepared by crosslinking method to extract lithium efficiently from shale gas

696 wastewater.

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