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3 **Efficient recovery of lithium from spent lithium-ion battery**
4 **raffinate by Mn and Al-based adsorbents: pretreatment,**
5 **adsorption mechanism, and performance comparison**

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19 **Abstract:**

20 As a strong wave of retired lithium-ion battery approaches, lithium extraction from
21 spent lithium-ion battery raffinate (SLR) becomes increasingly critical for
22 environmental protection and for sustainable lithium supply. To understand the factors
23 that affect maximum recovery of lithium from SLR, the organic and inorganic
24 components of SLR were initially determined. The organic matter content (up to 760.5
25 mg/L) seriously impacted the recovery rate of lithium. Therefore, SLR was managed
26 with a series of pretreatment techniques, including coagulation, biochar aerogel
27 adsorption, and ultrafiltration, achieving more than 84.3% removal of organic
28 substances. $\text{H}_{1.33}\text{Mn}_{1.67}\text{O}_4$ and Li/Al layered double hydroxides adsorbents were then
29 synthesized by solid state reaction method and hydrothermal method, respectively,
30 granulated into spheres with a PVC skeleton, and applied to recycle lithium from
31 pretreated SLR in a fixed bed adsorption column. The results indicated that both Mn
32 and Al-based adsorbents exhibited rapid adsorption kinetics, reaching saturation within
33 2 h. The Mn-based adsorbent exhibited superior adsorption selectivity for Li^+ and
34 higher Li^+/Na^+ separation factor ($\alpha_{\text{Na}}^{\text{Li}}$) compared to Al-based adsorbent, with partition
35 coefficients and $\alpha_{\text{Na}}^{\text{Li}}$ values equal to 6.62 mL/g, 8.79 for the former material, and 4.92
36 mL/g, 8.17 for the latter. On the other hand, the Al-based adsorbent displayed better
37 stability with negligible Al loss, while Mn loss from the related adsorbent was less than
38 0.2% in every adsorption-desorption cycle. Notably, both adsorbents demonstrated
39 excellent reusability with their adsorption capacity maintained after twenty adsorption-
40 desorption cycles.

41 **Key words:**

42 Spent lithium-ion battery raffinate; Pretreatment; Lithium recycling; Mn/Al-based
43 adsorbent; Comparative analysis.

44

45 **1. Introduction**

46 As a critical rare metal [1], lithium has extensive application in various industrial
47 applications, chiefly, in lithium batteries [2] due to its light mass density (0.534 g/cm^3)
48 [3], high electrode potential (-3.05 V) [4], low equivalent weight (6.94 g/Faraday) [5],
49 and long service life. In the context of “dual carbon” objective, the market for new
50 energy vehicles powered by lithium-ion batteries (LIB) has experienced exponential
51 growth as a response to the scarcity of fossil fuels and climate change [6], resulting in
52 a substantial increase in the production of lithium-ion batteries. By 2030, China’s
53 electric vehicle production is projected to reach 15 million per year [7], accounting for
54 45% of the global total electric vehicles based on reports from the International Energy
55 Agency [5]. However, after a lifespan of 3 to 10 years [8], a great deal of electric
56 vehicles will be retired, leading to a significant accumulation of spent LIBs [9,10]. The
57 China Society of Automotive Engineers estimates that, by 2030, the amount of
58 decommissioned power batteries will reach 3.5 million tons. However, the global
59 lithium recycling rate from LIBs is below 1% [11]. Survey of Development Research
60 of the State Council indicates that the standardized recovery rate of China’s new energy
61 vehicle power battery is less than 25% in 2023.

62 If handled improperly and if disposed as domestic waste, the heavy metals and
63 toxic electrolytes in spent LIBs will cause environmental problems and threats to
64 human health [12,13]. However, a large amount of valuable key metal ions, such as Li,
65 Co, Ni, and Mn in spent LIBs have high grade and are potentially easier to recover than
66 extraction from natural ores, which makes spent LIBs a secondary, economical source

67 of valuable minerals [10,14,15]. In particular, the content of Li in spent LIBs reaches
68 up to 5 to 7 wt% [16], which is substantially higher than any other lithium resource.
69 Therefore, recovering rare metals from spent LIBs is of great significance for mitigating
70 environmental pollution and ensuring a sustainable supply of lithium as raw material
71 for the manufacturing of new batteries.

72 Hydrometallurgy [17], pyrometallurgy [18], biometallurgy [19], and
73 electrochemical extraction [20] have been employed in research and industrial settings
74 for metals recovery from spent LIBs. Among these methods, hydrometallurgy
75 combined with leaching and extraction is the most common method adopted for metal
76 ion recycling [21]. The hydrometallurgy process requires a large volume of strong acid
77 and water for leaching, followed by pH adjustment, typically performed by addition of
78 NaOH, to extract Mn, Co, and Ni in sequence [22]. Spent lithium-ion battery raffinate
79 (SLR) is the leachate of spent LIBs obtained after the extraction of Mn, Co, Ni, and Li.
80 It contains large concentrations of Na and residual Li, and it is characterized by high
81 values of total dissolved solids (TDS) and total organic carbon (TOC). The lithium
82 concentration in the raffinate can reach up to 1000 mg/L, higher than that found in
83 traditional salt lake brine, seawater, or shale gas wastewater. It is thus potentially
84 feasible to further extract Li from the raffinate to further increase lithium supply and to
85 alleviate environmental pollution.

86 Currently, most literature studies on this topic focus on lithium recycling directly
87 from the spent LIBs or from salt lake brines, with limited attention paid to lithium
88 recycling from RSL. Presently, methods for lithium recovery from aqueous lithium

89 resources include evaporation and precipitation [23], solvent extraction [24],
90 adsorbents adsorption [25], membrane treatment [4,26], electrochemical methods [27],
91 or a combination of the above. Among these approaches, membrane and
92 electrochemical methods are not readily applicable, due to the high TDS and TOC
93 content of RSL. Instead, adsorbents have gained widespread attention due to their
94 simplicity in preparation, low synthesis contamination, high adsorption capacity and
95 selectivity, as well as reusability and economic potential [25].

96 There are three main types of inorganic metal-based lithium ion adsorbents
97 extensively applied for lithium extraction, including layered Al-based adsorption
98 materials, Mn-based ion sieves, and Ti-based ion sieves [25,28]. The lithium adsorption
99 process of these metal-based ion sieves is mainly governed by structural memory effect
100 [28]. Ti-based ion-exchange sieves have strong Ti-O bonds, which endow them with a
101 stable framework, excellent acid endurance, and exceptional Li adsorption ability [29].
102 However, high cost thwarts the practical application of these Ti-based materials. Al-
103 based adsorbents have exhibited better potential in industrial applications, owing to
104 their technological maturity, inexpensive raw materials, simple synthesis procedure,
105 and mild preparation conditions [30]. For example, Zhong et al [31]. synthesized two-
106 dimensional hexagonal Li/Al layered double hydroxides by coprecipitation to recover
107 Li from Qarhan salt lake brine at ambient temperature, with an adsorption capacity of
108 7.27 mg/g. Sun et al. prepared Li/Al layered double hydroxides and extracted Li from
109 Qaidam salt lake brine by hybrid method of reaction-coupled separation, reaching Li
110 loss lower than 3.93% [32]. In addition, Mn-based adsorbents present excellent

111 adsorption performance, selectivity, regeneration properties, and low cost [33].
112 Compared with $H_{1.6}Mn_{1.6}O_4$ and $HMnO_2$ [34], the synthesis of $H_{1.33}Mn_{1.67}O_4$ is simpler
113 due to lower energy requirement [35]. For instance, Tian et al. synthesized
114 $H_{1.33}Mn_{1.67}O_4$ and recovered lithium from shale gas wastewater, reaching a Li partition
115 coefficient higher than 1073 mL/g [36]. Both Al-based and $H_{1.33}Mn_{1.67}O_4$ adsorbents
116 have reliable application potential for lithium recovery from SLR.

117 This study discusses and evaluates the technical feasibility of lithium recycling
118 from SLR, as a novel potential source of lithium. We first investigate the characteristics
119 of SLR and the effect of pretreatment, including coagulation, biochar adsorption, and
120 ultrafiltration, on organic pollutant removal. Then, we discuss the synthesis of Li/Al
121 layered double hydroxides and of $Li_{1.33}Mn_{1.67}O_4$ adsorbent precursors by one step
122 method and solid-phase reaction method, respectively, and the granulation of the
123 adsorbents powder into spheres aimed at lithium recycling from SLR in a fixed bed
124 adsorption column. The adsorption kinetics, adsorption selectivity, multi-stage
125 adsorption performance, and regeneration capability of lithium recovery from SLR by
126 both Mn and Al-based adsorbent granules are evaluated. Adsorbents are also assessed
127 in terms of adsorption/desorption performance during 20 cycles of utilization. The main
128 objective is to verify the technical feasibility of lithium recovery from real SLR by
129 pretreatment combined with adsorption, which has important repercussions on further
130 development of lithium recycling strategies.

131 **2. Materials and methods**

132 2.1. Materials

133 AR-grade MnCO_3 , Li_2CO_3 , $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, NaOH , and HCl and were purchased
134 from Kelong Chemical Co., Ltd. (Chengdu, China) Polyaluminum chloride (PACl) was
135 purchased from Liming chemical plant (Zigong, China). Polyvinyl chloride (PVC) and
136 dimethylacetamide (DMAC) were supplied by Macklin Biochemical Co., Ltd.
137 (Shanghai, China). The raw SLR solution was provided by Btree Recycling
138 Technologies Co., Ltd. (Suzhou, China). All chemicals were used as received.

139 2.2. Synthesis of Mn and Al-based adsorbent powders precursor

140 The Mn-based adsorbent precursor for $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ was prepared by solid state
141 reaction method, with synthesis processes detailed in our previous work [36]. Briefly,
142 a proper amount of MnCO_3 and Li_2CO_3 powders with Li/Mn molar ratio of 1.33:1.67
143 were well-mixed in a ceramic mortar, then calcinated in a tube furnace at 500 °C for 4
144 h under ambient air with heating rate of 3 °C/min, followed by cooling to ambient
145 temperature. The Al-based lithium adsorbent precursor was synthesized by a one-step
146 method. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and LiCl were dissolved in ultrapure water at an Al/Li mole ratio
147 of 1.3:1. NaOH solution with a concentration of 5 mol/L was added dropwise to the
148 above solution with assistance of a peristaltic pump at a rate of 3.5 mL/min while
149 stirring at a speed of 150 r/min. The reaction temperature was 75 °C and the terminal
150 pH was 6-7. The obtained solid was separated from the aqueous solution by
151 centrifugation and dried to obtain the Al-based adsorbent precursor.

152 2.3. Granular Mn and Al-based adsorbent preparation

153 Adsorbent precursor powders were granulated into spheres by anti-solvent method,
154 as follows: 3.5 g PVC was added in 40 mL DMAC solution under magnetic stirring at

155 60 °C until dissolved completely. Then, 4.0 g adsorbent precursor powder was added to
156 this solution to form a uniform slurry. After that, the slurry was dripped by a syringe
157 pump into ultrapure water to form granules. The obtained spheres were rinsed in
158 ultrapure water to remove DMAC. Eventually, the Mn-based spheres and Al-based
159 spheres were separately eluted in 0.5 mol/L HCl solution and deionized water for 5 h
160 to eliminate the template Li⁺ ion and to obtain the granular adsorbent.

161 2.4. Experimental set-up

162 The lithium recycling system consisted of a pretreatment system and a fixed bed
163 adsorption stage, as depicted in Fig. 1. All the tests were conducted under ambient
164 temperature of roughly 25 °C. The raw raffinate of spent lithium-ion battery was
165 pretreated by coagulation, biochar aerogel adsorption, and ultrafiltration (UF), in
166 sequence. A commercial PACl coagulant with concentrations of 500, 1000, 1200, 1500,
167 2000 mg/L was tested to determine the optimum dosage. All the coagulation tests were
168 operated in a programmable jar test apparatus (ZR4-6, Zhongrun Water Industry
169 Technology Development Co., Ltd, China). The tests involved fast stirring at 200 rpm
170 for 2 min, followed by slow stirring at 40 rpm for 20 min and static precipitation for 30
171 min. The obtained supernatant liquid was collected for the subsequent tests. The biochar
172 aerogel was synthesized according to the protocol described in our previous works
173 [37,38]. The biochar aerogel adsorption process was conducted in a shaker at 150 rpm
174 for 2 h with the goal to remove additional organic matter on the clarified supernatant
175 from the previous coagulation step. Subsequently, the solution was pumped into the
176 ultrafiltration device to eliminate turbidity and further organic pollutant. The UF

177 treatment was performed in a cross-flow equipment at a constant pressure of 1.0 bar
178 with an effective membrane area of 17.6 cm². The UF process consisted of eight cycles,
179 each cycle including 1 h filtration and 5 min back washing with ultrapure water.

180 The lithium recovery procedure was conducted in a fixed bed column. Considering
181 the concentration of Li⁺ ion in the SLR and the adsorption capacity of the adopted
182 adsorbent based on previous studies [39], the volume ratio between adsorbent granules
183 and SLR was set to 1:1.5. To prepare the fixed bed for adsorption, 10 mL of Mn or Al-
184 based granules were placed in an adsorption column, while 15 mL of pretreated SLR
185 was put into a beaker as a feed solution to the column. Adsorption was conducted in a
186 closed-loop system, with the pretreated SLR circulating between the adsorption column
187 and the beaker for 5 h. Adsorption kinetic behaviors were explored by pseudo-first and
188 second-order models. The amount of adsorbed lithium at various times was computed
189 with Eq. (1):

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

190 where C_0 , m , and V represent the initial lithium concentration, the mass of the adsorbent
191 granules, and the solution volume, respectively. q_t and C_t stand for the adsorbed lithium
192 amount and the Li⁺ concentration in the solution at time t .

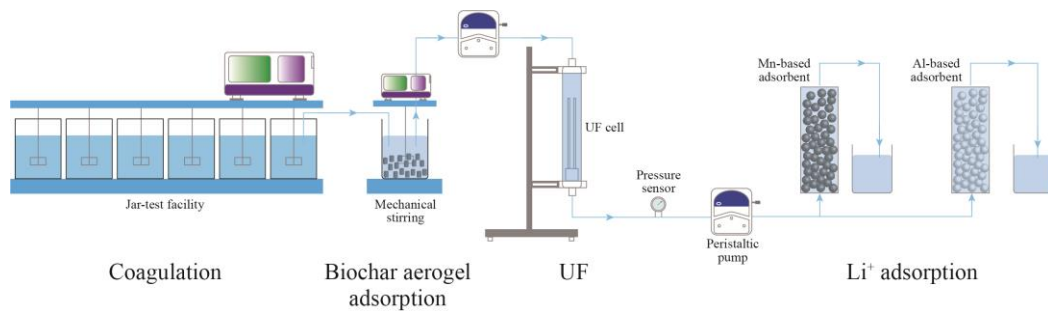
193 Adsorption selectivity of lithium with respect to other interfering metal ions was
194 assessed by determining the partition coefficient (K_d), the concentration factor (CF),
195 and the separation factor (α_{Me}^{Li}), calculated with the following Eqs. (2-4):

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (2)$$

$$CF = \frac{q_e(Me)}{C_0(Me)} \quad (3)$$

$$\alpha_{Me}^{Li} = \frac{K_d(Li)}{K_d(Me)} \quad (4)$$

196 The reusability of adsorbent granules was assessed by adsorption-desorption
 197 cycles, including adsorption, desorption, and ultrapure water washing steps.
 198 Specifically, the desorption process was carried out in the same way of the adsorption
 199 step described above, but with a solution consisting of 0.5 mol/L HCl for Mn-based
 200 adsorbent and ultrapure water for Al-based adsorbent, which recirculated between a
 201 beaker and the column for 5 h.



202

203 Fig. 1: Schematic flow diagram of the lithium recovery system comprising
 204 pretreatment and adsorption steps.

205

206 2.5. Analytical methods

207 Dissolved organic carbon (DOC), UV_{254} , and zeta potential of raw solution and
 208 coagulation supernatant under various coagulant dosage were measured with a TOC
 209 analyzer (TOC-L, Shimadzu, Japan), UV spectrophotometer (Orion AquaMate 8000,
 210 Thermo Fisher, USA), and Zeta-size nano instrument (Nano-ZS90, Malvern, UK),
 211 respectively. The three-dimensional excitation-emission matrix fluorescence spectra of

212 the raw SLR and the solutions obtained after each treatment step were analyzed with a
213 fluorescence spectrophotometer (F7100, Hitachi, Japan). The ion concentration in
214 solution was measured with an atomic absorption spectrometer (AAS, PinAAcle 900T,
215 PerkinElmer, USA) and with ion chromatography (Dionex Integriion HPLC, Thermo
216 Fisher, USA).

217 The crystalline structure of two types of adsorbent powders, their morphologies,
218 and the elemental distribution of granules were characterized with X-ray diffraction
219 (XRD, DX2700, China) and field emission scanning electron microscopy (FE-SEM,
220 Hitachi, Japan). Nitrogen adsorption-desorption isotherms were obtained with an ASAP
221 2460 analyzer (Micromeritics, USA) under liquid N₂ atmosphere (77 K). The specific
222 surface area and pore size distribution of the granules were determined applying the
223 Brunauer-Emmett-Teller equation and the Barrett-Joyner-Halenda (BJH) method,
224 respectively.

225 **3. Results and discussion**

226 3.1. Performance of SLR pretreatment and solution characteristics

227 The characteristics of raw SLR solution are summarized in Table 1. Effects of
228 PACl concentration on the TOC, UV₂₅₄, and zeta potential of the SLR solution are
229 instead presented in Fig. 2. When PACl dosage increased from 0 to 1500 ppm, TOC
230 and UV₂₅₄ values drastically decreased from 760.5 mg/L to 204.3 mg/L, and from 0.023
231 cm⁻¹ to 0.009 cm⁻¹, respectively. When PACl content further increased to 2000 ppm,
232 TOC and UV₂₅₄ values diminished only slightly to 194.8 mg/L and 0.007 cm⁻¹.
233 Therefore, the optimum PACl dosage was determined to be 1500 ppm. The addition of

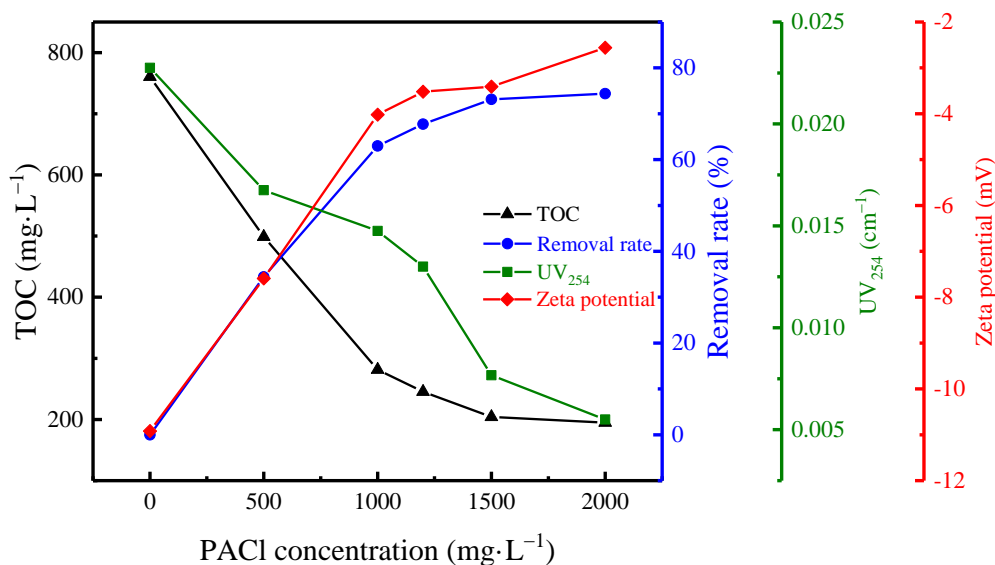
234 PACl decreased the absolute value of the zeta potential, which increased from -10.9
 235 mV (raw SLR) to -3.4 mV (PACl content of 1500 ppm) at the unadjusted pH equal to .
 236 A higher PACl concentration likely resulted in more hydroxide precipitation from the
 237 suspension [40]. Overall, PACl had remarkable performance on organic matter removal,
 238 removing up to 73% of organic matter and representing a suitable choice for SLR
 239 coagulation due to the availability and low cost of the coagulant.

240

241 Table 1: Characteristics of raw spent lithium-ion battery raffinate.

Parameter	Li (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	TOC (mg/L)	UV ₂₅₄ (cm ⁻¹)	TDS (mg/L)	pH
Values	11,470	31,210	126.4	54.56	57.50	769	0.023	112,000	5.54

242



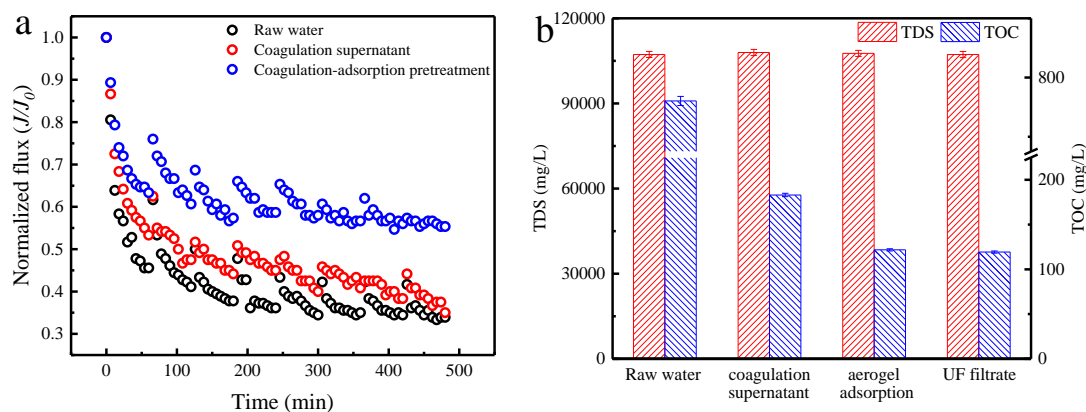
243

244 Fig. 2: Variation of TOC, UV₂₅₄, and zeta potential of the SLR solution with the
 245 increased dosage of PACl coagulant. Lines connecting the data points are only a guide
 246 for the eye.

247

248 Upon clarification, the supernatant was further treated with biochar aerogels and

249 UF membranes. The influence of coagulation and biochar aerogel adsorption processes
250 on UF membrane performance is presented in Fig. 3a. The use of raw SLR as feed
251 solution caused the severest UF membrane fouling, with the membrane flux declining
252 severely to 45.6% of the initial flux, and then recovering to 61.7% of the initial flux at
253 the end of the first cycle of filtration and backwashing. After 8 cycles, the observed flux
254 was only 33.9% of that measured with a pristine membrane, due to the high TOC value
255 of the raw SLR solution and the suspended materials blocking the membrane pores,
256 which was verified with SEM imaging, as shown in Fig. S2. The coagulation treatment
257 somewhat alleviated the UF membrane fouling. In particular, the membrane flux
258 decreased by roughly half in the first filtration cycle, and recovered to 62.5% of the
259 initial flux after backwashing. In this case, the flux decline was mainly attributed to
260 scaling and inorganic components depositing on the UF membrane surface (see Fig.
261 S2). The additional aerogel adsorption treatment further reduced membrane fouling. At
262 the end of first cycle, the flux declined to 63.3% of the initial flux and, after
263 backwashing, the flux recovered to 76.0% of the initial value. At the end of the eighth
264 cycle of filtration, the flux was approximately 55% of the flux measured with a pristine
265 membrane.

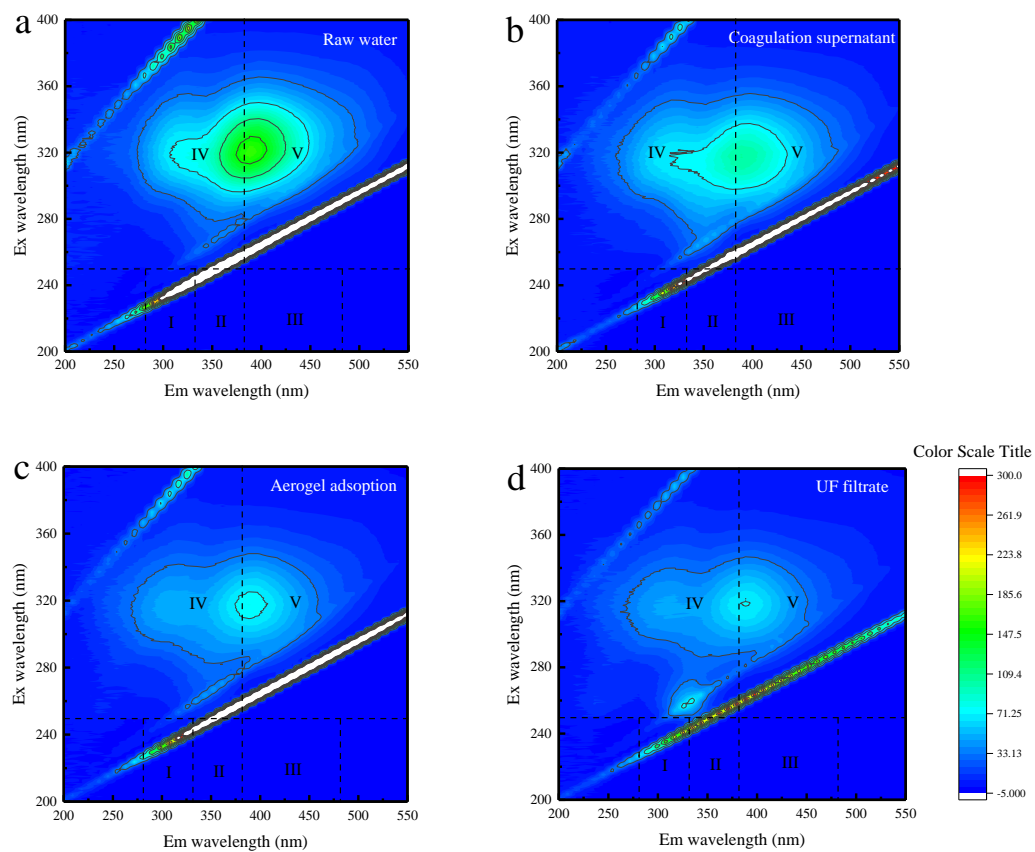


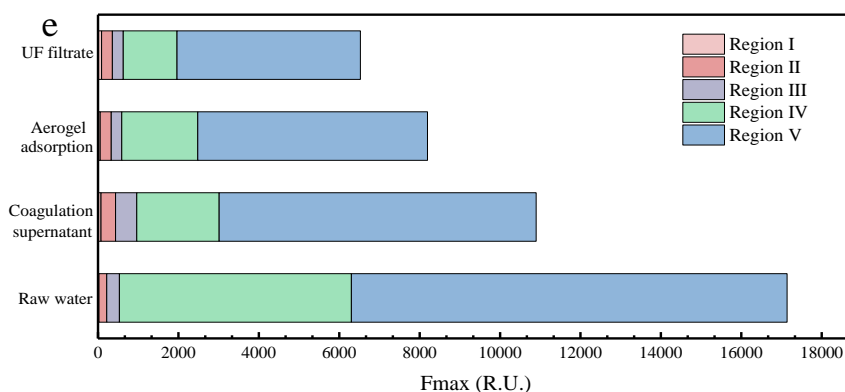
266 Fig. 3: (a) UF membrane performance for raw and pretreated raffinate of spent
 267 lithium-ion battery, and (b) related TDS, TOC variations.

268

269 As shown in Fig. 3b, the TOC decreased to 121.8 mg/L and 119.3 mg/L after
 270 aerogel adsorption and UF filtration, respectively. Throughout the various pretreatment
 271 processes, the TDS concentration remained constant; see Fig. 3b. The evolution of
 272 organic matter in the SLR solution was further investigated with three-dimensional
 273 fluorescence. Excitation-emission (EEM) spectra of raw SLR and the product stream
 274 from every processing stage are reported in Fig. 4(a-d), with the spectra divided into
 275 five regions based on previous research analyses [41]. One main peak of emission
 276 intensity was observed in all solution samples, centered between region IV and region
 277 V, which are related to soluble microbial byproducts and humic-like substance,
 278 respectively. The fluorescence regional integration (FRI) analysis indicated that DOM
 279 was mainly composed by soluble microbial byproducts (33.7%) and humic-like
 280 substances (63.2%); see Fig. 4e. Note that the organic matter composition may be
 281 altered in previous processing steps, including the organic extraction agent used for the
 282 recovery of rare earth metals from the spent lithium-ion battery.

283 The raw SLR solution had the highest fluorescence intensity. Upon treatment
284 through PACl coagulant and biochar aerogel adsorption, the peak intensity declined
285 sharply, and then it decreased slightly upon UF filtration. This result is consistent with
286 the TOC removal efficiency reported in Fig. 3b and with the trends in FRI values, which
287 suggest especially high removal of humic-like substances. Indeed, the biochar aerogel
288 typically exhibits a high affinity with humic-like matters, promoting their removal
289 through hydrogen bonding and hydrophobic interaction.





290 Fig. 4: Three-dimensional excitation-emission (EEM) fluorescence spectra of all SLR
 291 samples: (a) raw water, (b) supernatant from the coagulation step, (c) solution upon
 292 biochar aerogel adsorption, and (d) UF filtrate. (e) F_{\max} of EEM spectra obtained with
 293 fluorescence regional integration analysis.

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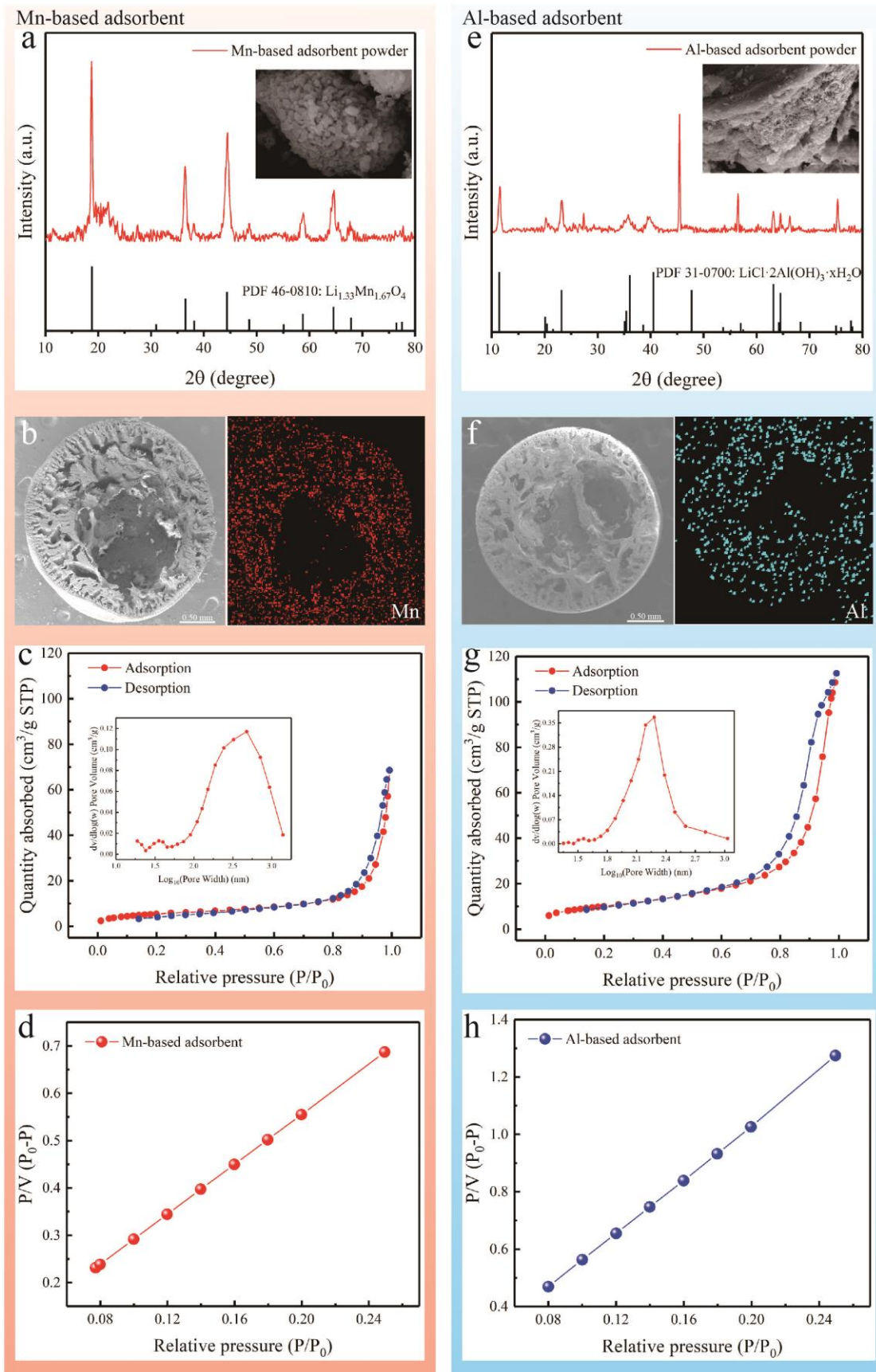
295 3.2.Characteristics of the Mn and Al-based adsorbents

296 Fig. 5a and 5e present representative XRD patterns and SEM micrographs of the
 297 two kinds of adsorbent precursor powders. The Mn-based powder showed nearly the
 298 same diffraction peaks of the standard XRD pattern (PDF No. 46-0810), with main
 299 peaks at $2\theta = 18.8^\circ, 36.5^\circ, 44.4^\circ,$ and 64.5° . The spinel structure of the adsorbent
 300 observed in the SEM analysis was similar with that described by previous research
 301 reports [36]. Both XRD and SEM results suggest the successful synthesis of the Mn-
 302 based adsorbent. The XRD pattern of Al-based adsorbent powder was also consistent
 303 with the diffraction peaks of the standard pattern (PDF No. 31-0700), with main peaks
 304 at $2\theta = 11.4^\circ, 23.2^\circ, 40.5^\circ,$ and 63.2° . The SEM analysis of the Al-based adsorbent
 305 suggested a lamellar structure, a layered crystal formed by superposition of octahedral
 306 layers of oxygen coordination, indicating the one step coprecipitation method

307 successfully synthesized the Al-based adsorbent.

308 Analyzing the granules produced by combining the precursor powders with PVC,
309 SEM cross-sectional micrographs presented in Fig. 5b and 5f suggest that both
310 adsorbent granules had a partly hollow and highly porous interior structure, with
311 micropores on the surface. The EDS mapping results indicate that Mn and Al were
312 finely distributed, suggesting that the adsorbent powders were uniformly incorporated
313 within the PVC skeleton. Nitrogen adsorption-desorption isotherms of both granule
314 adsorbents, presented in Fig. 5c and 5g, indicate that the adsorbents had mesopores,
315 because of the IV isotherm with an H3 hysteresis loop. The amount of adsorbed N₂ was
316 68.5 cm³/g and 112.6 cm³/g for the Mn and for the Al-based adsorbent, respectively.
317 The larger N₂ adsorption was attributed to the relative loose structure of layered Al-
318 based crystal compared to the spinel structure of the Mn-based adsorbent, as observed
319 with SEM analysis. The inset graphs in Fig. 5c and 5g display the pore size distribution
320 according to the BJH method. Mn-based adsorbent had bimodal mesoporous structure
321 distribution with a minor peak corresponding to a small portion of mesopores and a
322 major peak related to the main mesopores. Its mean pore size ranged from 21 to 24 nm.
323 In contrast, the Al-based adsorbent displayed a unimodal mesoporous structure
324 distribution with an average pore size in the range 15-18 nm. Based on BET surface
325 area plot (Fig. 5d and 5h), the Mn-based adsorbent possessed a BET surface area of
326 20.3 m²/g and a total volume of 0.106 cm³/g, while the corresponding values for the Al-
327 based adsorbent were 36.6 m²/g and 0.174 cm³/g, respectively. Overall, the structure,
328 surface area, and pore characteristics of the materials were highly suitable to achieve

329 potentially high Li adsorption capacity and kinetics, which are the topic discussed in
330 the following chapters.



331

332 Fig. 5: Mn and Al-based adsorbent properties: (a, e) XRD patterns of the precursor

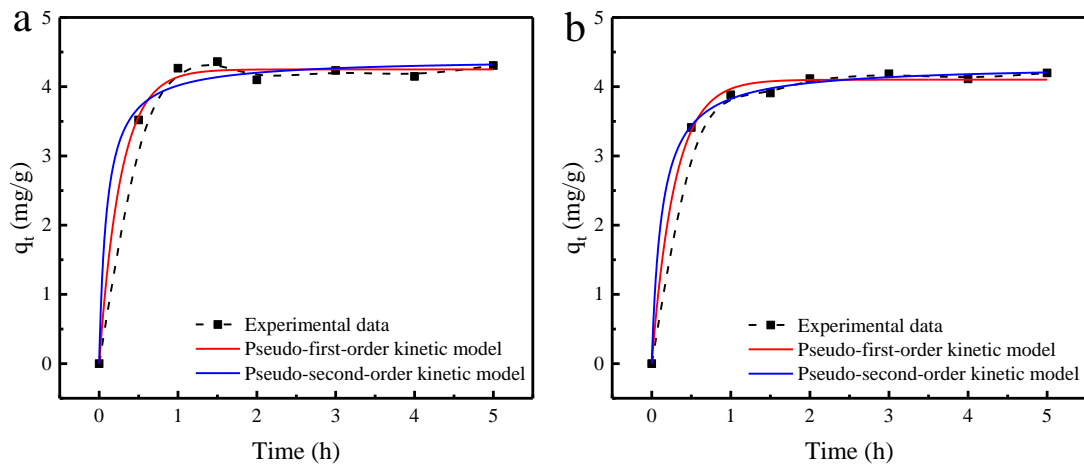
333 powders; (b, f) representative SEM micrographs and EDS mapping of the granules
334 obtained by combining the adsorbent powders with PVC; (c, g) N₂ adsorption-
335 desorption curves and resulting pore size distribution of the granules; (d, h) BET
336 surface area plot.

337

338 3.3. Adsorption kinetics

339 The lithium adsorption behavior of both Mn and Al-based adsorbent granules was
340 investigated through adsorption kinetics. The data were fitted to the pseudo-first and
341 second-order kinetic models and the results are displayed in Fig. 6. Both adsorbent
342 granules displayed a rapid lithium adsorption from the SLR solution within the first 1
343 h, followed by a substantial decrease in the adsorption rate until steady state was
344 reached after roughly 2 h. A relatively rapid adsorption rate observed in this work
345 compared with other previous research [42] may be partly attributed to the higher TDS
346 concentration of SLR (112.3 g/L). The osmosis pressure gradient generated by the
347 salinity difference between SLR solution and the adsorbent spheres may act as a driving
348 force that promotes the transfer of lithium ion from the aqueous phase to solid phase.
349 Fitted kinetic parameters summarized in Table 2 suggest that the differences in R²
350 values between pseudo-first-order kinetic model and pseudo-second-order kinetic
351 model were negligible. Therefore, the adsorption process was likely governed by a
352 combination of physical sorption and chemical sorption. According to previous studies,
353 the adsorption kinetics of Mn and Al-based adsorbents are mainly controlled by
354 chemical adsorption [31,36]. Some physical adsorption may possibly be attributed to

355 the interaction of lithium with the PVC skeleton, with ions sorbing onto the surface or
 356 the inner pore structure of the adsorbent granules.



357 Fig. 6: Results of lithium adsorption kinetics test onto (a) Mn-based adsorbent and (b)
 358 Al-based adsorbent. Data points were fitted using pseudo-first and pseudo-second
 359 order kinetics, with fitting results represented by a red and a blue line, respectively.

360

361 Table 2: Results of fitting the lithium adsorption kinetics data with pseudo-first-order
 362 and pseudo-second-order models.

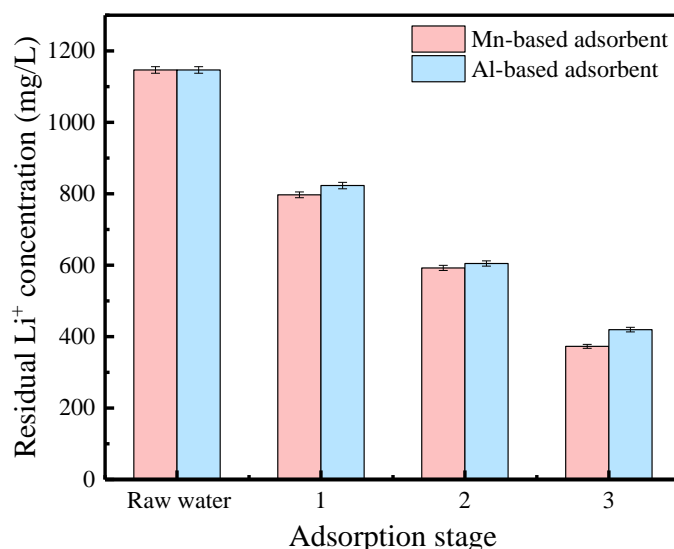
	Pseudo-first-model $q_{e,cal}$ (mg/g)	k_1 (min^{-1})	R^2	Pseudo-second-model $q_{e,cal}$ (mg/g)	K_2 ($\text{g}\cdot\text{min}^{-1}\text{h}^{-1}$)	R^2
Mn-based	4.25	3.66	0.9947	4.40	2.36	0.9867
Al-based	4.10	3.43	0.9955	4.31	1.81	0.9984

363

364 3.4. Performance of the integrated multiple stage adsorption process

365 An integrated three-stage adsorption process was designed and evaluated to
 366 maximize the recovery of lithium from SLR. Results presented in Fig. 7 imply that the
 367 adsorption on both adsorbent granules decreased in subsequent adsorption stages, likely
 368 due to the reduced concentration gradient. At the end of three-stage adsorption, the

369 concentration of Li^+ ion decreased from 1147 mg/L to approximately 373 mg/L and 420
 370 mg/L for Mn and Al-based adsorbent, respectively, and the recovery rate reached values
 371 of 67.5% and 63.4%. The Mn-based adsorbent displayed a relatively superior recovery
 372 performance, attributed to specific recognition of Li^+ ions by ion exchange of Li^+/H^+ ,
 373 which is possibly a more suitable mechanism compared to the intercalation phenomena
 374 characterizing the main adsorption mechanism of the Al-based adsorbent. However,
 375 overall, both adsorbents had a desirable performance for lithium recycling from
 376 raffinate of spent lithium-ion battery.



377

378 Fig. 7. Multi-stage adsorption performance of Mn and Al-based adsorbent granules.

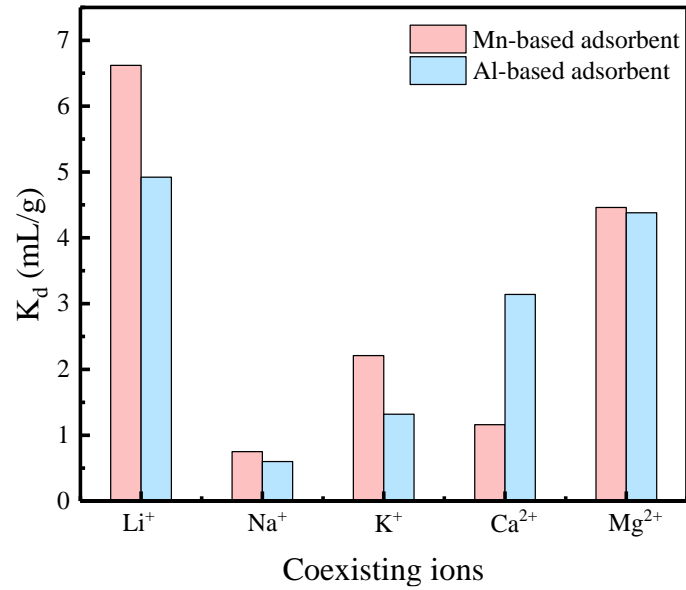
379

380 3.5. Selectivity performance

381 It is important to assess the selectivity of both Mn and Al-based adsorbents for
 382 lithium ion in the presence of interfering ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) in the SLR,
 383 especially the Na^+ ion characterized by high concentrations up to roughly 31200 mg/L.

384 Fig. 8 presents the partition coefficients (K_d), while other adsorption and selectivity

385 parameters are summarized in Table 3 and Table 4. The lithium partition coefficients
386 associated with both adsorbents were larger than those of other ions, particularly Na^+ .
387 Specifically, the K_d value characterizing the Mn-based adsorbent (6.62 mL/g) was
388 greater than that determined for the Al-based adsorbent (4.05 mL/g), consistent with
389 adsorption capacity results presented above. Compared with the layered crystal
390 structure of Al-based adsorbent, the relatively higher selective separation of Mn-based
391 adsorbent to lithium may be attributed to its spinel structure providing an ionic sieve
392 effect that promotes preferential adsorption of ions with radius similar to that of the
393 adsorption sites. It should be noted that the adsorption capacity for both adsorbents to
394 Na^+ was also large, which may be explained by the following reasons. On the one hand,
395 the concentration of Na^+ ion in SLR was 27.2 times higher than the Li^+ concentration,
396 which may promote much more substantial physical adsorption onto the surface and
397 inner cavity of the PVC skeleton. This hypothesis was corroborated by the EDS
398 mapping determined on granule adsorbent after they were used for adsorption; see Fig.
399 S3. On the other hand, although the selectivity for Li^+ with respect to Na^+ was high for
400 both adsorbent materials, a proportion of adsorption sites were indeed consumed by
401 Na^+ , which is an unavoidable phenomenon because of the concentration ratios in the
402 SLR solution. That being said, the combination of capacity and selectivity results
403 suggests the suitability of both adsorbent for lithium uptake from SLR, with a slight
404 preference for Mn-based materials, possibly due to their more appropriate structural
405 characteristics.



406

407

Fig. 8. Partition coefficients (K_d) determined for both adsorbent granules for coexisting cations.

408

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Table 3: Adsorption selectivity of Mn-based adsorbent from SLR.

	C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)	K_d (mL/g)	CF (mL/g)	α_{Me}^{Li}
Li ⁺	1,147	750	4.96	6.62	4.33	1
Na ⁺	31,200	29,400	22.2	0.75	0.71	8.79
K ⁺	126	107	0.24	2.21	1.88	3.00
Ca ²⁺	54.6	49.9	0.06	1.16	1.06	4.09
Mg ²⁺	57.5	42.4	0.19	4.46	3.29	1.49

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Table 4: Adsorption selectivity of Al-based adsorbent from SLR.

	C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)	K_d (mL/g)	CF (mL/g)	α_{Me}^{Li}
Li ⁺	1,147	823	4.05	4.92	3.53	1
Na ⁺	31,200	29,800	17.9	0.60	0.57	8.17
K ⁺	126	114	0.15	1.32	1.20	3.71
Ca ²⁺	54.6	43.6	0.14	3.14	2.51	1.41
Mg ²⁺	57.5	42.6	0.18	4.38	3.24	1.12

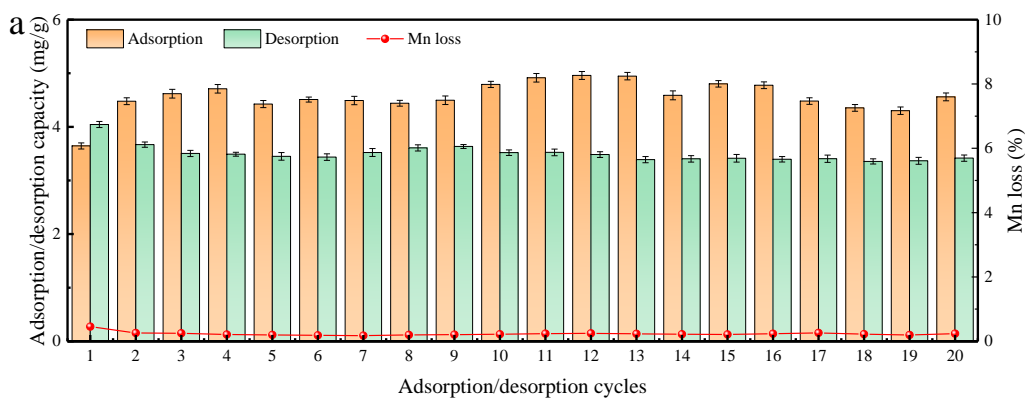
417

418 3.6. Reusability and stability of Mn and Al-based adsorbents

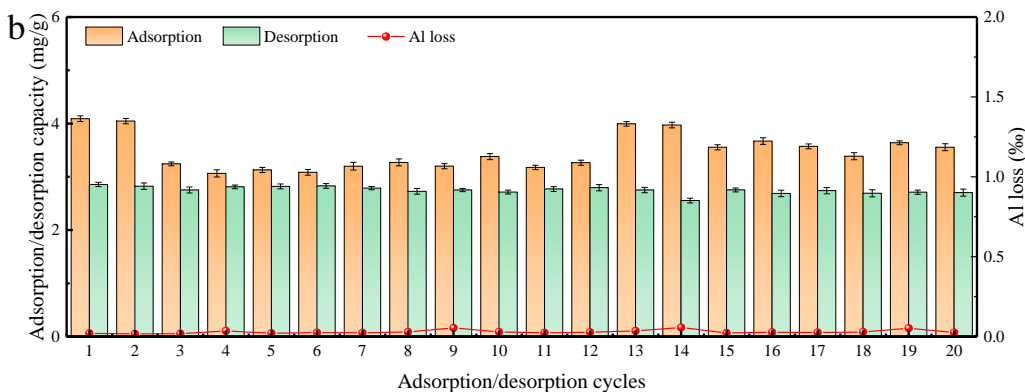
419 The reusability of both adsorbent granules was evaluated in twenty cycles of
420 adsorption and desorption. The lithium adsorption/desorption capacity assessed in
421 every cycle is presented in Fig. 9. The adsorbents exhibited relatively stable
422 performance, with adsorption capacities fluctuating around 4 mg/g for Mn-based
423 adsorbent and 3.5 mg/g for Al-based adsorbent across the cycles. Concurrently, both
424 adsorbents showed stable desorption behavior, with desorption capacities fluctuating
425 around 3.5 mg/g and 2.8 mg/g for Mn-based granules and Al-based granules,
426 respectively. For Mn-based granules, the seemingly inconsistent value of lithium
427 desorption compared to that of previous adsorption in the first cycle may be explained
428 with the incomplete washing out of adsorbent precursor from the synthesized material,
429 resulting in some template Li⁺ still occupying the binding sites during the first cycle of
430 adsorption, then washed out during the subsequent desorption step.

431 Fig. 9a presents results obtained in the investigation of the adsorbent stability. Mn
432 loss from Mn-based materials was 0.45% after the first cycle, and it decreased to around

433 0.2% for the following cycles. A higher Mn loss in the first cycle is likely ascribed to
 434 the incompletely fixed Mn element in the adsorbent crystal structure during the
 435 sintering procedure, with a portion of the element that was only attached to the surface
 436 of the powdered adsorbent, thus easily eluted once in contact with the desorption
 437 solution. The results presented in Fig. 9b suggest that during the 20 cycles, the Al-based
 438 granule suffered instead negligible Al loss, namely, less than 0.06%. A relatively larger
 439 Mn loss during all cycles may be attributed to the effect of acid treatment, which would
 440 likely induce electron transfer from trivalent manganese in the crystal structure to
 441 tetravalent manganese in the surface. After obtaining sufficient electrons, tetravalent
 442 manganese would convert to bivalent manganese, in turn subject to dissolution [43].
 443 Overall, the remarkable stability of both adsorbents imply the potential for long-term
 444 application of both adsorbents for lithium selective adsorption recovery.



445



446

447 Fig. 9: Adsorption-desorption capacity of Li^+ and related Mn, Al loss in different,
448 subsequent cycles of adsorption and desorption: (a) Mn-based adsorbent granules, (b)
449 Al-based adsorbent granules.

450

451 **4. Conclusion**

452 This paper discussed materials and their application in an integrated approach for
453 lithium recovery from spent lithium-ion battery raffinate (SLR), combining
454 pretreatment of the solution via PACl coagulation, biochar aerogel adsorption, and
455 ultrafiltration, with lithium adsorption onto Mn and Al-based adsorbent granules. The
456 pretreatment steps effectively removed organic constituents of the SLR, which
457 decreased from roughly 761 mg/L to 119 mg/L without observable lithium-ion loss.
458 Both Mn and Al-based adsorbent granules exhibited rapid adsorption of lithium from
459 the pretreated SLR, reaching saturation within 2 h, with final capacity in the range 4-5
460 mg of lithium per g of adsorbent granular material. Notably, the partition coefficients
461 of Li^+ for Mn-based (6.62 mL/g) and Al-based (4.92 mL/g) adsorbents were
462 significantly higher than those of other ions, particularly Na^+ (0.75 mL/g for Mn-based
463 adsorbent and 0.60 mL/g for Al-based adsorbent), suggesting effective separation of
464 Li^+ and Na^+ . The Mn-based adsorbent showed superior adsorption capacity compared
465 to Al-based adsorbent, attributed to its favorable structure. Both adsorbents also
466 presented remarkable reusability. After twenty adsorption/desorption cycles, the
467 adsorption capacities of Mn and Al-based adsorbents reached a stable behavior,
468 maintaining values of 4.5 mg/g and 3.5 mg/g, respectively, which was only about 10-

469 15% lower than the values measured for the as-synthesized materials in their first cycle
470 of application. While the Mn-based adsorbent provided a better adsorption capacity, it
471 experienced a relatively higher element loss, equal to approximately 0.2% Mn loss per
472 cycle. On the contrary, Al loss was negligible from Al-based materials. This study
473 indicates the effectiveness of pretreatment followed by Mn and Al-based adsorbent
474 adsorption as a promising and technically feasible strategy for lithium recovery from
475 SLR.

476

477 **Notes**

478 The authors declare no competing financial interests.

479

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