

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

*Original*

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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  $\text{Li}^+$  and  
34 higher  $\text{Li}^+/\text{Na}^+$  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 ( $0.534 \text{ g/cm}^3$ )  
48 [3], high electrode potential ( $-3.05 \text{ V}$ ) [4], low equivalent weight ( $6.94 \text{ g/Faraday}$ ) [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  $\text{MnCO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaOH}$ , and  $\text{HCl}$  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  $\text{MnCO}_3$  and  $\text{Li}_2\text{CO}_3$  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  $\text{LiCl}$  were dissolved in ultrapure water at an Al/Li mole ratio  
147 of 1.3:1.  $\text{NaOH}$  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  $\text{Li}^+$  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 cm<sup>2</sup>. 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<sup>+</sup> 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<sup>+</sup> concentration in the solution at time  $t$ .

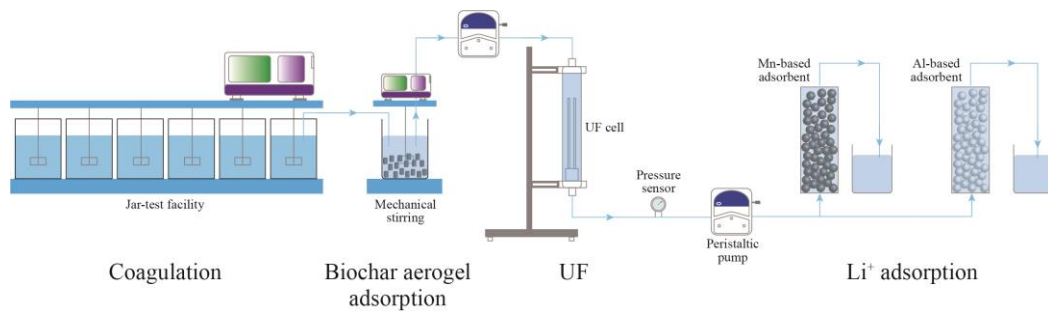
193 Adsorption selectivity of lithium with respect to other interfering metal ions was  
194 assessed by determining the partition coefficient ( $K_d$ ), the concentration factor (CF),  
195 and the separation factor ( $\alpha_{Me}^{Li}$ ), calculated with the following Eqs. (2-4):

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

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

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

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 N<sub>2</sub> 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, UV<sub>254</sub>, 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 UV<sub>254</sub> values drastically decreased from 760.5 mg/L to 204.3 mg/L, and from 0.023  
231 cm<sup>-1</sup> to 0.009 cm<sup>-1</sup>, respectively. When PACl content further increased to 2000 ppm,  
232 TOC and UV<sub>254</sub> values diminished only slightly to 194.8 mg/L and 0.007 cm<sup>-1</sup>.  
233 Therefore, the optimum PACl dosage was determined to be 1500 ppm. The addition of

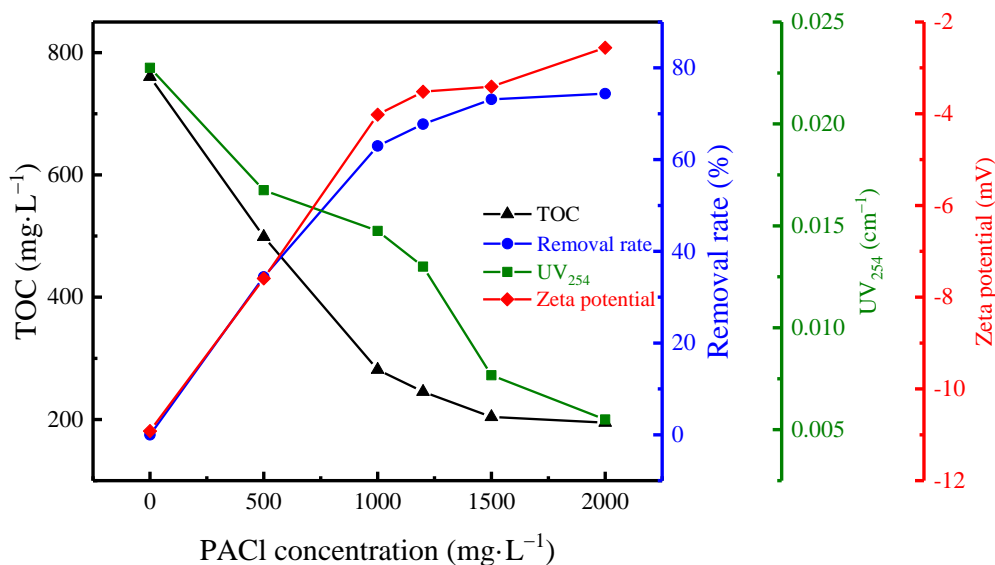
234 PACl decreased the absolute value of the zeta potential, which increased from  $-10.9$   
 235 mV (raw SLR) to  $-3.4$  mV (PACl content of 1500 ppm) at the unadjusted pH equal to .  
 236 A higher PACl concentration likely resulted in more hydroxide precipitation from the  
 237 suspension [40]. 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 <sub>254</sub> (cm <sup>-1</sup> ) | TDS (mg/L) | pH   |
|-----------|-----------|-----------|----------|-----------|-----------|------------|---------------------------------------|------------|------|
| Values    | 11,470    | 31,210    | 126.4    | 54.56     | 57.50     | 769        | 0.023                                 | 112,000    | 5.54 |

242



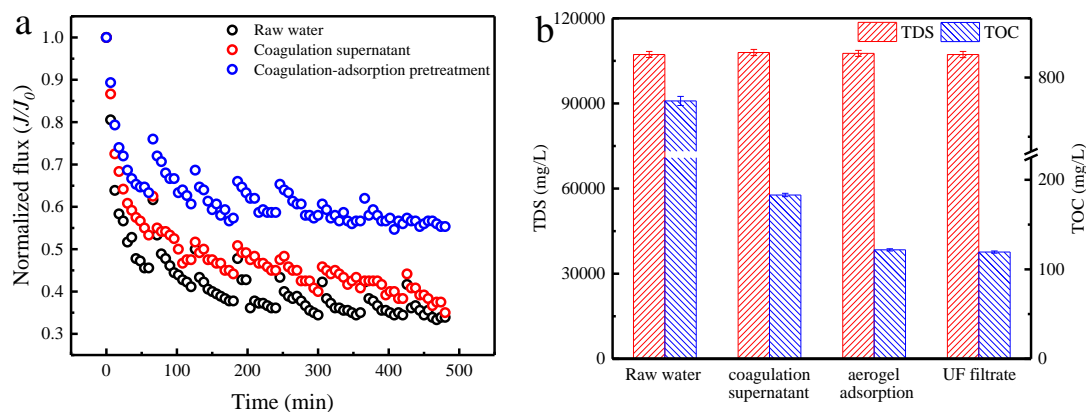
243

244 Fig. 2: Variation of TOC, UV<sub>254</sub>, 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.

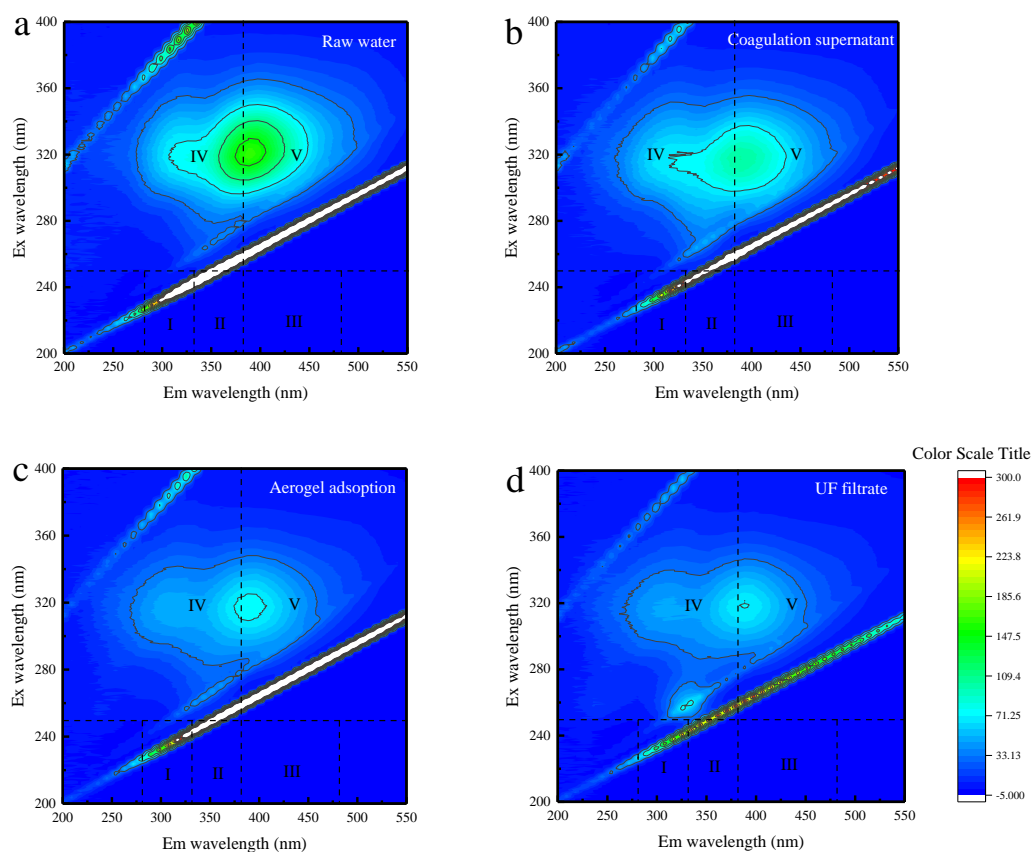


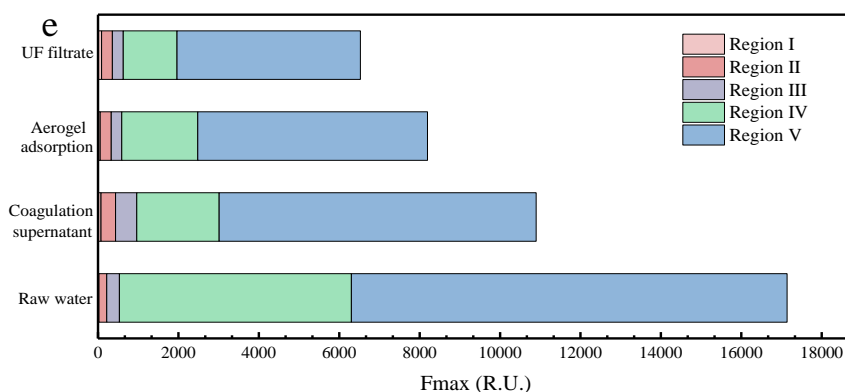
266 Fig. 3: (a) UF membrane performance for raw and pretreated raffinate of spent  
 267 lithium-ion battery, and (b) related TDS, TOC variations.

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.

294

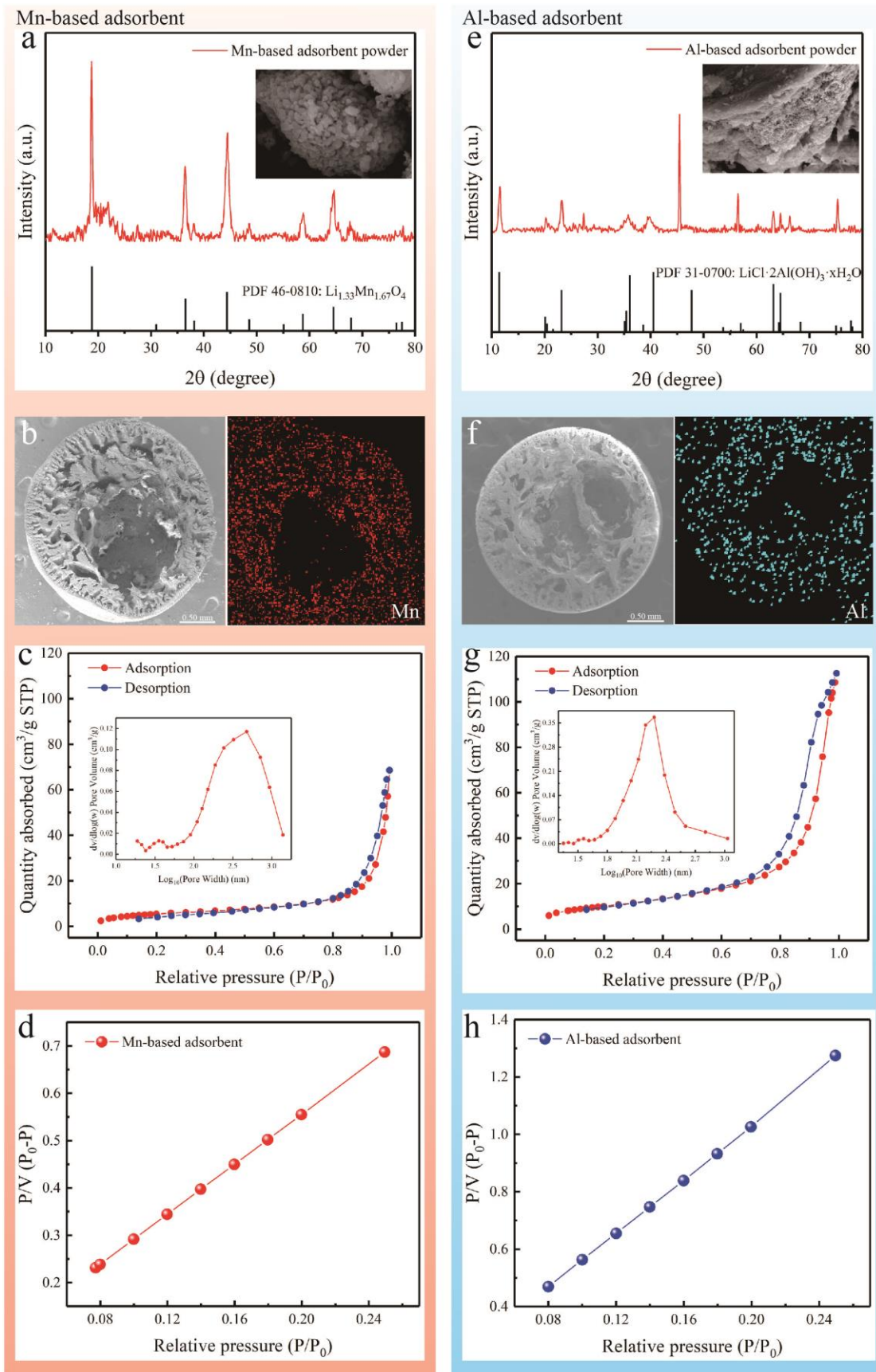
### 295 3.2.Characteristics of the Mn and Al-based adsorbents

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  $64.5^\circ$ . 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  $63.2^\circ$ . 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 N<sub>2</sub> was  
316 68.5 cm<sup>3</sup>/g and 112.6 cm<sup>3</sup>/g for the Mn and for the Al-based adsorbent, respectively.  
317 The larger N<sub>2</sub> 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 m<sup>2</sup>/g and a total volume of 0.106 cm<sup>3</sup>/g, while the corresponding values for the Al-  
327 based adsorbent were 36.6 m<sup>2</sup>/g and 0.174 cm<sup>3</sup>/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

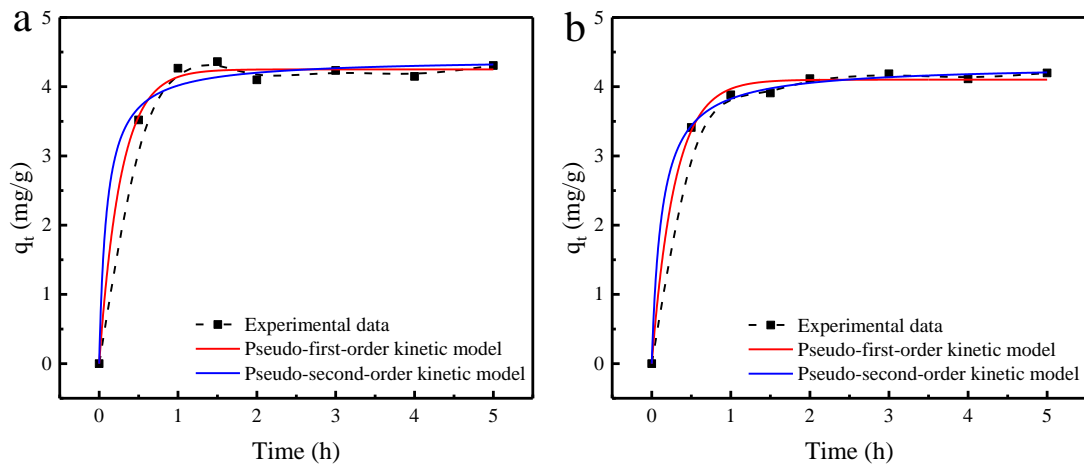
333 powders; (b, f) representative SEM micrographs and EDS mapping of the granules  
334 obtained by combining the adsorbent powders with PVC; (c, g) N<sub>2</sub> adsorption-  
335 desorption curves and resulting pore size distribution of the granules; (d, h) BET  
336 surface area plot.

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 R<sup>2</sup>  
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.

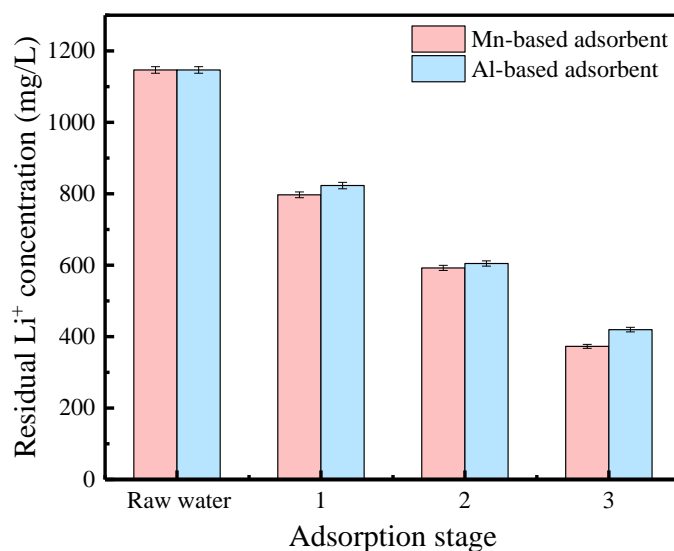
|          | Pseudo-first-model<br>$q_{e,cal}$ (mg/g) | $k_1$ ( $\text{min}^{-1}$ ) | $R^2$  | Pseudo-second-model<br>$q_{e,cal}$ (mg/g) | $K_2$ ( $\text{g}\cdot\text{min}^{-1}\text{h}^{-1}$ ) | $R^2$  |
|----------|--|-----------------------------|--------|---|---|--------|
| Mn-based | 4.25                                     | 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  $\text{Li}^+$  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  $\text{Li}^+$  ions by ion exchange of  $\text{Li}^+/\text{H}^+$ ,  
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.

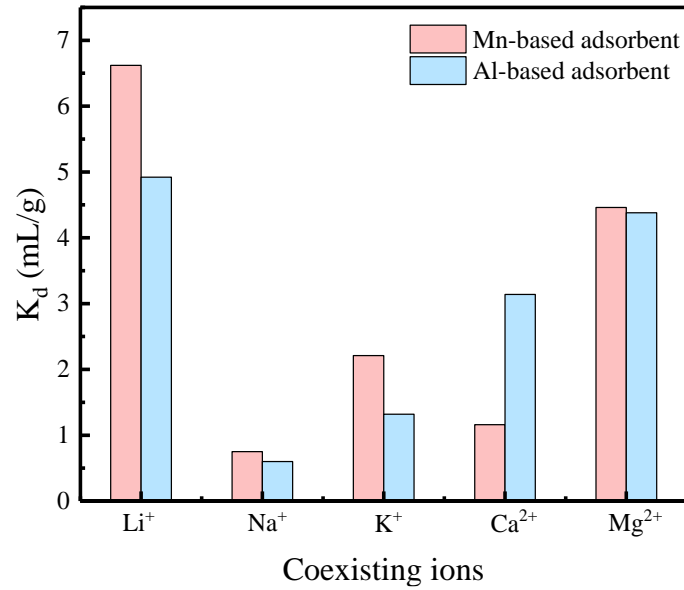
379

### 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 ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) in the SLR,  
383 especially the  $\text{Na}^+$  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  $\text{Na}^+$ .  
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  $\text{Na}^+$  was also large, which may be explained by the following reasons. On the one hand,  
395 the concentration of  $\text{Na}^+$  ion in SLR was 27.2 times higher than the  $\text{Li}^+$  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  $\text{Li}^+$  with respect to  $\text{Na}^+$  was high for  
400 both adsorbent materials, a proportion of adsorption sites were indeed consumed by  
401  $\text{Na}^+$ , 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

408

coexisting cations.

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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) | $\alpha_{Me}^{Li}$ |
|------------------|--------------|--------------|--------------|--------------|-----------|--------------------|
| Li <sup>+</sup>  | 1,147        | 750          | 4.96         | 6.62         | 4.33      | 1                  |
| Na <sup>+</sup>  | 31,200       | 29,400       | 22.2         | 0.75         | 0.71      | 8.79               |
| K <sup>+</sup>   | 126          | 107          | 0.24         | 2.21         | 1.88      | 3.00               |
| Ca <sup>2+</sup> | 54.6         | 49.9         | 0.06         | 1.16         | 1.06      | 4.09               |
| Mg <sup>2+</sup> | 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) | $\alpha_{Me}^{Li}$ |
|------------------|--------------|--------------|--------------|--------------|-----------|--------------------|
| Li <sup>+</sup>  | 1,147        | 823          | 4.05         | 4.92         | 3.53      | 1                  |
| Na <sup>+</sup>  | 31,200       | 29,800       | 17.9         | 0.60         | 0.57      | 8.17               |
| K <sup>+</sup>   | 126          | 114          | 0.15         | 1.32         | 1.20      | 3.71               |
| Ca <sup>2+</sup> | 54.6         | 43.6         | 0.14         | 3.14         | 2.51      | 1.41               |
| Mg <sup>2+</sup> | 57.5         | 42.6         | 0.18         | 4.38         | 3.24      | 1.12               |

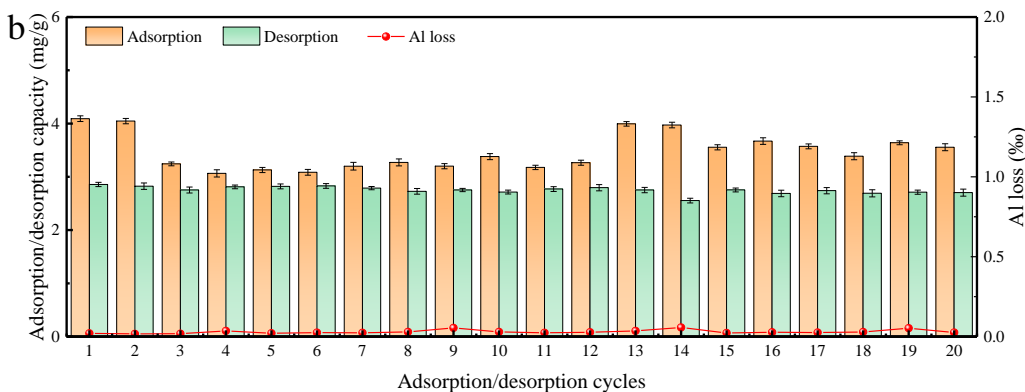
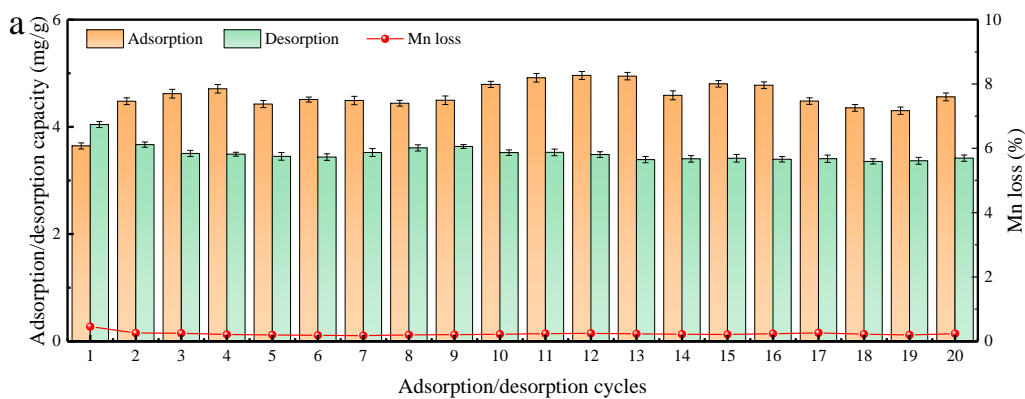
417

## 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<sup>+</sup> 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.



447 Fig. 9: Adsorption-desorption capacity of  $\text{Li}^+$  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  $\text{Li}^+$  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  $\text{Na}^+$  (0.75 mL/g for Mn-based  
463 adsorbent and 0.60 mL/g for Al-based adsorbent), suggesting effective separation of  
464  $\text{Li}^+$  and  $\text{Na}^+$ . 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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492

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