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Biochar-supported materials for lithium recovery: Comparison of ion-imprinted polymers, lithium ion sieves, and MnO_x composites

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Introduction

Biochar, a porous, carbonaceous material that is produced by pyrolysis of biomass (EBC, 2025), is increasingly studied as a low-cost, sustainable support material for engineered adsorbents

for targeted metal removal or recovery applications (Ahuja *et al.*, 2022). Its developed porous carbon structure and surface chemistry enable modifications for specific applications, including lithium recovery (Kamran and Park, 2022). Different materials have been developed and investigated for Li^+ recovery. Among selective materials, ion-imprinted polymers (IIP) and lithium ion sieves (LIS) have attracted considerable attention due to their high affinity and selectivity toward Li^+ .

To overcome limitations of IIP, such as low lithium binding kinetics due to deeply embedded sites, low site accessibility, and poor performance in real-world samples, several carbon-based supports have been investigated, including magnetic carbon nanotubes (Liang *et al.*, 2020), multi-wall carbon nanotubes (Huang and Wang, 2018), and biochar (Urbanová *et al.*, 2025). LIS materials are primarily challenged by poor chemical stability and regeneration issues. These factors motivate the development of environmentally friendly and economically favourable solutions. For example, Kamran and Park (2022) utilized the economic advantages of biochar and introduced Ni-doped MnO_2 nanorods onto biochar surfaces to prepare hybrid composites with high Li^+ removal efficiency.

Despite growing interest, the role of biochar as a support for such selective systems remains insufficiently understood, especially in terms of active phase stability and accessibility. The aim of this study was therefore to evaluate the potential of biochar from waste biomass as a porous support for both templated (IIP, LIS) and non-templated (MnO_x) materials for Li^+ recovery from aqueous solutions.

Materials and methods

Biochar preparation

Walnut shells (WS) and wood chips (WC) were utilized as feedstock materials for biochar production. WS was pyrolyzed using a continuous pyrolysis reactor Pyreka 2.1 (Pyreg, Germany) at 500 °C with a residence time of 20 min. Wood chips were processed in a continuous pyrolysis unit CTS20 (Carbon Technik Schuster GmbH, Germany) at 680 °C for 20 min. The resulting biochars were mechanically crushed and sieved to achieve a uniform particle size fraction of 500–1000 μm . This standardized material was subsequently used as a solid support for the synthesis of ion-imprinted polymers (IIP) and lithium-ion sieves (LIS).

Hybrid material preparation

Preparation of LIS material. Biochar derived from wood chips (WCB) with a particle size of 0.5–1.0 mm was used as a support for lithium ion sieve (LIS) synthesis. Prior to synthesis, biochar was demineralized and mildly oxidized by treatment in 1 M HNO_3 under ultrasonic conditions (120 min, 25 °C), followed by drying at 60 °C to introduce oxygen-containing functional groups ($-\text{COOH}$, $-\text{OH}$). The sample was subsequently neutralized using 1% NaHCO_3 and

thoroughly washed with deionized water to neutral pH. Hydrothermal synthesis was carried out by dissolving 1.66 g KMnO_4 and 1.4 g $\text{LiCl}\cdot\text{H}_2\text{O}$ in 50 mL of deionized water, followed by the addition of 5.0 g of pretreated biochar. The suspension was ultrasonicated for 15 min and then transferred into a Teflon-lined autoclave and heated at 160 °C for 12 h. After cooling to room temperature, the obtained composite was filtered and washed. To obtain the active ion sieve, the material was treated in 0.5 M HCl (24 h) to remove Li^+ ions from the MnO_x structure and generate selective adsorption sites. The final material (WCB-LIS) was washed with deionized water to neutral pH, dried at 55 °C for 48 h, and used in sorption experiments.

Preparation of IIP material. Ion-imprinted polymers (IIP) supported on biochar derived from walnut shells (WSB) were prepared using a bulk polymerization approach. Dibenzo-14-crown-4 (DB14C4), used as a selective ligand for Li^+ complexation, was synthesized according to a previously reported procedure (Urbanová *et al.*, 2025). For the preparation of IIP, 0.1 g of DB14C4 and 0.0689 g of LiNO_3 were dissolved in a mixture of methanol (20 mL) and dimethylformamide (DMF, 40 mL), followed by the addition of 0.17 mL α -methacrylic acid (α -MAA). The solution was stirred for 30 min to allow complex formation between Li^+ and the ligand. Subsequently, 0.4 g of WSB was added, and the suspension was ultrasonicated for 15 min to promote dispersion and infiltration into the porous structure. Then, 0.125 g of 2,2'-azobis(isobutyronitrile) (AIBN) and 3.96 g of ethylene glycol dimethacrylate (EGDMA) were added, and the mixture was purged with nitrogen for 15 min to remove dissolved oxygen. Polymerization was carried out at 70 °C for 12 h under continuous stirring. The obtained composite was washed sequentially with methanol, 1 M HNO_3 , and deionized water until neutral pH was reached, in order to remove template ions and unreacted species. After drying under vacuum for 12 h, the material (WSB-KL) was used in sorption experiments.

Preparation of MnO_x modified biochar. MnO_x -modified biochar was prepared via chemical impregnation followed by thermal treatment, as described by Akgül *et al.* (2019). Briefly, 3 g of WSB (particle size 0.5–1.0 mm) was mixed with 100 mL of 6 wt% KMnO_4 solution and agitated at 150 rpm for 4 h. The impregnated material was then filtered and dried at 100 °C. Subsequently, the dried sample was thermally treated in a muffle furnace at 300 °C to promote the formation of MnO_x phases on the WSB surface. The resulting material (WSB-IM) was used in sorption experiments.

Characterization of prepared materials

The prepared materials were characterized using ATR-FTIR spectroscopy (Cary 630, Agilent) equipped with a germanium crystal. The morphology and surface structure, together with elemental composition, were analyzed by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) using a JEOL JSM 7600F microscope (Japan). The measurements were performed at an accelerating voltage of 20 kV, a chamber pressure of 9.0×10^{-4} Pa, and magnifications ranging from 250× to 1500×.

Sorption experiments

Li^+ stock solution (1000 mg/l) was prepared by dissolving $\text{LiCl}\cdot\text{H}_2\text{O}$ in deionized water and diluted to obtain the desired concentrations ($\text{pH} \approx 6.4$). Initial screening experiments were performed by mixing 50 mg of sorbent with 10 mL of Li^+ solution (~ 2 and 20 mg/l) and agitating at 40 rpm for 24 h at room temperature (23 °C). Samples were centrifuged (8000 rpm, 5 min) and filtered (0.45 μm). Li^+ concentration was determined by atomic absorption spectrometer (Agilent, USA). All experiments were performed in duplicate. The adsorption capacity (Q , mg/g) was calculated using eq 1:

$$Q = \frac{(c_0 - c_f) \cdot V}{m} \quad (1)$$

where c_0 and c_f are the initial and equilibrium Li^+ concentrations (mg/l), V is the solution volume (l), and m is the sorbent mass (g).

Based on the results, only the WSB-IM material exhibited measurable Li^+ uptake, and therefore, subsequent experiments were conducted exclusively with this sorbent. Kinetic experiments were performed at contact times of 1, 6, and 24 h. Equilibrium adsorption studies were carried out in the concentration range of 2–80 mg/l. To evaluate the effect of competing ions, additional experiments were conducted in the presence of Na^+ and Mg^{2+} (10 mg/l), and in natural mineral water (Sulinka).

Equilibrium Li^+ adsorption on the WSB-IM material was described using the Langmuir (eq 2) and the Freundlich (eq 3) isotherm models.

$$Q_{eq} = \frac{b Q_{\max} C_{eq}}{1 + b C_{eq}} \quad (2)$$

$$Q_{eq} = K C_{eq}^{(1/n)} \quad (3)$$

where Q_{eq} (mg/g) is the equilibrium adsorption capacity, C_{eq} (mg/l) is the equilibrium concentration of Li^+ , and K and n are the Freundlich constants related to adsorption capacity and intensity, respectively. In the Langmuir model, Q_{\max} (mg/g) represents the maximum adsorption capacity and b (l/mg) is the affinity constant.

Results and discussion

Recent advances in Li^+ separation have focused on highly selective materials such as ion-imprinted polymers (IIP) (Huang and Wang, 2018; Qi *et al.*, 2024) and lithium ion sieves (LIS) (Bao *et al.*, 2026). However, their practical deployment remains limited by poor recoverability from aqueous systems. To address this challenge, we investigate the use of biochar from wood chips (WCB) and walnut shells (WSB) as a low-cost, porous support for immobilization of these active phases. In addition, MnO_x -modified biochar prepared by chemical impregnation was included as a non-templated reference material for comparison.

These materials were selected due to their alkaline character (pH 7.4–8.5) and well-developed pore structures with specific surface areas of 10.4 m²/g (WSB) and 397 m²/g (WCB). The alkaline nature of biochar may contribute to the stability and interaction of immobilized active phases and the specific surface area and pore structure are expected to influence the dispersion of IIP and LIS and the accessibility of Li⁺ adsorption sites.

Hybrid material characterization

The prepared hybrid materials were characterized using ATR-FTIR spectroscopy and SEM-EDX analysis to evaluate changes in surface functional groups and elemental composition after modification.

Figure 1 shows a comparison of ATR-FTIR spectra of the original and modified biochars (LIS-modified WCB and chemically impregnated WSB with thermal treatment). Significant changes are observed after both hydrothermal synthesis and chemical impregnation, particularly in the regions at 1700–1500, 1200–1000, and below 700 cm⁻¹. Changes in the 1200–1000 cm⁻¹ region indicate modification of oxygen-containing functional groups on the biochar surface, which can be attributed to oxidation and interaction with Mn species. The change in intensity at 1576 cm⁻¹ (aromatic C=C stretching vibrations) suggests partial reorganization of the carbon structure following thermal treatment. In addition, the increased intensity of bands in the ~1000–1200 cm⁻¹ region indicates the formation of new oxygen-containing functional groups due to KMnO₄ oxidation. A pronounced absorption band in the region of 610–640 cm⁻¹, characteristic of metal–oxygen vibrations, confirms the presence of Mn–O bonds (Qian *et al.*, 2020), indicating the formation of MnO_x on the biochar surface in both modification approaches. Due to the lower spectral limit of ATR-FTIR (~600 cm⁻¹), the exact Mn oxide phase cannot be unambiguously identified.

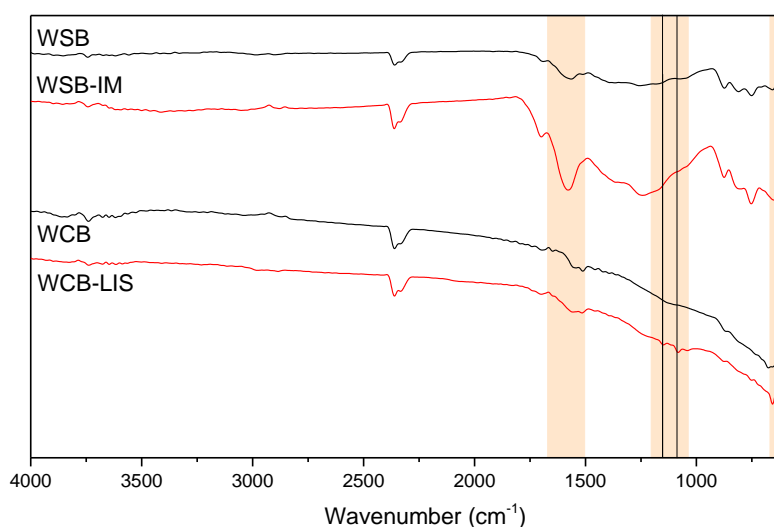


Fig. 1. ATR-FTIR spectra of original (WSB, WCB), LIS-modified (WCB-LIS), and chemically impregnated (WSB-IM) biochars.

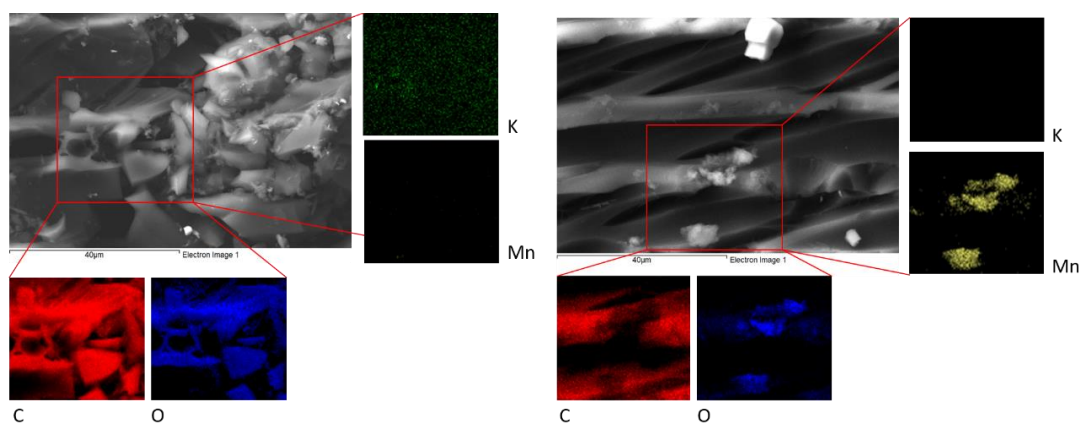


Fig. 2. EDX elemental mapping of WCB biochar before (left) and after (right) hydrothermal LIS synthesis.

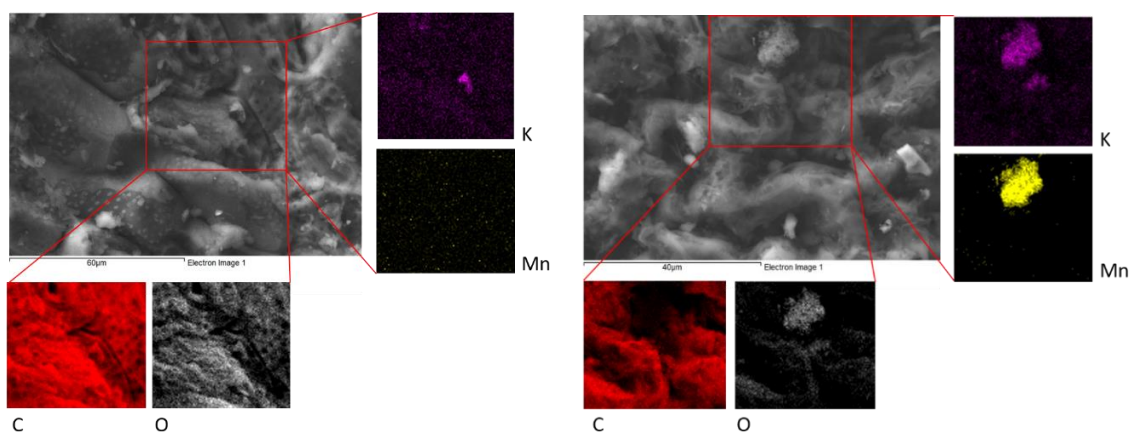


Fig. 3. EDX elemental mapping of WSB biochar before (left) and after (right) chemical impregnation with thermal treatment.

Figures 2 and 3 present SEM-EDX elemental mapping of WCB and WSB before and after hybrid material preparation (hydrothermal synthesis of LIS and chemical impregnation). In the original biochar, carbon and oxygen dominate and are uniformly distributed, while the manganese signal is negligible, confirming the absence of Mn in the original supports. After modifications, a clear change in elemental composition is observed. Mn appears as localized regions on the biochar surfaces, corresponding to the deposition of MnO_x phases, as indicated by its overlap with O signals (Fig. 2 and 3 left). At the same time, the distribution of C and O remains preserved, suggesting that the biochar retains its structural integrity and functions as a support. However, a non-uniform distribution of Mn is observed in both cases, indicating its deposition in the form of localized aggregates or crystallites rather than a continuous layer. This observation is consistent with ATR-FTIR analysis, where Mn–O vibrations were identified, confirming the formation of manganese oxide phases.

The ATR-FTIR spectra shown in Fig. 4 suggest the successful impregnation of biochar with the ion-imprinted polymer. Compared to the unmodified biochar (WSB), the modified material

(WSB-KL) exhibits several significant changes. A band observed at 1725 cm^{-1} corresponds to $\text{C}=\text{O}$ functional groups, indicating the presence of ester bonds from EGDMA and carboxyl groups from α -MAA. Changes around 1580 cm^{-1} (aromatic $\text{C}=\text{C}$ stretching vibrations) suggest interactions between the polymer phase and the carbon matrix. A pronounced increase in intensity at 1144 cm^{-1} ($\text{C}-\text{O}-\text{C}$ and $\text{C}-\text{O}$ vibrations) is characteristic of crown ether and ester structures within the polymer (Urbanová et al., 2025; Torrejos et al., 2015).

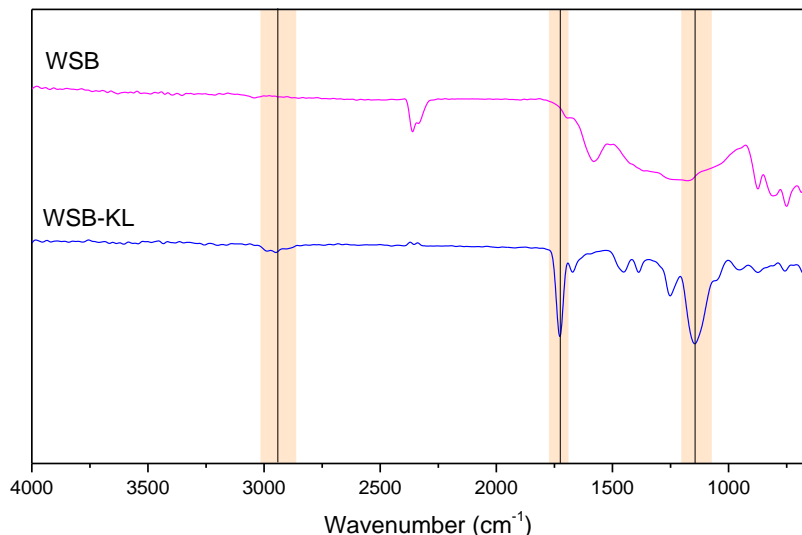


Fig. 4. ATR-FTIR spectra of WSB before and after IIP modification.

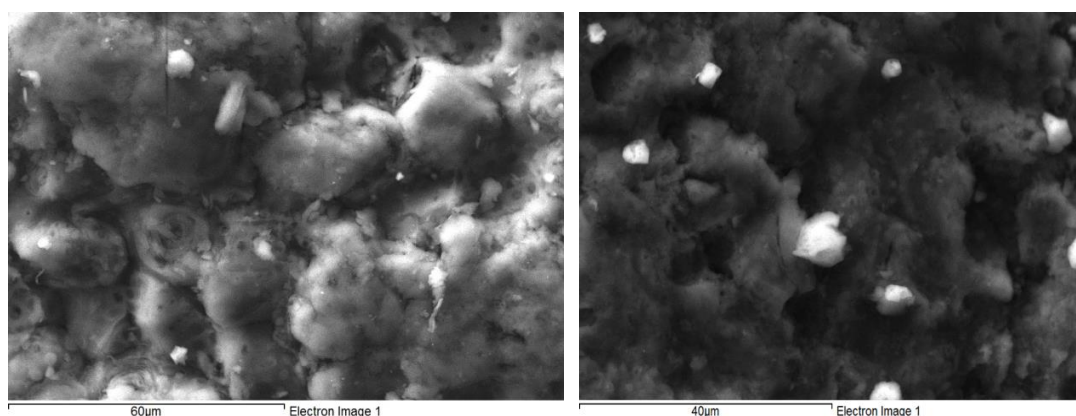


Fig. 5. SEM images of WSB before (left) and after (right) IIP modification.

SEM images (Fig. 5) reveal a significant change in surface morphology after IIP modification. The unmodified biochar exhibits a rough, porous surface, whereas the modified material shows a smoother, more compact structure, consistent with partial pore coverage by the polymer layer. In addition, the modified samples behaved as non-conductive during SEM analysis and required carbon coating, supporting the presence of an insulating polymer layer on the biochar surface.

Overall, analyses confirm the successful formation of hybrid materials with immobilized active phases. These structural and chemical modifications are expected to directly influence Li^+ uptake performance, as discussed in the following section.

Lithium adsorption experiments

The performance of the prepared materials toward Li^+ separation was evaluated using sorption experiments in model aqueous solutions (Table 1). As expected, both unmodified biochars (WCB, WSB) exhibited negligible Li^+ uptake, confirming the intrinsically low affinity of Li^+ ions toward carbon-based materials (Obar et al., 2024). However, unexpectedly limited adsorption was also observed for biochar-supported LIS and IIP systems. Despite ATR-FTIR and SEM-EDX analyses confirming the incorporation of MnO_x phases and ion-imprinted polymers, these materials did not exhibit the expected Li^+ uptake. For LIS-based materials, this behavior is likely related to the acid activation step (0.5 M HCl), which is required to exchange Li^+ ions in the crystal lattice with H^+ . Such treatment has been reported to induce partial structural degradation and Mn dissolution in lithium ion sieves (Qian *et al.*, 2020; Chen *et al.*, 2025), which may lead to loss of active sites.

In this case, the activation may have caused partial destabilization or leaching of the MnO_x phase from the WCB surface, as supported by its non-uniform distribution observed in WCB-LIS (Fig. 2). As a result, although the MnO_x phase was present, its accessibility and structural integrity were likely insufficient to enable effective Li^+ uptake.

Table 1. Li^+ adsorption by unmodified biochar and prepared hybrid materials from aqueous solutions ($C_0 = 2$ and 20 mg/l Li^+).

Sorbent	$Q_2 \text{ (mg/g)}$	$Q_{20} \text{ (mg/g)}$
WCB	0	0
WCB - LIS	0	0.011
WSB	0	0
WSB - IM	0.158	0.461
WSB – IIP	–*	0.012

* - negative sorption values were observed

No Li^+ sorption was observed for the WSB-IIP material, although both ATR-FTIR and SEM analyses confirmed the successful deposition of the Li-imprinted polymer onto the biochar support. A higher Li concentration was detected in the solution after sorption than before, indicating insufficient removal of template ions during synthesis and subsequent release of residual Li from the polymer matrix. This suggests that the imprinting process did not result in accessible or functional binding sites for Li^+ , but rather led to retention of Li^+ within the polymer structure. However, in our previous work (Urbanová et al., 2025) we reported effective Li^+ adsorption (0.57

mg/g) for Li-imprinted polymers prepared on K_2CO_3 activated WCB. This discrepancy may be attributed to differences in biochar activation and surface chemistry, which likely influence polymer anchoring, template removal efficiency, and accessibility of imprinted sites.

Among the prepared hybrid materials, only the sample obtained by chemical impregnation followed by thermal treatment (WSB-IM), without Li doping, exhibited measurable Li^+ uptake. The adsorption capacity reached 0.158 and 0.461 mg Li^+ /g depending on the initial Li^+ concentration (Table 1), indicating that the formed MnO_x phase provides active sites for Li^+ binding. In preliminary experiments, sorption kinetics were assessed at three time intervals (1, 6, and 24 h) without applying kinetic models. The results (Table 2) suggest a multi-stage adsorption process, characterized by rapid initial uptake within the first hour, followed by a slower phase approaching equilibrium. This behavior suggests that Li^+ adsorption is initially controlled by surface interactions, while subsequent uptake may be limited by diffusion into the porous structure or accessibility of active MnO_x sites.

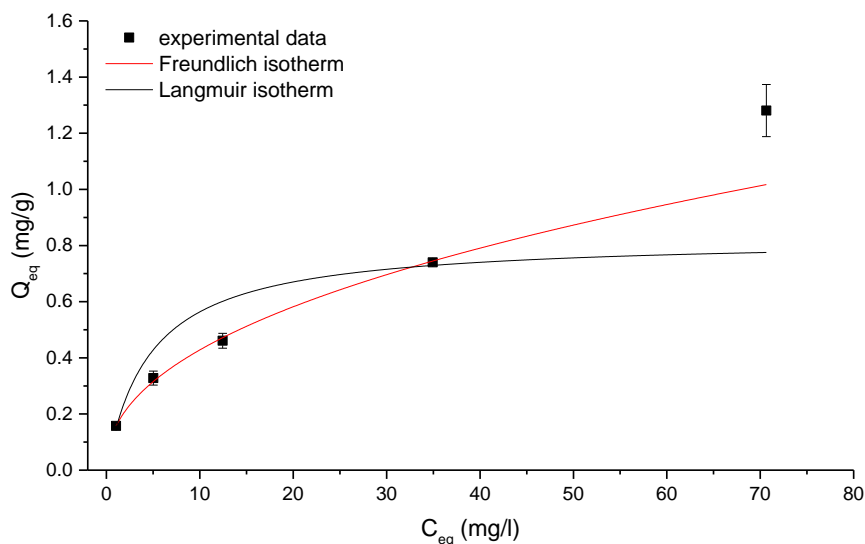


Fig. 6. Langmuir and Freundlich adsorption isotherms for Li removal calculated using non-linear regression analysis.

Table 2. Li^+ adsorption by WSB-IM in different time intervals ($C_0 = 2$ mg/l Li^+).

Sorbent	Q (mg/g)		
	1h	6 h	24 h
WSB - IM	0.113	0.142	0.158

The comparison of determination coefficients (R^2) indicates that Li^+ adsorption on WSB-IM is better described by the Freundlich isotherm. $1/n < 1$ further indicates favorable adsorption on a heterogeneous surface. The maximum sorption capacity (Q_{max}) calculated from the Langmuir model was 0.83 ± 0.07 mg/g (Table 3), whereas the experimentally determined value reached 1.28 mg/g.

Table 3. Parameters of Langmuir and Freundlich adsorption isotherms for Li^+ by WSB-IM ($T = 24\text{h}$, $\text{pH} = 6.4$).

Isotherm	Q_{\max} (mg/g)	b (l/mg)	K (l/g)	$1/n$	R^2
Langmuir	0.83 ± 0.07	0.21 ± 0.05	-	-	0.975
Freundlich	-	-	0.16 ± 0.01	0.44 ± 0.01	0.997

Table 4 demonstrates a significant competitive effect of Na^+ and Mg^{2+} ions on Li^+ sorption by the WSB-IM material. A stronger competition was observed in the presence of Mg^{2+} ions, which is consistent with the well-known diagonal relationship between Li and Mg (Dai *et al.*, 2025). As a result, both elements exhibit comparable chemical properties and ionic radii, making their selective separation more challenging.

A substantial reduction in Li^+ adsorption was further observed in mineral water (Sulinka), where the adsorption capacity decreased from 0.158 to 0.02 mg/g. This effect can be attributed to the high ionic strength and the presence of multiple competing ions (Na^+ , Mg^{2+} , Ca^{2+} , HCO_3^-), which significantly limit the accessibility of active adsorption sites. These results indicate that, although MnO_x modified biochar exhibits measurable Li^+ uptake, its non-templated nature results in limited selectivity compared to IIP and LIS systems, making it more susceptible to competitive ion interference.

Table 4. Li^+ adsorption by WSB-IM from model solution and mineral water (Sulinka) in the presence of competing ions Na^+ ($C_0 \text{ Li} = 1.75 \text{ mg/l}$), Mg^{2+} ($C_0 \text{ Li} = 1.56 \text{ mg/l}$) and in mineral water Sulinka ($C_0 \text{ Li} = 2.28 \text{ mg/l}$).

Sorbent	Q (mg/g)			
	Without competition	Na^+ (10 mg/l)	Mg^{2+} (10 mg/l)	Sulinka*
WSB – IM	0.158	0.083	0.068	0.02

* Na^+ ($c = 760 \text{ mg/l}$), Mg^{2+} ($c = 254 \text{ mg/l}$), Ca^{2+} (221 mg/l), NO_3^- ($c = <1,0 \text{ mg/l}$), Cl^- ($c = 25,9 \text{ mg/l}$), HCO_3^- ($c = 3831 \text{ mg/l}$)

Conclusions

Our results show that although advanced Li^+ selective materials such as IIP and LIS can be immobilized on biochar supports, their practical performance is strongly limited by structural instability and insufficient accessibility of active sites. On the contrary, non-templated MnO_x -modified WSB exhibited measurable Li^+ uptake with experimental Q_{\max} of 1.28 mg/g, indicating the importance of phase stability over intrinsic selectivity. The pronounced effect of competing ions and complex matrices confirms that real-water conditions remain the main challenge for effective Li^+ recovery.

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