

Circular Upcycling of Waste Paper into a Cellulose– $\text{H}_4\text{Mn}_5\text{O}_{12}$ Ion-Sieve Biocomposite for Selective Lithium Recovery

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Article

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Posted Date: August 7th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10418713/v1>

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Additional Declarations: No competing interests reported.

Circular Upcycling of Waste Paper into a Cellulose–H₄Mn₅O₁₂ Ion-Sieve Biocomposite for Selective Lithium Recovery

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Abstract

The increasing demand for lithium has intensified interest in efficient and sustainable recovery technologies from aqueous resources. In this study, a cellulose-based composite adsorbent (Cell-HMO) was fabricated by incorporating protonated lithium manganese oxide (H₄Mn₅O₁₂) into a regenerated cellulose matrix derived from waste paper. Structural characterization using XRD, FTIR, FESEM, and EDS confirmed the successful incorporation and homogeneous distribution of HMO particles within the cellulose framework. The adsorption process was optimized using the Taguchi experimental design, which identified solution pH and adsorbent dosage as the most influential factors affecting lithium recovery. Under the optimized conditions, the Cell-HMO composite exhibited a maximum adsorption capacity of 4.842 mg g⁻¹ and a lithium recovery efficiency of 96.2%. Selectivity experiments demonstrated preferential adsorption of Li⁺ over competing K⁺ and Mg²⁺ ions, supporting the ion-sieving behavior of the composite. These findings indicate that waste-paper-derived Cell-HMO is a promising sustainable adsorbent for selective lithium recovery from aqueous solutions.

Keywords: Lithium recovery; waste paper; cellulose-based adsorbents; Hydrogen manganese oxide (HMO); Ion-sieve selectivity; Taguchi optimization

1. Introduction

The global demand for sustainable energy storage has intensified due to the depletion of fossil fuels and increasing environmental concerns [1-4]. Among electrochemical technologies, lithium-ion batteries (LIBs) are widely recognized for their high efficiency, stability, and reliability, driving a rapid increase in lithium demand [3, 5-7]. Lithium and its compounds are not only essential in batteries but also find applications in glass, ceramics, catalysis, pharmaceuticals, and the nuclear industry. However, the quality and availability of natural lithium ores have declined due to overexploitation, making alternative sources such as seawater and salt lake brines increasingly important. Recovering lithium from these aqueous resources represents a strategic and sustainable approach to ensure a long-term supply for industrial applications [8-11].

Lithium-ion sieves (LIS) are specialized adsorbents with high selectivity for lithium ions (Li^+), offering a promising solution for lithium recovery from aqueous media. Spinel-type manganese oxides (MnO_2) have emerged as efficient LIS materials due to their favorable structural and chemical properties. Acid-leached manganese spinel oxides derived from precursors such as LiMn_2O_4 , $\text{Li}_4\text{Mn}_5\text{O}_{12}$, and $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ exhibit high chemical stability, low toxicity, and strong selectivity at relatively low cost [12]. Various forms, including hydrated MnO_2 ($\text{MnO}_2 \cdot 0.5\text{H}_2\text{O}$), have been synthesized for Li^+ extraction from brine and seawater, and their ion-exchange properties can be tailored through structural and compositional modifications [12, 13]. Despite their excellent adsorption performance, most LIS materials are in fine powder form, which limits practical handling and industrial application. Strategies such as granulation, membrane fabrication, and incorporation into composite matrices have been explored to overcome these challenges, improving mechanical stability, processability, and reducing material loss during aqueous operations [12]. Synthesis routes for LIS, including solid-state reaction, hydrothermal processing, and sol-gel methods, have been optimized to produce $\text{Li}_4\text{Mn}_5\text{O}_{12}$ -based materials with desirable structural and adsorption properties [14, 15].

Polymer composites are widely used as structural materials due to their high mechanical strength, low density, and versatility. Recent emphasis on sustainability has increased interest in bio-based composites derived from renewable resources [16-18]. Natural fibers, including cellulose, starch, alginic acid, chitosan, and cyclodextrins, offer biodegradable and environmentally compatible

alternatives to synthetic reinforcements. Among these, cellulose, the most abundant natural polymer on Earth, is particularly attractive for industrial applications due to its non-toxicity, biodegradability, biocompatibility, low cost, and versatility. However, its complex structure, consisting of crystalline and amorphous regions stabilized by strong intra- and intermolecular hydrogen bonds, presents challenges for dissolution and uniform chemical modification [19, 20]. The dissolution of cellulose is critical for producing derivatives and composites with consistent properties. This process involves solvent penetration into fibers and separation of polymer chains, which depends on the type of cellulose and solvent system [21-25]. Derivatizing solvents disrupt hydrogen-bond networks by reacting with hydroxyl groups, facilitating dissolution, though some solvents, such as ionic liquids, have limitations due to water sensitivity and difficult purification [25-28]. Water-based solvents, including NaOH or NaOH-urea systems, are inexpensive and environmentally friendly but primarily dissolve low-molecular-weight cellulose, often forming granules from native fibers [25, 29-31]. Pretreatment, typically via acid hydrolysis, is therefore required to reduce polymer chain length and enhance accessibility [25, 32, 33]. Hydrolysis in alcoholic media can accelerate cellulose degradation due to higher hydrogen ion activity compared with aqueous systems, though the effect on solubility and dissolution mechanisms remains underexplored [25, 34-36].

Chemical crosslinking further enhances the structural integrity and functionality of cellulose-based materials. Hydroxyl and carboxyl groups on cellulose chains react with crosslinkers via mechanisms such as ether formation, esterification, Michael addition, or free-radical polymerization. Epichlorohydrin (ECH) is a widely used covalent crosslinker under alkaline conditions, forming intermolecular networks by reacting with hydroxyl groups [19, 37]. Pre-crosslinking prevents molecular aggregation during phase separation and allows the formation of hierarchical architectures with unique microstructures [38]. Crosslinking improves thermal stability, surface area, swelling capacity, and mechanical strength, which are critical for applications in hydrogels, pollutant adsorption, and controlled release systems. While other crosslinkers such as glutaraldehyde and citric acid are also used, ECH has gained attention due to its efficiency in producing stable three-dimensional cellulose networks [19]. Lignocellulosic biomass derived from wood, bamboo, grasses, and sugarcane bagasse represents a sustainable source of organic carbon and energy [39]. Concurrently, municipal solid waste, particularly waste

paper constituting 25–40% of global waste, poses significant environmental challenges. Recycling and valorizing waste paper into high-value biomaterials not only reduces environmental burden but also provides sustainable feedstocks for functional composites. Utilizing cellulose from waste paper for composite adsorbents aligns with circular economy principles, enhancing both environmental and economic benefits [18, 19, 40].

Despite the considerable progress in lithium ion-sieve materials, their practical application remains limited by poor mechanical stability, difficult solid-liquid separation, and the loss of fine particles during repeated adsorption processes. Although several polymer-supported lithium ion sieves have been reported, most studies have relied on commercial cellulose, chitosan, or synthetic polymer matrices. The development of lithium ion-sieve composites using waste-paper-derived cellulose remains scarcely explored, particularly in combination with statistical process optimization. Therefore, converting waste paper into a regenerated cellulose matrix for immobilizing HMO particles provides a sustainable strategy to improve adsorbent handling while promoting circular utilization of waste biomass.

In this study, a sustainable cellulose-based composite adsorbent was developed using waste paper as a renewable cellulose source and protonated lithium manganese oxide (HMO) as the active ion-sieving phase for selective lithium recovery. The composite was fabricated by incorporating HMO into a regenerated cellulose matrix, while epichlorohydrin was employed to improve structural stability through chemical crosslinking. The structural, morphological, and adsorption properties of the prepared composites were systematically characterized using XRD, FTIR, FESEM, and EDS analyses. Process parameters influencing lithium adsorption were optimized using the Taguchi experimental design. Compared with conventional powder-type lithium ion sieves, the developed composite offers improved handling and mechanical integrity while maintaining high lithium selectivity. In addition, this study demonstrates the feasibility of converting waste paper into a value-added adsorbent for sustainable lithium recovery, thereby contributing to both circular resource utilization and environmentally friendly adsorption technologies.

2. Materials and Methods

All chemicals used, including lithium carbonate, manganese carbonate, sodium hydroxide, hydrochloric acid, boric acid, ethanol, triethanolamine, urea, epichlorohydrin, lithium chloride, magnesium chloride, and potassium chloride, were of analytical grade and procured from Merck (Germany). Waste paper was collected from local municipal waste streams, cleaned thoroughly before use, and utilized as the cellulose source without further chemical modification prior to pretreatment.

2.1. Synthesis of LMO and HMO Ion-Sieve Materials

Lithium manganese oxide precursor and its protonated ion-sieve form were synthesized via a solid-state combustion method [12]. Lithium carbonate (Li_2CO_3) and manganese carbonate (MnCO_3) were mixed at a molar ratio of $\text{Li/Mn} = 0.8$ and ground for 15 min in a Herzog attrition mill using triethanolamine as a dispersing agent to ensure homogeneous mixing. The resulting mixture was further homogenized and calcined in a muffle furnace at 270 °C for 2 h, followed by 400 °C for 6 h, to obtain a crystalline spinel-type lithium manganese oxide precursor (LMO). To prepare the protonated spinel lithium manganese oxide ($\text{H}_4\text{Mn}_5\text{O}_{12}$, denoted as HMO), 8 g of the as-synthesized lithium manganese oxide precursor was dispersed in 500 mL of 1.5 mol L^{-1} hydrochloric acid solution and stirred at 50 °C for 24 h [15]. During acid treatment, lithium ions were extracted from the spinel lattice and replaced by protons through a Li^+/H^+ ion-exchange process, yielding the protonated spinel phase ($\text{H}_4\text{Mn}_5\text{O}_{12}$). The resulting gray HMO powder was thoroughly washed with deionized water until neutral pH was achieved, followed by filtration and drying at room temperature.

2.2. Preparation of Cellulose-Based Composite Adsorbents

2.2.1. Preparation of Waste Paper Pulp

Waste paper was collected from environmental sources and thoroughly cleaned to remove surface impurities and contaminants. The waste paper was cut into small pieces and soaked in hot water for 24 h with periodic replacement of the soaking water to facilitate fiber disintegration and pulp formation. The resulting pulp was washed, oven-dried at 100 °C, and subsequently milled to obtain a fine cotton-like texture.

2.2.2. Acid Hydrolysis of Waste Paper

To prepare hydrolyzed cellulose, 100 mL of ethanol (92.5 wt%) was preheated to 75 °C in a water bath, followed by the addition of 4 mL of hydrochloric acid (37 wt%). Once the temperature was stabilized, 4 g (dry weight) of the prepared waste paper pulp was added, and the mixture was stirred to ensure uniform dispersion. The hydrolysis reaction proceeded for 3 h at 75 °C. The reaction was quenched by adding 900 mL of cold distilled water, and the resulting ethanol–acid–water mixture was immediately filtered. The hydrolyzed cellulose was thoroughly washed with distilled water, neutralized to $\text{pH} \approx 7$, and immersed in 1 L of distilled water overnight to ensure complete solvent exchange. Finally, the pulp was filtered and oven-dried at 60 °C overnight to obtain dry, crystalline cellulose fibers [25].

2.2.3. Preparation of Cellulose Solution

A NaOH/urea/water solution (7:12:81 wt%) was prepared by dissolving sodium hydroxide and urea in distilled water in a 250 mL beaker, followed by storage in a refrigerator until the temperature reached -13 °C. Subsequently, 3 g of pre-hydrolyzed waste-paper cellulose was gradually added to the precooled solvent under vigorous stirring for 5 min at 25 °C to form a transparent cellulose dope solution. The resulting solution was centrifuged at 4000 rpm for 10 min at 10 °C to remove undissolved residues and trapped air bubbles [41].

2.2.4. Preparation of CELL–HMO Adsorbent

For the preparation of the cellulose–hydrogen manganese oxide (CELL–HMO) composite, 10 mL of the prepared cellulose solution was placed in a 100 mL beaker and gently mixed with 1 g of HMO powder. The resulting homogeneous mixture was transferred into a large syringe and dropwise introduced into 500 mL of 2 M hydrochloric acid solution to induce coagulation and granulation. The obtained granules were aged in the acidic medium for 24 h, then filtered, thoroughly washed with distilled water until neutral pH, and dried at room temperature [42, 43].

2.2.5. Preparation of CELL–ECH–HMO Adsorbent

The crosslinked cellulose–HMO composite (CELL–ECH–HMO) was synthesized following the same procedure as above, with the addition of epichlorohydrin (ECH) as a crosslinking agent. Briefly, 1 mL of ECH was added to 10 mL of centrifuged cellulose solution under continuous stirring in an ice-water bath (0 °C) for 1 h to ensure homogeneous crosslinking. Subsequently, 1 g of HMO powder was gradually introduced into the solution with gentle stirring. The resulting viscous mixture was transferred into a syringe and dropped into 500 mL of 2 M HCl solution to induce coagulation and form spherical granules. The beads were aged for 24 h, filtered, washed with distilled water until neutral, and dried at room temperature [38, 42, 44].

2.3 Characterization

The crystalline structures of LMO, HMO, Cell–HMO, and Cell–ECH–HMO were characterized using X-ray diffraction (XRD, PHILIPS PW1730, Netherlands) with Cu K α radiation ($\lambda = 1.54056$ Å). Surface morphology was examined by field-emission scanning electron microscopy (FESEM, VEGA3 TESCAN, Czech Republic), while elemental composition was analyzed using energy-dispersive X-ray spectroscopy (EDS). Functional groups were identified by Fourier transform infrared spectroscopy (FTIR, Thermo AVATAR, USA).

2.4. Experimental Design and Optimization

To optimize the adsorption performance of the CELL–ECH–HMO composite adsorbent and to evaluate the relative influence of key process parameters, the Taguchi experimental design method was employed. This statistical approach enables the systematic assessment of multiple variables with a minimal number of experimental trials, providing reliable and reproducible optimization while reducing cost and time [45, 46]. The objective of the experimental design was to identify the operating conditions that maximize lithium adsorption capacity and recovery efficiency. Using Qualitek-4 software, the selected operational parameters, such as solution pH, adsorbent dosage, initial ion concentration, and contact time, were entered into the program. Based on the orthogonal array methodology, the software recommended an L9 (3³) design matrix, allowing the evaluation of individual and interactive effects of the factors on adsorption performance. The detailed experimental layout and factor-level combinations are summarized in Table 1a. The experimental

results were statistically evaluated using analysis of variance (ANOVA) to determine the significance and relative contribution of each parameter to adsorption performance as shown in Table 2. ANOVA was performed to evaluate the statistical significance and relative contribution of each experimental factor to lithium adsorption capacity and recovery efficiency. The optimal conditions obtained from the Taguchi design were subsequently verified through confirmation experiments, ensuring the accuracy and reproducibility of the optimized parameters.

Table 1. a) Factors and their level conducted in the experiment, b) Experimental design matrix and expected response

a)					
Independent variables	Code	Level 1	Level 2	level 3	
pH	A	9	11	13	
Adsorbent dosage (g)	B	0.5	1.25	2	
Li ⁺ initial concentration (mg L ⁻¹)	C	10	30	50	
b)					
Run No.	Adsorption process variables			Adsorption Efficiency	
				Cell-HMO	
	A	B	C	Recovery (%)	Ads. Capacity (mg g ⁻¹)
1	9	0.5	10	31.4	0.628
2	9	1.25	30	29.86	0.7168
3	9	2	50	35.64	0.891
4	11	0.5	30	46.666	2.8
5	11	1.25	50	49.82	1.99
6	11	2	10	82.1	0.415
7	13	0.5	50	45.76	4.576
8	13	1.25	10	82.1	0.656
9	13	2	30	80.5	1.20

2.5. Determination of Selectivity Performance

The selectivity of lithium ions was evaluated in the presence of competing cations of the same group, specifically K⁺ and Mg²⁺, in aqueous solution. Selective adsorption experiments were conducted under the optimal operating conditions obtained from the Taguchi experimental design. The tests were performed using a mixed-ion solution containing 50 mg L⁻¹ of each ion, with an adsorbent dosage of 1.25 g in 100 mL of solution. The adsorption was carried out at ambient temperature for contact times of 1 and 2 h to reach equilibrium. The selectivity performance of the adsorbent was quantified using the equilibrium adsorption capacity (Q_e), distribution coefficient

(K_d), separation factor (α_{Me}^{Li}), and concentration factor (CF), which were calculated according to the following equations [3, 44]:

$$K_d = (C_{0.Me} - C_{e.Me}) / C_{e.Me} \times \frac{V}{W} \quad \text{Eqn. 1}$$

$$\alpha_{Me}^{Li} = K_{d.Li} / K_{d.Me} \quad (Me = K^+, Mg^{2+}, Li^+) \quad \text{Eqn. 2}$$

$$C_F = Q_{e.Me} / C_{0.Me} \quad (Me = K^+, Mg^{2+}, Li^+) \quad \text{Eqn. 3}$$

where $C_{0.Me}$ and $C_{e.Me}$ are the initial and equilibrium ion concentrations in the saline solution (mg L⁻¹), V is the solution volume (mL), and W is the mass of HMO used (g).

3. Results and Discussion

3.1. FTIR Analysis

The FTIR spectra of waste paper, acid-hydrolyzed cellulose, and the composite adsorbents (CELL-HMO and CELL-ECH-HMO) are presented in Figure 1. The raw waste paper exhibits characteristic cellulose absorption bands at 3431–3426 cm⁻¹ (O–H stretching), 3133–3128 cm⁻¹ (C–H stretching), 1646–1641 cm⁻¹ (C–OH stretching and bending of adsorbed water), 1163–1160 cm⁻¹ (asymmetric C–O stretching), and 1075–1017 cm⁻¹ (C–O–C ether vibrations), confirming its lignocellulosic structure [47]. After acid hydrolysis, the appearance of a peak at 874 cm⁻¹ corresponding to the crystalline cellulose band (C–O stretching and β -1,4-glycosidic linkage) and additional peaks at 1111, 1400, and 1453 cm⁻¹ indicate that the extracted nanocellulose largely preserves the cellulose backbone [48]. Upon HMO incorporation (CELL-HMO), the O–H stretching vibration shifts to 3331 cm⁻¹ with reduced intensity, suggesting weakened hydrogen-bonding interactions between cellulose chains due to hydrogen manganese oxide incorporation [49]. In the crosslinked composite (CELL-ECH-HMO), absorption bands at 3426 cm⁻¹ (O–H stretching), 3130 cm⁻¹ (C–H stretching), and 1164 cm⁻¹ (asymmetric C–O and C–O–C stretching) become more intense with increasing epichlorohydrin (ECH) content, confirming successful

crosslinking. The broadening and intensification of the O–H and C–H bands reflect the reaction between ECH–Cl and cellulose –OH groups, generating additional –CH₂ and –CH₃ functionalities on the cellulose surface. Overall, the FTIR results indicate that the cellulose framework was preserved during processing, while HMO incorporation and ECH crosslinking modified the hydrogen-bonding environment and surface chemistry of the composite. These structural changes are expected to contribute to the observed adsorption performance [40].

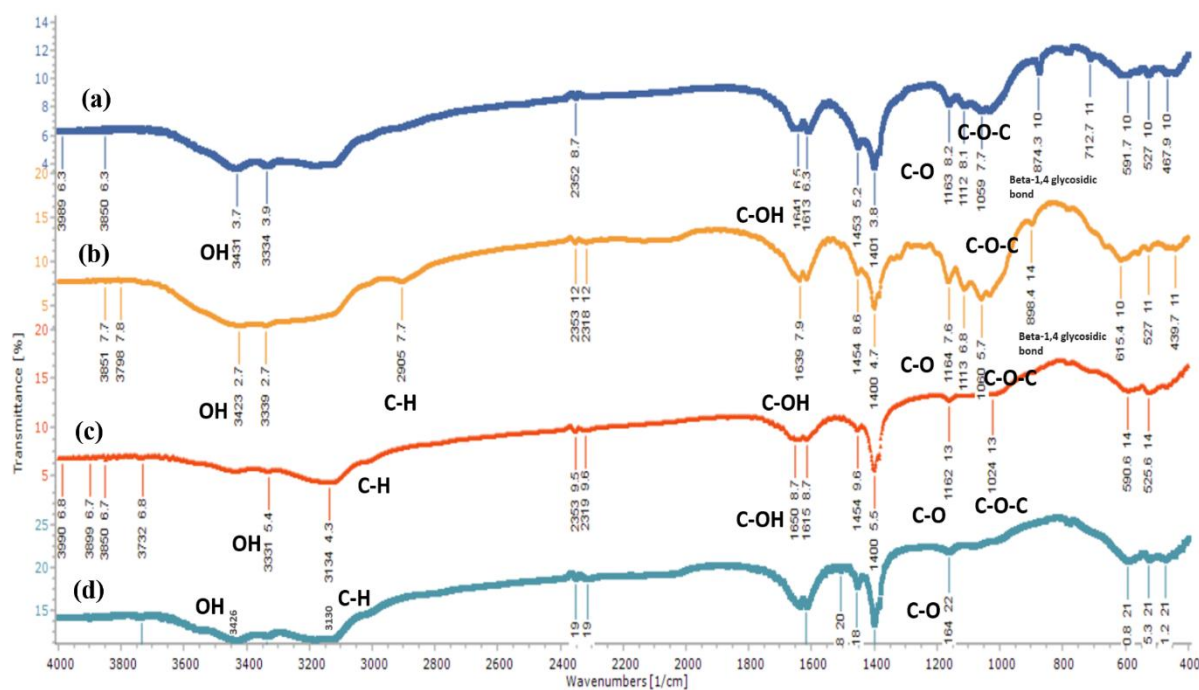


Figure 1. FTIR spectra of (a) raw waste paper, (b) acid-hydrolyzed cellulose, (c) CELL-HMO, and (d) CELL-ECH-HMO

3.2. Morphological Properties

3.2.1. XRD Analysis

The X-ray diffraction (XRD) patterns of the spinel lithium manganese oxide precursor (LMO), the protonated ion-sieve phase ($\text{H}_4\text{Mn}_5\text{O}_{12}$, denoted as HMO), and the cellulose-based composite adsorbents (Cell-HMO and Cell-ECH-HMO) are presented in Figure 2. After calcination, the

LMO precursor exhibited characteristic diffraction peaks corresponding to a crystalline spinel-type lithium manganese oxide structure. Phase identification was performed using JCPDS reference cards and X'Pert HighScore software, confirming the formation of lithium-containing spinel phases. The well-defined diffraction peaks indicate successful crystallization and structural development of the LMO precursor during thermal treatment. Following acid leaching, the XRD pattern of the protonated phase (HMO) remained largely similar to that of the LMO precursor, indicating that the fundamental spinel framework was preserved during Li^+ extraction. However, slight shifts of diffraction peaks toward higher 2θ values and minor reductions in peak intensity were observed. These changes can be attributed to lattice contraction resulting from Li^+ removal and subsequent proton insertion through the Li^+/H^+ ion-exchange process. The retention of the spinel structure confirms the successful formation of the protonated ion-sieve phase ($\text{H}_4\text{Mn}_5\text{O}_{12}$) without collapse of the manganese oxide framework [15, 49].

For the composite adsorbents (Cell-HMO and Cell-ECH-HMO), the characteristic diffraction peaks of HMO were still detectable, although with reduced intensity due to the presence of the amorphous cellulose matrix. The absence of new impurity peaks indicates that incorporation into the cellulose network did not alter the crystalline structure of the ion-sieve material. This structural stability demonstrates that the active adsorption phase remained intact after composite fabrication. The preservation of the spinel framework suggests that the structural features responsible for lithium-ion exchange were retained after composite fabrication. The XRD results confirm successful synthesis of the LMO precursor, formation of the protonated HMO ion-sieve through acid treatment, and preservation of the crystalline spinel structure after incorporation into the cellulose matrix [50].

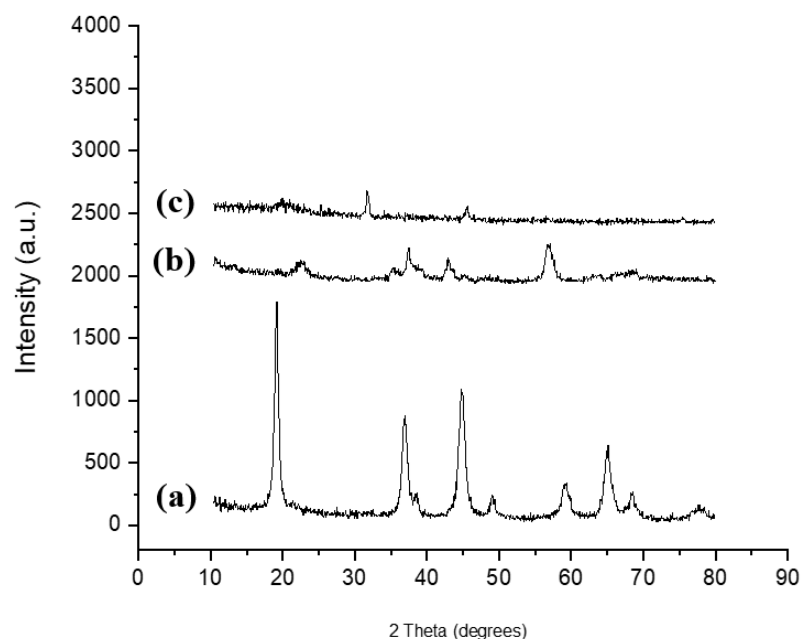


Figure 2. XRD patterns of (a) LMO precursor, (b) HMO ion-sieve material, (c) Cell-HMO composite, and (d) Cell-ECH-HMO composite.

3.2.2. FESEM Analysis

The FESEM images (Figure 3a–f) display the morphological features of the synthesized cellulose-based composites. The spherical Cell-HMO particles exhibit a three-dimensional porous network typical of regenerated cellulose, confirming the preservation of the natural polysaccharide framework. At higher magnifications (Figure 3a–c), uniformly distributed quasi-spherical HMO nanoparticles (tens to a few hundred nanometers) are clearly observed within the cellulose matrix, indicating successful in situ incorporation during granulation. Lower-magnification images (Figure 3d–f) reveal a rough and porous surface morphology that enhances the specific surface area and facilitates mass transfer during adsorption. The close interfacial contact between cellulose and HMO particles suggests strong physical and hydrogen-bonding interactions, providing excellent structural stability and dispersion. Overall, the FESEM results confirm that the cellulose matrix effectively stabilizes and supports the HMO nanoparticles, forming a porous composite scaffold with high surface accessibility, which is expected to facilitate mass transfer during lithium adsorption [32, 49].

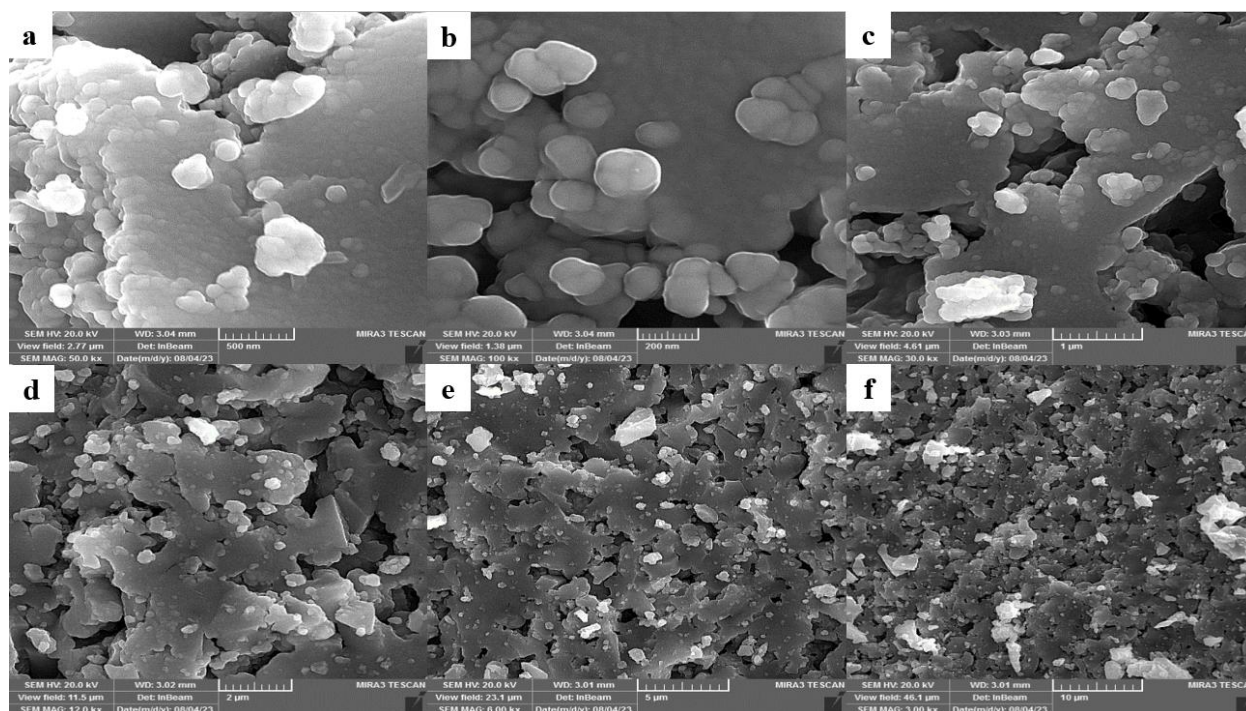


Figure 3. FE-SEM images of the CELL–HMO composite at different magnifications: (a) 500 nm, (b) 200 nm, (c) 1 μ m, (d) 2 μ m, (e) 5 μ m, and (f) 10 μ m

3.2.3. EDX Analysis of CELL–HMO

As shown in the EDX elemental mapping results (Figure 4a), HMO particles are uniformly distributed within the porous cellulose matrix. The fine particle distribution increases the exposed surface area of the active phase, which may improve the accessibility of adsorption sites (Figure 4b). The particle size histogram of CELL–HMO (Figure 4c) indicates that particle sizes are not skewed to either side of the distribution but are clustered around the mean, suggesting a normal particle size distribution. A significant amount of HMO powder is clearly observed on the cellulose surface (Figure 4d). The uniform dispersion of HMO powder aligns with the distribution of Mn and O elements in the EDX elemental mapping, confirming homogeneous incorporation of the ion-sieve material within the cellulose matrix.

The FTIR, XRD, FESEM, and EDS results demonstrate successful incorporation of HMO particles within the regenerated cellulose matrix while preserving the structural integrity of both components. The cellulose network provides mechanical support, preserves accessible adsorption sites, and allows for successful crosslinking via ECH, enhance lithium recovery performance [44].

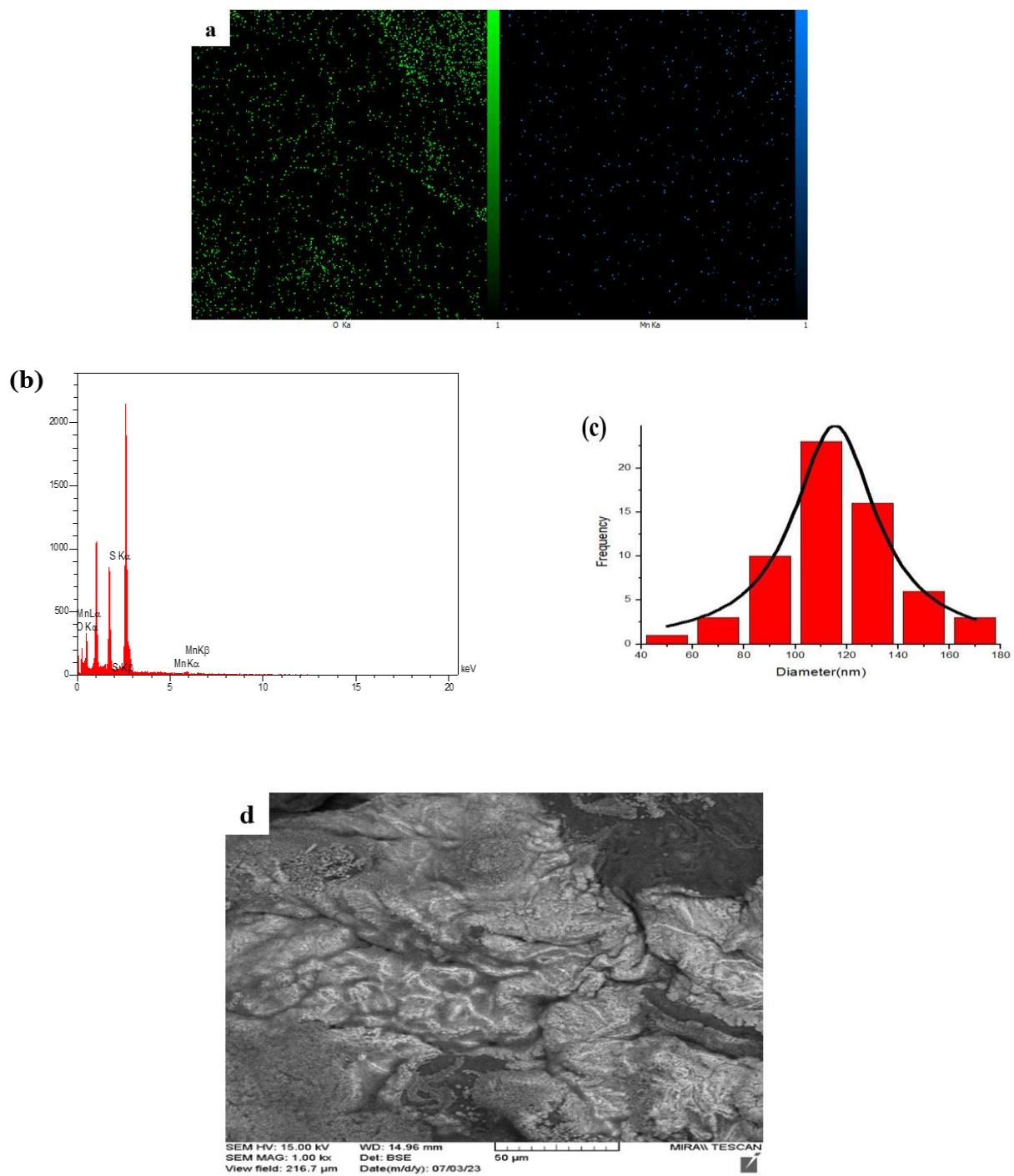


Figure 4. EDX analysis of CELL-HMO composites: (a) elemental mapping; (b) partial surface concentration of HMO particles on CELL-HMO; (c) particle size histogram; (d) FE-SEM image showing abundant HMO powder on the cellulose surface.

3.3 Statistical analysis of Lithium Adsorption Capacity and Recovery Efficiency

The experimental results obtained from the Taguchi design are summarized in Table 1b. After performing the proposed experimental runs, the adsorption capacity (Q_e) and lithium recovery efficiency (R%) were selected as the response variables, each measured in duplicate to ensure data reliability. Since the main objective of this study was to maximize lithium recovery from aqueous solutions, the quality characteristic in the Taguchi design was defined as “larger is better.” The statistical evaluation of the experimental data was conducted using analysis of variance (ANOVA), and the results are summarized in Table 2. Initial lithium concentration and adsorbent dosage were identified as the most influential factors affecting adsorption capacity and recovery efficiency according to the ANOVA results. These results indicated that the interaction between pH and biosorbent dosage also had a statistically significant influence on lithium adsorption capacity and recovery efficiency [45]. The effects of the interactions among the different parameters on lithium adsorption capacity and recovery percentage are summarized in Table 2.

Table 2. ANOVA table for Taguchi regression model: a) R(%), b) q_t					
<i>a) Li recovery percent as response</i>					
Source	DF	Seq. SS	Variance	PS	Contribution (%)
	Cell-HMO	Cell-HMO	Cell-HMO	Cell-HMO	Cell-HMO
A	2	67.839	33.919	67.344	67.284
B	2	19.802	9.901	19.307	19.29
C	2	11.952	5.976	11.457	11.447
Error	2	0.494	0.247		1.979
Total	8	100.088			100
<i>b) Li adsorption capacity as response</i>					
Source	DF	Seq. SS	Variance	PS	Contribution (%)
	Cell-HMO	Cell-HMO	Cell-HMO	Cell-HMO	Cell-HMO
A	2	68.058	34.028	67.658	17.888
B	2	113.484	56.742	113.086	29.9
C	2	196.274	98.137	195.875	51.789
Error	2	0.397	0.198		0.423
Total	8	378.214			

3.3.1. *Effect of pH*

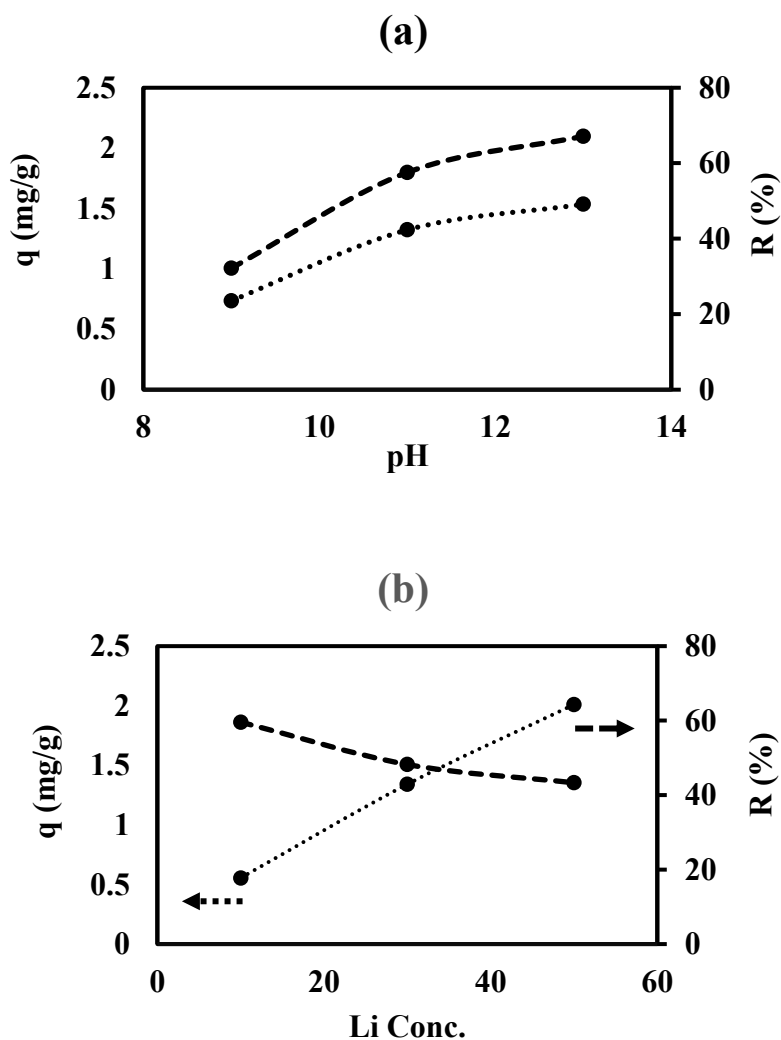
Figure 5a illustrates the effect of pH on the lithium recovery process. Overall, these results indicate that solution pH strongly influences lithium adsorption by affecting the surface charge characteristics of the composite and the Li^+/H^+ ion-exchange process. Under acidic conditions, the presence of excessive H^+ ions suppresses Li^+ uptake due to competitive adsorption and surface protonation, which reduces the availability of negatively charged active sites. As the solution becomes more alkaline, deprotonation of surface functional groups generates abundant negatively charged sites, thereby strengthening the electrostatic attraction between Li^+ and the ion-sieving Mn–O framework. The moderately alkaline environment (pH 11–13) was thus found to be optimal for lithium recovery, as it simultaneously minimizes ionic competition and promotes structural diffusion of Li^+ into the spinel lattice. However, at excessively high pH values, the formation of $\text{Mn}(\text{OH})_2$ or Mn–O–H complexes destabilizes the ion-sieve structure by partially dissolving the manganese oxide phase into the solution [51]. Such structural changes may reduce the number of accessible adsorption sites and consequently decrease lithium adsorption performance. Therefore, maintaining an appropriate alkaline pH appears to be important for preserving adsorption performance under the investigated conditions.

3.3.2. *Effect of initial lithium concentration*

Figure 5b illustrates the influence of the initial lithium ion concentration on the adsorption capacity and lithium recovery efficiency of the Cell-HMO composite. The adsorption capacity was observed to increase directly with increasing initial Li^+ concentration. Increasing the initial lithium concentration increased the driving force for mass transfer, resulting in higher adsorption capacity until the available adsorption sites approached saturation. However, when the initial Li^+ concentration increased from 10 ppm to 50 ppm, the recovery efficiency gradually decreased. This trend can be attributed to the higher ratio of Li^+ ions relative to the available spinel lattice sites in the composite adsorbent, which leads to saturation of the crystal structure cavities and limits the accessibility of additional Li^+ ions. Consequently, while the total adsorption capacity increases, the percentage of Li^+ removed from the solution declines at elevated concentrations [50, 51].

3.3.3. Effect of composite adsorbent dosage

Figure 5c shows the effect of the composite adsorbent dosage on lithium adsorption capacity and recovery efficiency. At higher dosages, the adsorption capacity exhibited a decreasing trend, which can be attributed to aggregation and overlapping of active sites within the spinel layers. This behavior may be attributed to partial aggregation of adsorbent particles, which can reduce the effective surface area available for adsorption [52]. Conversely, increasing the adsorbent dosage from 0.5 g to 2 g led to an enhancement in lithium recovery efficiency. The recovery percentage is directly related to the available surface area, the density of active sites, and the ion-exchange and redox capacity of the adsorbent. Higher dosages provide greater accessibility to active sites, thereby improving Li^+ uptake from the solution.



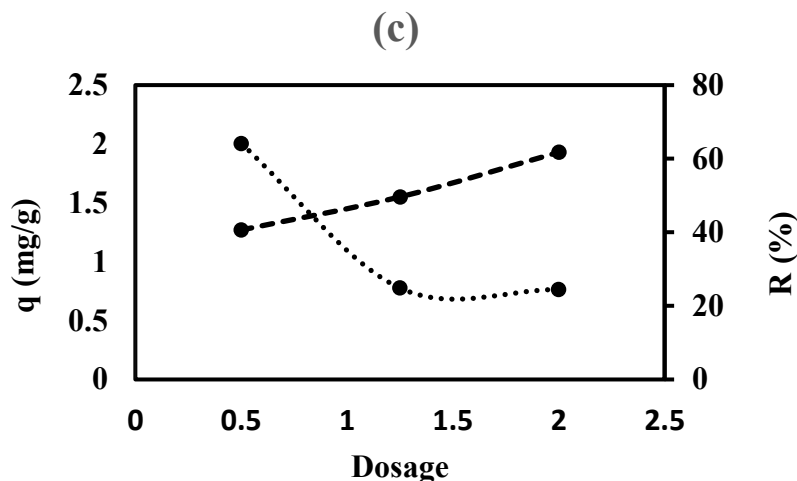


Figure 5. Effect of (a) solution pH, (b) initial lithium ion concentration; (c) Cell-HMO composite dosage on the lithium adsorption capacity and recovery efficiency of the Cell-HMO composite.

3.3.4. Optimization of lithium adsorption and recovery efficiency

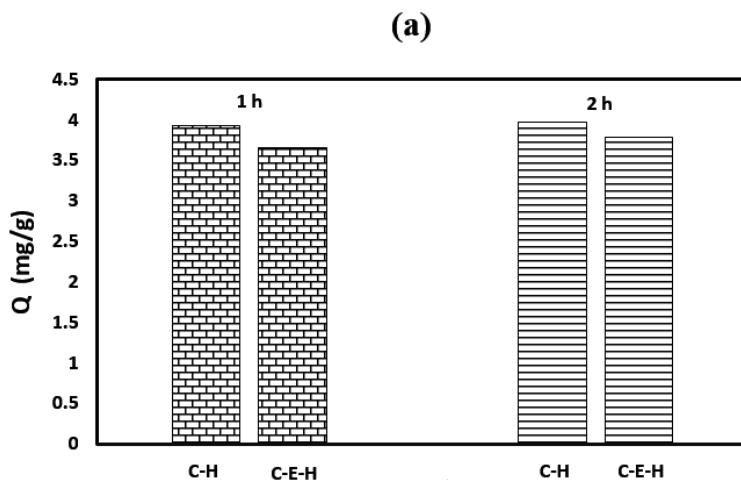
The Taguchi optimization results (Table 3) demonstrate that the C–HMO composite achieved maximum lithium adsorption under highly alkaline conditions. The optimal parameters were pH = 13, adsorbent dosage = 0.5 g, and initial Li^+ concentration = 50 mg L^{-1} for adsorption capacity, and pH = 13, dosage = 2 g, and concentration = 10 mg L^{-1} for recovery efficiency. The predicted lithium recovery efficiency and adsorption capacity were 99.06% and 4.726 mg g^{-1} , while the corresponding experimental values were 96.2% and 4.842 mg g^{-1} . The close agreement between the experimental and predicted values indicates that the Taguchi method provided reliable optimization of the investigated operating parameters.

Table 3. Optimal conditions for Cell-HMO adsorption based on R% and Q_e

	Cell-HMO	
	(R%)	Q_e (mg g^{-1})
pH	13	13
Adsorbent dosage (g)	2	0.5
Li^+ initial Conc. (mg/L)	10	50
Expected value	99.06	4.73
Actual value	96.2	4.84

3.4. Comparison of Cell-HMO and Cell-ECH-HMO Composites

The lithium adsorption performance of the two composite adsorbents, CELL–HMO and CELL–ECH–HMO, was compared under optimized conditions determined from the Taguchi experimental design as shown in Figure 6. The data obtained from the comparative study of the two adsorbents indicate that the non-crosslinked Cell-HMO exhibited higher lithium adsorption than the crosslinked Cell-ECH-HMO. The lower lithium uptake observed for Cell–ECH–HMO is likely associated with the presence of epichlorohydrin, which may partially restrict the accessibility of HMO active sites by forming a more compact crosslinked network [40]. Although the ECH crosslinker improves the mechanical properties of the adsorbent and reduces the leaching of cellulose carbon and manganese from the HMO ion-sieve, it simultaneously decreases the hydrophilicity of the composite. The reduced adsorption capacity may also be related to the lower hydrophilicity generally associated with crosslinked cellulose networks, although this effect was not directly quantified in the present study [44].



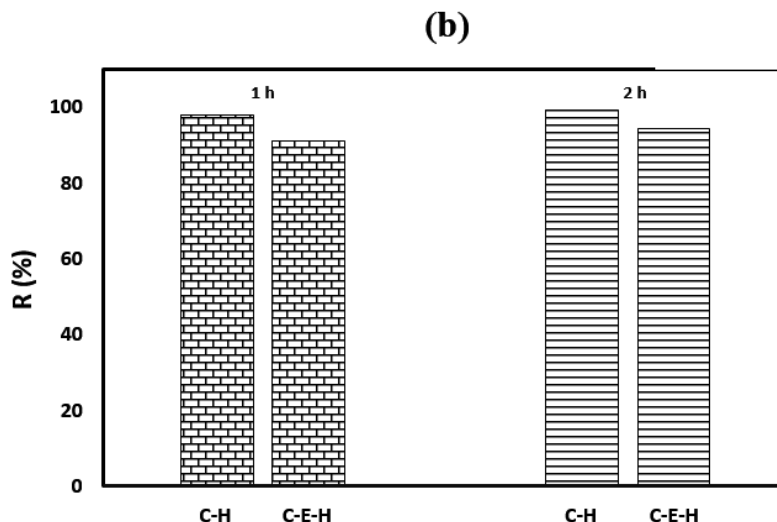


Figure 6. Comparison of Lithium Adsorption Performance between Cell-HMO and Cell-ECH-HMO Composites in terms of (a) the lithium adsorption capacity and (b) the lithium recovery efficiency (after 1 and 2 hr of adsorption time)

3.5. Selectivity of the Cell-HMO Adsorbent

The selectivity of the Cell-HMO adsorbent was evaluated by comparing its adsorption behavior toward lithium ions with other coexisting ions in solution, namely K^+ and Mg^{2+} . As shown in Table 4 and Figure 7, the equilibrium distribution coefficients (K_d) followed the order $K^+ < Mg^{2+} < Li^+$, indicating the preferential adsorption of lithium ions over the competing cations investigated in this study. The K_d values for Li^+ were one to two orders of magnitude higher than those of competing cations, indicating markedly stronger affinity and pronounced ion-sieving behavior. The selectivity factors ($\alpha_{Li/Mg}$) further demonstrate the preferential uptake of Li^+ over Mg^{2+} and K^+ , reflecting the structural memory effect of the protonated spinel $H_4Mn_5O_{12}$ framework. The observed selectivity is consistent with the ion-sieving characteristics of protonated $H_4Mn_5O_{12}$ reported in previous studies, where the ionic radius and structural compatibility of Li^+ favor its insertion into the spinel framework [53]. In contrast, larger cations such as K^+ and the divalent Mg^{2+} are primarily restricted to surface adsorption due to steric and electrostatic limitations. These results confirm that lithium uptake is governed predominantly by the ion-sieving mechanism rather than nonspecific surface adsorption.

Table 4. Lithium adsorption selectivity parameters of the Cell-HMO composite after 1 hour and 2 hours.

Ion	Time (h)	C ₀ (mg L ⁻¹)	C _e (mg L ⁻¹)	Q _e (mg g ⁻¹)	R (%)	K _d (mL g ⁻¹)	Selectivity (α)
Li ⁺	1	50	2.5	3.8	95.0	1520	1.00
	2	50	1.4	3.9	97.2	2777.14	1.00
Mg ²⁺	1	50	31.1	1.5	37.8	48.62	31.26
	2	50	29.4	1.6	41.2	56.02	49.54
K ⁺	1	50	39.0	0.9	22.0	22.56	67.36
	2	50	36.2	1.1	27.6	30.50	91.06

Note: C₀ and C_e are the initial and equilibrium concentrations, respectively. Q_e is the equilibrium adsorption capacity. R is the removal efficiency (%). K_d is the distribution coefficient. α selectivity factor

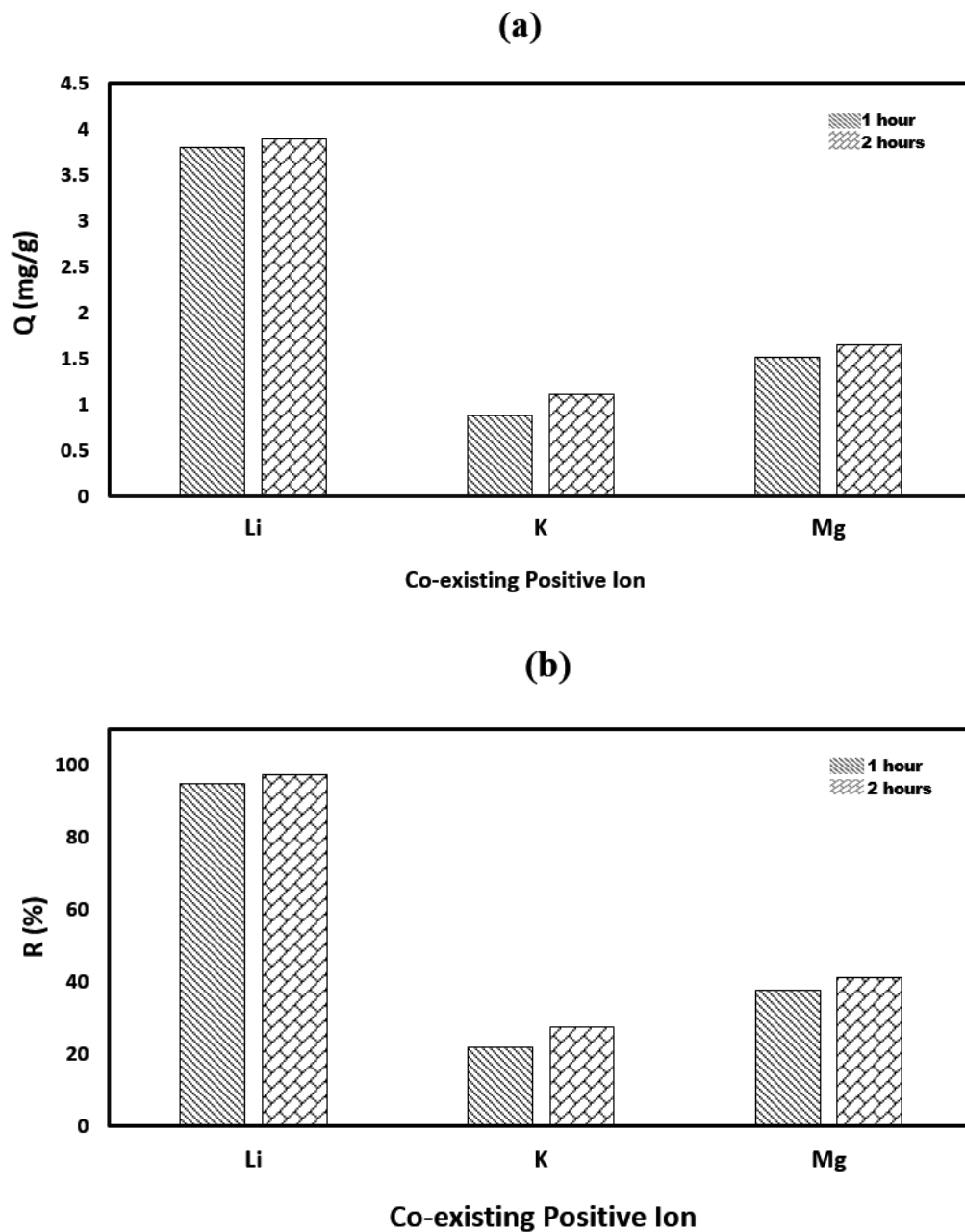


Figure 7. Simultaneous effect of different competing cations (K^+ and Mg^{2+}) on (a) the lithium adsorption capacity and (b) the lithium recovery efficiency of the Cell-HMO composite.

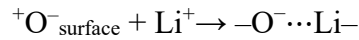
3.6. Proposed Mechanism of Lithium Adsorption by Cellulose–HMO Composite

Based on the experimental observations and previous reports, lithium adsorption is proposed to occur through a combination of electrostatic surface adsorption, ion exchange, and intercalation

into the spinel HMO structure. Lithium uptake primarily follows a multi-stage process, although partial overlap between stages may occur depending on Li^+ concentration and accessibility of active sites. The redox/disproportionation mechanism, typically observed during acidic activation of Li–Mn oxides, is not active under these alkaline conditions.

- *Electrostatic surface adsorption*

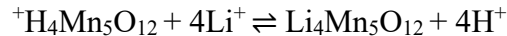
Li^+ ions are initially attracted to the negatively charged surface sites of HMO and deprotonated hydroxyl groups of cellulose:



The initial adsorption step is proposed to involve electrostatic interactions between Li^+ ions and negatively charged surface sites. The process is reversible and rapid, and typically precedes penetration into the lattice [44, 51, 54].

- *Ion exchange*

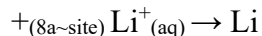
After the initial surface adsorption, Li^+ gradually diffuses into the interior of HMO particles and approaches the tetrahedral 8a sites of the spinel lattice. This stage is commonly described by the H^+/Li^+ exchange reaction, in which Li^+ replaces surface-bound H^+ within the spinel channels. This diffusion-controlled step is expected to be slower than the initial surface adsorption process:



This process, often described by the stage model, governs selective lithium uptake and preserves the structural integrity of the spinel framework. Stage 2 occurs over minutes to hours and may partially overlap with surface adsorption, especially at higher Li^+ concentrations. This mechanism is consistent with the established ion-exchange behavior of protonated $\text{H}_4\text{Mn}_5\text{O}_{12}$ reported in previous studies [44, 51, 54].

- *Intercalation and structural accommodation*

Finally, lithium ions are proposed to intercalate into the tetrahedral 8a sites of the spinel lattice:



- The spinel framework accommodates Li^{+} while retaining structural integrity.
- Intercalation provides high selectivity and stability of Li^{+} adsorption under alkaline conditions [44, 51, 54].

- *Role of the Cell–HMO Composite Structure*

The cellulose matrix is not expected to participate directly in lithium ion exchange but provides structural support for the active HMO phase by:

- Preventing aggregation of HMO particles,
- Increasing accessible surface area and porosity,
- Facilitating Li^{+} diffusion through surface –OH groups, and
- Improving mechanical stability and potentially supporting reusability over multiple adsorption-desorption cycles.

4. Conclusion

A novel Cell-HMO composite was synthesized by embedding lithium ion-sieving HMO particles into a cellulose matrix derived from waste paper. Structural and morphological analyses (FESEM, XRD, FTIR, and EDS) confirmed uniform dispersion of HMO particles within the cellulose framework. The adsorption performance of Cell-HMO for lithium recovery from aqueous solutions was systematically evaluated using Taguchi experimental design. Statistical analysis revealed that solution pH and adsorbent dosage significantly influenced lithium uptake. Optimal conditions yielded a maximum adsorption capacity of 4.842 mg g^{-1} and a recovery efficiency of 96.2%. Lithium selectivity tests showed that, among competing cations (K^{+} and Mg^{2+}), Li^{+} was preferentially adsorbed, demonstrating the high selectivity of the composite. Overall, the results demonstrate that waste-paper-derived Cell–HMO is an effective and sustainable adsorbent for selective lithium recovery from aqueous solutions. The combination of renewable cellulose with protonated manganese oxide provides a mechanically stable composite while maintaining high lithium selectivity. Although additional studies on regeneration performance, long-term stability, and application to real brine systems are required, the present work establishes a sustainable

platform for developing waste-derived adsorbents for lithium recovery and circular resource utilization.

Declarations

Funding

No funds, grants, or other support was received for the submitted work.

Competing Interests

The authors have no competing interests to declare that are relevant to the content of this article.

Author Contributions

Naeim Aghazadeh: Material preparation, Data Collection & analysis; Investigation; Validation.

Elham Jalilnejad: Conceptualization; Resources; Data Curation; Writing – Review & Editing; Supervision; Project administration.

Reza Rafiee: Conceptualization; Review & Editing; Supervision.

Hedayat Khalili: Data Curation and analysis. All authors read and approved the final manuscript.

Data availability

The datasets generated and/or analyzed during the current study are provided in full within the article and excel files are available from the corresponding author on request. Please contact E. Jalilnejad (Email address: e.jalilnejad@uut.ac.ir; elham.jalilnejad@gmail.com).

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