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Characteristics of organic-inorganic composite sorbent prepared using lithium hydroxide and manganese oxide for recovery of lithium ions

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ABSTRACT

For recovering lithium ions from aqueous solutions, organic sorbents were prepared with polyacrylonitrile (PAN). The physical properties and adsorption ability of hydrous manganese oxide (HMnO) and organic sorbents were investigated. The lithium sorption capacity of HMnO increased rapidly with an increase in solution pH. The prepared PAN/HMnO sorbent was characterized using differential scanning calorimetry, thermogravimetric analysis, and microscope observations. The specific surface areas of the sorbent with 20%, 30%, and 40% PAN content were recorded to be 25.77 m^2/g, 18.36 m^2/g, and 12.90 m^2/g, respectively. The synthesis conditions with PAN/HMnO organic sorbent at 30% PAN content were identified to be most optimal. Further, this sorbent showed a regeneration efficiency of approximately 70%, even when it was washed 5 times with HCl solution. In general, the PAN organic sorbents with immobilized HMnO were found to be suitable for the recovery of lithium ions from water.

Keywords: Sorption; Lithium; Hydrous manganese oxide (HMnO); Polyacrylonitrile (PAN)

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1. Introduction

Lithium, a rare metal with very low global reserves, has wide-ranging applications. It is used in secondary batteries and as a raw material for aircraft light alloys and fuel for nuclear power generation. The global lithium reserves are estimated to be around 4 million tons [1]. With ever-increasing industrial development, the demand for lithium has been increasing [2], leading to the gradual exhaustion of its land sources; this has resulted in an increase in mining cost. The lithium concentration in seawater of 0.17 mg/L is very low; however, the total quantity is very large at approximately 2.5×10^{14} kg. Therefore, there is a growing research interest in the recovery of lithium ions from seawater [3–9].

Lithium manganese oxide (LMO) has shown a sorption of 27 mg/g of lithium ions, which is significantly higher than for other sorbents [1,10–12]. In addition, it is reported to be selective to lithium ions [13–17]. However, since it is used as a fine powder, it may leak out during the sorption process and lead to a pressure drop in the column [16–18].

To resolve this issue, studies have been conducted on the fabrication of LMO beads and PVC membranes. However, these materials have certain issues, such as the loss of active sites for lithium sorption owing to the encapsulation of PVC and restriction on the amount of sorbent that could be embedded into the membrane. In addition, considering the economic aspects, pressurized flow systems involve

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consumption of high energy for the recovery of lithium from seawater [16,18].

Polyacrylonitrile (PAN) is one of the better-suited organic binders due to its characteristic features, such as excellent pelletizing property, good solubility in organic solvents, strong adhesion with inorganic materials, and chemical stability. Therefore, PAN-based composite ion exchangers show high selectivity and result in high inherited sorption capacity for the inorganic sorbents [19,20].

The aim of this study is to devise a relatively more economical and environmentally friendly method of preparation of organic sorbents and determine the effectiveness of the prepared product in tackling the issues associated with the use of powder sorbents. For this purpose, organic sorbents were synthesized using bead-shaped PAN; further, the physical properties and sorption capacity of hydrous manganese oxide (HMnO) were evaluated and compared with that of its combination products with PAN in varying concentrations.

2. Materials and methods

2.1. Preparation of hydrous manganese oxide (HMnO)

The inorganic sorbent hydrous manganese oxide (HMnO) was synthesized using manganese oxide (MnO_2, Sigma Aldrich, USA) and lithium hydroxide monohydrate ($LiOH·H_2O$, Sigma Aldrich, USA) [11]. Firstly, 100 g of manganese oxide and 2 L of 4 M lithium hydroxide were mixed for 24 h and filtered. The mix was dried at 60°C for 24 h and calcined in an electric furnace at 600°C for 4 h to form LMO; further, it was stirred in 0.5 M HCl solution for 24 h to obtain HMnO. This was washed thoroughly with distilled water and dried at 60°C for 24 h; the final product was used as a sorbent.

2.2 PAN/HMnO sorbent synthesis

A 1-liter three-neck flask was used for the preparation of the composite. Firstly, specific amounts of HMnO powder were mixed with dimethyl sulfoxide (DMSO, Sigma Aldrich, USA) and a few drops of TWEEN-80 surfactant (Sigma Aldrich, USA), and stirred at 50°C for 1 h to form a homogeneous solution. Thereafter, specific amounts of PAN (polyacrylonitrile, Sigma Aldrich, USA) powder (MW 1,300,000) were added to this solution while stirring at 50°C for 5 h. As a result, bead-type organic sorbent was prepared. The slurry containing HMnO and PAN was hardened by dropping it into distilled water using a syringe of 1 mm diameter. The beads were washed several times with distilled water to obtain desired PAN organic sorbent. Thereafter, the beads were dried at 60°C, and immersed in a nitric acid (HNO_3) solution (pH 1–3) to remove the residual material. The final product was washed with water.

2.3. Surface characterization

The thermal properties of PAN organic sorbents were determined by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) using a thermal analyzer (Universal V2.6D, TA Instruments, US). The thermal profiles were recorded at a heating rate of 20°C/min at temperatures of 50–600°C under nitrogen stream. The surface morphologies of the sorbents were observed using a KES 2006 video optical microscope that uses the ITPro software Version 3.03, both of which were developed by Sometech Inc. (Seoul, Republic of Korea). The specific surface area and porosity of the PAN organic sorbents were measured using the BET surface area and porosimetry system (ASAP 2020, Micromeritics Instruments, Atlanta, GA).

2.4. Sorption experiment

The Sorption equilibrium experiment was conducted to evaluate the sorption characteristics of HMnO in lithium-ion-containing seawater and artificial wastewater. 0.1 g of sorbent was added to 1 L of lithium-ion-containing artificial wastewater in an Erlenmeyer flask. The mixture was stirred at 25°C a rate of 120 rpm in a constant temperature stirrer for 72 h. Subsequently, it was suction filtered through a 0.45 µm filter paper. The lithium content in the filtrate was analyzed by means of inductively coupled plasma atomic emission spectrometry (ICP-AES) (730ES, Varian, Australia). The adsorbed amount was calculated as the difference between the amount of lithium in the test liquid and the filtrate after the sorption reaction.

$$q = \frac{V\left(C_o - C\right)}{W} \tag{1}$$

Here C_o and C are the lithium concentrations (mg/L), before and after the sorption experiment, V is the volume of the test solution (mL), and W is the amount of HMnO (g).

2.5. Continuous column test

The seawater used for testing lithium recovery was taken from the Yellow Sea off the coast of Korea. Ninety-milliliter columns made of cylindrical acryl were used; their inflow and outflow vents were blocked using absorbent cotton, and the column was packed with 5 g of PAN/HMnO. The packing superficial velocity, adsorbent volume, and pore volume were 0.15 cm/s, 46.8 cm^3, and 22.1 cm^3, respectively. The wastewater and HCl regenerant solution were pumped upstream from the seawater with a metering pump and collected over a period of 3 days. The presence of Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} was evaluated using ICP-AES.

3. Results and discussion

3.1. Properties of HMnO

Lithium ions were removed completely from synthesized LMO by means of wet mixing using hydrochloric acid solution [17–19]. The HMnO sorbent has a high affinity for lithium ions and the sorption properties of HMnO have been investigated by Park et al. [11].

The pHpzc value for HMnO is 2.8, determined from the point of intersection of zeta potential and pH curves (Fig. 1). Its capacity for sorption of Li ions is high in the alkaline region that was not influenced significantly by the presence of competing cations, such as Na^+, K^+, Mg^{2+}, and Ca^{2+} [11,21–22].

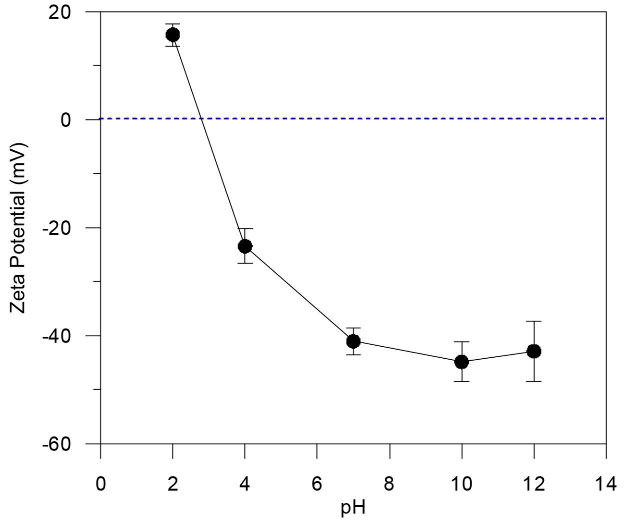

Fig. 1. Zeta potential of HMnO as a function of pH.

3.2. Synthesis of PAN/HMnO sorbent

The particle size of HMnO is less than 10 µm. Due to its fine size, it can cause a pressure drop in the fixed bed reactor when used with seawater, which is not the case with a bead-type adsorbent. This is a limiting factor for its direct application [16–18]. In order to resolve this issue, we synthesized bead-type organic sorbents by immobilizing HMnO on 20–40% PAN (weight/weight); thereafter, the effectiveness of HMnO was tested by comparing its physical properties and sorption capacity with that of the organic sorbent.

Further, the thermal properties of the organic sorbents with different PAN content were characterized by means of TGA and DSC (Fig. 2). With a decrease in PAN content from 40% to 20%, a weight loss was observed at low temperatures. Specifically, weight reduction of the sorbent was observed when the PAN content was reduced from 40% to 20% at approximately 300°C; further, the weight was lower when the temperature was 300°C, as compared to when it was 100°C.

The decrease in weight at a temperature range of 300–800°C shows that the weight loss increases proportionally with PAN content, which can be attributed to pyrolysis of PAN.

The changes in the thermal properties of the organic sorbents revealed from TGA are corroborated by DSC results. The DSC curves of the organic sorbents with PAN content of 20%, 30%, and 40% are shown in Fig. 2. Exothermic peaks are detected at approximately 100, 200, and 300°C. Considering that the melting point of PAN is 300°C, the corresponding exothermic peak can be ascribed to the thermal decomposition of functional groups in PAN such as –CH$_2$ or –C$_2$HN.

The HMnO particle size was less than 2 µm in its powder form that decreased after the acid treatment (Fig. 3). From the BET sorption experiment, we estimated the specific surface area and pore volume of HMnO to be 42.72 m^2/g and 0.14 cm^3/g, respectively. As the PAN content was increased, the specific surface area decreased. The specific surface areas in case of 20%, 30%, and 40% PAN content were 25.77 m^2/g, 18.36 m^2/g, and 12.90 m^2/g, respectively (Table 1).

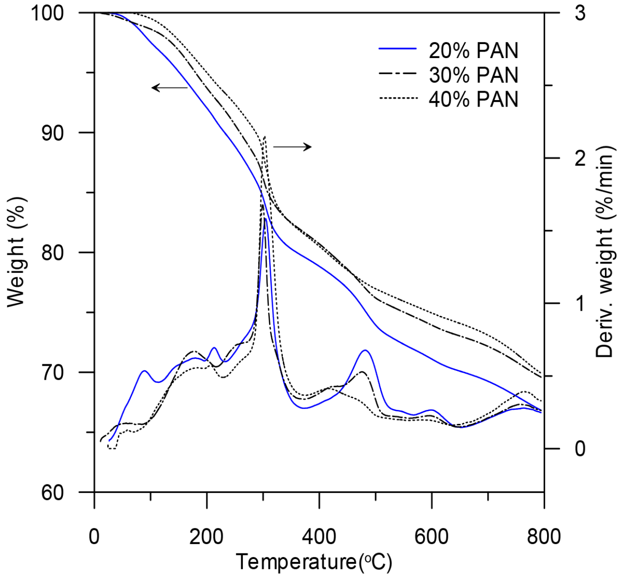

Fig. 2. TGA and DSC profiles of PAN/HMnO composite sorbents prepared with different PAN content.

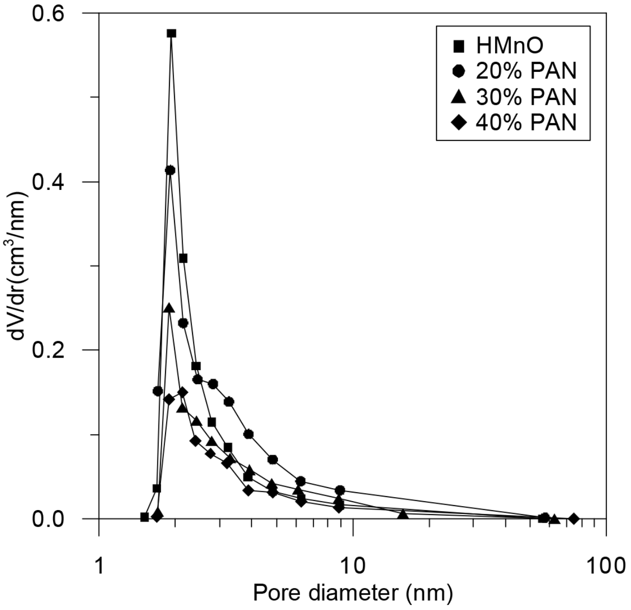

Fig. 3. Pore-size distribution of the PAN/HMnO composite sorbents prepared with different PAN content.

Table 1
Structural properties of PAN/HMnO sorbent based on their relative content

Sample	BET surface area (m^2/g)	Pore volume (cm^2/g)	Pore width (nm)
HMnO	42.72	0.1356	12.69
20% PAN	25.77	0.0793	12.31
30% PAN	18.36	0.0695	15.14
40% PAN	12.90	0.0663	15.56

We studied the morphologies of the organic sorbent using a microscope (Fig. 4); the surface and the internal layers of the bead-type sorbents with varying PAN content were observed. The surface of the sorbent with 20% PAN content was cracked and HMnO powder was observed on it. When the PAN content was high, the bead was nearly spherical-shaped and the bonding of the surface was relatively better. As we observed the internal structure of the 20% PAN/HMnO sorbent, the pore size was in the range of 50–80 µm. In the case of 30% PAN/HMnO sorbent, the pores were sized 100–200 µm and were distributed more evenly. The pore size of internal layers of the 40% PAN/HMnO sorbent was in the range of 80–120 µm; further, the corresponding number of pores was negligible as compared to 20% and 30% PAN/HMnO sorbents.

3.3. Sorption properties of HMnO

The sorption equilibrium rate for lithium using organic sorbents with HMnO and 20%–40% PAN content was measured. For this purpose, 0.1 g of the sorbent was added to 1 L of solution containing 5 mg/L of lithium. By stirring at 120 rpm and room temperature for 72 h, the adsorbed amount of lithium per unit of stirring time can be obtained (Fig. 5). The concentration of lithium in the supernatant collected after an interval was measured, and the amount of sorption was calculated by comparing it with the initial concentration [Eq. (1)].

The sorption rate of the HMnO and PAN organic sorbent increased gradually up to 24 h, after which it decreased; the process reached equilibrium at 48 h. While, the sorption rate changed negligibly with an increase in PAN content, the sorption capacity decreased. The corresponding values for sorbents with 0% (pure HMnO), 20%, 30%, and 40% PAN content were 3.3 mg/g, 2.9 mg/g, 2.5 mg/g, and 2.0 mg/g, respectively. The trend can be explained as follows: The surface of the sorbent is dense and hard on which PAN layer is formed as per the PAN content. This results in a decrease in the specific surface area with active sorption sites and therefore, the sorption capacity with an increase in PAN content.

The variation in sorption capacity with PAN content and outflow state of immobilized HMnO is displayed in Table 2. In the case of sorbent with 20% PAN content, the adsorbed amount was higher than that of HMnO by 88%;

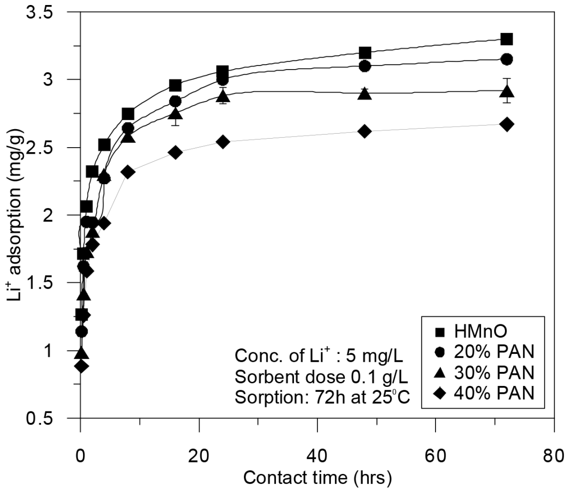

Fig. 5. Lithium sorption kinetics of pure HMnO and PAN/HMnO sorbents.

Table 2
Variation in lithium sorption capacity with PAN content

PAN content (%)	Sorption amount (mg/g)	Removal efficiency (%)	Remark (%)
HMnO	3.3	100.0	20 ± 8 leak
20	2.9	87.8	15 ± 5 leak
30	2.5	75.2	3 ± 2 leak
40	2.0	61.5	No leak

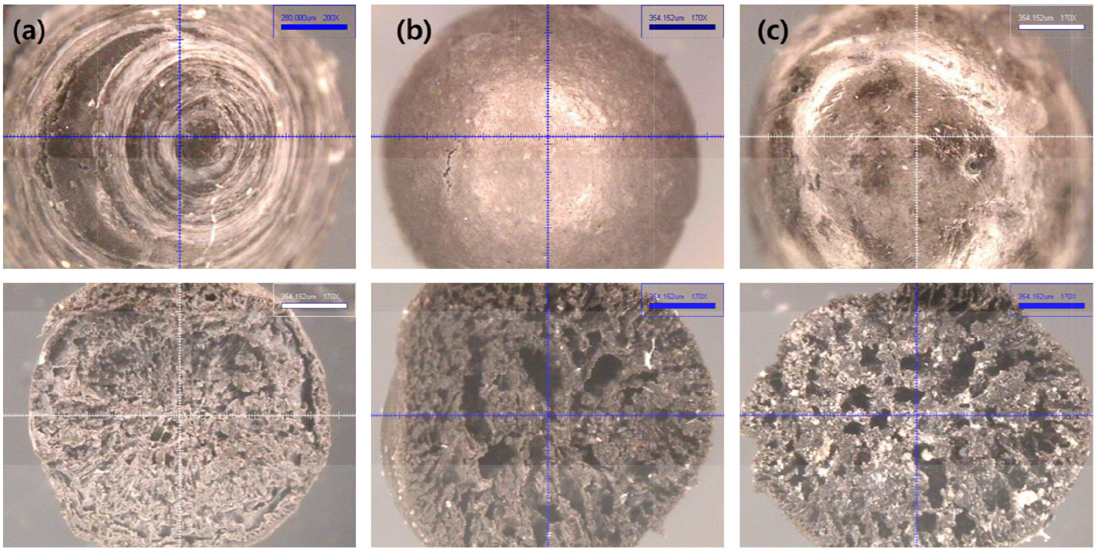

Fig. 4. Microscope images of the PAN/HMnO composite sorbents prepared with different PAN content: (a) 20%, (b) 30%, and (c) 40%.

however, the bead form did not sustain during the sorption experiment and the sorbent leaked out of the column. This is possibly because the PAN content was relatively smaller than HMnO, resulting in beads having a less rigid structure. However, the PAN sorbent with 30% and 40% PAN content retained the bead form. This is possibly because the high amount of PAN completely encapsulated the HMnO particles, and thus, significantly reduced the lithium-ion-removal rate. The differences in the structural and physical properties of the sorbents with different PAN content were confirmed by SEM as well as visual observations.

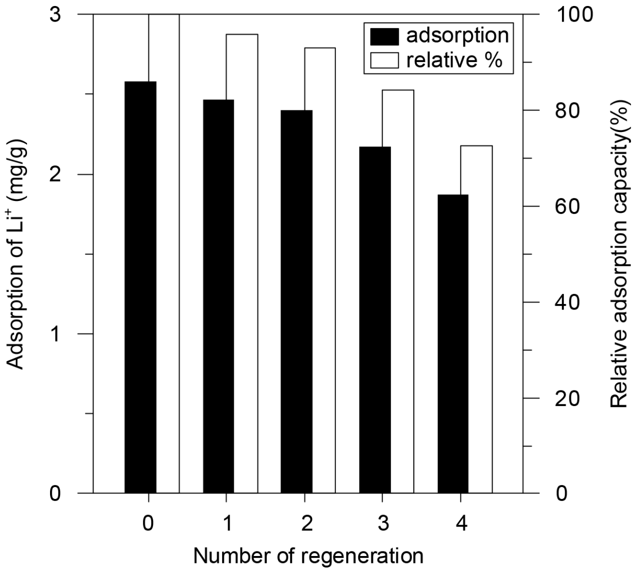

Fig. 6. Regeneration efficiency of HMnO with 30% PAN organic sorbent using 0.5 N HCl for washing.

3.4. Regeneration study

In order to assess the possibility of recycling the sorbent for use in multiple sorption cycles, lithium-desorption experiments were conducted with used organic sorbent of HMnO with 30% PAN content and 0.5 N HCl solution. We found that the lithium desorption values for five successive regeneration cycles were 100, 95, 93, 84, and 72%, respectively (Fig. 6). Fig. 7 shows the microscope images of the organic sorbent HMnO with 30% PAN content for the five successive regeneration cycles. The surface structure of the before and after regeneration of sorbents were little difference. However, the regenerated sorbent exhibited a bit rough surface structure as compared to the virgin sorbent. Although further systematic work is required to optimize the regeneration process, we can conclude that the organic sorbent of HMnO with 30% PAN content can maintain a sorption rate of 70% even as it undergoes 5 successive cycles of desorption using electrolytes like HCl.

3.5. Seawater applicability evaluation

Sorption experiments of organic sorbents were also performed with seawater to evaluate their application. The sample of seawater, which was used to test the collection of lithium, was collected from the Yellow Sea off the coast

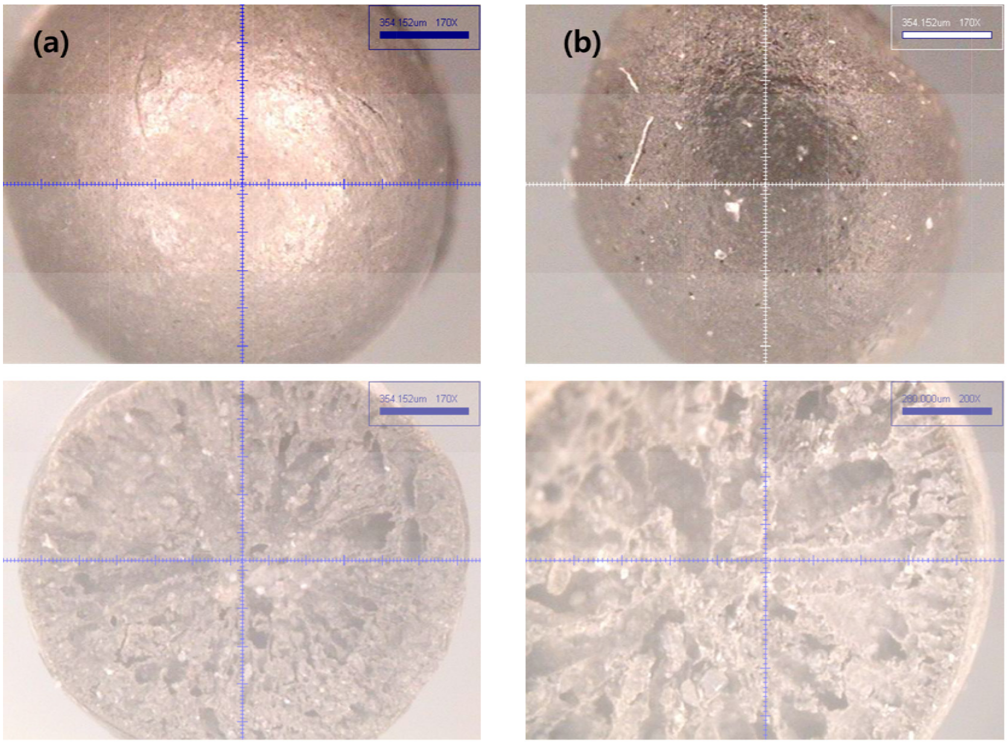

Fig. 7. Microscope images of the organic sorbent HMnO with 30% PAN content (a) after Li⁺ sorption, and (b) after being regenerated five times and treated with 0.5 N HCl.

Table 3
Metal ion uptake by PAN/HMnO sorbent

Metal ion	HMnO		20% PAN		30% PAN		40% PAN		C.S. (mg/dm^3)
	Uptake (mg/g)	C.F. (dm^3/kg)	Uptake (mg/g)	S.E. (%)	Uptake (mg/g)	S.E. (%)	Uptake (mg/g)	S.E. (%)	
Li$^+$	3.12	1836	2.09	66.84	1.57	50.15	1.38	44.06	0.17
Na$^+$	22.5	2.14	17.87	79.54	13.37	59.50	10.49	46.70	10500
K$^+$	2.35	6.18	1.84	78.59	1.15	49.11	1.03	43.92	380
Mg^{2+}	2.90	2.15	1.81	62.45	1.63	56.02	1.43	49.22	1350
Ca^{2+}	4.81	12.03	2.95	61.25	1.41	29.24	1.24	25.69	400

C.F.: concentration factor, S.E.: sorption efficiency by HMnO, C.S.: concentration in seawater, Column Diameter 10 mm, Length 90 mm, Sorbent dose 5.0 g, Superficial velocity 0.15 cm/s, Sorption 3 d

of Korea; it consisted of 0.17 mg/L Li$^+$, 11500 mg/L Na$^+$, 380 mg/L K$^+$, 1410 mg/L Mg^{2+}, and 385 mg/L Ca^{2+}. As shown in Table 3, the sorption rate of lithium by HMnO was 97.3%, and the sorption capability for selectivity of 3.12 mg/g of lithium (Li$^+$) was 0.22 mg/L for 5 g/L of HMnO. The concentration factors (CFs) of Na$^+$, K$^+$, Mg^{2+}, and Ca^{2+} were in the range of 2–12, while that of Li$^+$ was approximately 1000 times greater than that of all the other examined ions.

The sorption capacity of sorbent (HMnO) with 0% PAN content was the highest at 3.12 mg/g, while it was the lowest at 1.38 mg/g for the sorbent having 40% PAN content, which is consistent with the results of its batch sorption. Further, these results revealed that the organic sorbent with 30% PAN content possesses the most effective sorption capacity and the best structure.

4. Conclusions

We developed organic sorbents with HMnO immobilized on PAN for the collection of lithium ions from water. The thermal analysis showed that the HMnO particles combined effectively with PAN. Further, the beads prepared with different PAN content as observed with SEM were spherical in shape with a size of 2 mm, and had a porous structure. The HMnO and PAN organic sorbents attained sorption equilibrium at 48 h. While the sorption rates did not differ significantly with PAN content, the sorption capacity decreased with increasing PAN content. When the PAN organic sorbent was used in seawater, it retained HMnO's high lithium selectivity. The sorption capacity of sorbent with 20% PAN content was higher than of pure HMnO by 88%; however, HMnO could not sustain its bead shape during the sorption experiment. Therefore, the synthesis conditions of the organic sorbent with 30% PAN content were identified as most optimal. We conclude that the PAN organic sorbents with immobilized HMnO are suitable for the recovery of lithium ions from water.

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