Solid phase extraction of lithium ions from water samples using K-birnessite with layer-structure material form (KBRLSM)

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Harun Ciftci & Cigdem Er

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ABSTRACT

Layer-structure materials have attracted considerable interest for the removal, separation, and preconcentration of trace metals in analytical and environmental chemistry. In the present work, we developed a separation and preconcentration method for lithium ions from water samples using K-birnessite with layer-structure material (KBRLSM) form. The experimental parameters that affected the extraction efficiency of the method such as pH, flow rate and volume of the sample solution, concentration of eluent, amount of adsorbent, effect of common matrix ions, and capacity of adsorbent were investigated and optimized. The adsorbed Li ions on KBRLSM were eluted with 5 mL of $1 \, mol \, L^{-1}$ HCl solutions and their concentrations were determined by high resolution-continuum source flame atomic absorption spectrometry. The adsorption isotherm studies indicate that the adsorption of Li ions follows both the Langmuir and Freundlich isotherms. The Langmuir monolayer adsorption capacities (q_{max}) were estimated as $2.77 \, mg \, g^{-1}$. A constant of the energy (K_L) for Li was calculated as $0.35 \, L \, g^{-1}$. The optimum pH value for quantitative sorption of Li ions was found between 5.0 and 7.0. The preconcentration factor was found as 40 for 200 mL aqueous solution containing 5 µg Li ions. The developed method was successfully applied to some water samples.

Keywords: Birnessite; Ion-exchanged birnessite; Adsorption; Separation; Lithium

1. Introduction

Lithium and its compounds have been used in many fields of science and technology such as heat-resistant glass and ceramics, high strength-to-weight alloys used in aircraft, lithium-ion batteries, lubricating greases, pyrotechnics, optics, organic and polymer chemistry, tritium production, and neutron absorber [1]. Recently, alternative resources for lithium have been investigated. Many researches have been investigated for the separation and recovery method of lithium ions from water samples which have an attractive source of this element.

Separation and preconcentration procedures have a very important role for sample preparation, removing process, and inorganic and organic trace analysis in environmental and analytical purposes. Separation procedures based on solid-phase extraction (SPE) have been widely used to remove certain components of the sample, commonly toxic metal ions and/or harmful organic compounds from various samples [2]. A

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number of separation procedures for trace metals involving cloud-point extraction, (SPE), co-precipitation, and solvent extraction have been used in literature [3–5]. Among these preconcentration techniques, SPE is an efficient, sensitive and inexpensive technique to perform removal of metal ions from environmental samples, preconcentration of metal ions for analytical purposes [2].

SPE has some advantages such as rapidity, simplicity, low solvent usage and lower extraction time, higher sensitivity, and lower cost according to classic liquid–liquid extraction methods [6]. Many metal and organic species can be separated when SPE is used with batch or column techniques [7].

Recent tendency in the field of solid phase extraction is related to the synthesis of new sorbent materials [2].

Recently, there are increasing interests to layer-structure materials due to their potential applications such as adsorption, catalysis, ion-sieves, and rechargeable batteries [8–10]. Manganese oxides with layer-structure material forms are interesting materials because of their extremely high selective affinity for lithium ions [11,12]. Birnessite is a layer-structure manganese oxide with edge-sharing MnO_6 octahedra, and has been a subject of intensive investigations due to its ion exchange, sorption, and redox properties. MnO_6 layers of birnessite comprise edge-sharing $Mn(IV)O_6$ octahedral, $Mn(III)O_6$ octahedral and, cation vacancies [13–16]. The vacancies in the structure of birnessite commonly account for the negatively charged layers, partially causing adsorption of heavy metals and other pollutants in contaminated water systems and soils [17].

In the present work, we have developed a separation and preconcentration method for lithium ions from water samples using K-birnessite with layer-structure material (KBRLSM) form. Various experimental and analytical parameters, such as sample solution pH, sample volume, flow rate of sample solution and eluent, volume and concentration of eluent, amount of adsorbent, effect of other ions, and capacity of adsorbent, were investigated. The method was successfully applied to separate the trace amounts of Li from water samples.

2. Experimental

2.1. Apparatus

The analysis was performed by ContrAA 300, a high resolution-continuum source flame atomic absorption spectrometer (HR-CS FAAS) (GLE, Berlin, Germany), equipped with a 50 mm burner head. All absorption lines of elements in the spectral range of 185–900 nm can be analytically evaluated by using a Xe short-arc lamp as a continuum lamp source. The spectral background of the sample in the HR-CS FAAS is always corrected directly on the analysis line simultaneously and independently. All measurements were carried out under optimum conditions in three replicates. All pH measurements were made with an Orion Star (Thermo Fisher, USA) model pH meter. The operating conditions for Li by HR-CS FAAS are given in Table 1.

2.2. Reagents and solutions

All solutions were prepared using ultrapure water (specific resistance 18 MΩ cm) from a Milli-Q purification system (Millipore Corporation, Massachusetts, USA). Standard solutions of analytes were prepared from their 1,000 mg L^{-1} stock solutions (Merck).

All pH adjustments were made using the following buffer solutions: H_3PO_4/NaH_2PO_4 for pH 3, CH_3COOH/CH_3COONa for pH 4–6, $NaHPO_4$/KH_2PO_4 for pH 6–8, and NH_3/NH_4Cl buffer solution for pH 8–10. These buffer solutions were prepared from 1 mol L^{-1} solutions of their components. All glassware was cleaned using ultrapure water, kept in nitric acid for 24 h, and washed again with ultrapure water.

2.3. Synthesis of KBRLSM

KBRLSM was prepared according to the study of Eren et al. [17]. 2.85 g of $Mn(NO_3)_2$ was dissolved in 450 cm^3 distilled water. The 100 cm^3 of a solution containing 1.1 g $KMnO_4$ and 0.8 g KOH was added from a fast-dripping burette. A dark brown to black precipitate was formed immediately and the solution was stirred continuously for 1 h. After stirring, the suspension was settled for 30 min. Then, the excess supernatant was removed and the concentrated suspension was centrifuged and washed several times with distilled water. The KBRLSM was treated with a

Table 1
The operating conditions for HR-CS FAAS

Parameters	Li
Wavelength, nm	670.7845
Flow rate of C_2H_2-air, L h^{-1}	60
Burner height, mm	5
Evaluation pixels, pm	3
Background correction	Simultaneous

Table 2
Effect of type, concentration, and volume of eluent on Li ion recovery

Eluent	Recovery (%)* Li
0.1 mol L^{-1} HCl, 5 mL	74 ± 1
0.5 mol L^{-1} HCl, 5 mL	88 ± 2
1 mol L^{-1} HCl, 5 mL	96 ± 2
1 mol L^{-1} HNO$_3$, 5 mL	90 ± 2

*Results are mean ± standard deviation of three replicate analyses.

1 mol L^{-1} HCl solution for one day at room temperature, washed with distilled water, and dried at 70°C.

2.4. Preparation of separation column

A glass column, which was 10.0 cm in length, 0.8 cm in internal diameter, and had a 250 mL tank on top of the column and a stopcock at the bottom of the column for the adsorption of Li metal ions, was used. A small amount of glass wool was placed on the top and the bottom of the KBRLSM to avoid disturbance during the sample passage. The adsorbent bed height in the column was approximately 1.0 cm. This system was cleaned with water and 1 mol L^{-1} HCl solutions.

2.5. Separation/adsorption procedure

The proposed procedure was tested with model solutions. For the model solution, 2.5 mL of 2.0 mg L^{-1} Li$^+$ solutions and 2 mL of buffer solutions were added to a flask. Then, the final volume was completed to 50 mL by deionized water. The column was preconditioned by passing the aqueous solutions of working pH through column and then, the model solution was passed through the column at a flow rate of 1.5 mL min^{-1}. Afterwards, the column was rinsed with 10 mL of water, and the retained metal ions on the KBRLSM were eluted with 5 mL of 1 mol L^{-1} HCl solutions at a flow rate of 1.0 mL min^{-1}. The metal concentration in the eluate solution was determinated by HR-CS FAAS. The recovery of the analyte was calculated from the ratio of the concentration found by FAAS.

3. Results and discussion

The effects of some experimental parameters such as pH of the sample solution, kind of elution agent, flow rate and volume of the sample, interfering ions, and the amount of KBRLSM were optimized using column procedures.

3.1. Effect of sample solution pH

pH is an important factor for adsorption processes for the purposes of separation and preconcentration. In order to find the optimum pH, the model solution was adjusted to the desired pH with the buffer solution. These solutions were then passed through the column at 1.5 mL min^{-1}. It was found that the maximum recovery of Li$^+$ ions was achieved at pH 5.0–7.0 (Fig. 1). The recovery of Li ions begins to decrease when the solution is over pH 7.0. Hence, pH 7.0 was selected as an optimum pH and NaHPO$_4$/KH$_2$PO$_4$ was used as buffer solutions for the separation of the Li$^+$ ions for further experiments.

3.2. Effect of type, concentration, and volume of eluent

The elution of Li$^+$ ions on KBRLSM was studied by using HCl solution at varying concentrations (0.1–1.0 mol L^{-1}) as a stripping agent. The optimum eluent for Li$^+$ ion was found to be 5 mL of 1 mol L^{-1} HCl solutions (Table 2).

3.3. Effect of sample solution flow rate

The effect of flow rate of sample loading was examined under the optimum conditions. The influences of the sample flow rate on the recovery of the Li$^+$ ions were investigated in the range of 0.2–2.0 mL min^{-1}. The recovery was greater than 95% at a flow rate between 0.2 and 1.5 mL min^{-1} (Fig. 2). However, at a flow rate above 1.5 mL min^{-1}, there was a decrease in the sorption percentage.

3.4. Effect of eluent flow rate

The flow rates of eluent solution (5 mL of 1 mol L^{-1} HCl) were examined in the range of 0.2–2.0 mL min^{-1}
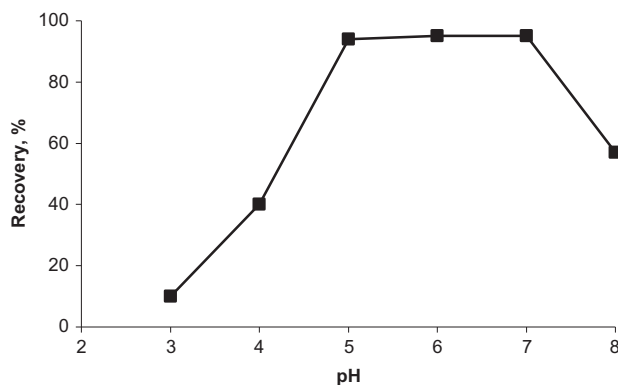

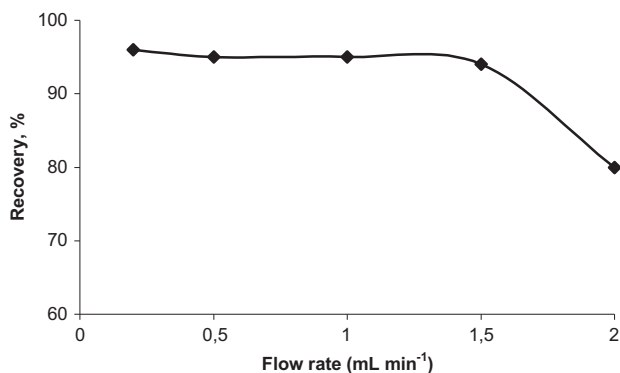Fig. 1. The effect of pH of sample solution on the recovery of Li.

Fig. 2. Effect of flow rate of sample solution on the recovery of Li.

at optimum conditions. The recovery of analyte ions ranged between 95 and 100% at the eluent flow rates varying up to 1.0 mL min^{-1}. To decrease the analysis time, eluent flow rate was selected as 1 mL min^{-1}.

3.5. Effect of sample volume

In order to deal with real samples, especially water samples containing very low concentrations of the metal ions, the maximum applicable sample volume must be obtained. For this purpose, a series of model solutions in the range of 100–500 mL of containing 5.0 μg of Li$^+$ ions was prepared and passed through a column. The recoveries of analyte were quantitative (>95%) for sample volumes up to 200 mL (Fig. 3). Preconcentration factors (PF) were obtained by the following equation: PF = (V_S/V_E), where V_S is the maximum volume of passed solution (200 mL) and V_E is the volume of eluate (5 mL) [18,19]. A maximum PF was found to be 40.
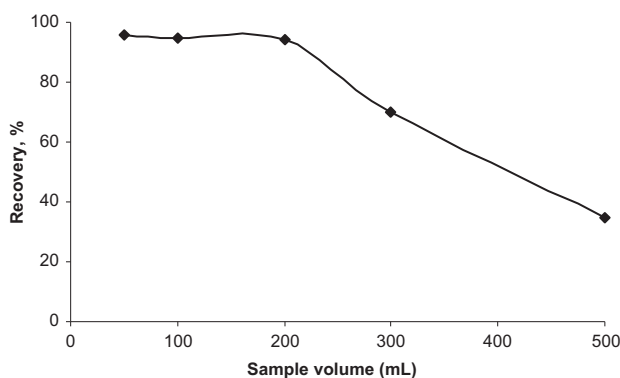
3.6. Effect of KBRLSM amount

The effect of the amount of KBRLSM on recoveries of Li$^+$ was studied. For this purpose, different amounts of sorbent (200–600 mg) were tested into the adsorption column. A 50 mL of model solution including 5 μg of analyte were passed through the column at optimum experimental conditions (pH 7; flow rate 1.5 mL min^{-1}; eluent 5 mL of 1 mol L^{-1} HCl). The results showed that the recovery of the analytes increase up to 300 mg of KBRLSM and remain constant above this value (Fig. 4). Therefore, the minimum sorbent amount for the maximum recovery of Li$^+$ ions was selected as 300 mg for further studies.

3.7. Effect of other ions

Matrix effects are an important problem in the determination of heavy metals by atomic spectroscopic techniques in real samples. Other ions present in the sample solution also affect the retention of the analytes on the sorbent and thus the recovery of them. Therefore, the effects of common coexisting ions on the determination of Li$^+$ ions were investigated. For this purpose, synthetic 50 mL solutions containing 5 μg of Li$^+$ ion and various amounts of possible interfering ions (their nitrate or chloride salts) were used. The results showed that in excess of 1,000 mg L^{-1} of common ions (sodium, calcium, magnesium, chloride, nitrate, bromide, and sulfate) and 10 mg L^{-1} of silver, nickel, copper, zinc, manganate(II), lead(II), cadmium, aluminum and iron(III) and chrome(III) ions had no significant interference on quantitative recovery (>95%) of Li$^+$ ions.

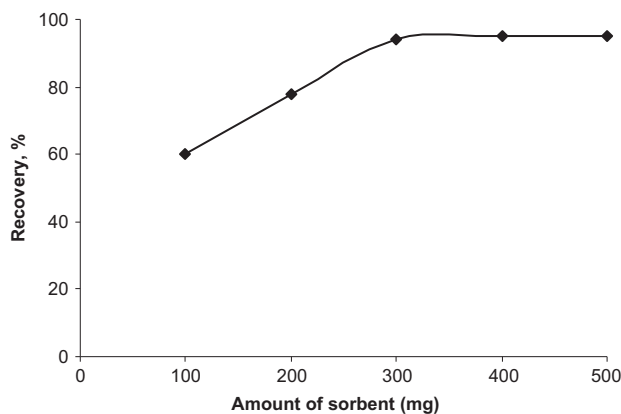Fig. 3. Effect of sample volume on the recovery of Li.

Fig. 4. Effect of sorbent amount on the recovery of Li.

3.8. Capacity of the KBRLSM and adsorption models

Adsorption capacity of KBRLSM was obtained by batch experiments. For this purpose, 50 mg of KBRLSM was added into a 250 mL flask containing 100 mL of model solution which has various concentrations of analyte ions under the optimum experimental conditions. The prepared solutions containing different amount of analytes were shaken for 1 h at 150 rpm at room temperature. Then, 5 mL of supernatant was taken from each solution and the amount of residual Li^+ in the solution was determined using HR-CS FAAS.

There are several isotherm equations available for analyzing experimental adsorption equilibrium data. In this study, the equilibrium experimental data for adsorbed Li^+ ions on KBRLSM were analyzed using the Langmuir and Freundlich models. These isotherms are as follows:

(a) Langmuir isotherm model

The linearized equation form of the Langmuir model used to evaluate maximum metal uptake is expressed by the following equation:

$$C_e/q_e = C_e/q_{max} + 1/K_L q_{max} \qquad (1)$$

where C_e is the final metal concentrations in the solution at equilibrium (mg L^{-1}), q_e is the amount of sorbed metal ions per gram of sorbent at equilibriums (mg g^{-1}), K_L is a constant related to the energy of adsorption/desorption (L g^{-1}), and q_{max} is the maximum adsorption capacity of sorbent (mg g^{-1}).
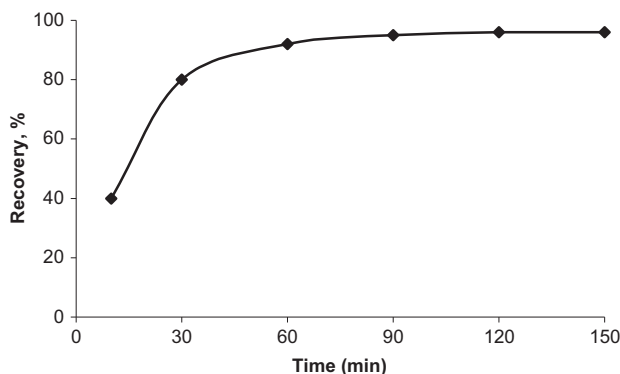
(b) Freundlich isotherm model:

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (2)$$

where K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

Langmuir model had been shown to fit the experimental data well with the correlation coefficients (R^2), 0.9835 for Li ions. The Langmuir monolayer adsorption capacities (q_{max}) were estimated at 2.77 mg g^{-1}. A constant of the energy (K_L) for Li was calculated as 0.35 L g^{-1} (Figs. 5–7). High correlation coefficients indicate that the adsorption of Li on the sorbent comply with the Langmuir adsorption isotherm. This means that the solid surface presents a finite number of identical sites that are genetically uniform, and there are no interactions between the adsorbed species, and a monolayer adsorption is formed when the solid surface reaches saturation [20].

The equilibrium data also fitted to Freundlich equation, a fairly satisfactory empirical isotherm that can be used for non-ideal adsorption. K_F relates the multilayer adsorption capacity to n intensity of adsorption, which varies with the heterogeneity of the adsorbent [21]. A relatively $n \ll 1$ indicates that the adsorption intensity is favorable over the entire range of concentrations studied, while $n > 1$ means that the adsorption intensity is favorable at high concentrations but much less at lower concentrations [22]. The Freundlich adsorption capacity (K_F) was found to be 1.15 (mg$^{(1-1/n)}$ L$^{1/n}$ g^{-1}). In the adsorption system, the n values are calculated as 2.55 from slopes of curves in Fig. 8. Those values indicate that adsorption intensities are favorable at high concentrations.

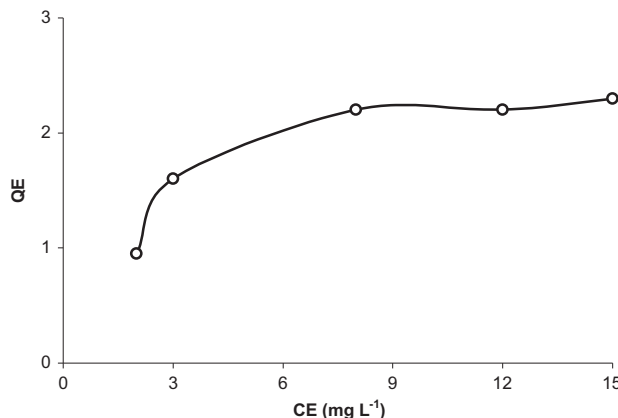Fig. 5. Time course of Li recovery by K-birnessite.

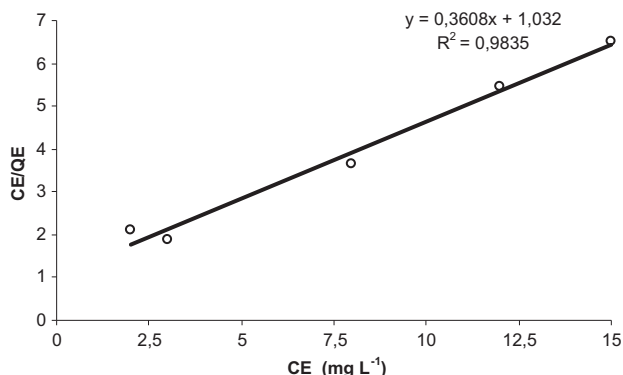Fig. 6. Langmuir isotherm obtained from the Li adsorption on K-birnessite.

Fig. 7. Linearized Langmuir isotherm plot for the adsorption of Li onto K-birnessite.
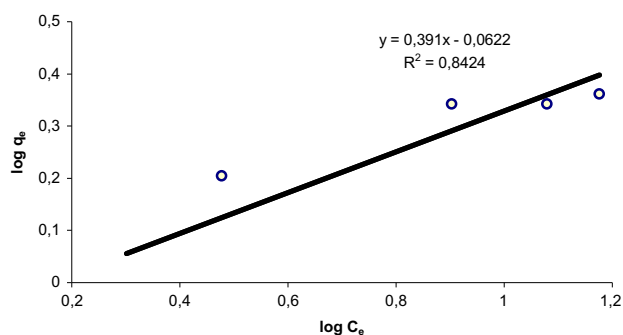

Fig. 8. Freundlich isotherm plot for adsorption of Li onto K-birnessite.

3.9. Reusability of the sorbent

The stability and reusability of the sorbent were evaluated by determining the recovery of the analyte by applying adsorption-elution cycles. One adsorption-elution cycle was considered as follow: the passage of 50 mL of the model solution, 5 mL of eluent solution and 50 mL of deionized water through the column loaded with 300 mg of sorbent, respectively. The adsorbent was always stored in water when it was not in use. The capacities of the adsorbent did not significantly change up to 60 cycles.

3.10. Applications

In order to show the applicability of the method, it was applied for the separation and recovery of Li ions in real samples under optimal experimental conditions. The accuracy of the method was checked by determining the percent relative error of spiked real samples. The results obtained are given in Table 3. A good agreement was obtained between added and found value of the analyte.

Table 3
Application of method for Li ions in water samples

Sample	Added ($\mu g\,L^{-1}$)	Found* ($\mu g\,L^{-1}$)	Relative error (%)
Tap water	0	96 ± 3.6	
	100	202 ± 8.5	3.1
River water	0	128 ± 6.5	
	100	225 ± 12	−1.3
Waste water	0	768 ± 35	
	200	925 ± 42	−4.4
Dam water	0	165 ± 7.6	
	100	260 ± 10	−1.9

*Mean and standard deviation from three determinations.

4. Conclusions

We developed a SPE procedure for the separation and recovery of lithium ions in water samples on KBRLSM form. The developed method provides a simple, accurate, and an economical procedure for separation, removal, and preconcentration of lithium from water samples.

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