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Development of synthetic solid inorganic material as adsorbents of Li and K from the enrichment brine

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ABSTRACT

The disposal concentration from seawater desalination plant has a significant impact on environment, which needs to pay strict attention due to the rapid development of desalination plant. The chemical elements extracted from seawater are very scarce on land such as potassium or very expensive such as lithium. The abstraction selectivity of them as the salt co-products using the synthesis solid inorganic material was tested in the lab. The results show that the technology is feasible to recover lithium as LiCl by ion sieve material (denoted IS-Li) which has good selectivity for lithium ions from the concentrated brine and the adsorption capacity is 25 mg g^{-1}. And there are insignificant effect from the competed ions, although the order of effect on the capacity is K > Ca > Mg > Na. The material (denoted A-K) which obtained from zeolite has good adsorption capacity of potassium of about 20 mg g^{-1} in the condition of mixed concentrated brine, but the maximum adsorption amount decreased due to the effect of other ions. The effect of coexisting ions other than the uptake of lithium is in the order of Na > Ca >Mg. The selectivity of the inorganic material for lithium and potassium and preliminary process design with the seawater desalination were provided in this paper.

Keywords: Brine; Desalination; Lithium; Potassium; Environmental impact; Adsorption

1. Introduction

It has been recognized that seawater desalination can be costly and supplied in large quantity of fresh water, which plays an important role to solve the scarcity of fresh water for human consumption, for industrial and agricultural use. The desalination, which has been well established since the mid twentieth century, is already a means of compensating fresh water resources in many parts of the world, including the Middle East, North Africa, USA and European Union. Recently, expanding desalination capacities can be found in the United States, Europe and China. In 2004, a total of 17,348 desalination units with a total capacity of 37.75 million m^3 of desalted water have been installed in the world. Similarly, 20 new desalination projects are underway in California and will be constructed by 2030 [1–4].

Desalination plants extract large volumes of seawater and discharge hypersaline brine back to the sea, thus have detrimental impact on the environment. Even though the early researches report that the effects of brine disposal from desalination plant on the marine fauna have not been considered due to its insignificance, more researchers appraised that the effect of high concentration brine

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should not be ignored, especially with the rapid development of seawater desalination plants day by day without adequate treatment. Therefore, the sustainability assessment and environmental studies related to desalination technologies are being conducted, most of which are in connection with brine disposal problems [5–8]. At present, the concentrated water from seawater desalination projects is almost poured into sea directly. Although the concentrate contains materials which are originated in the sea, there are high salt concentrations with about double of seawater and will be continue to increase due to the new technology application for higher possible product recovery ratio, higher temperature and turbidity, and some chemicals like biocide, coagulants, anti-scale and inhibition corrosion in the concentration brine. It results the marine environmental pollution, causes the death of fish, alga, and worsens the ecological environment gradually [9–11]. A very important aspect of desalination with respect to both technical and economical performance is the strategy for handling the concentrate process. It obliges researchers and engineers of desalination to take new measures for treating the vast concentrated brine. Some studies are required to ascertain proper discharge to minimize the possible adverse effects on the marine life. The new disposal options such as injection of brine into deep wells to recharge aquifer to prevent regress of seawater inland in the coastal regions is under investigation, or to install longer pipes into the sea for proper dilution of the brine should be done away from the shore, and several injection pumps for spray brine. In addition, the quality of the water in the area should be monitored periodically [12–15]. However, this intake might affect different marine species due to its limitation.

On the other hand, concentrated brine contains vast chemical elements which are very expensive or scarce on land. It casts our eyes along the reuse and recycling of them from concentrated brine. Many researchers reported the recovery of salt co-products from the concentrate of desalination plant or salt lake water by the multi-evaporation process, evaporation pond and separation using extraction and ion exchange technique [16–19]. Some researchers indicated separation is important and the ion-exchange resin is impractical due to the very low efficiency [18]. Synthesis materials used for the extraction of useful metal ions were widely adopted in the literature. The growing number of desalination plants worldwide and the increasing need of metal ions recycling emphasize the necessity for developing newer materials and greener desalination technologies.

The lithium resources play a very important role in the industrial, energy, pharmaceutical and economic sectors. In the last decade, the demand for lithium has been growing for promising use in many fields, such as high-performance batteries [20–22]. Meanwhile, the potassium, which is used mostly as agricultural fertilizer, is very scarce on land, calling for the need of extracting potassium from seawater and saline [16,18]. Based on this, lithium and potassium were selected for extraction in the present study. The adsorbents of lithium and potassium were tested in competition system from common coexisting ions such as Na^+, Ca^{2+} and Mg^{2+} in the laboratory, in order to evaluate the selectivity and feasibility of the lithium and potassium recovery and obtain more information for a new measure to treat concentrated brine in seawater desalination in the future.

2. The material and methods

The adsorbent of lithium (termed as the IS-Li) and adsorbent of potassium (termed as the A-K) were synthesized using the $MnCO_3$-LiOH-HCl and zeolite-Na_2AlO_2-Na_2O-NH_4Cl/NaCl, respectively [23,24]. Powder X-ray diffraction (XRD) analysis was carried out to identify the phase of the samples using a Shimadazu XRD-6000 X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) monochromated by graphite at 40 kV and 30 mA. Infrared spectra were obtained on a Bruker TENSOR 27 FTIR Spectrometer with the KBr method.

The evaluations and tests for the selectivity of adsorption were carried out in the batch system. 0.1 g of adsorbent was added into the pointed mixed solution and shaked for scheming time, the concentration of adsorbate after separation was analysed by the atomic absorption spectrometry. The uptake values were calculated by the change in solution concentration using the equation below:

$$q = \frac{V\left(C_0 - C_f\right)}{W} \tag{1}$$

where q is the uptake of lithium or potassium per unit (mg g^{-1}), C_0 and C_f is the initial and final concentrations of adsorbate (mg l^{-1}), respectively. V is the volume of solution and W is the mass of adsorbent of IS-Li or A-K used (g).

The most common models used for sorption processes are the Langmuir and Freundlich isotherms which is described by Eqs. (2) and (3):

$$q_e = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \tag{2}$$

$$q_e = k {C_{eq}}^{1/n} \tag{3}$$

where q_e is the amount of adsorbed ion per unit weight of adsorbent (mg g^{-1}), q_{max} is the maximum amount of adsorbate per unit weight of adsorbent forming a complete monolayer on the surface (mg g^{-1}) and C_{eq} is the remaining or equilibrium ion concentration in bulk solution (mg l^{-1}). The magnitude of b reflects the slope of the adsorption isotherm, which is a measure of adsorption affinity coefficient (1 mg^{-1}). k and $1/n$ are adsorption constants of Freundlich isotherm, that indicate relative capacity and adsorption intensity, respectively.

3. Results and discussion

3.1. Characteristic of IS-Li and A-K

The materials were prepared by the $MnCO_3$, LiOH and dislithium using HCl solution [23]. Fig. 1(a) shows the XRD patterns of materials of IS-Li. The patterns indicate a face-centered cubic system and spinel structure [23]. The absorption bands at 3317 and 3471 cm^{-1} in Fig. 1(b) are the stretching vibration of hydroxyl groups. The band at 910 cm^{-1}, which could be ascribed to the coupled lattice vibration of protons, suggests the presence of hydroxyl groups in a more ordered state. The bands below 800 cm^{-1} correspond to Mn-O stretching vibrations, its formula is $MnO_2 \cdot 0.5H_2O$ [25,26].

The adsorbents of A-K were prepared by modificating zeolite, Na_2AlO_2 and $NH_4Cl/NaCl$ [24]. The natural zeolite was employed from the Liaoning of China, and the general formula is: $(Na_2, K_2)\ OAl_2O_3\ 10SiO_2\ 8H_2O$. The chemical composition is (in %): SiO_2–67.92; Al_2O_3–12.74; Fe_2O_3–1.78; MgO–0.32; CaO–0.50; Na_2O–5.24; K_2O–0.57; whereby the content of the main mineral is 85 ± 6%. SiO_2, K_2O, CaO and MgO were decreasing and Al_2O_3, Na_2O were increasing in the modification process.

As can be seen from Fig. 2(a), the XRD patterns show that the clinoptilolite zeolite adsorbent of A-K is obtained and the FTIR bands connect with the internal Si-O(Si) and Si-O(Al) vibrations in tetrahedral or alumino- and silico-oxygen bridges lie in the range of 1200–400 cm^{-1} (Fig. 2(b)). The bands due to the presence of zeolite water lie in the range of 1600–3700 cm^{-1}, and the band at 1070 cm^{-1} is ascribed to the asymmetric valence vibrations in SiO_4. The bands at 476 and 617 cm^{-1} are corresponded to the O-Si-O and O-Al-O vibrations (Fig. 2b) [24,27–29].

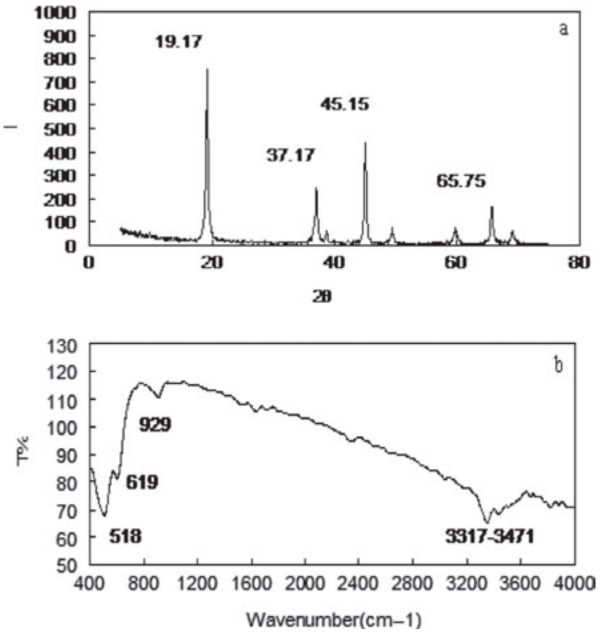

Fig. 1. (a) The XRD pattern and (b) FTIR spectrum of the IS-Li.

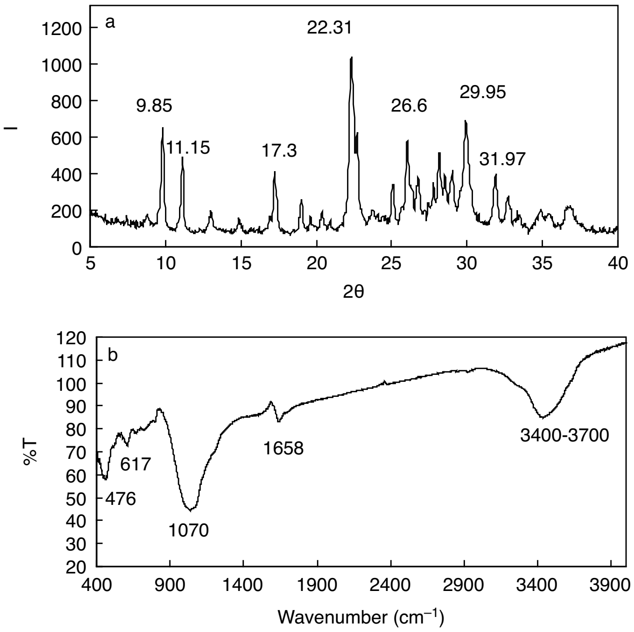

Fig. 2. (a) The XRD pattern and (b) FTIR spectrum of the A-K.

3.2. Results of abstracting lithium by IS-Li

The effects of contact time on the uptake of lithium from the mixed solution (molar ratio of Li:Na:K:Ca:Mg is 1) were tested in a batch reactor. Fig. 3 shows the results of lithium uptake onto IS-Li in the simulated concentration with 10 mg l^{-1} lithium ions, it implies that the IS-Li

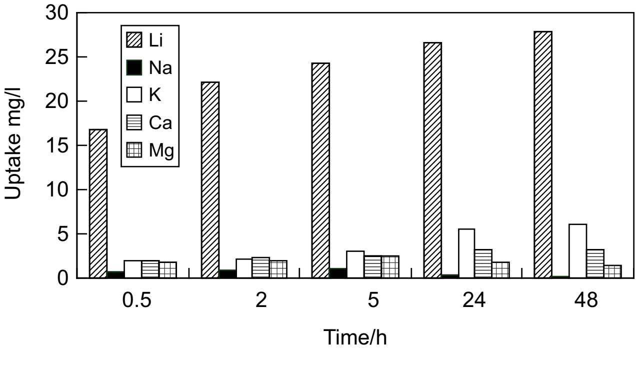

Fig. 3. The results of uptake of lithium versus contact time with coexisting ions.

has good selectivity for the lithium ion and the capacity is over 25 mg g^{-1} and the maximum uptake at contact time keeps 24 h. It also indicates the order of effect on the uptake of lithium ion is K > Ca > Mg > Na.

The result of variety of uptake with different initial concentration of lithium under conditions of mixed solution with TDS kept as 1000 mg l^{-1} and shaked for 12 h is presented in Fig. 4. As can be seen, the uptake increases with the increase of initial lithium concentration, it may attribute to its strong diffusion force at high concentration conditions. The fitting results of Langmuir and Freundlich isotherm are listed in Table 1. It indicates that the Freundlich isotherm fits better than Langmuir isotherm to describe the process of Lithium by the ion sieve, since the correlation coefficient R^2 for Freundlich and Langmuir is 0.995 and 0.410, respectively. It implies the multi-layer adsorption in the surface and physical adsorption is the main pattern.

3.3. Results of abstracting of potassium by A-K

The effects of contact time on the uptake of potassium were measured by the batch reactor in the single system and the result was presented in Fig. 5. The maximum uptake of potassium is observed at 140 min and after 140 min its value shows no further increase with time increasing. It suggests that the equilibrium is achieved when contacting for140 min and the maximum uptake of potassium is about 61.0 mg g^{-1}.

Fig. 6 presents the influence of Na, Ca and Mg on potassium adsorption by A-K from mixed solution for 140 min. It can be seen that the effect of coexisting ions such as sodium, calcium and magnesium ions on the uptake of potassium is different.

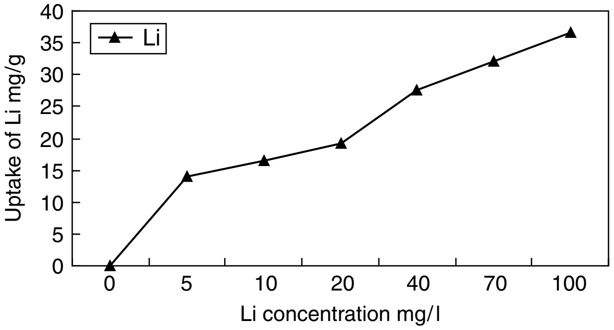

Fig. 4. The uptake of Li versus initial concentration.

Table 1
Fitting parameters of Langmuir and Freundlich isotherm

Freundlich isotherm			Langmuir isotherm		
k (mg g^{-1})	n	R^2	q_e (mg g^{-1})	b (l mg^{-1})	R^2
27.495	2.916	0.995	3.17×10^3	1.428×10^{-4}	0.410

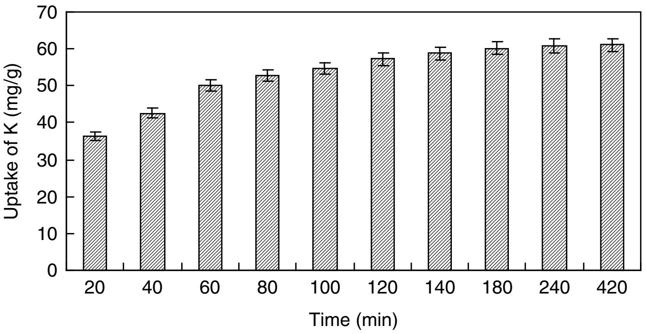

Fig. 5. Effect of contact time on the uptake of potassium.

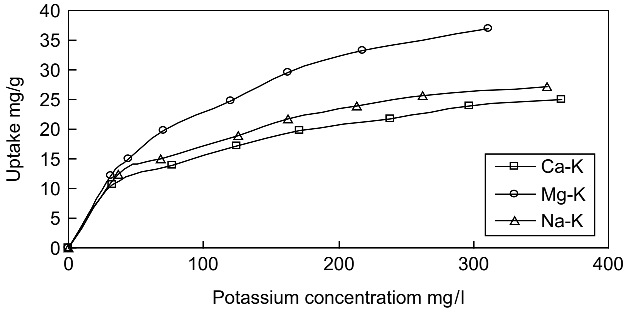

Fig. 6. The influence of coexisting ions on the uptake of potassium.

Table 2 lists the fitting parameters of Langmuir isotherm and Freundlich isotherm. It shows that potassium adsorption onto the adsorbent of A-K in the coexisting ions system obeys the Freundlich isotherm as the correlation coefficient R^2 is 0.998. It indicates the multi-player adsorption in the surface and physical adsorption is the main pattern and the adsorbate–adsorbent interaction is stronger than adsorbate–adsorbate interaction according to the n values ($n > 2$).

Fig. 7 presents the uptake of potassium versus molecule ratio of sodium, calcium and magnesium ions with potassium ions. The results show that the order of effect on the uptake of potassium onto A-K is Na > Ca > Mg. The capacity is decreasing with the concentration of

Table 2
Freundlich and Langmuir isotherm parameters

Item	Freundlich isotherm			Langmuir isotherm		
	k mg g^{-1}	N	R^2	q_e (mg g^{-1})	b (l mg^{-1})	R^2
Ca	2.969	2.749	0.998	4.22×10^3	2.049×10^{-5}	0.52
K-Mg	2.684	2.158	0.998	4.82×10^3	3.15	0.65
K-Na	3.39	2.783	0.996	4.31×10^3	2.34	0.48

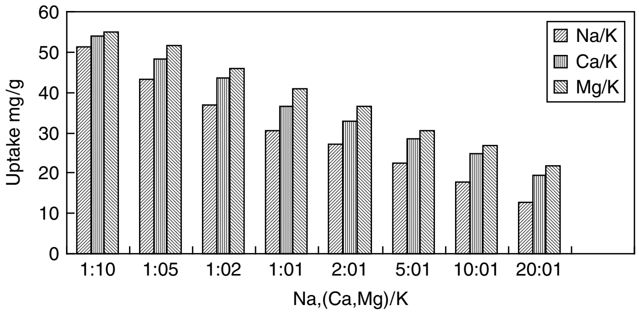

Fig. 7. Influence of main competed ions on adsorption of potassium.

competed metal ions increases, but the minimized level remains close to 20 mg g^{-1}.

3.4. The scheme of adsorption regeneration of lithium and potassium

Although the concentration of lithium is low in the concentrated seawater, the IS-Li that loaded to the column can be reused after being washed with HCl solution, meanwhile, the concentration of LiCl solution is obtained. The repeating loading-regeneration procedures of the adsorbents have been tested and the results are shown in Fig. 8. The adsorption capacity dereases slightly with the increase of reused times. After reusing for five times, the uptake capacity remains 93% of the initial capacity.

Similar to the recovery of lithium, the A-K loaded with potassium ions is washed with HCl or NaCl solution, then the A-K is reused in the adsorption and higher concentration KCl solution is obtained in the elute solution. It is shown that about 95% uptake capacity is achieved after five times used due there are still exist Li^+ and K^+ in recovered materials.

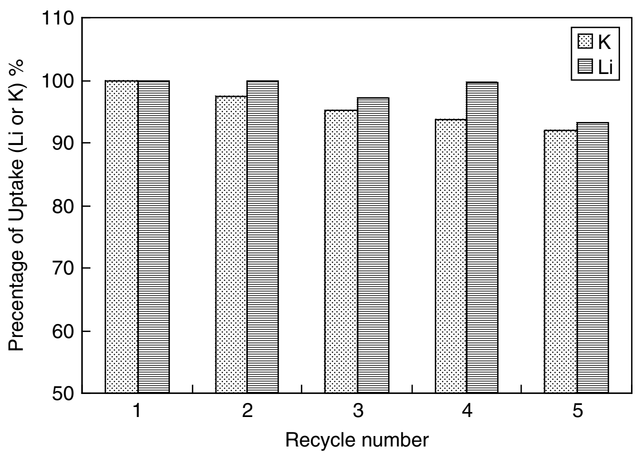

Fig. 8. Relation of reuse times and uptake capacity of lithium and potassium.

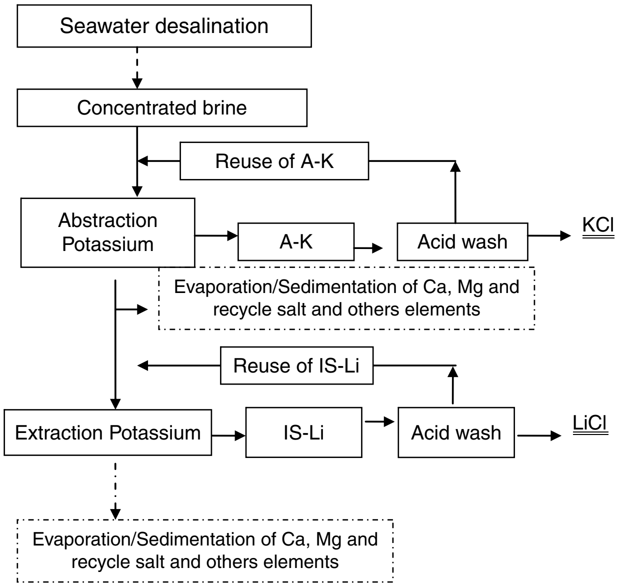

Fig. 9. Scheme of recycle of adsorption for Lithium and Potassium.

As is stated above, the lithium and potassium ions were selected to be separated from the simulated concentrated brine by the solid materials IS-Li and A-K, respectively. Saline solution with higher ion concentration such as lithium chloride (LiCl) and potassium chloride (KCl) were obtained from the regeneration process, the concentration values depend on the ratio of liquid with solid and other operated parameters. The average ratio of liquid of eluation with adsorbent (L/S) was 3:1 in this study and about 700 mg l^{-1} of LiCl and 600 mg l^{-1} KCl were obtained, respectively. The purity of LiCl and KCl is close to 98% and 93%, respectively, even now the reasonable process based on the first investigation combines with the seawater desalination plant as showed in Fig. 9 of LiCl and KCl, for recovery.

In fact, the algae and other organism and microorganism will affect the adsorption behavior and the dynamic parameters. The influence of colloid such as turbidity on the uptake was measured in the lab, the results found that turbidity under 25 NTU was not evident (data not shown here). The consummate of dynamic parameters in the column system, including the organic matter effect on the adsorption and elute process, will provide more useful information for industrial application. The column pilot test will be carried out in the near further, and it will not only reduce the cost, eliminate the impact on the environment but also reasonably establish the new industry base on the seawater desalination plant.

4. Conclusions

The main conclusions can be listed below:

- The IS-Li ion sieve material has excellent selectivity for lithium ions from the concentrated brine and the maximum adsorption amount is 25 mg g^{-1} with the lithium ions concentration of 10 mg l^{-1} and there are insignificant effect from the competed ions, however, the order of effect on the capacity is K > Ca > Mg > Na.
- The clinoptilolite material of A-K which is obtained from nature zeolite has good adsorption capacity for potassium, but the capacity decreased to the half due to the competed ions effect, while close to about 20 mg g^{-1}. The order of effect of coexisting ions is Na > Ca > Mg.
- The lithium and potassium were recycled from concentration brine by the novel inorganic material and it can be regenerated by the acid for reuse.

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