

Modified Phillipsite as a Novel Ion-Exchanger for Potassium Extraction from Seawater

Chunxia MENG^{1,2}, Jin HOU^{1*}

¹ College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

² College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

crossref <http://dx.doi.org/10.5755/j01.ms.25.4.19961>

Received 16 January 2017; accepted 03 May 2018

Template-free preparation of phillipsite as a novel K⁺ ion-exchanger was studied systematically by hydrothermal synthesis. The alkalinity, dosage of water glass, dosage of H₂O, aging time, reaction temperature and time of hydrothermal synthesis were discussed in detail. The optimized material obtained about phillipsite through the synthesis and testing methods was performed. The K⁺ ion-exchange capacity and selectivity coefficient were tested. The molar composition for preparing high performance phillipsite obtained was 2K₂O:18SiO₂:Al₂O₃:510H₂O by optimizing synthetic conditions. The K⁺ ion-exchange capacity of phillipsite was 57.3 mg/g in seawater. The K⁺ selectivity coefficient was 88.6 in an equimolar K⁺ and Na⁺ mixed solution. Phillipsite can selectively capture K⁺ over other ions, and therefore can be used for potassium extraction selectively from seawater. Phillipsite was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The XRD pattern indicated that the synthetic zeolite was phillipsite. The phillipsite particles exhibited cross-like shape and the average particle size was about 2.5 μm. The synthetic phillipsite was mainly consisted of Si, Al, K and O elements.

Keywords: phillipsite, extracting potassium, ion-exchange, template-free, seawater.

1. INTRODUCTION

Zeolites are silicate crystalline materials with regular pore size and structure. They have been applied to ion-exchange, adsorption and catalyst as one of the most important industrial raw materials [1–5]. Ion-exchange is an inherent feature for most of the zeolites. The high ion-exchange capacity and selectivity to certain cations result in their wide application in adsorption and separation industry [6]. Actually phillipsites have been reported about their remarkable selectivities for certain cations. For instance, Colella reported the ion-exchange selectivity of three phillipsites towards Cs and Sr [7]. Pepe studied the mixed phillipsite and chabazite for removing Ba²⁺ by ion-exchange [8].

Potassium is one of the essential nutrient elements for plant growth. Potassium resources are lacking on land, but enormous in seawater. So many public attentions have been gained for potassium extraction from seawater. At present, magnetic zeolite P and zeolite W have been reported as ion-exchangers for extracting potassium from seawater. Cao synthesized a series of magnetic zeolites P and studied the behavior of K⁺ ion-exchange in seawater [9]. We reported the preparation of zeolite W and its K⁺ ion-exchange property in seawater [10].

In this work, phillipsite used as K⁺ ion-exchanger was studied systematically. The alkalinity, dosage of water glass, dosage of H₂O, aging time, temperature and time of hydrothermal synthesis were discussed in detail. The optimal preparation method for high performance phillipsite was obtained by optimizing synthetic

conditions. Phillipsites were characterized by XRD, SEM and EDS.

2. EXPERIMENTAL DETAILS

2.1. Materials

The raw materials used included sodium aluminate (NaAlO₂, Aladdin), water glass (27.8 wt% SiO₂, 8.93 wt% Na₂O, 63.27 wt% H₂O, Dongyue), potassium hydroxide (KOH, Aladdin), ammonium chloride (NH₄Cl, Aladdin) and sodium chloride (NaCl, Aladdin).

2.2. Template-free synthesis of zeolite

Template-free zeolite was synthesized from a synthetic solution by dissolving NaAlO₂ and water glass in de-ionized water firstly, and then KOH solution was added to the mixture. The molar composition of the resulting synthetic gel was as follows: xK₂O:ySiO₂:Al₂O₃:zH₂O. The gel was aged at a variable time at room temperature, and then transferred to a teflon-lined stainless steel autoclave and hydrothermally treated in an oven. Zeolite was recovered after hydrothermal treatment, washed with deionized water and dried at 110 °C. Zeolite was successively modified with 20 wt.% NH₄Cl and 20 wt.% NaCl heated solutions for testing its K⁺ ion-exchange property, and then modified zeolite was obtained.

2.3. The K⁺ ion-exchange equilibrium and ion-exchange capacity of zeolite in seawater

0.30 g modified zeolite was added to 200 mL seawater at room temperature. The concentrations of main cations in seawater were shown in Table 1. The residual K⁺ concentration in the liquid phase was tested by atomic

* Corresponding author. Tel.: +86-532-66782223.
E-mail address: houjinqd@163.com (J. Hou)

absorption spectrophotometer at a variable time. The equation for ion-exchange capacity is as follows:

$$Q_{K^+} = \frac{(c_0 - c) \times V}{m}, \quad (1)$$

where Q_{K^+} stands for the K^+ ion-exchange capacity of zeolite (mg/g); c_0 is the K^+ concentration before ion-exchange (mg/L); c is the K^+ concentration after ion-exchange (mg/L); V represents the volume of seawater (L); m represents the dosages of zeolite (g).

Table 1. Concentrations of main cations in seawater

Ion	Mass concentration, mg·mL ⁻¹	Molar concentration, mmol·L ⁻¹
K ⁺	0.38	9.74
Na ⁺	10.62	461.74
Ca ²⁺	0.40	10.00
Mg ²⁺	1.28	53.33

2.4. The K^+ selectivity coefficient of zeolite in an equimolar K^+ and Na^+ mixed solution

0.30 g modified zeolite was added to 200 mL equimolar K^+ and Na^+ mixed solution stirred continuously at room temperature. The contents of K^+ and Na^+ ions in the above mixed solution are both 10 mmol/L. The concentrations of K^+ and Na^+ ions in the liquid phase were measured by atomic absorption spectrophotometer respectively after the liquid phase and solid phase were separated. Then the selectivity coefficient was calculated.

The ion-exchange selectivity is defined by the following equation:

$$K_t = A_S B_L / B_S A_L, \quad (2)$$

where K_t is the K^+ selectivity coefficient of zeolite; A_S and B_S represent the molar fraction of K^+ and Na^+ in the zeolite phase respectively; A_L and B_L represent the molar fraction of K^+ and Na^+ in the liquid phase respectively.

2.5. Characterization

The structure of synthetic zeolite was identified by X-ray diffraction (XRD, D8-Advance, German Bruker). The image of synthetic zeolite was observed by scanning electron microscopy (SEM, S-4800, Japan Hitachi). Elemental analysis of synthetic zeolite was carried out by energy-dispersive X-ray spectroscopy (EDS, E-max, Japan Hitachi). The cation concentrations were tested by atomic absorption spectrophotometer (AAS, TAS-990, Beijing, China).

3. RESULTS AND DISCUSSION

3.1. The K^+ ion-exchange equilibrium of zeolite in seawater

The K^+ ion-exchange equilibrium curve of zeolite in seawater was tested. The K^+ ion-exchange capacities of zeolite in seawater at different time are shown in Fig. 1. The K^+ ion-exchange rate of zeolite was a fast process and reached an ion-exchange balance in about 20 min. In order to ensure the complete ion-exchange, the ion-exchange time of subsequent experiments was set to 50 min.

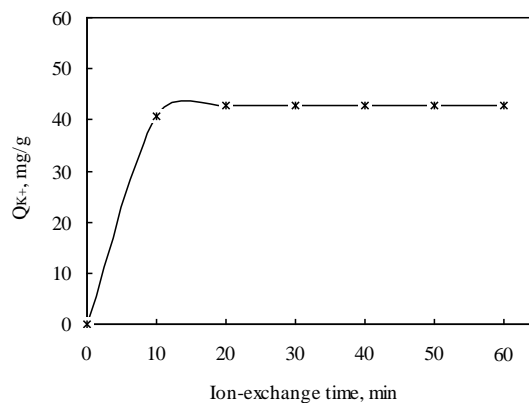


Fig. 1. The K^+ ion-exchange capacity of zeolite at different time in seawater

3.2. The K^+ ion-exchange properties of zeolite in seawater

3.2.1. Effect of K_2O/Al_2O_3 molar ratio

Five groups of experiments with various K_2O/Al_2O_3 molar ratios were completed to test the ion-exchange capacity. The resulting synthetic gel with molar ratio of $xK_2O:18SiO_2:Al_2O_3:570H_2O$ was continuously aged for 10 hours, and then prepared by hydrothermal method at 160 °C for 24 hours. The K^+ ion-exchange capacities of prepared zeolites are shown in Fig. 2. The results showed that the K_2O/Al_2O_3 molar ratio of 2 was an optimum proportion for the K^+ ion-exchange capacity. The maximum value of ion-exchange capacity was 42.8 mg/g. The additive of KOH provided not only an alkaline environment but also excess K^+ ion, which had a significant part in the synthesis of phillipsite.

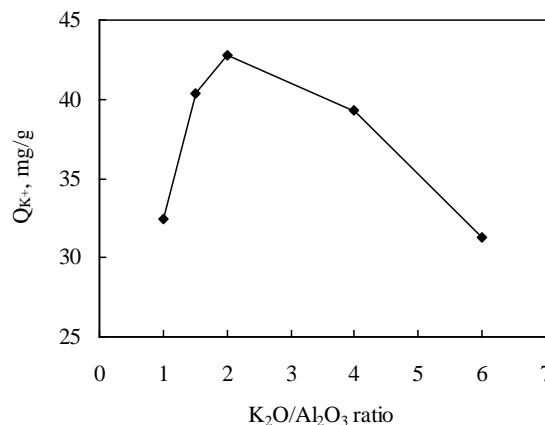


Fig. 2. The influence of K_2O/Al_2O_3 molar ratio on the ion-exchange capacity

3.2.2. Effect of SiO_2/Al_2O_3 molar ratio

Five sets of experiments with various SiO_2/Al_2O_3 molar ratios were completed to test the influence of aluminum dosage on the ion-exchange capacity. The aluminum amount in the zeolite structure was directly proportional to the charge balance material, K^+ amount. Zeolites were gained in the synthetic gel with the molar ratio of $2K_2O:ySiO_2:Al_2O_3:570H_2O$ after aged for 10 hours, and then prepared by hydrothermal method at

160 °C for 24 hours. Fig. 3 shows the K^+ ion-exchange capacities of synthetic zeolite with various SiO_2/Al_2O_3 molar ratios. The results show that the K^+ ion-exchange capacity reached a maximum value when the SiO_2/Al_2O_3 molar ratio is 18. The optimum value of ion-exchange capacity is 42.8 mg/g.

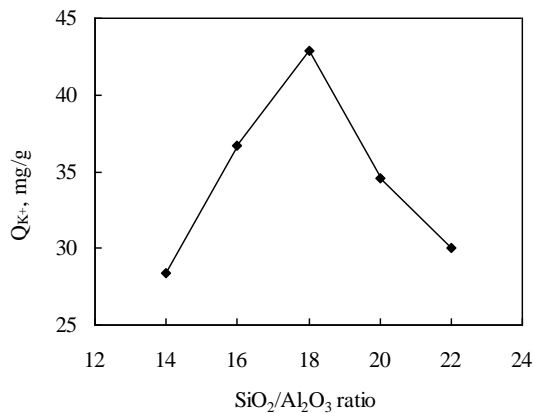


Fig. 3. The influence of SiO_2/Al_2O_3 molar ratio on the ion-exchange capacity

3.2.3. Effect of H_2O/Al_2O_3 molar ratio

Fig. 4 shows the K^+ ion-exchange capacities of zeolites received with various H_2O dosages from $2K_2O:18SiO_2:Al_2O_3:zH_2O$ after aged for 10 hours, and then prepared by hydrothermal method at 160 °C for 24 hours. The results show that the K^+ ion-exchange capacity reached a maximum value when the H_2O/Al_2O_3 molar ratio was 510. The optimum value of ion-exchange capacity was 44.8 mg/g. Kim reported that the less the amount of water, the faster the crystallization process [11]. This indicated that a short distance between nutrients in solution would improve the nucleation and further crystallization. However high concentration normally causes crystal aggregation.

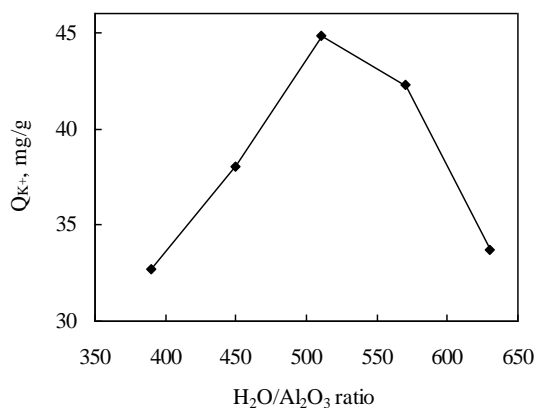


Fig. 4. The influence of H_2O/Al_2O_3 molar ratio on the ion-exchange capacity

3.2.4. Effect of aging time

Fig. 5 shows the K^+ ion-exchange capacities of synthetic zeolite at various aging time. Zeolites were obtained in the synthetic gel with the molar composition of $2K_2O:18SiO_2:Al_2O_3:510H_2O$ after aged, and then prepared

by hydrothermal method at 160 °C for 24 hours. The result shows that the optimum aging time was 14 hours, so the optimum value of ion-exchange capacity was 53.1 mg/g at the above conditions. In general, Aging offers a required time to obtain the generation of crystalline nucleus with dissolution of solid fine particles, which resulted in the generation of smaller crystals. Aging at low temperature accelerated nucleation and rose the amount of crystalline nucleus in the preparation process.

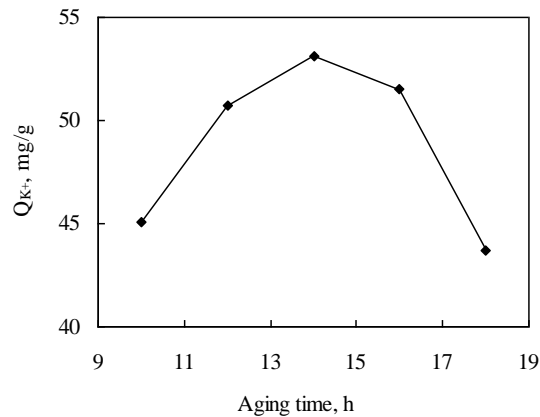


Fig. 5. The influence of various aging time on the ion-exchange capacity

3.2.5. Effect of synthesis temperature

Five groups of experiments at various synthesis temperature were completed to test the ion-exchange capacity. The resulting synthetic gel with molar ratio of $2K_2O:18SiO_2:Al_2O_3:510H_2O$ was continuously aged for 14 hours, and then prepared by hydrothermal method for 24 hours. The K^+ ion-exchange capacities of prepared zeolites are shown in Fig. 6. The results show that the preferred synthetic temperature was 140 °C, and the optimum value of K^+ ion-exchange capacity was 57.3 mg/g. The high temperature could enhance concentration of reactants in synthetic gel and was also propitious to crystallization.

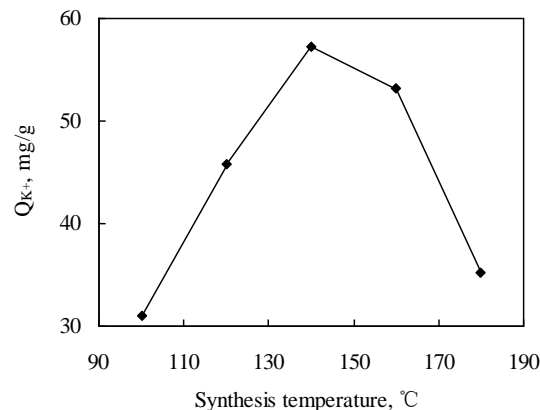


Fig. 6. The influence of various synthetic temperature on the ion-exchange capacity

3.2.6. Effect of synthesis time

Five groups of experiments at various synthesis time were completed to test the ion-exchange capacity. The

resulting synthetic gel with molar ratio of $2K_2O:18SiO_2:Al_2O_3:510H_2O$ was continuously aged for 14 hours, and then prepared by hydrothermal method at $140\text{ }^\circ\text{C}$. The K^+ ion-exchange capacities of prepared zeolites are shown in Fig. 7. The results show that the preferable synthetic time was 24 hours, and the optimum value of K^+ ion-exchange capacity was 57.3 mg/g . However, the ion-exchange capacity of zeolite P reported was 14.8 mg/g [9]. K^+ ion-exchange capacity would reduce when the prepared time was too long or too short. A short prepared time led to incomplete crystal skeleton, and a long prepared time resulted in the formation of large crystal particles.

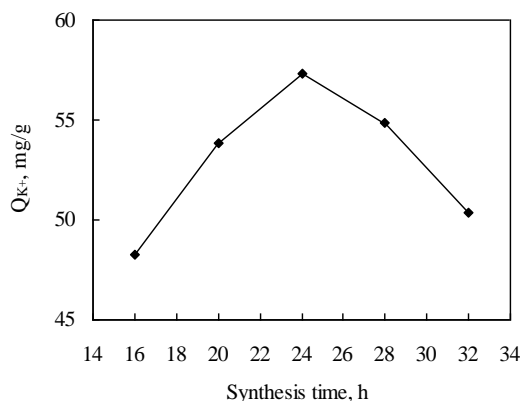


Fig. 7. The influence of different synthesis time on the ion-exchange capacity

3.3. The K^+ selectivity coefficient of zeolite in an equimolar K^+ and Na^+ mixed solution

Zeolite tested was prepared according to the above optimal synthetic conditions, that is, the synthetic gel with the molar ratio of $2K_2O:18SiO_2:Al_2O_3:510H_2O$ was aged for 14 hours at room temperature, and then prepared by hydrothermal method at $140\text{ }^\circ\text{C}$ for 24 hours.

The K^+ selectivity coefficient of the zeolite is 88.6 in an equimolar K^+ and Na^+ mixed solution. So the zeolite can be used for extracting potassium selectively.

3.4. Characterization of zeolite

Zeolite characterized was synthesized according to the above optimal synthetic conditions. The molar ratio of synthetic gel was $2K_2O:18SiO_2:Al_2O_3:510H_2O$, which was aged for 14 hours at room temperature, and then prepared by hydrothermal method at $140\text{ }^\circ\text{C}$ for 24 hours.

The XRD of synthetic zeolite was analyzed. The XRD pattern are shown in Fig. 8. The results indicate that the diffraction peaks ($2\theta = 10.85^\circ, 12.45^\circ, 16.60^\circ, 17.85^\circ, 21.00^\circ, 21.85^\circ, 23.55^\circ, 25.75^\circ, 26.85^\circ, 27.65^\circ, 28.10^\circ, 29.85^\circ, 30.35^\circ, 32.75^\circ$ and 33.50°) correspond to the characteristic peaks of phillipsite [12, 13]. So the synthetic zeolite is phillipsite.

The synthetic phillipsite was tested by SEM. Fig. 9 shows the SEM image for magnification of 10000 times. The morphology of phillipsite particles present cross-like shape. The average particle size is about $2.5\text{ }\mu\text{m}$.

The element compositions of the synthetic phillipsite were analyzed by EDS. The results as shown in Fig. 10 indicate that phillipsite mainly consist of Si, Al, K and O elements. So the chemical constitution of synthetic phillipsite is Si-Al-K aluminosilicate.

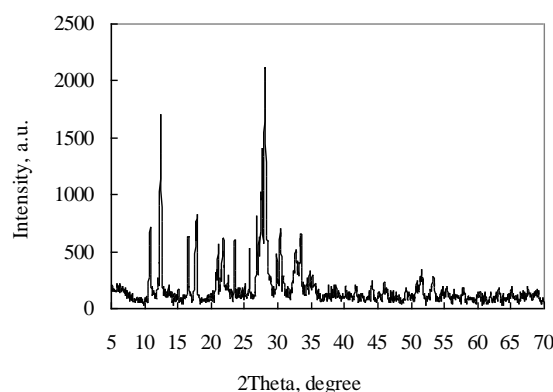


Fig. 8. XRD pattern of synthetic zeolite

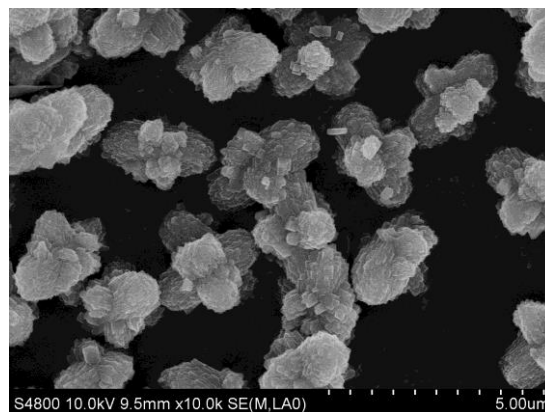


Fig. 9. SEM image of synthetic phillipsite

The element compositions of the synthetic phillipsite were analyzed by EDS. The results as shown in Fig. 10 indicate that phillipsite mainly consist of Si, Al, K and O elements. So the chemical constitution of synthetic phillipsite is Si-Al-K aluminosilicate.

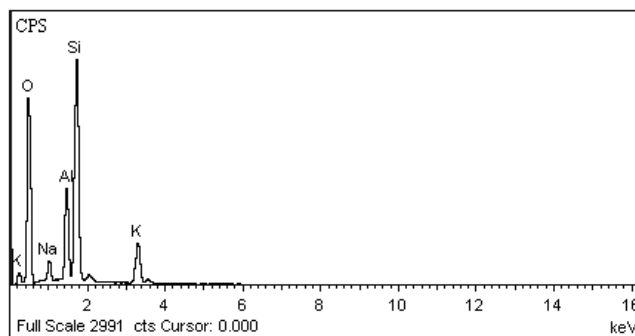


Fig. 10. EDS of synthetic phillipsite

4. CONCLUSIONS

Phillipsite was obtained with high K^+ ion-exchange performance. The optimal synthetic conditions were obtained. The molar ratio of synthetic gel was $2K_2O:18SiO_2:Al_2O_3:510H_2O$, which was aged for 14 hours

at room temperature, and then prepared by hydrothermal method at 140 °C for 24 hours. The K⁺ ion-exchange capacity of phillipsite was 57.3 mg/g, and the K⁺ selectivity coefficient was 88.6 in an equimolar K⁺ and Na⁺ mixed solution at the optimal synthetic conditions. Phillipsite could selectively capture K⁺ ion over other ions. So it could be used for extracting potassium selectively from seawater. The chemical constitution of synthetic phillipsite was Si-Al-K aluminosilicate.

Phillipsite was synthesized through high temperature and hydrothermal synthesis under the alkaline (KOH) environment. The additive of KOH provided not only an alkaline environment but also excess K⁺ ion, which had a significant part in the synthesis of phillipsite. Phillipsite had the memory function for K⁺ ion introduced as a particular target ion in the preparation process, so the synthetic phillipsite had the special selective separation property for K⁺ ion.

Acknowledgments

The authors thank the Natural Science Foundation of Shandong Province (NO. ZR2016BM06) for financial support.

REFERENCES

1. **Jung, D., Lee, S., Na, K.** RuO₂ Supported NaY Zeolite Catalysts: Effect of Preparation Methods on Catalytic Performance During Aerobic Oxidation of Benzyl Alcohol *Solid State Sciences* 72 2017: pp. 150–155. <https://doi.org/10.1016/j.solidstatesciences.2017.08.022>
2. **Lim, J.B., Jo, D.H., Hong, S.B.** Palladium-Exchanged Small-Pore Zeolites with Different Cage Systems as Methane Combustion Catalysts *Applied Catalysis B: Environmental* 219 (15) 2017: pp. 55–162. <https://doi.org/10.1016/j.apcatb.2017.07.032>
3. **Feng, P., Zhang, G.Q., Zang, K.L., Li, X.J., Xu, L.Y., Chen, X.F.** A Theoretical Study on the Selective Adsorption Behavior of Dimethyl Ether and Carbon Monoxide on H-FER Zeolites *Chemical Physics Letters* 684 (16) 2017: pp. 79–284. <https://doi.org/10.1016/j.cplett.2017.07.005>
4. **Hanim, S.A.M., Malek, N.A.N., Ibrahim, Z.** Analyses of Surface Area, Porosity, Silver Release and Antibacterial Activity of Amine-Functionalized, Silver-Exchanged Zeolite NaY *Vacuum* 143 2017: pp. 344–347. <https://doi.org/10.1016/j.vacuum.2017.06.038>
5. **He, Y.H., Lin, H., Dong, Y.B., Wang, L.** Preferable Adsorption of Phosphate Using Lanthanum-Incorporated Porous Zeolite: Characteristics and Mechanism *Applied Surface Science* 426 2017: pp. 995–1004. <https://doi.org/10.1016/j.apsusc.2017.07.272>
6. **Xue, Z.T., Li, Z.L., Ma, J.H., Bai, X., Kang, Y.H., Hao, W.M., Li, R.F.** Effective Removal of Mg²⁺ and Ca²⁺ Ions by Mesoporous LTA Zeolite *Desalination* 341 2014: pp. 10–18. <https://doi.org/10.1016/j.desal.2014.02.025>
7. **Adabbo, M., Caputo, D., de Gennaro, B., Pansini, M., Colella, C.** Ion Exchange Selectivity of Phillipsite for Cs and Sr as a Function of Framework Composition *Microporous and Mesoporous Materials* 28 (2) 1999: pp. 315–324.
8. **Pepe, F., de Gennaro Aprea, B.P., Caputo, D.** Natural Zeolites for Heavy Metals Removal from Aqueous Solutions: Modeling of the Fixed Bed Ba²⁺/Na⁺ Ion-Exchange Process Using a Mixed Phillipsite/Chabazite-Rich Tuff *Chemical Engineering Journal* 219 2013: pp. 37–42. <https://doi.org/10.1016/j.cej.2012.12.075>
9. **Cao, J.L., Liu, X.W., Fu, R., Tan, Z.Y.** Magnetic P Zeolites: Synthesis, Characterization and the Behavior in Potassium Extraction from Seawater *Separation and Purification Technology* 63 (1) 2008: pp. 92–100. <https://doi.org/10.1016/j.seppur.2008.04.015>
10. **Hou, J., Yuan, J.S., Shang, R.** Synthesis and Characterization of Zeolite W and its Ion-Exchange Properties to K⁺ in Seawater *Powder Technology* 226 2012: pp. 222–224. <https://doi.org/10.1016/j.powtec.2012.04.046>
11. **Kim, S.D., Noh, S.H., Seong, K.H., Kim, W.J.** Compositional and Kinetic Study on the Rapid Crystallization of ZSM-5 in the Absence of Organic Template under Stirring *Microporous and Mesoporous Materials* 72 (1–3) 2004: pp. 185–192. <https://doi.org/10.1016/j.micromeso.2004.04.024>
12. **Fukui, K., Katoh, M., Yamamoto, T., Yoshida, H.** Utilization of NaCl for Phillipsite Synthesis from Fly Ash by Hydrothermal Treatment with Microwave Heating *Advanced Powder Technology* 20 (1) 2009: pp. 35–40. <https://doi.org/10.1016/j.apt.2008.10.007>
13. **Rawajfih, Z., Mohammad, H.A., Nsour, N., Ibrahim, K.** Study of Equilibrium and Thermodynamic Adsorption of α -picoline, β -picoline, and γ -picoline by Jordanian Zeolites: Phillipsite and Faujasite *Microporous and Mesoporous Materials* 132 (3) 2010: pp. 401–408. <https://doi.org/10.1016/j.micromeso.2010.03.019>