Journal of Cleaner Production 195 (2018) 821–830

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Investigations of the possibility of lithium acquisition from geothermal water using natural and synthetic zeolites applying poly(acrylic acid)

Małgorzata Wiśniewska [a,*], Gracja Fijałkowska [a], Iwona Ostolska [a], Wojciech Franus [b], Agnieszka Nosal-Wiercińska [c], Barbara Tomaszewska [d], Joanna Goscianska [e], Grzegorz Wójcik [f]

[a] Department of Radiochemistry and Colloid Chemistry, Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland
[b] Department of Geotechnics, Civil Engineering and Architecture Faculty, Lublin University of Technology, Nadbystrzycka Street 40, 20-618 Lublin, Poland
[c] Department of Analytical Chemistry and Instrumental Analysis, Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland
[d] Department of Fossil Fuels, Faculty of Geology, Geophysics and Environmental Protection, AGH - University of Science and Technology, Mickiewicza 30 Av., 30-059 Kraków, Poland
[e] Laboratory of Applied Chemistry, Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska Street 89b, 61-614 Poznań, Poland
[f] Department of Inorganic Chemistry, Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland

ARTICLE INFO

Article history:
Received 26 October 2017
Accepted 31 May 2018
Available online 1 June 2018

Keywords:
Zeolites
Clinoptilolite
Lithium recovery
Geothermal water
poly(acrylic acid)

ABSTRACT

The purpose of the paper was to investigate the possibility of obtaining lithium from geothermal water using natural and synthetic zeolites applying poly(acrylic acid). The efficiency of lithium ion sorption was determined depending on the type of tested zeolite, pH of the solution and the presence of anionic poly(acrylic acid). It was shown that the adsorption amount on the surface of aluminosilicates depends on their structure (size of specific surface area and porosity). Moreover, it was proved that the amount of adsorbed lithium ions increases with the increasing pH value of the solution. This is due to an increase in the concentration of negatively charged groups on the zeolite surface that capture the lithium cations from the solution effectively. In general, the addition of anionic polymer increases lithium ions sorption from the LiCl solution at pH 9, at which about 100% recovery of Li cations by Na-X zeolite was obtained. Under these conditions the poly(acrylic acid) carboxyl groups are completely dissociated which guarantees effective formation of polymer-metal complexes and results in the increase of amount of adsorbed lithium ions. The important parameter affecting lithium ions sorption amount is the order of adsorbates addition to the system since the polymer adsorption modifies surface properties of the solid thus influencing the ion exchange process of metal cations. The maximum recovery of lithium cations from geothermal water (at the natural pH 5.5) was obtained in the system containing natural clinoptilolite and anionic polymer. It amounted to almost 5 mg/L (with the initial content of Li^+ ions in water about 10 mg/L).

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Lithium is a chemical element belonging to the alkali metal group. It is the lightest metal with high reactivity that is why it does not occur in the free state in nature. This element is used in many areas e.g. as an additive for metal alloys and pyrotechnic materials, a catalyst or a component of drugs affecting the central nervous system (Krebs, 1990; Chałupnik et al., 2013; Martinez and Corma, 2011; Schou, 1957; Guzetta et al., 2007; Gelenberg et al., 1989).

Nowadays lithium plays a major role in industry as “a chemical source of electricity” because it is used in the production of lithium ion batteries characterized by high energy density and low weight (Molenda, 2006; Bruce et al., 2008; Languang et al., 2013). Due to this fact they are used in a variety of devices or as a power source in

* Corresponding author.
E-mail address: wisniewska@hektor.umcs.lublin.pl (M. Wiśniewska).

https://doi.org/10.1016/j.jclepro.2018.05.287
0959-6526/© 2018 Elsevier Ltd. All rights reserved.

electric cars. Because of intensive technology development, demand and utilization of lithium increase year by year up to 10% (Park, 2012).

Lithium is relatively widely distributed in nature because it is a constituent of igneous rocks and minerals. This element also occurs in salt lakes, underground brine deposits or sea water. Only a few of these natural formations can be an industrial source of lithium because they mostly form too small deposits or the lithium ions content is too small (in the sea water, in which the content of Li^+ is the highest, its concentration is only 1 mg/L) (Keslera et al., 2012; Schwochau, 2005).

At present the most popular method of lithium acquisition is brine evaporation in which it is pumped out of aquifers located beneath the surface of Earth crust into special tanks. After a few months a concentrated mineral containing lithium remains on the reservoir bottom as a result of water evaporation due to the sunlight. This method is only cost-effective in the regions where brine deposits occur naturally and rainfalls are very small (Garrett, 2004).

The lithium recovery process from ores (lepidolite, spodumene, petalite, amblygonite) is accomplished by the use of the following methods: hydro- and pyro-metallurgy, pressure leaching and bioleaching (Swain, 2017). On the other hand, the most important methods for Li acquisition from brine are: precipitation, chromatography, ion-exchange, liquid-liquid extraction (also using ionic liquids) and membrane processes. Recovery from the sea water includes co-precipitation, ion-exchange, liquid-liquid extraction, membrane processes and also sorption using different natural and synthetic sorbents. The combined techniques are recently developed to increase the efficiency of lithium acquisition from aqueous solutions. For example, new electrodialysis combined with the polar membrane system was developed to separate lithium ions (Bunani et al., 2017a, 2017b). The hybrid capacitive deionization mode was used for selective extraction of lithium ions from water (Siekierka et al., 2018). The lithium selective cathode and activated carbon anode coated with the anion-exchange membrane were used. Suzuki et al. (2017) applied displacement chromatography using the synthesized cation exchange resin with 50% cross-linkage for lithium removal from solution.

It was observed that the concentration of lithium ions near the geothermal sources is higher than in the sea water reaching 16 mg/L (Siekierka et al., 2018). Geothermal fluids may contain high levels of arsenic, mercury, lithium and boron because of the underground contact between the hot fluids and rocks (Kabay et al., 2018; Tomaszewska et al., 2017a, b). In the future geothermal waters can be analyzed as a source of clean energy and at the same time they become a potential source of Li (Tomaszewska and Szczepański, 2014). They wash out lithium present in the minerals while penetrating the Earth surface. This element can be recovered by filtration or adsorption using such adsorbents as zeolites.

Zeolites are porous sorption materials which form a group of crystalline aluminosilicates containing a network of channels and pores of different sizes. This microporous structure endows zeolites with some specific properties e.g. well-developed surface area, molecular-sieve activity and ion-exchange ability. For this reason both natural and synthetic zeolites are used as adsorbents. Furthermore, their price is low and they are readily accessible. Synthetic zeolites can be obtained from waste materials such as fly ashes (Franus, 2012; Wdowin et al., 2014; Franus and Wdowin, 2010; Bandura et al., 2016, 2017; Kołodyńska et al., 2017,).

The use of zeolites as sorption materials in lithium extraction from geothermal water is beneficial for the environment and can be a faster and cheaper alternative to traditional mining and brine methods.

Owing to the capability of using geothermal water as a potential source of microelements such as Li, the purpose of this study was to investigate the possibilities of its recovery from geothermal water using natural and synthetic zeolites. The effect of zeolite type, solution pH value and the addition of poly(acrylic acid) on the amount of adsorbed lithium was also determined.

Poly(acrylic acid) - PAA was chosen for the experiments because its macromolecules adsorbed on the zeolite surface can capture lithium ions effectively from geothermal water. This results from its specific structure, each segment contains the functional carboxyl group. The dissociation degree of these groups is dependent on solution pH. With the pH increase, polymeric chains gain more and more negative charge. For this reason a single molecule of PAA with the molecular weight 240 000 Da (composed of 5455 segments and also containing 5455 carboxyl groups) adsorbed on the unit of the solid surface can bind a significantly larger number of lithium ions compared to the zeolite surface not covered with the polymer. Such possibility is caused by the specific conformation of adsorbed PAA macromolecules which can be spatially developed towards the solution consuming only a few adsorption sites on the solid surface. In addition, poly(acrylic acid) is non-toxic and is characterized by good biodegrability which does not burden the natural environment.

2. Materials and methods

2.1. Zeolite preparation and characterization

Natural clinoptilolite was obtained from the zeolite tuffs located in the Sokyrnytsya Mine in the Transcarpathian area of Ukraine. Synthetic Na-X zeolite was prepared on a semi-technical scale using a prototype installation for the synthesis of zeolites from fly ash (Fig. 1). For this purpose 10 kg of fly ash was mixed with 25 L of NaOH solution of the concentration 3 moL/L. The reaction time was 48 h and the reaction temperature was 80 °C (Wdowin et al., 2014). Surface properties and elemental composition of zeolites were determined by the BET method (Micromeritics ASAP, 2020 analyzer) and the XRF technique (Panalytical ED-XRF type Epsilon 3 spectrometer), respectively. The obtained results are presented in Table 1. The XRD method (Panalytical X'PERT PRO MPD) was applied for determination of crystalline structure of zeolites studied (Fig. 2). Additionally, the SEM technique (FEI Quanta 250 FEG) enabled determination of surface morphology of the examined solids (Fig. 3).

2.2. Geothermal water characterization

Geothermal water from the natural geothermal sources of Rabka Zdrój (southern part of Poland) was used in the study. As for the geological conditioning, Rabka Zdrój is situated in the area of the Magura Nappe composed of sandstone-shale, Cretaceous-Paleogene flysch (Ciężkowski et al., 2010). This is a large complex where geothermal and curing waters have been exploited for several years. Currently Rabka Zdrój has nine working exploitation boreholes where the lithium composition varies from 10 to 16 mg/L. Similar geothermal water was discovered in the Poręba Wielka village, situated 6 km from Rabka Zdrój.

Using the XRF method, its elemental composition was determined (Table 2). Measurements were performed before and after the water filtration. However, no apparent differences in the elemental composition were observed. The Li content in water was determined using an ICP-OES spectrometer, due to the fact that the XRF method cannot be applied to determine its concentration. The lithium content was about 10 mg/L.

In order to take into account Na ions co-adsorption (Table 3),

Download English Version:

https://daneshyari.com/en/article/8094276

Download Persian Version:

https://daneshyari.com/article/8094276

Daneshyari.com