Chemical Bulletin of "Politehnica" University of Timisoara, ROMANIA
Series of Chemistry and Environmental Engineering
Chem. Bull. "POLITEHNICA" Univ. (Timisoara) *Volume 58(72), 1, 2013*

Use of Magnesium Silicate Functionalized with Dibenzo-18-Crown-6 for Environmental Protection

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Abstract: In this present paper the removal of Sr(II), Tl(III), Cs(I), Nd(III), Eu(III), La(III) through adsorption was studied. The adsorption occurred on a solid support (magnesium silicate) functionalized with dibenzo-18-crown-6. The obtained material was characterized by SEM and EDX. On the adsorption process the equilibrium adsorption capacity, the influence of the contact time on the adsorption capacity and on the separation efficiency were investigated.

Keywords: magnesium silicate, crown ether, removal, adsorption

1. Introduction

Separation of metals from different sources of water is a worldwide problematic. Different techniques have been developed for specific metals and water pollution. An advanced technique for metal separation and removal is the adsorption.

Many new adsorbent materials are investigated in order to find the best material for the removal or separation of a specific substance. Mostly for the adsorption process a solid support is functionalized with an extractant to achieve better adsorption proprieties. As solid supports substances with high specific areas, narrow pore size distribution range and high porosity such as silica or magnesium silicate are chosen.

Crown ether is a widely used extractant for functionalization of solid supports because it is an ion-selective reagent and is can form complexes with positive ions [1-5]. Because of this property crown ethers are used as efficient extractants. The efficiency is also given by the good match between the cavity of the crown ether and the ionic radius of the metal ion [6].

Lanthanum, neodymium and europium are part of the rare earth elements (REE) and have unique proprieties and wide applicability such as in metallurgy, ceramic industry and nuclear fuel industry [7].

Cesium and strontium are find in radioactive liquid waste. It is important to separate them from radioactive liquid waste because they are harmful for vitrification and for the final geological storage [8, 9].

Thallium is a rare element distributed in almost all natural environments. Thallium and its compounds are used in numerous industries such as ceramic semiconductors, alloys and electronic devices. Thallium is a highly toxic element than conventional heavy metals for the human body [10].

This study reveals the adsorption of metal ions (Sr(II), Tl(III), Cs(I), Nd(III), Eu(III), La(III)) on magnesium silicate functionalized with crown ether (dibenzo-18-crown-6). By the separation of these metal ions through adsorption the equilibrium concentration was established and the influence of the contact time on the adsorption capacity and on the separation efficiency was studied.

2. Experimental

Magnesium silicate was used as solid support and was functionalized with crown ether (dibenzo-18-crown-6) using the dry method. 0.01 g crown ether dissolved in 25 mL ethyl alcohol were added over 5 g magnesium silicate and kept in contact for 24 hours. After that it was dried at 323 K for another 24 h.

The functionalized material was characterized by energy dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM), using a scanning electron microscope Quanta FEG 250, equipped with energy dispersive X-ray quantifier (EDAX ZAF).

In order to make the adsorption experiments and establish the equilibrium concentration of the functionalized solid support for each metal, the initial concentration of the metal solution was varied (10, 50, 100, 150, 200 mg/L). For this a stock solutions of the concentration 1g/L of each metal (Sr(II), Tl(III), Cs(I), Nd(III), Eu(III), La(III)) was used. Solutions of each metal having concentrations of 10, 50, 100, 150, 200 mg/L were prepared by dilution. 25 mL of these obtained solution were mixt with 0.1 g functionalized solid support for one hour using a Julabo SW23 mechanical shaker bath at 200 rot/min and 298 K. After mixing the samples were filtered and analysed using an inductively coupled plasma mass spectrometry ICP-MS Bruker Aurora M90.

For studying the influence of the contact time 0.1 g functionalized material was put in contact with 25 mL 10mg/L solution for each metal and shaked for 120 minutes. After 15, 30, 60, 90, 120 minutes samples were taken, filtrated and the concentration of metal ions analysed.

3. Results and Discussion

3.1. Characterisation of the functionalized solid support

After functionalization of the magnesium silicate, the material was analysed by SEM and EDX in order verify if the functionalization occurred. Fig. 1 presents the morphology of the obtained material. It can be observed that white spots are situated on the surface of the solid support. These are associated to the soft crown ether used for functionalization.

The presents of the used extractant is also highlighted by the EDX spectrum presented in Fig. 2. Beside of the elements of the solid support Si, Mg, specific elements for the crown ether as C are present.

Figure 1. SEM image of the functionalized material

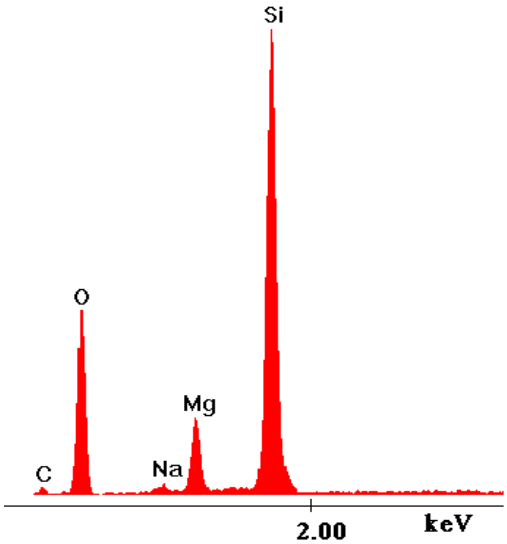

Figure 2. EDX spectrum of the functionalized material

3.2. Influence of the initial metal concentration and contact time

The experimental data regarding the influence of the initial metal concentrations over the adsorption capacity of the obtained material is shown in Fig. 3. By increasing the initial concentration, the equilibrium concentration increases and this leads to the increase of the adsorption capacity of the obtained material in the adsorption process of the metal ions Sr(II), Tl(III), Cs(I), Nd(III), Eu(III), La(III) until it reaches a constant value at the equilibrium concentration.

The adsorption capacity was calculated using the following equation:

$$q = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

where C_0 is the initial metal concentration (mg/L), C_t the equilibrium concentration of the metal solution at time t (mg/L), V is the volume of metal solution (L), m is the amount of solid support (g).

In the adsorption process of different metal ions on the obtained functionalized solid support high adsorption capacities were registered for Eu(III) 12.5 mg/g, Nd(III) 12.46 mg/g and La(III) 11.45 mg/g, respectively and lower capacities for Sr(II) 6.23 mg/g, Cs(I) 5.75 mg/g, Tl(III) 4.73 mg/g respectively. For all studied metal ions the material reached the equilibrium concentration at about 100 mg/L.

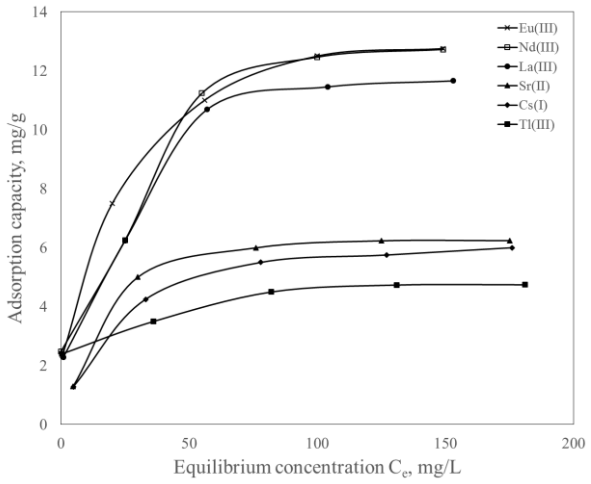

Figure 3. Adsorption isotherm of the metal ions on the obtained material

The influence of the contact time on the adsorption capacity of the obtained material and on the separation efficiency of the adsorption process was also studied. Fig. 4 and Fig. 5 show the influence of the contact time on the adsorption capacity and on the separation efficiency. The equilibrium adsorption capacity is reached after increasing with the contact time in about 60 minutes. The separation efficiency reaches the maximum point also after 60 minutes. The highest efficiencies are obtained for Nd(III), Tl(III), Eu(III), La(III) 95% and the lowest are for Sr(II) and Cs(I) 50%.

The efficiency was calculated using the following formula:

$$\eta = \frac{(C_0 - C_t)}{C_0} 100 \qquad (2)$$

where C_0 is the initial metal concentration (mg/L), C_t the equilibrium concentration of the metal solution at time t (mg/L).

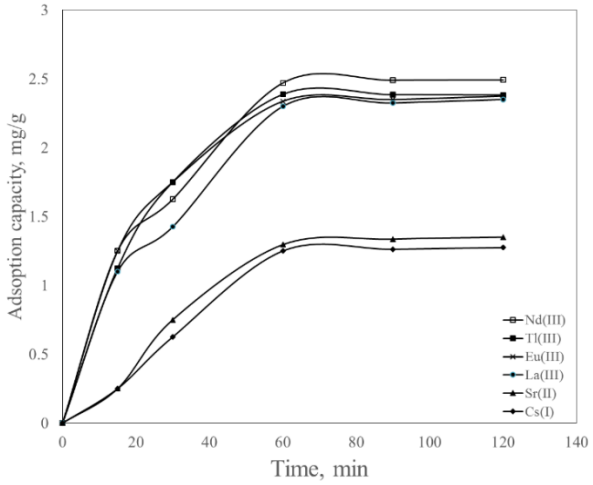

Figure 4. Influence of the contact time on the adsorption capacity of the adsorption process

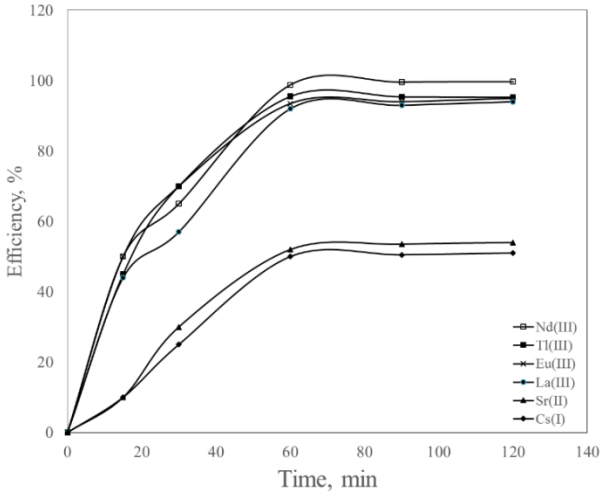

Figure 5. Influence of the contact time on the separation efficiency of the adsorption process

4. Conclusions

The solid support magnesium silicate was functionalized with divbenzo-18-crown-6 using the dry method. The SEM and EDX analysed effectuated on the adsorbent material revealed a successful functionalization. The obtained material was used in the adsorption process of Sr(II), Tl(III), Cs(I), Nd(III), Eu(III), La(III) metal ions. The highest adsorption capacity was obtained for Eu(III) 12.5 mg/g, Nd(III) 12.46 mg/g and La(III) 11.45 mg/g and the highest separation efficiency for Nd(III), Tl(III), Eu(III), La(III) 95%. The adsorption equilibrium capacity as well as the separation efficiency reached the maximum value after 60 minutes.

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Received: 16 May 2013
Accepted: 24 June 2013