Equilibrium Studies for Crown Ether Impregnated Solid Support Used in the Removal Process of Nd(III), La(III), Sr(II), Tl(I), Eu(III)

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In this paper, the equilibrium adsorption capacities of styrene-divinylbenzene copolymer, grafted with aminophosphonic groups and impregnated with dibenzo-18-crown-6 in the removal process of Nd(III), La(III), Sr(II), Tl(I), Eu(III) from aqueous solution were determined. The obtained material was characterized with Fourier Transform Infrared spectroscopy. The experimental data was fitted to three adsorption models: Langmuir, Freundlich, and Temkin. The Langmuir model best described the adsorption process of the metals used. The highest adsorption capacity was obtained for Eu(III) 2.30 mg/g and the lowest for Sr(II) 0.90 mg/g. The other capacities were situated slightly under the maximum capacity.

Keywords: adsorption, crown ether, impregnation, isotherms

IUPAC defines the fifteen lanthanides plus scandium and yttrium as rare earth elements (REE). These have a wide application in different fields such as: industry, medicine and agriculture. Through their extensive use they have become pollutants of soils, the hydrosphere and the biosphere [1]. Lanthanum, neodymium, europium are three of these REE. Lanthanum(III) is one of the reactive elements and is used in super alloys, catalysts, special ceramics and in organic synthesis. The effluent origin from the industries where lanthanum is used as semi- conductor, in ceramic industries, chemical engineering, electronics and electrooptics, biomedicine has often a high metal concentration [2-4]. Lanthanum is also used in manufacturing special lenses because of it is special optical qualities. Together with fluorine and oxygen, lanthanum is used in the motion pictures industry for making of carbon arc lamps [5]. Neodymium is widely used in *syntered Nd-Fe-B permanent magnetic materia*l but also for the electronic instruments and by manufacturing laser equipment's [1].

Europium is used in optoelectronic devices and only the trivalent oxidation state is stabile in water [6, 7]. Strontium appears in nature in the earth's crust an in the sea water. Only the natural minerals strontianite (strontium carbonate) and celestite (strontium sulfate) are used in industries. Strontium in form of strontium carbonate is used for manufacturing of X-ray absorbing glass, in the removal of lead from zinc sulfate solutions. It is also used in certain optical material and in pyrotechnic. The toxicity of strontium is related to the anion forming compound [8]. Strontium can be also radioactive. $_{90}$Sr is considerate to be dangerous because of its long half-life of 28 years. Over long term radiation it can be retained by the human body or other lives [9]. Thallium is a rare metal and it is distributed in all environmental media. It appears in the continental and oceanic crust. Thallium is used for manufacturing imitation of jewelry, thermometers, semiconductor, alloys and electronic devices [10, 11]. It was also used as insecticide because of it is highly toxicity. Thallium exists in two oxidation stats Tl(I), Tl(II) in water, where Tl(I) is more toxic because of its higher solubility of its compounds and therefor it can be easily transported in aqueous mediums. For humans thallium is very harmful because it can displace potassium from bodily fluids [12, 13]. All these studied elements have a negative effect on the environment and on the human health in time. Different technics have been used to remove metals ions from aqueous solutions such as solvent extraction, ion exchange, solid-phase extraction. One of the best methods to remove substances from water is the adsorption due to its cost and operation simplicity. The adsorption takes place through attraction between the adsorbent sites and adsorbate. In recent times in order to improve the adsorption capacity of various adsorbent materials different solid supports, grafted or impregnated with functional groups, were studied [2, 14-16]. Characteristics such as high specific area, mechanical strength and low solvent swelling during the impregnation process make macroporous polymeric resin suitable to incorporate large amounts of extractant. They also have an organophilic nature due to their hydrophobic surface [17, 18]. Crown ether compounds have the ability to form stabile complexes with metal ions. This ability is due to its structure so that ions can be fitted in their circular cavity or three dimensional cavities [19-22]. The novelty of this study is the used solid support, which is obtained through synthesis of St-DVB copolymer (styrene-divinylbenzene copolymer), grafted with aminophosphonic groups. The material was also impregnated with dibenzo-18-crown-6, used as extractant. The aminophosphonic groups, as well as crown ether, have affinity for bonding with metals ions. The obtained material is used for the removal of Nd(III), La(III), Sr(II), Tl(I), Eu(III) from aqueous solutions. Equilibrium studies were conducted in order to determine the adsorption performances of the obtained materials in removing the studied metal ions from aqueous solutions.

Experiemntal part

Materials and methods

Impregnation of the solid support

St-DVB copolymer grafted with aminophosphonic groups was impregnated with crown ether using the dry method. The impregnation of crown ether (dibenzo-18-crown-6) (Merck, Germany) was made as followed: 0.01

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g crown ether dissolved in 25 mL acetone (VWR Prolabo Chemicals, France) was mixt with 1 g St-DVB copolymer and kept in contact for 24 h. The samples were then dried at 323K for 24 h.

Characterization of the obtained material

The obtained material St-DVB copolymer grafted with aminophosphonic groups and impregnated with crown ether was characterized by FTIR analysis. The FTIR spectra (KBr pellets) of the obtained adsorbent were recorded on a Shimadzu Prestige- 21 FTIR spectrophotometer in the range 4000–400 cm^{-1}.

Adsorption experiments

This experiment was carried out in order to determinate the equilibrium adsorption capacity of the material for each metal used (Nd(III), La(III), Sr(II), Tl(I), Eu(III)). 0.1 g of impregnated material was mixt with 25 mL solution of each metal ion having different concentrations (5, 10, 25, 50, 75, 100 mg/L). The solutions for each metal ion were prepared through appropriate dilution from a stock solution with the concentration of 1000 mg/L. The samples were shacked for one hour at room temperature in a Julabo SW23 mechanical shaker bath. After the time expired, they were filtered and the metal residual concentrations in the filtrate were analyzed using inductively coupled plasma mass spectrometry (ICP-MS Bruker aurora M90).

Results and discussions

Characterization of the obtained material

The structure of the St-DVB copolymer grafted with aminophosphonic groups is presented in figure 1.

The FT-IR spectrum of the St-DVB copolymer grafted with aminophosphonic groups is presented in figure 2. It

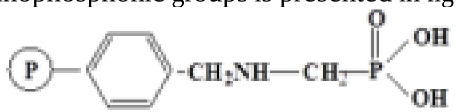

Fig. 1. The structure of St-DVB copolymer grafted with aminophosphonic groups

can be observed the formation of aminophosphonic acid groups grafted on polymer. The amino group adsorption band is at 1545 cm^{-1}. In addition, the bands from 1295 cm^{-1} and 1071 cm^{-1}, from the spectrum were assigned to group P=O and P-OH [23]. Bonds associated to crown ether are visible at 2922 cm^{-1} for the stretching bond C-H and at 1446 cm^{-1}, 1319 cm^{-1} for the stretching bond O-H.

Concentration dependence and adsorption isotherms

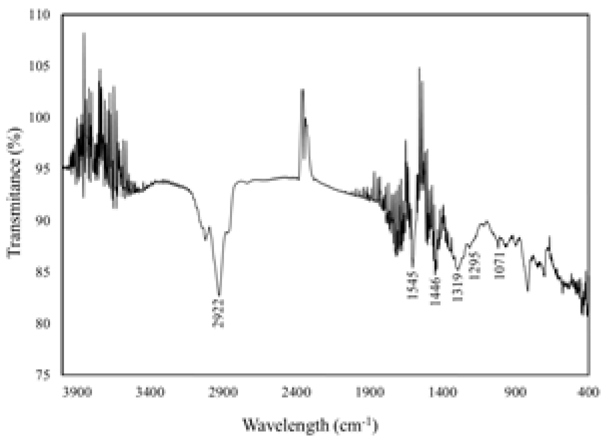

Fig. 2. IR spectrum of the studied adsorbent material

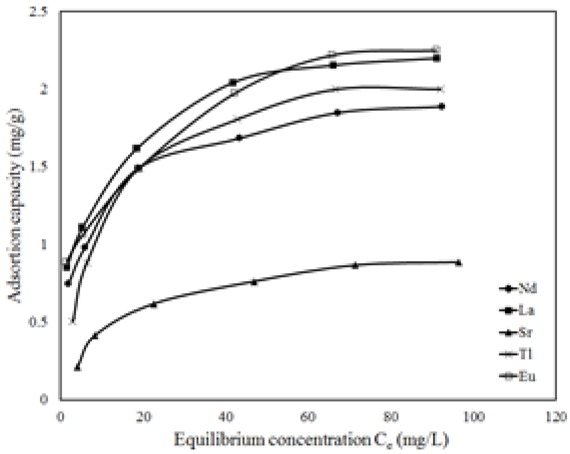

Fig. 3. Adsorption isotherm of metal ions onto the obtained material

The impregnated material was used in the removal process of Nd(III), La(III), Sr(II), Tl(I), Eu(III) from aqueous solutions. Equilibrium studies were carried out in order to determine the maximum adsorption capacity of impregnated for the used metals. The effect of the initial metal ions concentrations upon the adsorption capacity of the impregnated material is presented in figure 3.

It can be observed that the adsorption capacity increases with increasing of the initial metal ions concentrations till it reaches a constant value. The lowest adsorption capacity was obtained for Sr(II) about 0.90 mg/g and the highest for Eu(III) about 2.30 mg/g. The other capacities from the removal process of La(II), Tl(I), Nd(III) are situated slightly under the highest obtained adsorption capacity. The obtained adsorption equilibrium data are correlated with four adsorption isotherm models: Langmuir, Freundlich, and Temkin. The Langmuir adsorption isotherm model describes that the maximum adsorption possible corresponds to a monolayer and that the interaction forces between adsorbed molecules are negligible. The Langmuir model is given by the linearized form as [24- 26]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$$

where q_e is the amount of metal adsorbed per gram of adsorbent, qm is the monomolecular adsorption capacity (mg/g), C_e the equilibrium concentration of the adsorbate in solution after the adsorption, K_L the Langmuir constant. The Langmuir isotherm parameters (q_m, K_L) can be given by plotting C_e/q_e versus q_e. The Langmuir isotherms of metal ions adsorption onto the studied material are given in figure 4. The Langmuir isotherm parameters together with the correlation coefficients are given in table 1.

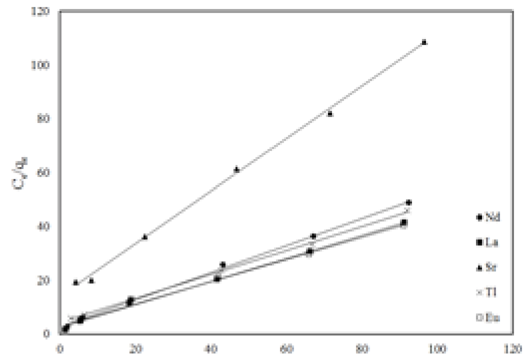

Fig. 4. Langmuir isotherm of metal ions adsorption onto the obtained material

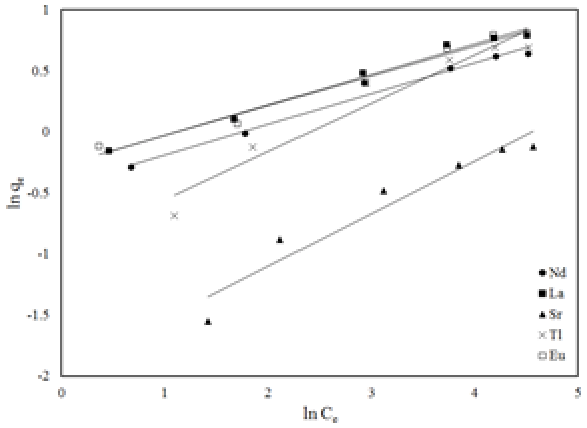

Fig. 5. Freundlich isotherm of metal ions adsorption onto the obtained material

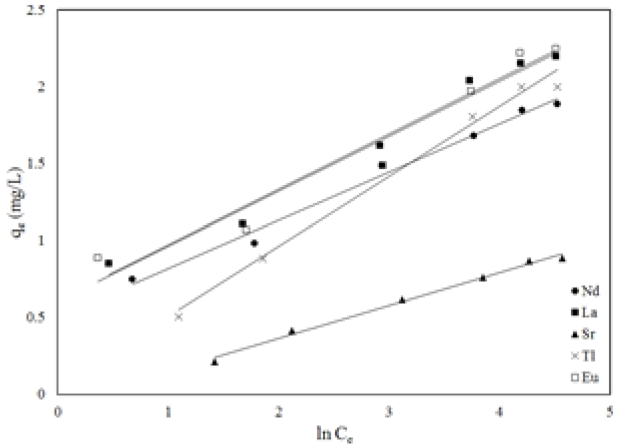

Fig. 6. Temkin isotherm of metal ions adsorption onto the obtained material

Table 1
EQUILIBRIUM ISOTHERM PARAMETERS

Isotherm	Parameter	Nd(III)	La(II)	Sr(II)	Tl(I)	Eu(III)
Langmuir	q_m, mg/g	2	2.32	1.02	2.25	2.40
	K_L, L/mg	0.1822	0.185	0.069	0.102	0.143
	R^2	0.9982	0.9977	0.9983	0.9992	0.9922
Freundlich	K_F mg/g	0.64	0.75	0.1406	0.385	0.7639
	1/n	0.2502	0.2489	0.4304	0.3962	0.2434
	R^2	0.9786	0.9875	0.9319	0.9379	0.978
Temkin	K_T, L/g	5.013	5.44	0.734	1.11	5.42
	b_T	7.83	6.80	11.39	5.37	6.84
	R^2	0.9876	0.9819	0.9926	0.9859	0.9482
	ΔG^0, kJ/mol	-3.95	-4.15	0.75	-0.25	-4.14

The shape of the Langmuir isotherm is given by the dimensionless constant equilibrium parameter R_L from as:

$$R_L = \frac{1}{1 + K_L C_0}$$

where K_L is the Langmuir constant and C_0 is the initial metal concentration. The R_L values offers information about the nature of the adsorption process. The type of the Langmuir isotherm is given by the R_L values as been unfavorable for $R_L>1$, linear for $R_L=1$, favorable for $0<R_L<1$ and irreversible for $R_L=0$. The values calculated for the entire concentration range are situated in the interval $0<R_L<1$ which shows a favorable adsorption process of the studied metals onto the impregnated material. The Freundlich adsorption isotherm model is used to describe the adsorption characteristics for a heterogeneous surface. The Freundlich model is given by the linearized form as [23-25]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where qe is the amount of metals adsorbed per gram of adsorbent, Ce the equilibrium concentration of the adsorbate in solution after the adsorption, KF the Freundlich constant. By plotting qe against Ce parameters like 1/n and KF can be calculated. The Freundlich isotherm of the studied metal ions onto impregnated material is given in figure 5. The Freundlich isotherm parameters together with the correlation coefficients are given in table 1.

Parameters like K_F which describes the quantity of the adsorbed metal for a unit equilibrium concentration and 1/n which measures the adsorption intensity or the surface heterogeneity are important for the characterization of the Freundlich isotherm. The values of 1/n can be classified as followed: 1/n>1 indicates a cooperative adsorption involving strong interactions between the molecules of adsorbate, 1/n=1 means that concentration does not influence the partition between the two phases and 1/n<1 corresponds to a normal L-type Langmuir isotherm. The obtained values are 1/n<1 which suggests that the Langmuir isotherm model better describe the absorption process of the studied metals onto impregnated material than the Freundlich model. The Temkin isotherm model takes in account the interactions between adsorbent and adsorbate and assumes that the heat of adsorption decreases linear with the surface coverage rather than logarithmic. The Temkin model is given by the linearized form as [27, 28]:

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e$$

where RT/b_T is the heat of adsorption (J/mol), K_T is the Temkin isotherm constant (L/mg), R is the universal gas constant (J/mol . K) and T the absolute temperature. Plotting q_e against $\ln C_e$, KT and b_T can be calculated. The Temkin isotherm for the metal ions adsorption onto impregnated material is given in figure 6. The Temkin isotherm parameters are given in table 1.

To determine the Gibbs free energy of adsorption, the calculated K_T value was used conform:

$$K_T = \exp\left(-\frac{\Delta G^0}{RT}\right)$$

Negative values of ÄG^0 were obtained for all metals exception Sr(II). These confirm that the adsorption has a spontaneous nature. The fact that the Sr(II) adsorption process is not spontaneous may be the reason why in this case was obtained the lowest maximum adsorption capacity of the studied material.

Comparing the isotherms applied to the experimental data and the calculated isotherm parameters. The Langmuir isotherm gives the best fit, followed by Temkin and Freundlich. The Langmuir isotherm describes efficient the adsorption process of the studied metals onto the impregnated material due to its correlation coefficient closed to unit. The calculated adsorption capacities of the studied material for the metals from aqueous solutions are closed to the experimental obtained. The R_L value indicates a favorable adsorption process conform the Langmuir isotherm and the Freundlich parameter $1/n<1$ corresponds to a normal L-type Langmuir isotherm.

Conclusions

The novelty of this study was the modification of the St-DVB copolymer by grafting it with aminophosphonic groups and impregnating it with dibenzo-18-crown-6, in order to improve its adsorption proprieties of metal ions from aqueous solutions. The functional groups that define the adsorption proprieties of the studied material were highlighted through FTIR spectroscopy.

The proposed method is easy, requires a less time and the obtained results show a good accuracy. The efficiency of the material for simultaneously removing Nd(III), La(III), Sr(II), Tl(I) and Eu(III) is demonstrated from the adsorption isotherm, which reveals the good adsorption proprieties. Equilibrium studies were performed in order to determine the maximum adsorption capacities and the experimental data were fitted with Langmuir, Freundlich and Temkin adsorption models, where the Langmuir model offers the best result. The highest adsorption capacity was obtained for Eu(III) - about 2.30 mg/g and the lowest for Sr(II) - 0.90 mg/g. The adsorption capacities for La(II), Tl(I), and Nd(III) are found in the1.90 mg/g – 2.25 mg/g range. The high affinity of crown ether for metals is well known from literature but the added nitrogen and phosphor functional groups from the solid support cause the formation of hydrogen bonds which contribute to the adsorption of the metal ions.

This work reveals the fact that the use of solid supports with various functional groups and also impregnated with crown ether are suitable to be used in the removal process of metal ions from aqueous solutions. The proposed study presents the advantage that a lower quantity of crown ether is used and combining its advantages with the properties of the solid supports, which leads to the improvement of the adsorption performance of the obtained adsorbent.

References

1.CHUNHUA, X., XINYI, C., CAIPING, Y., Journal of Rare Earths, **29,** 2011, p. 979

2.TADJARODI, A., JALALAT, V., ZARE-DORABEI, R., Material Research Bulletin, **61**, 2014., p.113

3.TRIYOSO, D. H., GILMER, D. C., JIANG, J., Droopad, R., Microelectronic Engineering, **85,** 2008, p. 1732

4.DAS, D., SRE, J., VARSHINI, C., DAS, N., Minerals Engineering, **69**, 2014, p. 40

5.AWWAD, N. S., GAD, H.M.H., AHMAD, M.I., ALY, H.F., Colloids and Surfaces B: Biointerfaces, **81**, 2010 , p. 593

6.ZAKI, A.A., EL-ZAKLA, T., ABED, M., EL GELEEL, Journal of Membrane Science, **401– 402**, 2012. p. 1

7.SHARMA, P., TOMAR, R., Microporous and Mesoporous Materials, **116**, 2008. P. 641

8.CHEGROUCHE, S., MELLAH, A., BARKAT, M., Desalination, **235**, 2009, p. 306

9.WU, P., DAI, Y., LONG, H., ZHU, N., LI, P., WU, J., DANG, Z.,. Chemical Engineering Journal **191**, 2012, p.288

10.KARSKI, S., WITONSKA, I., Kinetics and Catalysis, **45**, 2004, p. 256

11.CHOUDHARY, V.R., JANA, S.K., Journal of Catalysis, **201**, 2001, p. 225

12.WAN, S., MA, M., LV, L., QIAN, L., XU, S., XUE, Y., MA, Z., Chemical Engineering Journal, **239**, 2014, p. 2000

13.SANGVANICH, T., SUKWAROTWAT, V., WIACEK, R. J., GRUDZIEN, R. M., FRYXELL, G. E., ADDLEMAN, R.S., TIMCHALK, C., YANTASEE, W., Journal of Hazardous Materials, 2010. **182**, p.225.

14.BADIEI, A., BONNEVIOT, L., CROWTHER, N., MOHAMMADI ZIARANI, G., Journal of Organometallic Chemistry, **691**, 2006, p.5923

15.BADIEI, A., NOROUZI, P., TOUSI, F., European Journal of Scientific Research **12**, 2005, p. 39

16.BIRUNGI, Z.S., CHIRWA, E.M.N., Bioresource Technology, **160**, 2014, p. 43

17.EL-SOFANY, E.A., Journal of Hazardous Materials **153**, 2008. p. 948

18.RAO, T.R., BIJU, V.M.N., Reviews in Analytical Chemistry **21**, 2002, p. 233

19.NEGREA, A., POPA, A., CIOPEC, M., LUPA, L., NEGREA, P., DAVIDESCU, C. M., MOTOC, M., MINZATU, V., Pure Applied Chemistry, **86**, 2014, p. 1729

20.ALEXANDRATOS, S. D., STINE, C. L., SACHLEBEN, R. A., MOYER, B. A., Polymer **46**, 2005, p. 6347

21.DUMAN, O., AYRANCI, E., Journal of Hazardous Materials, **176**, 2010, p. 231

22.MOHAPATRA, P. K., LAKSHMI, D. S., BHATTACHARYYA A., MANCHANDA, V. K., Journal of Hazardous Materials, **169**, 2009, p. 472

23.DAVIDESCU, C.M., CIOPEC, M., NEGREA, A., POPA, A., LUPA, L., DRAGAN, E.S., ARDELEAN, R., ILIA, G., ILIESCU, S., Polymer Bulletin, **70**, 2013, p. 277

24.VIJAYARAGHAVAN, K., MAHADEVAN, A., JOSHI, U.M., BALASUBRAMANIAN, R., Chemical Engineering Journal, **152**, 2009, p. 116

25.XIONG, C., RAO, C., Indian Journal of Chemical Technology, **19**, 2012, p. 392

26.BIRUNGI, Z.S., CHIRWA, E.M.N., Bioresource Technology, **160**, 2014, p.43

27.NEGREA, A., CIOPEC, M., LUPA, L., DAVIDESCU, C. M., POPA, A., ILIA, G., NEGREA, P., Journal of Chemical & Engineering Data, **56**, 2011, p.3830

28.POPA, A., CIOPEC, M., NEGREA, A., LUPA, L., NEGREA, P., DAVIDESCU, C. M., ILIA, G., DUTEANU, N., Pure Applied Chemistry, **86,** 2014, p. 1741

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