New Materials, Compounds and Applications
Vol.1, No.1, 2017, pp.27-35

ADSORPTION STUDY OF SOME SORBENTS BASED ON MALEIC ANHYDRIDE STYRENE COPOLYMER AND SULFODIMEZINE AND TRIAZINE AS LINKABLE AMINES

A.F. Alieva[1], F.E. Huseynov[1], E.J. Eyyubova[1*], N.T. Shamilov[1], F.M. Chiragov[1]

[1]Baku State University, Baku, Azerbaijan

Abstract. Based on the copolymer of styrene with maleic anhydride and amines - sulfodimezine and triazine, new modified adsorbents have been obtained. Sorption characteristics of synthesized sorbents with respect to Ce (III) ions are studied. In the course of research, the influence of various parameters such as pH, the influence of ionic strength, the time necessary for establishing complete sorption equilibrium, the effect of the initial concentration of metal ions was studied. Also, the reverse desorption process was studied and the optimum eluent was established. Chemical structure of synthesized products was set by IR-spectroscopy.

Keywords: *Sorption, Ce(III), chelating sorbent, preconcentration.*

Corresponding Author: *Esmira Eyyubova, Department of Analytical Chemistry, Baku State University, Z. Khalilov str. 23, Baku, Azerbaijan, Tel.:+994 55 685 86 51, e-mail: esmira024@yahoo.com*

Manuscript received: *4 November 2017*

1. Introduction

Heavy metal ions are among the most dangerous and toxic pollutants of the environment. Therefore, extracting them from objects of different purposes is of particular importance for living organisms. Hence, the development of various methods for extracting them is an urgent task.

At present, various technologies for the concentration of different metal ions have been proposed. Among them, adsorption is the simplest and cheapest technology. Usually, due to high surface activity, microporous structure and high adsorption capacity, activated carbon is used as an adsorbent substance [8, 10, 11].

In recent years, considerable success has been achieved in the use of organic and inorganic adsorbents for the selective extraction of elements [1, 7, 12]. From this point of view, polymeric chelating-forming adsorbents occupy an important place [3, 6, 9, 13].

Methods for the preparation of various modified adsorbents based on a copolymer of styrene with maleic anhydride and the corresponding amines are provided. This work is devoted to the study of the adsorption of Ce (III) ions from its aqueous solutions by a polymeric chelating-forming adsorbent. Various adsorption characteristics, in particular the effect of pH, time, ionic strength, initial concentration of the metal ion, were studied during the studies. Also, desorption process was studied and the optimum eluent was established.

2. Experimental part

2.1. Preparation of solutions

For the experiment, an aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ was used. The standard solution is prepared by dissolving $2 \cdot 10^{-3}$ M metal in distilled water. The equilibrium concentrations of metal ions in the solution are determined using the appropriate reagent 3- [2- (4, 4- dimethyl- 2, 6- dioxocyclohexylidene) hydrazinyl] -2-hydroxy-5-nitrobenzene-1-sulfonic acid (Figure 1). For this purpose, a $2 \cdot 10^{-3}$ M solution of the reagent was prepared by dissolving it in distilled water. Optical densities of the solutions were measured on KFK-2 and optimal pH = 3 and λ = 440 nm were established. For adsorption studies, a 10^{-2} M metal ion solution was used.

In the course of the studies, the effect of pH on the adsorption capacity of the sorbent was studied [4]. Buffer solutions from 3 to 8 were prepared on the basis of 0.1 N solutions of CH_3COOH and $NH_3 \cdot H2O$.

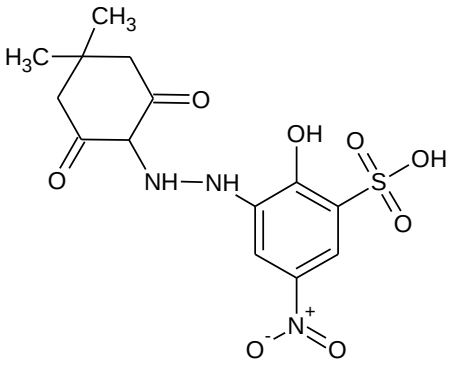


Figure 1. Molecular structure of the reagent

To study the effect of ionic strength on the sorption capacity of the sorbent, a 2 M KCl solution was used, as well as a 2 M KOH solution to study the desorption process.

For the synthesis of the sorbent, a copolymer of styrene with maleic anhydride (Figure 2) and sulphodimezine (S_1) (Figure 3) and triazine (S_2) as amines were used (Figure 4).

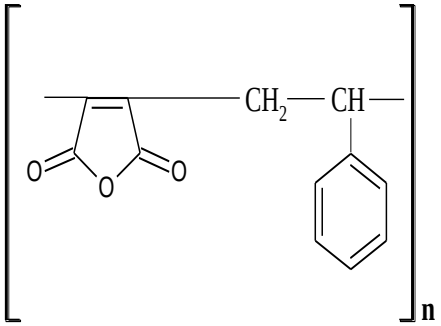


Figure 2. The molecular structure of a copolymer of styrene with maleic anhydride

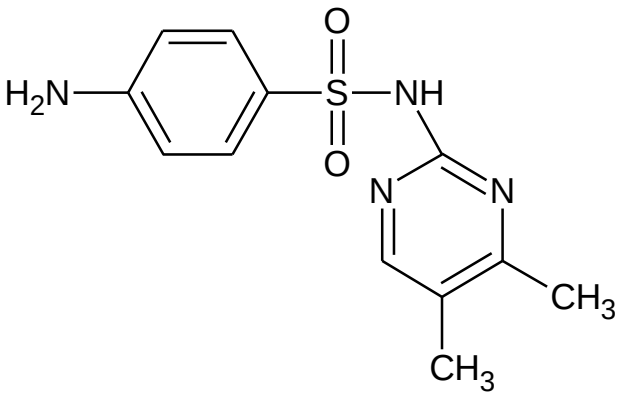


Figure 3. Molecular structure of sulphodimezine

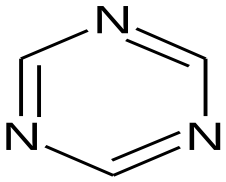
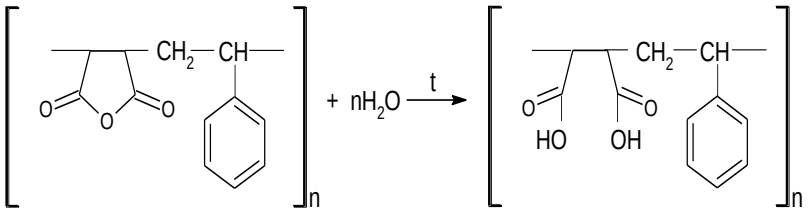


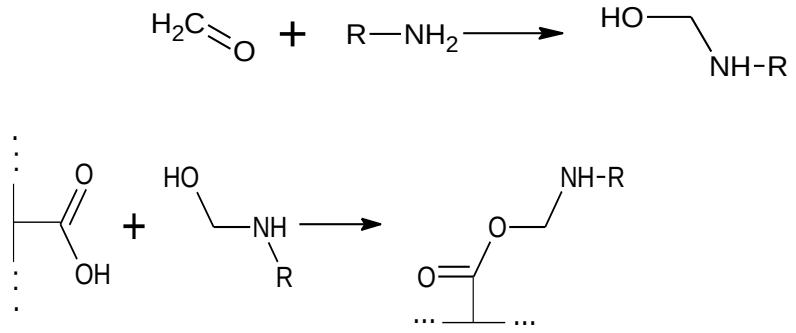
Figure 4. Molecular structure of triazine

2.2. Synthesis of sorbent

Synthesis of the adsorbent was carried out according to a known technique [2]. As the polymer matrix for the synthesis of the sorbent, a styrene-maleic anhydride copolymer and sulphodimezine and triazine as amines were used. For that purpose, 3 g of copolymer, previously weighed on analytical scales, were added to the round bottom flask. Subsequently, the appropriate amount of sulphodimezine was weighed, dissolved in water and added to the original contents of the flask. The synthesis was carried out in the presence of formalin, as a cross-linking agent. The reaction was carried out at a temperature of 60-70 ℃, for 30-40 minutes. During the reaction, the following transformations were observed (Scheme 1):



Since the process is carried out in an aqueous medium, the anhydride groups of the polymer undergo hydrolysis.



Scheme 1. The mechanism of the sorption process

As a result of the mutual influence of formaldehyde and amine, an unstable carbonylamine is formed. The resulting carbonylamine interacts with the carboxyl groups of the macromolecule and thus the amine is introduced into the macromolecule.

At the end, the resulting synthesis product is passed through a filter paper, washed, dried, grinded and used for further research.

By the same procedure, a sorbent was prepared on the basis of the amine triazine.

2.3. Concentration

Adsorption studies of Ce (III) ions were carried out at room temperature. The experiments were carried out in a static mode. For each experiment, 2 ml of a metal ion solution with a known concentration (10^{-2} M) was added to 50 ml conical flasks. To each flask, 30 mg of the adsorbent previously weighed on the analytical balance and the corresponding pH was added. The pH of the solutions was monitored with a pH meter of Ionomer I-130. The resulting mixture was kept for 24 hours. The contents of the flask were then passed through a filter paper and the liquid phase was separated from the solid phase. Subsequently, 1 ml samples were taken from each flask, diluted with photometric pH 3, and the final concentrations of Ce (III) ions on CPA-2 at 440 nm were determined.

The degree of metal ion extraction was calculated by the following formulas:

$$R,\% = \frac{C_0 - C_e}{C_e} x100,$$

where R is the percentage recovery of the metal ion

$$q_e = \frac{(C_0 - C_e)V}{m},$$

where C_0 is the initial concentration of the metal ion, C_e is the equilibrium concentration of the metal ion, V is the volume of the solution, and m is the mass of the sorbent.

2.4. Desorption process

Studies of desorption were carried out using various inorganic acids with the same concentration, namely: 0.5 M solutions of HNO_3, HCl, H_2SO_4 and CH_3COOH acids.

2.5. Equipment

The optical densities of the solutions were measured on KFK-2. pH values on the pH meter Ionomer I-130. Infrared measurements of S_1 and S_2 before were obtained using a Varian 3600 Fourier transform spectrometer from 400 to 4000 cm^{-1}.

3. Results and discussion

3.1. Infrared Spectroscopy

Results of Infrared Spectroscopy of S_1 is shown on the Figure 5.

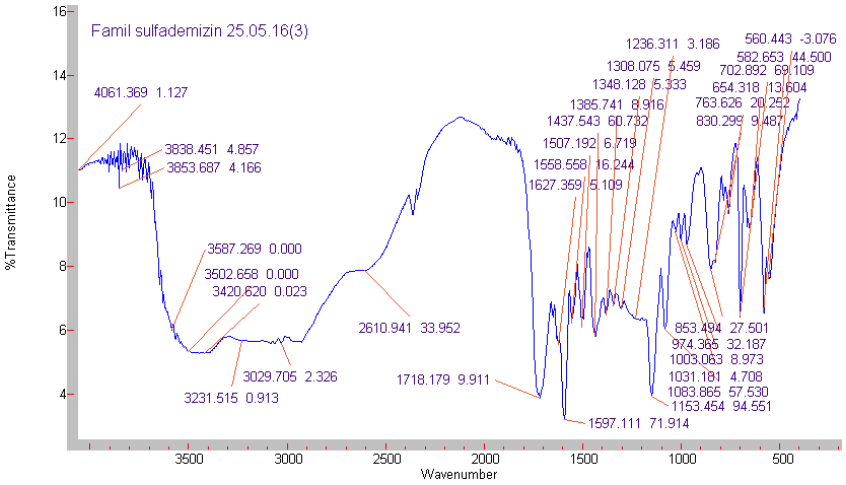


Figure 5. IR spectrum of sulphodimezine

In the IR spectrum of the sorbent, absorption bands of 3600-3100 cm^{-1} are seen [stretching vibrations of hydroxyl groups present in carboxyl groups and valence vibrations of -NH groups (3400-3200 cm-1)], 1750-1715 cm^{-1} (valence vibrations of -C = O groups present in carboxyl groups), 1570-1550 cm^{-1} (valence vibrations of C-N groups and deformation vibrations of NH groups), 1610-1510 cm^{-1} (stretching vibrations of C-C groups in the benzene ring), 710- 680 cm^{-1} (deformation vibrations of C-C groups in the benzene ring). Thus, the IR spectrum of the sorbent confirms the proposed structure.

3.2. Effect of pH on the degree of extraction of Ce (III)

Depending on the pH and the presence of certain components in the solution, the ion can exist in the form of various complex particles. One of the most important parameters that affect the degree of adsorption of Ce (III) ions is the acidity of the contacting solution. Therefore, studying the effect of pH on the degree of adsorption is an important task.

For this purpose, 30 mg of sorbent was weighed and added to the flask. Further, 2 ml of a 10^{-2} M metal ion solution and 18 ml of a corresponding pH of 3 to 8 were added. The contents of the flask were stored for 24 hours. After one day, the optical densities of the heterogeneous mixtures were measured for KFK-2 at photometric pH 3 and the wavelength of 440 nm. The results of the studies showed that the greatest metal recovery is observed at a pH value of 5.0 for both sorbents. Further experiments were carried out at a given pH value of 5.0. The graphical representation of the data is shown in Figure 6.

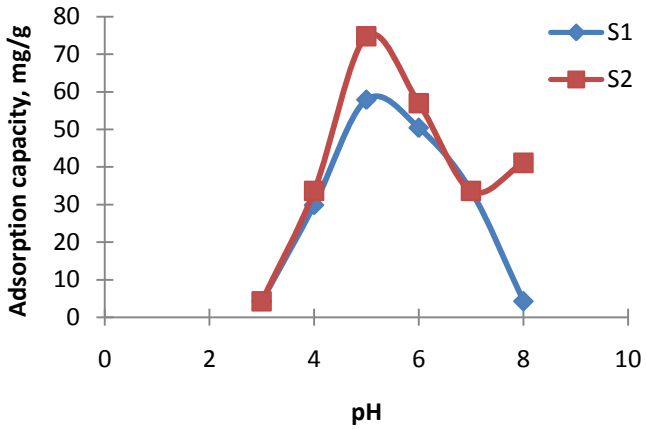


Figure 6. Dependence sorption capacity sorbent on pH
$m_{sorb.}$=30 mg, $V_{gen.}$=20 ml, $C_{Me}=10^{-2}$ M

3.3. Effect of time on the degree of extraction of the metal ion

The effect of time on the adsorption capacity of the Ce (III) metal ion is shown in Figure 7. To study this parameter, measurements were made in the interval from 0 to 270 minutes. The equilibrium concentrations of metal ions in the sample were determined at appropriate time intervals on KFK-2 at pH 3.0 and λ = 440 nm.

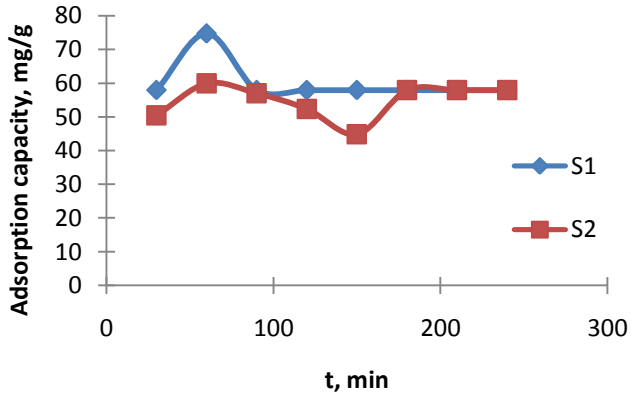


Figure 7. The influence of time on the sorption capacity of the sorbent
$m_{sorb.}$=30 mg, $V_{gen.}$=20 ml, $C_{Me}=10^{-2}$ M, t_1=90 min, t_2=180 min, pH=5.0

As can be seen from Figure 7, in the period from 0 to 150 minutes, the degree of sorption varies chaotically, and from 90 minutes remains constant for S_1 and 180 minutes for S_2. This indicates the attainment of complete sorption equilibrium.

3.4. Effect of ionic strength on the sorption capacity of the sorbent

In the course of the study, the effect of ionic strength on the degree of extraction of the Ce (III) ion was investigated. For these purposes, a 2 M potassium chloride KCl solution was used. The results are shown in Figure 8.

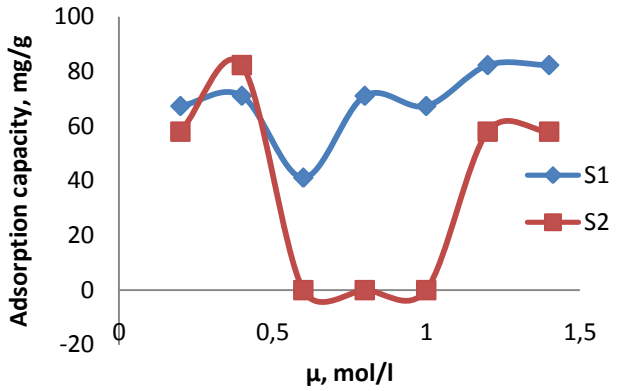


Figure 8. Effect of ionic strength on the sorption capacity of the sorbent
$m_{sorb.}$=30 mg, $V_{gen.}$=20 ml, $C_{Me}=10^{-2}$ M, t_1=90 min, t_2=180 min, pH=5.0

Studies have shown that within the range of μ = 0.2-1.0 mol/l, the presence of KCl has a negligible effect on the extraction of metal ions in case of S_1. In case of S_2 it`s apparent that KCl greatly affects adsorption of Ce(III) ions by the synthesized sorbent.

3.5. Effect of the initial concentration of Ce (III) ions on the sorption capacity of the sorbent

This work includes studying the influence of the initial metal ion concentration on the degree of cure by the synthesized sorbent was studied. For this purpose, the concentration of Ce (III) ions was varied from 0.2·10-3 mol/l to 8.0·10-3 mol/l at pH 5.0. For this, 30 mg of an appropriate adsorbent were weighed, the corresponding volumes of the metal ion solution and pH 5.0 were added. After 3 hours, the optical densities of the heterogeneous solutions were measured on KFK-2, at pH 3.0 and λ = 440 nm. The degree of extraction of the metal ion was calculated according to a well-known formula (See 2.3). The results are graphically depicted in Figure 9 and Table 1.

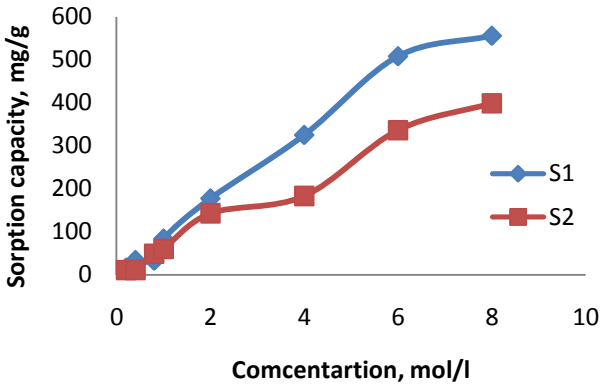


Figure 9. Effect of the initial concentration of Ce (III) ions on the sorption capacity of the sorbent
$M_{sorb.}$=30 mg, $V_{gen.}$=20 ml, $C_{Me}=10^{-2}$ M, t_1=90 min, t_2=180 min, pH=5.0, μ=1,0 mol/l

The results of the studies have shown that the greatest sorption capacity is observed at a concentration of Ce (III) ions $8{,}0 \cdot 10^{-3}$ mol/l.

Table 1. Degree of extraction and sorption capacities of Ce (III) ions by synthesized S_1 and S_2

C_{Me}, mmol/l	0.2	0.4	0.8	1.0	2.0	4.0	6.0	8.0
Adsorption Capacity S_1, мg/g	16.191	34.095	32.694	84.072	177.485	325.078	508.164	555.788
R_1,%	86.6%	91.25	43.75	90%	95%	86.99%	90.66%	91.99%
Adsorption Capacity S_2, мg/g	10.898	11.209	48.574	59.784	142.922	183.100	336.288	398.563
R_2,%	58.33	30%	65%	64%	76.5%	49%	60%	53.33%

3.6. Desorption process

An important task in the use of sorption technique is the search for the appropriate substances for desorption of the desired component. This work also involves studying the reverse process-desorption. The presence of the necessary eluents for desorbing the metal ion is an important task. In our article, this process is carried out by using different inorganic acids with the same concentration, in particular 0.5 M solutions of HNO_3, HCl, H_2SO_4 and CH_3COOH acids. The results of the studies are presented in Table 2.

Table 2. Results of desorption of Ce(III) by the synthesized adsorbents

Acid, mol·L^{-1}	**HNO_3**	**HCl**	**H_2SO_4**	**CH_3COOH**
Adsorption capacity S_1, мg/g	51.377	57.916	46.706	15.26
Adsorption capacity S_2, мg/g	64.865	49.509	59.784	19.685

Table 2 shows that an appropriate eluent in case of S_1 is 0.5 M solution of HCl and 0.5 M solution of HNO_3 acid in case of S_2.

4. Conclusion

The present work has shown that the synthesized sorbent can be successfully applied for the extraction of Ce (III) ions from aqueous solutions of its salts. The results of the studies are quite high, in particular when studying the effect of the initial concentration of metal ions on the adsorption capacity of the adsorbent, the maximum adsorption capacity of the sorbents are 555.788 and 398.563 mg/g. The foregoing allows us to assume the possibility of using the synthesized products, based on a

copolymer of styrene with maleic anhydride and sulphodimezine and triazine, to extract Ce (III) ions from various natural and industrial objects.

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