

СОРБЦИЯ ИОНОВ ЦЕРИЯ (III) НА ПОЛИМЕРНОМ ХЕЛАТООБРАЗУЮЩЕМ СОРБЕНТЕ**А.Ф. Алиева, Ф.Э. Гусейнов, Н.Т. Эфендиева, Н.Т. Шамилов, Ф.М. Чырагов**

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В настоящей работе были исследованы методы концентрирования Се (III) из водных растворов на синтетическом полимерном адсорбенте. Изучено сорбционно-фотометрическое определение микроколичеств ионов церия с помощью нового полимерного хелатообразующего сорбента, модифицированного дитизоном. Сорбционный процесс проводился в статических условиях. Установлены оптимальные характеристики сорбционного процесса: влияние рН, время контакта, влияние начальной концентрации металла, влияние ионной силы. Для извлечения ионов церия рН = 5, время контакта составляет 210 мин. Оптимальная ионная сила достигается при значении $\mu = 0,6$. Сорбционную емкость сорбента и процентное извлечение определяли по разности начальных и конечных концентраций церия (III) в растворе. Сорбируемость ионов церия (III) составляла 91,38%, сорбционная емкость сорбента по отношению к ионам церия составляла 682,85 мг г⁻¹. На конечном этапе был проведен процесс десорбции с использованием различных (органических и минеральных) кислот с одинаковыми концентрациями (0,5, 1,0, 1,5 и 2,0 М). Наибольшей элюирующей способностью по отношению к ионам церия (III) обладает 1М HCl. Сорбент, модифицированный дитизоном на основе сополимера малеинового ангидрида со стиролом (СМА), предлагается в качестве синтетического сорбента с лучшими аналитическими свойствами (высокая сорбционная емкость, время контакта 3 ч по отношению к ионам церия. Возможно многократное использование регенерированного сорбента для концентрирования. Разработанные методики могут быть использованы для определения Се (III) в стандартных образцах, почве и водопроводной воде.

Ключевые слова: церий, сорбируемость, хелатообразующий сорбент, концентрация, десорбция

SORPTION OF CERIUM(III) IONS ONTO CHELATING POLYMERIC SORBENT**A.F. Alieva, F.E. Guseynov, N.T. Afandiyeva, N.T. Shamilov, F.M. Chyragov**

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In a present paper methods of concentration of Ce(III) from aqueous solutions onto synthetic polymer adsorbent. The sorption-photometric determination of the microquantities of cerium ions by new polymeric chelating sorbent, modified with dithizone has been studied. Sorption process was carried out under static conditions. Optimal characteristics of the sorption process: influence of pH, time of contact, effect of the initial concentration of metal, influence of ionic strength were studied. pH for extracting Ce is 5; the residence time is 210 min. Optimal ionic strength was achieved at a value of $\mu = 0.6$. The sorption capacity of the sorbent and the percentage recovery were determined from the difference in the initial and final concentrations of cerium(III) in the solution. The sorbability of cerium(III) ions was 91.38%, sorption capacity of sorbent with respect to cerium ions is $682.85 \text{ mg}\cdot\text{g}^{-1}$. At the final stage, a desorption process was carried out using different (organic and mineral) acids with the same concentrations (0.5, 1.0, 1.5, and 2.0 M). 1M HCl has the highest eluting ability with respect to cerium (III) ions. Sorbent modified with dithizone based on a styrene-maleic anhydride (SMA) copolymer is proposed as synthetic sorbent with the best analytical properties (high sorption capacity, residence time 3 h with respect to cerium ions). Multiple use of the regenerated sorbent for concentration is possible. The developed techniques can be used to determine Ce(III) in standard samples, soil and tap water.

Key words: cerium, sorbability, chelating-forming sorbent, concentration, desorption

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INTRODUCTION

Heavy metal ions are in the number of the environmental pollutants. Low doses of rare-earth elements have some positive effects on physiological and biochemical reactions for plants and animals. Rare-earth elements are widely used as plant growth regulators for crops and as feed additives for livestock, poultry and aquaculture [1, 2]. As a result, rare-earth elements from agriculture will be present in agricultural products and enter the human body through the food chain. So it is necessary to obtain the impact of heavy metal ions to the environment from the analytical point of view [3].

Cerium is one of the toxic rare earth elements. The global demand for rare-earth elements and their compounds has over the past decades due to their chemical, catalytic, electrical, magnetic, and etc. properties [4].

For this purpose, recently sorption methods have been widely used, especially with the use of polymeric chelating-forming sorbents (PCC).

The methods of separation and concentrating of rare-earth elements associated with their toxicity are of great interest. The most widespread methods for the determination of heavy metal ions are flotation, coagulation and adsorption [5-8].

Among the widespread known techniques for extracting microquantities of rare-earth elements from solutions, the sorption method is effective. This method

allows to reduce the detection limit for microquantities of elements. For extract heavy metal ions both natural [9, 12, 14, 16] and synthetic [10, 11, 13, 15-19] sorbents are used. Spectrophotometric methods of determination due to simplicity, reproducibility and cheapness of equipment are more universal.

The aim of this work is the study of optimal characteristics of the sorption process – influence of pH, residence time, effect of the initial concentration of metal, influence of ionic strength of sorbent modified with dithizone based on a styrene-maleic anhydride (SMA) copolymer. The criterion for optimality of the process of sorption of cerium cations from aqueous solutions by a polymeric sorbent is its maximum absorption and the achievement of a high sorption capacity. At the final stage the desorption process was carried out.

EXPERIMENTAL PART

Equipment

The pH of the solutions was measured with an ionomer PHS-25 with a glass electrode. The optical density of the solutions was measured on a KFK-2 photocolimeter ($l = 1 \text{ cm}$). To mix the solutions, an ORBITAL SHAKER TS-1 thermomixer was used. Sorbent was dried in a Zymark TurboVap LV drying cabinet.

Solutions and reagents

All reagents used are chemically pure. For the photometric determination of cerium, 3-[2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl]-2-hydroxy-5-nitrobenzene-1-sulfonic acid was used as the

reagent. The solution of reagent ($2 \cdot 10^{-3}$ M) was prepared by dissolving it in an appropriate amount of distilled water. The cerium solution was prepared by dissolving in an appropriate amount of distilled water the salt of cerium $Ce(NO_3)_3 \cdot 6H_2O$. Working solutions were prepared by diluting with distilled water aliquots of the stock solution. The pH of the solutions was maintained constant using an ammoniated acetate buffer (pH 3-11).

Synthesis of a sorbent

Synthesis of sorbent was carried out according to a known method. The sorbent were synthesized by adding a certain amount of dithizone and formaldehyde to the copolymer of styrene with maleic anhydride. The reaction proceeds in a sand bath at 60-70 °C with continuous stirring for 45-50 min. Due to the fact that the reaction takes place in an aqueous medium, the anhydride groups included in the copolymer are hydrolyzed. In the reaction of formaldehyde and dithizone, an unstable carbonylamine is formed. The resulting carbonylamine reacts with carboxyl groups and the amine fragment enters to the macromolecule. A schematic representation of the polycondensation process is shown in Fig. 1:

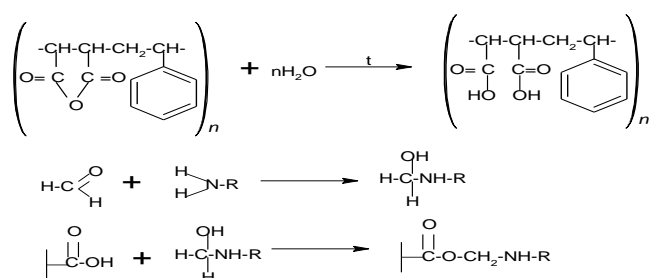


Fig. 1. A schematic representation of the polycondensation process
Рис. 1. Схематическое изображение процесса поликонденсации

The resulting sorbent were washed 4-5 times with distilled water. The resulting mass was then dried in an oven.

Sorption studies

Sorption process was carried out under static conditions. To carry out sorption studies, 30 mg of sorbent, 2 ml of a solution of Ce (III) ion and corresponding amount of pH = 5 were added to sorption flasks. The absorption capacity of the cerium ion sorbed by sorbent was calculated from the following equation.

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

where Q is the sorption capacity of sorbent, V – volume of solution, C_0 – is the initial concentration of cerium ions ($mg \cdot l^{-1}$), C is the concentration of cerium ions after the sorption process ($mg \cdot l^{-1}$) and m-mass of the sorbent (mg). The maximum sorption capacity of sorbent with respect to cerium ions is $682.85 \text{ mg} \cdot g^{-1}$.

The percentage recovery of cerium ions was calculated by the ratio of the difference in the concentrations of cerium ions in the solution before and after sorption to the concentration of cerium ions in the solution before sorption using the following equation:

$$\%R = \frac{C_0 - C_e}{C_0} \cdot 100,$$

where R is the percentage recovery, C_0 and C_e are the initial and equilibrium concentrations of the cerium ion. The maximum percentage recovery of cerium ions from the solution when using a sorbent modified with dithizone was 91.38%.

Influence of acidity of environment

The effect of pH is one of the main characteristics of sorption process. The sorption process was carried out under static conditions. The time for studying the effect of pH was 24 h. The influence of pH on the sorption of Ce(III) by polymer sorbent in the pH range 3-8 was studied. For this aim 30 mg of sorbent were placed in the sorption flasks, 2 ml of a 10^{-2} M solution of cerium is added to the sorption flasks and left in a buffer medium at pH = 3-8. After concentrating, the photometric determination of cerium ions in solutions was studied. For this aim, the 1.5 ml of reagent 3-[2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl]-2-hydroxy-5-nitrobenzene-1-sulfonic acid was added to the aliquot part of the sorbent solution with a volume of 1 ml and diluted to a mark with pH = 5. The results of the studies showed that at pH = 5 the maximum sorption of cerium ions is observed. Finally, a graphical dependence of the sorption capacity on the medium acidity was drawn. Figure 1 shows the dependence of the sorption capacity on the medium acidity.

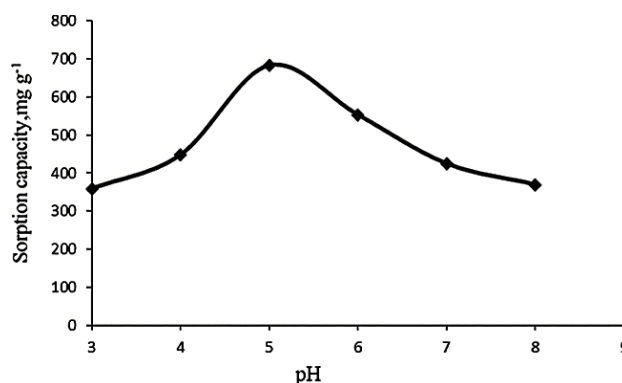


Fig. 2. Influence of medium acidity on the sorption process.
 $C_{Ce} = 10^{-2} \text{ mol l}^{-1}$, $m_{\text{sorb}} = 30 \text{ mg}$, $\lambda = 440 \text{ nm}$
Рис. 2. Влияние кислотности среды на процесс сорбции.
 $C_{Ce} = 10^{-2} \text{ моль л}^{-1}$, $m_{\text{сорб}} = 30 \text{ мг}$, $\lambda = 440 \text{ нм}$

Residence time

The time necessary to achieve complete sorption equilibrium was studied. For this purpose 30 mg of sorbent were placed in the sorption flasks, 2 ml of a 10^{-2} M cerium solution and 18 ml of pH = 5 were

added. To study the influence of time, measurements were made within 210 min. Every 30 min an aliquot of 1 ml was taken from the solution. It was found, that time required for establishing complete sorption equilibrium is 210 min. Fig. 2 shows the dependence of the sorption capacity on the residence time.

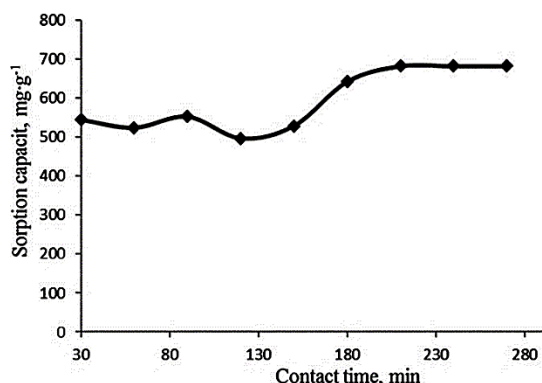


Fig. 3. Influence of residence time on the sorption process.

$C_{Ce} = 10^{-2} \text{ mol l}^{-1}$, $\text{pH} = 5$, $m_{\text{sorb}} = 30 \text{ mg}$, $\lambda = 440 \text{ nm}$

Рис. 3. Влияние времени контакта на процесс сорбции.

$C_{Ce} = 10^{-2} \text{ моль л}^{-1}$, $\text{pH} = 5$, $m_{\text{сорб}} = 30 \text{ мг}$, $\lambda = 440 \text{ нм}$

Effect of the initial concentration of the metal

To study the influence of the initial concentration of cerium ion on the sorption process, 30 mg of sorbent is placed in the sorption flasks, a certain amount of a 10^{-2} M solution of cerium is added and left in a buffer medium at $\text{pH} = 5$. The results of the analysis showed that at a concentration of $80 \cdot 10^{-4} \text{ M}$, the maximum sorption capacity of sorbents to cerium ions is observed.

Influence of ionic strength

The effect of ionic strength on the sorption of the Ce(III) by polymer sorbent is studied. To study the effect of ionic strength on the extraction of metal ions, a solution of 2M KCl was used. It was found that the optimal ionic strength on sorbent modified with dithizone is achieved at a value of $\mu = 0.6$. Fig. 3 shows the dependence of the sorption capacity on the ionic strength.

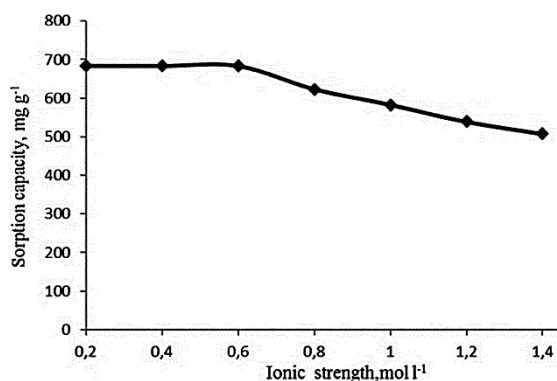


Fig. 4. Influence of ionic strength on the sorption process.

$C_{Ce} = 10^{-2} \text{ mol l}^{-1}$, $\text{pH} = 5$, $m_{\text{sorb}} = 30 \text{ mg}$, $\lambda = 440 \text{ nm}$

Рис.4. Влияние ионной силы на процесс сорбции. $C_{Ce} = 10^{-2} \text{ моль л}^{-1}$, $\text{pH} = 5$, $m_{\text{сорб}} = 30 \text{ мг}$, $\lambda = 440 \text{ нм}$

The desorption process

For the extraction of cerium ions absorbed by polymeric sorbent, a desorption process was carried out at the final stage. Mineral and organic acids HCl, HNO_3 , H_2SO_4 , CH_3COOH of different concentrations (0.5 M, 1 M, 1.5 M, 2 M) were used to extract metal ions absorbed by sorbents modified with dithizone. The results of the conducted studies showed that the best desorbing ability with respect to the cerium ions is in 1M HCl. After washing the sorbent with 1M hydrochloric acid, a 90% desorption of cerium ions is achieved.

CONCLUSION

Thus, adsorption of Ce(III) from aqueous solutions onto synthetic polymer adsorbent is characterized by high degrees of recovery and adsorption capacity. The pH for extracting cerium ions is $\text{pH} = 5$; the residence time is 210 min; optimal ionic strength was achieved at a value of $\mu = 0.6$. The developed techniques can be used to determine Ce(III) in standard samples, soil and tap water.

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