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SYNTHETIC CHELATING SORBENT BASED ON MALEIC ANHYDRIDE WITH STYRENE AND 4-NITROANILINE-2-ARSONIC ACID FOR PRECONCENTRATION OF SILVER(I)

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ABSTRACT

This article is devoted to the extraction of silver (Ag) ions in an acidic medium at pH 5 by a copolymer of maleic anhydride with styrene (MASC), chemically modified with 4-nitroaniline-2-arsonic acid (NAA). The structure of the sorbent CSMA-4-nitroaniline-2-arsonic acid was studied by IR spectroscopy methods. The study of Ag(I) ion sorption was carried out under static conditions. The influence of various parameters on the process of Ag(I) ion sorption was studied. Maximum sorption of metal ions is observed at pH 5. The sorption equilibrium was established after 3 hours. As the concentration of sorbed metal ion increases, it reaches its maximum at $6 \cdot 10^{-3}$ M. To study desorption, the effect of different acids - HNO_3, CH_3COOH with the same concentrations on the desorption of Ag(I) from the sorbent was studied. The experiment showed that the maximum desorption of Ag(I) occurs in 2 M nitric acid (HNO_3).

Introduction

Sorption technologies have been widely used for the preconcentration of heavy and hazardous metal ions [1-7]. Chelating sorbents are of particular interest as sorption material. More efficient is the use of modified forms of the MASC. For example, chelating sorbents, which are fixed on organic compound·s matrices [8–9]. According to recent papers, the MASC is a potential matrix for the synthesis of chelating sorbents, as well as the preconcentration and determination of heavy metal ions [10-13].

Ag(I) is among heavy and toxic metal ions. It can accumulate on skin and prolonging contact with it results in argyria [14-15]. Therefore, it is actual from analytical point of view the sorption preconcentration of Ag(I) as heavy and toxic metal ion from aqueous solutions.

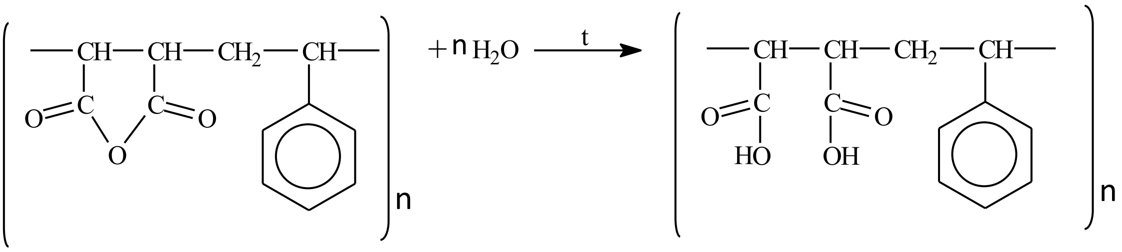
The main goal in the present work is to study the conditions for the preconcentration of Ag(I) with a new chelating sorbent based on MASC modified with NAA, followed by determination of Ag ions by photometric spectrometry to remove Ag(I) from aqueous solutions.

Experimental technique

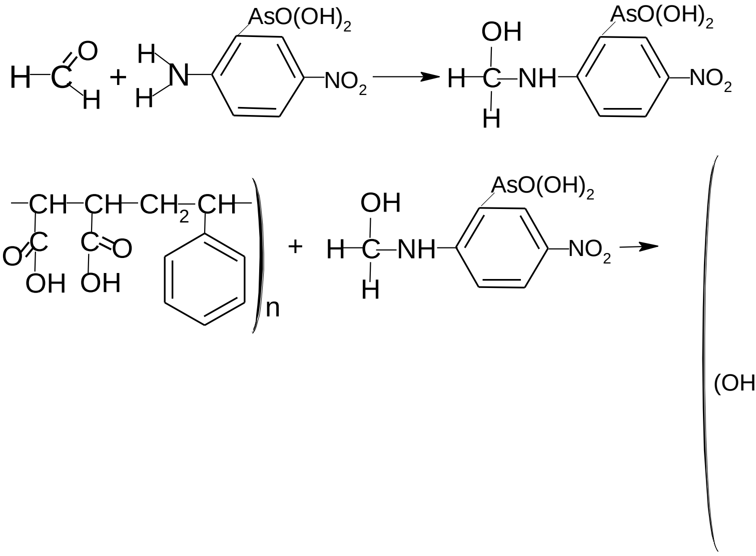
Sorbent. To investigate the sorption preconcentration of Ag, a synthetic chelating sorbent based on MASC and NAA was used for preconcentration of Ag(I).

Synthesis of sorbent.

The sorbent synthesis is carried out according to the method [16]. The sorbent used in this study was created by modifying a macroporous MASC. NAA was applied as an amine. To begin, weigh 3 g of copolymer using an analytical scale before transferring it into the round bottom flask. The appropriate amount of NAA was weighed, dissolved in water, and added to the flask's original contents. In the synthesis, formalin was utilized as a cross-linking agent. The reaction was conducted at 60-70 °C for 30-40 minutes. The following stages were observed in the polycondensation reaction (Scheme 1):



Because the procedure is carried out in an aqueous medium, the polymer's anhydride groups undergo hydrolysis.



The combination of formaldehyde with 4-nitroaniline-2-arsonic acid creates an unstable carbonylamine. Unstable carbonylamine interacts with the macromolecule's carboxyl groups, introducing the amine into it.

Before conducting experimental studies, the synthetic chelating sorbent was purified. To conduct the experiment on the sorption of silver ions, the sorbent was ground in an agate mortar and sifted through a sieve with 14 mm pores.

Figure 1 shows the molecular structure of the amine.

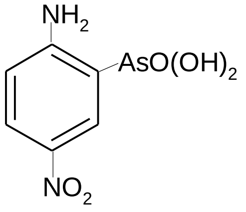


Fig 1. Molecular structure of 4-nitroaniline-2-arsonic acid

Solutions. The standard solution of Ag(I) was prepared by dissolving an accurate mass of the metal salt $AgNO_3$ (chemically pure) in distilled water [17]. Spectrophotometric measurements were performed using a Lambda Perken Elmer spectrophotometer and a KFK-2 photoelectric colorimeter. Working solutions were obtained by appropriate dilution of the stock solutions.

To create the required acidity ammonium acetate buffer solutions (pH 3–11) were used. The determination of silver in solutions was carried out by the spectrophotometric method using the reagent - 2,2',3,4-tetrahydroxy-3'-sulfo-5'-nitroazobenzene.

Study of metal sorption. Metal sorption isotherms were obtained under static conditions at 20°C. The sorption value and the degree of metal extraction were calculated from their equilibrium concentration in the solution by the spectrophotometric method [18]. The degree of extraction (R, %) and the value of sorption (q_e, mg/g) for the studied analyte were calculated using the formulas:

$$R,\% = \frac{C_0 - C_e}{C_e} x100 \text{ (1)},$$

$$q_e = \frac{(C_0 - C_e)V}{m} \text{ (2)},$$

where C_o and C_e are the initial and residual (equilibrium) concentrations of the adsorbate, respectively, $mg \cdot L^{-1}$; V is the volume of the solution, L; m is the mass of the sorbent, g.

When studying sorption in a static mode, $5 \cdot 10^{-3}$ M of Ag(I) metal aqueous solution was introduced into a test tube with a ground stopper, and an ammonium acetate buffer solution was added to create the required acidity to a total volume of 20 ml. 30 mg of the sorbent was added to a test tube, closed with a cork, and intensively stirred for 1–150 min. The solution was separated from the sorbent by filtration.

Study of metal desorption. The dependence of metal desorption from the modified sorbent surface on acidity and eluent concentration was studied under static conditions. A portion of the modified sorbent weighing 30 mg was placed in a 50 ml conical flask with a metal solution and left for three hours with stirring. Then, the sorbent was separated from solution by filtration. At the final stage, the concentration of desorbed silver(I) ions was determined in the obtained filtrate.

Results and discussions

Sorbent identification.

IR spectroscopy.

The structure of the synthetic sorbent CSMA-4-nitroaniline-2-arsonic acid was studied by IR spectroscopy methods. The following vibrations are observed in the IR spectrum of CSMA-4-

nitroaniline-2-arsonic acid: 3600-3100 cm^{-1} (stretching vibrations of the –OH group, as well as stretching vibrations of the –NH group (3400-3200 cm^{-1})], 1775-1745 cm^{-1} (stretching vibrations of the -C=O group in the carboxyl group), 1585-1565 cm^{-1} (stretching vibrations of C-N and deformation vibrations of N-H), 1605-1515 cm^{-1} (stretching vibrations of C-C in the benzene ring), 730-695 cm^{-1} (deformation vibrations of C-C in the benzene ring).

Influence of pH on sorption. The static sorption capacity of a synthetic chelating sorbent depends on the content of functional-analytical groups in the sorbent matrix and the acidity of the medium. The sorption of silver(I) by synthetic sorbent was influenced by pH.

The study of the effect of pH (in the range of 3-8) on the preconcentration of silver(I) ions under static conditions showed that the quantitative extraction of metal ions is achieved at pH 5.

This effect of the medium pH value on the preconcentration of silver(I) ions can be explained as follows: at a low pH value, -AsO_3H_2 and NH_2 functional groups of the polymer sorbent easily form protonation and in this case, competition between the formed protons and silver ions with subsequent electrostatic repulsion of silver ions is observed in the aqueous solution. In this case, the adsorption value decreases. With a further increase in the pH value, these functional groups are no longer protonated and therefore the previously observed process of electrostatic repulsion of the silver ions decreases. The result of this process is an increase in the adsorption value of the silver ion.

At pH=5 of the environment, at which maximum adsorption is observed, the metal ion in the aqueous solution is in the form of Ag^+.

The pH or acidity value of the medium at which hydrolysis of a metal ion begins depends on its charge and radius. Thus, the greater the charge and the smaller the radius of the cation of a metal element, the lower the pH value of the medium at which hydrolysis of the metal begins. [19] For silver ions in aqueous solution, at pH values greater than 8, the hydrolysis process begins.

Figure 2 represents the dependence of adsorption capacity on medium pH.

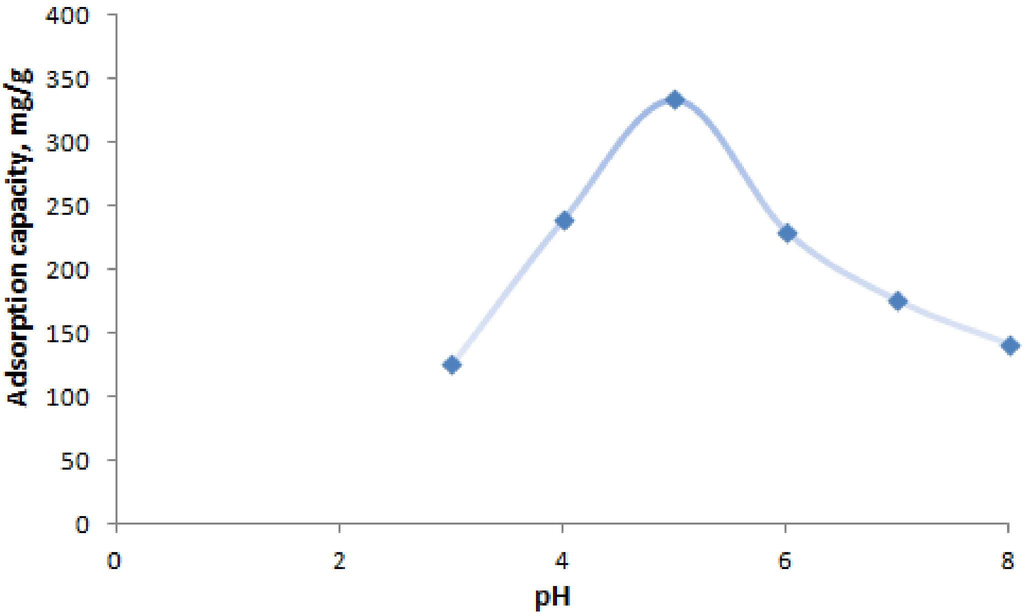


Fig.2. Effect of medium pH on adsorption capacity.

Fig. 2 shows that the maximum degree of silver extraction by sorbent is achieved from solutions with pH 5. So, all further studies were carried out at pH=5.

Effect of time on sorption. It was found that the sorption equilibrium in the "sorbent - liquid phase" system is achieved after 3 hours of contact. For all further experiments, the time to establish the sorption equilibrium was 3 hours.

Influence of silver (I) concentration. The initial concentration of metal affects the value of the sorbent sorption capacity. The study of the dependence of the sorption capacity (SC) on the concentration of silver (I) showed that the sorption value changes with the concentration of the silver ions. Figure 3 shows the dependence of the sorption capacity of the sorbent on the initial concentration of silver ions. As can be seen from the figure, the maximum sorption capacity of the sorbent is achieved at an initial metal concentration of $6 \cdot 10^{-3}$ M. So, with an increase in the concentration of the silver ion in the solution, the amount of adsorbed metal increases, and at a concentration of $6 \cdot 10^{-3}$ M it becomes maximum (pH=5, $C_{Ag+}=6 \cdot 10^{-3}$ mol/l, $V_{tot.}$=20 ml, SC = 334,08 mg/g).

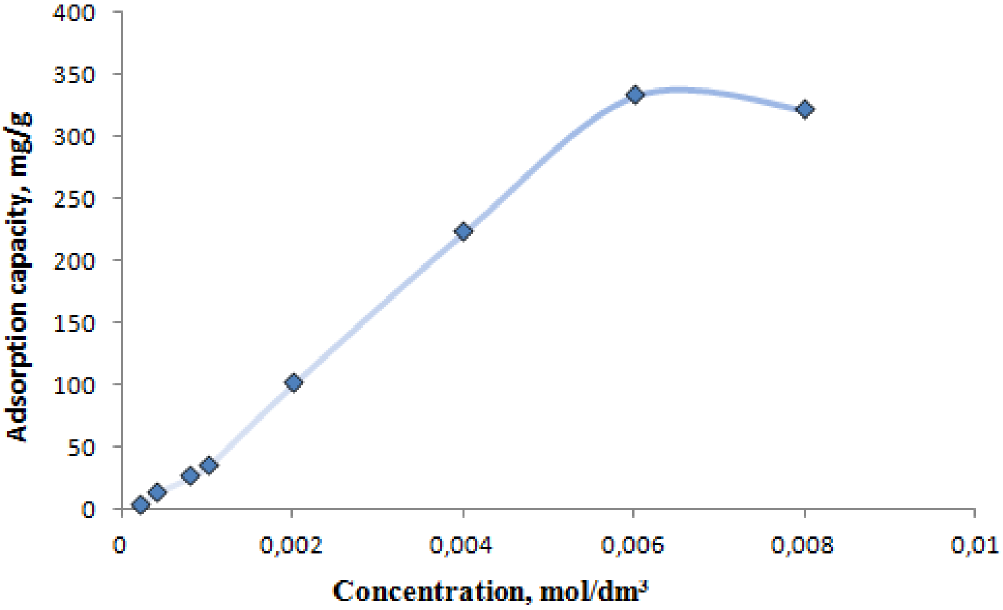


Fig.3. Effect of initial concentration of metal on adsorption capacity.

Study of the desorption of the absorbed silver ion from a polymeric sorbent. The technique of adsorption has a number of benefits, including great reversibility, which enables recycling of wasted adsorbent by desorption.[20] Furthermore, desorption and regeneration of the sorbent is the economical process of removal silver(I) ions. This process allow the repeated use of sorbent. In this process a precipitate of silver (I) with sorbent was formed, filtered off, washed 2-3 times with distilled water in order to remove the diluents, and then dried. To select a suitable eluent, as desorbing agents various acids were tested – mineral HNO_3 and organic CH_3COOH. It was found that the desorption capacity of HNO_3 is higher than that of CH_3COOH. A study of the influence of the HNO_3 concentration showed that Ag(I) ions are maximally desorbed in a nitric acid with concentration of 2.0 M.

Effect of concentration of different acids on the degree of extraction (%) of silver(I)

Acid	Concentration, mol/l	Degree of desorption, %
HNO_3	0,5	65
	1,0	79
	2,0	87
CH_3COOH	0,5	60
	1,0	71
	2,0	76

Adsorption isotherm. The adsorption isotherm depicts the connection between the adsorbate in the surrounding phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium and constant temperature. This graph is extremely important for research on adsorption studies. [21] Adsorption isotherm will be linear only in small ranges, at low sufficient concentrations the linear adsorption isotherm can be applied. [22-23]

In this work, Langmuir adsorption isotherm model was used to explain adsorption process.

Langmuir isotherm. [Langmuir, 1918]: Langmuir's model is widely used to depict physical and chemical adsorption. The Langmuir isotherm model is defined by the following equation:

$$q_e=\frac{q_m K_L C_e}{1+K_L C_e}, \quad (1)$$

In the equation, C_e (mmol/dm^3) represents the adsorbate concentration in the aqueous phase at the adsorption equilibrium, q_e (mmol/g) represents the equilibrium adsorption capacity or the quantity of metal adsorbed on the adsorbent's surface at the adsorption equilibrium, q_m is the maximum adsorption capacity equal to q_e for the complete monolayer, and K_L (dm^3/mmol) is the Langmuir isotherm constant.

A graph showing the dependence of 1/qe on 1/Ce has been produced. The q_{max} and K_L values were calculated using the plot's slope and intercept, respectively. Table 1 illustrates Langmuir isotherm parameters.

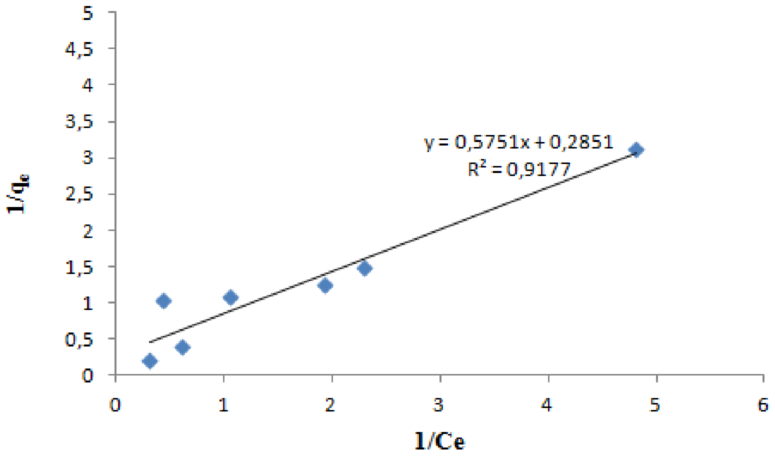


Table 1. Langmuir isotherm parameters .

Langmuir			
$q_{max,}$ mg/g	$K_{L,}$ dm^3/mg	R_L	R^2
3.507	0.004	0.996	0.9177

R_L is a crucial adsorption equilibrium characteristic that determines whether the isotherm is irreversible ($R_L = 0$), favorable ($R_L<1$), linear ($R_L=1$), or unfavorable ($R_L>1$). The Langmuir isotherm model factor R_L may be derived using the following equation:

$$R_L=\frac{1}{1+K_L C_O}, \quad (2)$$

where K_L is the Langmuir constant(dm^3/mmol), C_0 is the initial concentration of adsorbate (mmol/dm^3).

The results obtained reveal that R_L is between 0 and 1 and equivalent to 0.996, indicating that adsorption is favorable under the given circumstances using the Langmuir model. Furthermore, the coefficient of regression R^2=0.9177 indicates that the isotherm model matches well with experimental adsorption values.

Conclusion. For the first time, the preconcentration of silver ions with a synthetic sorbent based on MASC modified with NAA was investigated. The most effective conditions for silver sorption on the adsorbent were identified. Silver removal by adsorbent is most effective in pH 5 solutions. After 3 hours of contact, the "adsorbent - liquid phase" system reached sorption equilibrium. The Langmuir adsorption isotherm was used to describe the adsorption process. As the concentration of silver ions in the solution rises, sorbed metal increases until it reaches its maximum at $6 \cdot 10^{-3}$ M. The results demonstrated that the suggested sorbent may be utilized to preconcentrate silver in aqueous solutions. The regenerated sorbent can be reused for further preconcentration processes.

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СИНТЕТИЧЕСКИЙ ХЕЛАТООБРАЗУЮЩИЙ СОРБЕНТ НА ОСНОВЕ МАЛЕИНОВОГО АНГИДРИДА СО СТИРОЛОМ И 4-НИТРОАНИЛИН-2-АРСОНОВОЙ КИСЛОТОЙ ДЛЯ КОНЦЕНТРИРОВАНИЯ СЕРЕБРА(I)

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Аннотация: Статья посвящена извлечению ионов серебра(Ag) в кислой среде при pH 5 сополимером малеинового ангидрида со стиролом(СМАС), химически модифицированным 4-нитроанилин-2-арсоновой кислотой(НАК). Исследование сорбции ионов Ag(I) проводилось в статических условиях. Изучено влияние различных параметров на процесс сорбции ионов Ag(I). Максимальная сорбция ионов металла наблюдается при pH 5. Сорбционное равновесие устанавливается через 3 часа. Количество сорбированного иона металла увеличивается и при концентрации $8 \cdot 10^{-3}$ М становится максимальным. Для изучения десорбции Ag(I) с сорбента исследовано влияние различных кислот - HNO_3, CH_3COOH с одинаковыми концентрациями. Эксперимент показал, что максимальная десорбция Ag(I) происходит в 2М азотной кислоте (HNO_3).

Ключевые слова: синтетический хелатообразующий сорбент, сорбционная емкость, серебро(I), сорбция, десорбция.

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MALEİN ANHİDRİDİ-STİROL SOPOLİMERİ ƏSASINDA 4-NİTROANİLİN-2-ARSON TURŞUSU İLƏ GÜMÜŞ(I) QATILAŞDIRILMASI ÜÇÜN SİNTETİK XELATƏMƏLƏGƏTİRİCİ SORBENT

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Xülasə: Məqalə gümüş(Ag) ionlarının 4-nitroanilin-2-arson turşusu(NAT) ilə kimyəvi modifikasiya olunmuş, malein anhidridi-stirol sopolimeri(MASS) ilə turş mühitdə pH 5 sorbsiya olunmasına həsr edilmişdir. Ag(I) ionunun sorbsiyasının tədqiqi statik şəraitdə aparılmışdır. Ag(I) ionlarının sorbsiya prosesinə müxtəlif parametrlərin təsiri öyrənilmişdir. Metal ionlarının maksimal sorbsiyası pH 5-də müşahidə edilir. Sorbsiya tarazlığı 3 saatdan sonra əldə olunur. Udulmuş metal ionunun miqdarı artır və $8 \cdot 10^{-3}$ M qatılığında maksimuma çatır. Ag(I)-in sorbentdən desorbsiyasını öyrənmək üçün eyni qatılıqlı müxtəlif turşuların - HNO_3, CH_3COOH təsiri öyrənilmişdir. Təcrübə göstərdi ki, Ag(I)-nin maksimum desorbsiyası 2M azot turşusunda (HNO_3) baş verir.

Açar sözlər: sintetik xelatəmələgətirici sorbent, qatılaşdırma, gümüş(I), sorbsiya, desorbsiya.