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SILVER(I) PRECONCENTRATION USING *m*-AMINOPHENOL CONTAINING SORBENT FROM AQUEOUS SOLUTIONS

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The influence of sorption characteristics on the removal of silver(I) has been examined. The sorption capacity of chelating polymeric sorbent, based on maleic anhydride styrene copolymer modified with *m*-aminophenol, towards Ag(I) ions was studied. The pH of sorption was maximum at the value 6. With the increasing of initial metal concentration, sorption of silver(I) increases and reached maxima at value $80 \cdot 10^{-3}$ M. At the final stage, the elution process of Ag(I) was established and find that HNO₃ 1 M is the best elution agent. Multiple use of the regenerated sorbent for sorption process is possible. This study shows that using of mentioned sorbent modified with *m*-aminophenol is effective for removal of silver(I) ions from aqueous solutions.

Keywords: preconcentration, removal, silver(I), *m*-aminophenol, aqueous solution.

doi

Introduction

Heavy metal ions have a strong ability to collect in objects of environments and consider to be one of it's main pollutants. They can get to human body through different sources, such as aquatic environment and show toxicity even at low doses. So, there is a need to reduce their concentration in environmental samples by using modern analysis methods.

Silver is among of heavy metal ions [1]. Due to the excellent physical properties, such as the highest thermal conductivity it widely used in industry, production of jewellery, coins, photography and etc. On the other hand, being one of the potential toxicants, it's show a big damage to humans life. Increasing content of silver and silver compounds in environment cause several disease, the main and well-known of which is argyria. Therefore, the determination of silver(I) in objects of environment is actual problem.

Various treatment methods, such as sorption, flotation were used to remove silver and its compounds and reduce their concentration [2–20]. Among of them sorption is the most widely used method in recent years. The main advantages of method is simplicity, cost-effectiveness and applicability for the removal of number heavy metal ions from water and wastewater.

Natural adsorbents, such as activated car-

bons were used in absorption of chemicals in environmental objects, such as water, because it has an ability to improve water quality by removing the chemicals [20]. On the other hand, it is not effective for adsorption of total dissolved solids as unable by sorption, hardness, or heavy metals. So, there is a need to use the effective adsorbents, which have high sorption capacity and can selectively absorb the heavy metal ions from aqueous solutions.

In recent years, polymeric chelating sorbents are widely used for preconcentration and removal of heavy metal ions, because of number of advantages, such as higher adsorption capacity, selectivity, than natural one. They allow to determine the trace amounts of elements. Especially, nitrogen and sulfur containing sorbents reveals high selectivity towards silver(I) ions in aqueous solutions. Thus, due to the number of advantages polymeric chelating sorbents are widely used for sorption of silver(I) ions from aqueous solutions.

In present work polymeric sorbent of maleic anhydride styrene copolymer (MASC), modified with *m*-aminophenol was used as an adsorbent for the preconcentration and spectrophotometric determination of silver(I) ions from aqueous solutions. In this regard, the proposed technique is based on the preliminary

concentration of silver(I) from the object using a polymeric chelating sorbent containing fragments of *m*-aminophenol.

Materials and methods

Chemicals and Equipment. The chemicals used in the present study were of analytical grade. The stock solution of Ag(I) was prepared from its salt AgNO₃ by diluting with deionized water till mark. The working solutions were prepared by diluting the appropriate amount of the stock solution. The pH values were maintained constant by using solutions of HCl, NaOH and ammonia-acetate buffer solutions. [21] To maintain a constant ionic strength, a KCl solution was used. Reagent 2,2'-di(2,3,4-trihydroxyphenyl-azo)biphenyl (R) was prepared by the azo combination of a diazotized amine with pyrogallol. In order to use in the analysis, the sorbent pellets were ground in an agate mortar and sieved through a sieve with diameter 0.14 mm. Each experiment was repeated twice. To study the sorption of silver, we used a chelating sorbent based on a copolymer of maleic anhydride with styrene, containing fragments of *m*-aminophenol (Scheme 1).

Scheme 1. Molecular structure of *m*-aminophenol.

Adsorbent synthesis

Adsorbent synthesis was carried out by the known technique [22]. For each experiment 3 g of maleic anhydride styrene copolymer was measured and the corresponding quantity of amine added to a flask. *m*-Aminophenol was solved in hot water. Reaction proceeds in the presence of formalin at 330–340 K and lasts approximately 30–40 min. The reaction is carried out in sandy bath by continuous mixing. Since the reaction is carried out in aquatic environment anhydride groups of copolymer subject to hydrolysis. Because of the mutual influence of formaldehyde and amine nonstable carbonylamine is formed. The resulting carbonylamine mutually interacts with carboxyl groups of mac-

romolecule and the amine fragment enters the macromolecule.

For removal of remaining parts of reaction product sorbent has been rinsed several times with distilled water. Then constant mass was dried in vacuum desiccators at 323 K, grinded and skipped through sieve with 0.14 mm of pore diameter. The resulting product was used as the solid phase in current research.

Adsorption experiments

Sorption process was carried out under static conditions. For each experiment 2 ml of metal ion solution with a known concentration (10⁻² mol/L) was added into 50 ml conical flasks. The pH of solutions were adjusted with pH meter Ionomer I-130 by using of 0.1 mol/L of NH₄OH and 0.1 mol/L CH₃COOH. The final concentrations of Ag(I) ions in the filtrate determined at λ=540 nm.

The absorption capacity of Ag(I) ions sorbed by sorbent was calculated from the following equation:

$$Q = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where Q – is the sorption capacity of sorbent, mg/g, V – volume of solution, C_0 – is the initial concentration of silver ions mg/l, C is the concentration of silver ions after the sorption process (mg/l) and m – mass of the sorbent (mg). The maximum sorption capacity of sorbent with respect to silver ions is 230.4 mg/g.

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

$$\% R = \frac{C_0 - C_e}{C_0} \times 100, \quad (2)$$

where R is the percentage recovery, C_0 and C_e are the initial and equilibrium concentrations of the silver ion. The maximum percentage recovery of silver ions from the solution when using a sorbent modified with *m*-aminophenol was 88%.

Fig. 1. The FTIR spectra of the sorbent.

Results and discussions

The structure of the obtained sorbent was studied by FTIR spectroscopy.

FTIR spectroscopy

The FT-IR spectroscopy of the sorbent has been studied. In IR spectrum of sorbent are observed the following vibrations: stretching dances of NH group at $3400\text{--}3200\text{ cm}^{-1}$, stretching dances of OH group at $355\text{--}3200\text{ cm}^{-1}$, --C=O group stretching dances of carboxyl group at $1750\text{--}1715\text{ cm}^{-1}$, C–N stretching dances and N–H deformation dances at $1570\text{--}1550\text{ cm}^{-1}$, valent dances in benzene ring at $1610\text{--}1510\text{ cm}^{-1}$, deformation dances in benzene ring at $710\text{--}680\text{ cm}^{-1}$.

Influence of pH

pH of solution is one the most important characteristics, determining the behavior of ions in aqueous solutions. The effect of pH on the sorption of silver(I) was studied by varying the pH within the range of 3–7. Sorption of silver ions was carried out in static conditions from aqueous solutions. Sorption of the silver(I) was carried out from the volume of 25 ml of the solution. Due to this, was added 1.5 ml of the reagent solution to the aliquot part of the sorbent solution with a volume of 1 ml and diluted till mark with pH. The optical density of the solution is measured on a photocolorimeter KFK-2 at $\lambda = 440\text{ nm}$.

The results showed that the recovery of silver was maximized in the pH of solution 6. At pH 6 the degree of sorption passes through a maximum. So, the sorption capacity of sorbent was pH dependent and in order to achieve the maximum efficiency, selectivity of the silver(I) extraction, a pH of 6 was selected for the subsequent studies.

Influence of contact time

The effect of contact time on the removal of silver(I) from aqueous solutions was studied. In order to carry out the influence of contact time on adsorption of silver(I) from aqueous solutions, an aliquot part of solution was taken every 30 minutes and analyzed by AAS. Results of two parallel analysis were averaged. By the results, the sorbent is fully saturated with silver(I) after 210 min. The recovery of silver reached 91%. Further increasing in saturation time wasn't significantly change the adsorption. Thus, saturation time of 210 min was chosen for further experiments.

Influence of initial Ag^+ concentration

Influence of initial metal concentration is one of the main parameters affecting sorption process. Effect of initial Ag(I) concentration on sorption was studied. It is found, that with increasing the initial concentration of metal in the solution, sorption of silver ion increases and, reached a maximum at concentration $80 \cdot 10^{-3}\text{ M}$.

(pH 6, $C_{Ag^+} = 80 \cdot 10^{-3}$ M, $V_{total} = 20$ ml, $m_{sorbent} = 0.03$ g). At this value all the Ag^+ ions are adsorbed by solid phase. Then the sorption process reached equilibria.

Influence of ionic strength

Effect of ionic strength on sorption of silver(I) was studied. Silver(I) was sorbed from aqueous solutions containing 0.1–1.4 M KCl. The presence of KCl increased the adsorption capacity due to value of $\mu=0.6$. Further, there is a significant decrease in metal(I) sorption from solutions with a concentration of more than 0.6 M. Therefore, all further experiments were carried out in aqueous solutions with an ionic strength of 0.6 M.

Effect of coexisting ions

The effect of co-existing ions on Ag(I) adsorption process was studied. By the results of experiments it can be seen, that sorbent could adsorb Ag(I) ions in the presence of alkali and alkaline-earth ions, such as Na^+ , K^+ , Ca^{2+} . Transition metals, such as Zn^{2+} , Ni^{2+} , Cr^{3+} and Pd^{2+} also couldn't prevent to the Ag(I) adsorption process. This process indicates, that the occurring adsorption is selective and in the same conditions adsorbent could separate more silver(I) ions than other metal ions.

The desorption process

Desorption and regeneration of the sorbent is the economical process of recovering metal ions. This process allow the repeated use of sorbent. In this process a precipitate of Ag^+ with sorbent was formed, filtered off, washed 2–3 times with distilled water in order to remove the diluents, and then dried. As desorbing agents used the 0.5M, 1M, 1.5M, 2M solutions of H_2SO_4 and HNO_3 . The best elution properties toward silver(I) ions possessed the 1 M nitric acid solution.

The sorption-desorption process is carried out until the used sorbent does not lose its quality in the process of concentration. The results of the studies showed that the copolymer of styrene with maleic anhydride modified with m-aminophenol can be used 7 times for the concentration process without changing its qualities.

Adsorption isotherms

Adsorption isotherms are used in order to explain the adsorption process between adsorbent and adsorbate. Adsorption isotherms were obtained by varying the initial concentration of Ag(I) ions from $2 \cdot 10^{-3}$ mol/L to $80 \cdot 10^{-3}$ mol/L. The maximum adsorption capacity of adsorbent toward silver(I) was determined using Langmuir isotherm model.

Langmuir adsorption isotherm

Adsorption of Ag(I) can be easily explained using Langmuir adsorption isotherm. Langmuir adsorption model based on the assumption that molecules are adsorbed at a fixed adsorption site.

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

where C_e (mg/L) is the equilibrium concentration of Ag^+ in solution, q_e (mg/g) is the equilibrium adsorption capacity, q_m (mg/g) is the adsorption capacity of monolayer and K_L (L/mg) is the Langmuir constant. Langmuir adsorption isotherm constants were calculated from the linear plot of dependence of C_e/q_e on C_e , which is shown in Figure 2.

The main characteristic of the Langmuir isotherm is a separation factor R_L , which can be calculated by the following equation:

$$R_L = \frac{1}{1 + b C_0} \quad (2)$$

where b is the Langmuir constant (L/mmol), C_0 is the initial concentration of silver(I) ions (mg/L). The value of equilibrium parameter R_L between 0 and 1 shows favorable adsorption process. By the results of adsorption study R_L found to be 0.996, which indicates to adsorption favorable by Langmuir model. The value of the regression coefficient $R^2=0.9971$ indicates that Langmuir isotherm model fits good with experimental adsorption data.

Langmuir isotherm parameters for the adsorption of Ag(I) ions onto adsorbent

Adsorbent	Langmuir			
	(q_{max} , mg/g)	(K_L , L/mg)	(R_L)	(R^2)
m-aminophenol	333.3	0.0035	0.996	0.9971

Fig. 2. Langmuir adsorption isotherm.

Conclusions

Current research represents a very simple, rapid, sensitive and inexpensive method for the selective removal of silver(I) ions from aqueous solutions. This study is characterized by high removal efficiency, which reveals, that MASC modified with *m*-aminophenol was suitable for removal of silver(I) ions from aqueous media. Various sorption factors, such as pH, contact time, initial metal ion concentration and ionic strength effect the adsorption of silver(I) ions.

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GÜMÜŞ(I)-in *m*-AMİNOFENOL FRAQMENTLİ SORBENTLƏ SULU MƏHLULLARDAN QATILAŞDIRILMASI

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Sorbsiya parametrlərinin gümüş(I)-in çıxarılmasına təsiri öyrənilmişdir. Malein anhidridi stiroil sopolimeri əsasında, *m*-aminofenol ilə modifikasiya olunmuş xelatəmələgətirici polimer sorbentin Ag(I)-ə qarşı sorbsiya tutumu öyrənilmişdir. Sorbsiya pH 6 qiymətində maksimum olur. Metalın ilkin qatılığı artdıqca, gümüş(I)-in sorbsiyası artır və $80 \cdot 10^{-3}$ M maksimum olur. Son mərhələdə, Ag(I)-in desorbsiya prosesi öyrənilmiş və 1 M HNO₃-ün ən yaxşı elyurədicisi agent olduğu müəyyənleşdi. Bərpa olunmuş sorbentin sorbsiya prosesi üçün çoxlu sayda istifadəsi mümkündür. Hazırkı araşdırma göstərir ki, anhidridi stiroil sopolimeri əsasında, *m*-aminofenol ilə modifikasiya olunmuş xelatəmələgətirici polimer sorbentin istifadəsi gümüş(I)-in sulu məhlullardan çıxarılması üçün effektivdir.

Keywords: *qatılaşıdırılma, çıxarılma, gümüş(I), m-aminofenol, sulu məhlul.*

КОНЦЕНТРИРОВАНИЕ СЕРЕБРА(I) СОРБЕНТОМ, СОДЕРЖАЩИМ *m*-АМИНОФЕНОЛ, ИЗ ВОДНЫХ РАСТВОРОВ

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Изучено влияние сорбционных характеристик на извлечение серебра(I). Изучена сорбционная ёмкость хелатообразующего полимерного сорбента на основании малеинового ангидрида со стиролом, модифицированного *m*-аминофенолом по отношению к ионам Ag(I). Сорбция максимальна при pH 6. С увеличением начальной концентрации металла сорбция серебра(I) увеличивается и достигает максимума при значении $80 \cdot 10^{-3}$ М. Изучен также процесс десорбции Ag(I) и найдено, что 1 М HNO₃ является лучшим элюирующим агентом. Возможно многократное использование регенерированного сорбента для процесса сорбции. Данное исследование показывает, что использование хелатообразующего полимерного сорбента на основании малеинового ангидрида со стиролом, модифицированного *m*-аминофенолом является эффективным для извлечения серебра(I) из водных растворов.

Ключевые слова: *концентрирование, извлечение, серебро(I), m-аминофенол, водный раствор.*