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PRECONCENTRATION OF SILVER (I) ON THE MODIFIED SORBENT FROM AQUEOUS SOLUTIONS

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Abstract.   Preconcentration of silver (I) on the modified sorbent from aqueous solutions has been experimentally carried out. For this aim synthetic polymeric chelating sorbent based on maleic anhydride styrene copolymer modified with 1,2,3-triphenylguanidine has been synthesized. Some important sorption characteristics and experimental parameters of synthesized synthetic polymeric chelating sorbent toward silver (I) ions have been studied. Influence of pH, contact time, effect of initial metal concentration, ionic strength on the sorption of silver (I) on synthetic polymeric chelating sorbent modified with 1,2,3-triphenylguanidine from aqueous solutions has been studied. The structure of the obtained sorbent was studied by FTIR spectroscopy. Adsorption capacity and maximum removal efficiency of synthetic chelating sorbent toward silver (I) ions have been calculated. The highest adsorption capacity of modified synthetic chelating sorbent toward silver (I) ions is 462,8 mg g^{-1}. The maximum removal efficiency is equal to 92%. The desorption process using some organic and mineral acids as the desorbing agents has been investigated. The results of experiments shows synthetic polymeric chelating sorbent based on maleic anhydride styrene copolymer modified with 1,2,3-triphenylguanidine show a high selectivity and sensitivity on silver (I) extraction.

1.   Introduction

Heavy metal ions are one of the main pollutants of environment. They are found naturally in the earth, become concentrated as a result of human caused activities and can enter plant, animal, and human tissues via inhalation, manual handling etc.

Silver is a white noble metal. It is widely distributed throughout the world and occurs as the metal and also as sulfide ores (e.g. argentite). It is found in the environment in four oxidation states: 0, 1+, 2+ and 3+, with 0 and 1+ being the most common, while 2+ and 3+ are seldom seen naturally in the environment (Ansari, 2008). Silver has unique physic-chemical properties, such as malleability, ductility, and resistance to atmospheric oxidation. Due to these unique properties silver has long been used in the manufacture of coins, ornaments, and jewelry. On the other hand, silver is a toxic heavy metal according to World Health Organization. Average silver concentrations in natural waters are 0.2–0.3 µg/litre (World Health Organization, 2003). Therefore, preconcentration of silver(I) ions from aqueous solutions is extremely important and actual from the point of view of its toxicity.

In order to reduce the quantum of silver(I) ions in aqueous solutions different treatment methods, such as coagulation, floatation, adsorption, extraction, ion-exchange, metal replacement, electrolysis and electrodialysis have been developed (Calace, 2003;

Bowe, 2003; Akgul, 2006; Hasany, 2001; Manzoori, 2003; Dimeska, 2006). Adsorption from aqueous solutions is easy to carry out, this method is economic and an efficient for the removal or recovery of silver ion from aqueous solutions. Taking into account the above mentioned advantages, the sorption preconcentration of silver (I) with subsequent photometric determination is an effective method for silver (I) recovery from aqueous solutions.

Activated carbon is one of the most effective adsorbents used to remove a number of substances from objects of environment, including silver ion (Adams, 1992). Activated carbons have a developed porous structure, which is characterized by pore size. The disadvantage of activated carbon is that the adsorption on it is often irreversible.

Synthetic polymeric adsorbents are widely used for preconcentration of silver (I) from aqueous solutions (Alieva, 2019; Bahmanova, 2018; Nazarova, 2019). Synthetic polymeric sorbents with functional groups, containing nitrogen, sulfur, oxygen etc. due to high adsorption capacity have a high value of selectivity. These advantages of analytical characteristics allow to use synthetic polymeric sorbents for extraction and preconcentration of silver (I) from aqueous solutions.

Present research devoted to preconcentration of silver (I) on the modified sorbent from aqueous solutions. For this purpose synthetic polymeric chelating sorbent based on maleic anhydride styrene copolymer modified with 1,2,3-triphenylguanidine has been synthesized. Some important sorption characteristics and experimental parameters of synthesized synthetic polymeric chelating sorbent toward silver (I) ions have been studied.

2. Experimental

2.1. Reagents

All of the chemicals and reagents used in analysis were of analytical grade. The standard solution of Ag(I) was obtained by dissolving an appropriate amount of $AgNO_3$ in distilled water and adding 2-3 drops of concentrated HNO_3 in order to prevent hydrolysis. Working solutions were prepared from the standard solution by dilution with distilled water. The solution of reagent 2,2'-di (2,3,4- trihydroxyphenylazo) biphenyl with concentration $1.0x10^{-3}$ mg L^{-1} was prepared by bidistilled water. Equilibrium concentration of silver (I) ions were determined in the liquid phase using adsorption spectrophotometry at 540 nm, pH 6.0. (Bulatov, 1972; Mammadov, 2018) Adsorption studies were carried out by using $1.0x10^{-2}$ mg·L^{-1} water solution of $AgNO_3$.

The effect of pH on the adsorption of Ag(I) ions was studied at the range of pH=3-8 respectively. The pH of the buffer solutions with concentration 0,1 N was maintained constant using an acetic acid and ammonium hydroxide solutions respectively. The effect of ionic strength on the adsorption was studied using 2 mol L^{-1} KCl solution. Solution of 0.5 mol L^{-1} KOH was used in desorption process.

2.2. Apparatus

The optical density of the test solutions has been measured on phototocolorimeter КФК-3. pH of the solutions was measured using an ionomer И-130. For each experiment the contents of the sorption flasks were continuously stirred using a stirrer ORBITAL SHAKER TS-1. The sorbent was dried on evaporator ZymarkTurboVap LV. The IR spectra of the sorbent were recorded on a LUMOS IR
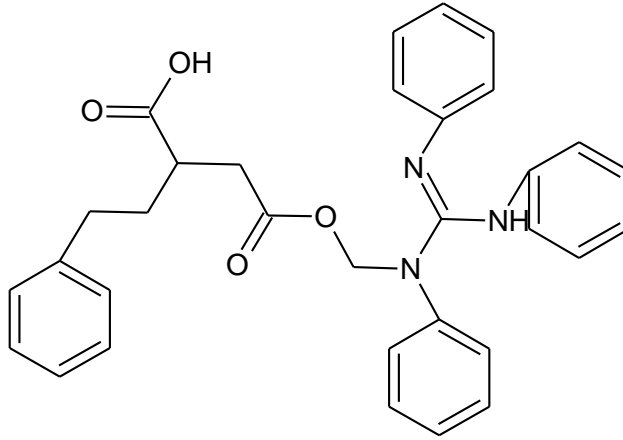
Fourier microscope (BRUKER Germany).

Figure 1. Molecular structure of 1,2,3-triphenylguanidine

2.3. Synthesis of chelating adsorbent.

Adsorbent synthesis was carried out by the known technique (Akperov, 2002). For each experiment 3 g of maleic anhydride styrene copolymer was measured and the corresponding quantity of 1,2,3-triphenylguanidine added to a flask. 1,2,3-triphenylguanidine was solved in water. Reaction proceeds in the presence of formalin at 333.15-343.15 K and lasts approximately 35-45 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 macromolecule and the amine fragment enters the macromolecule.
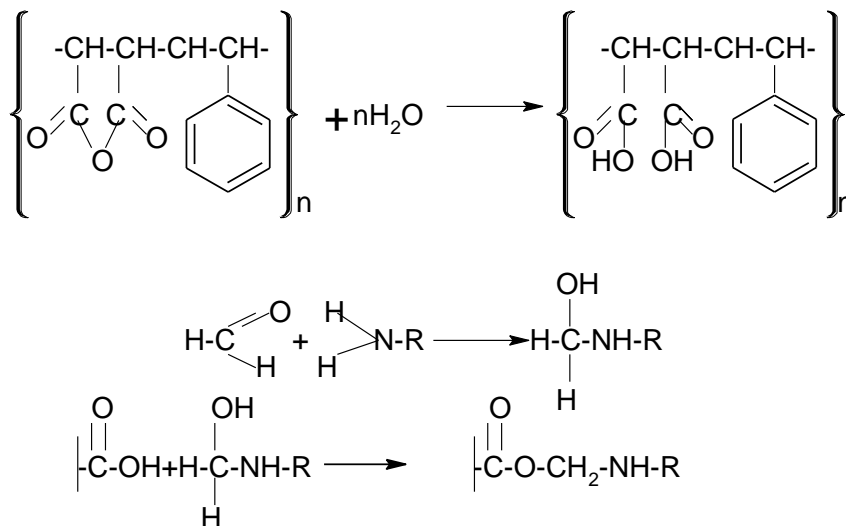

Figure 2. Representation of the polycondensation process

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 investigated by Infrared spectroscopy and then was used as the solid phase in current research. The schematic representation of considered reaction is shown in Fig. 1.

3.   Results and discussion

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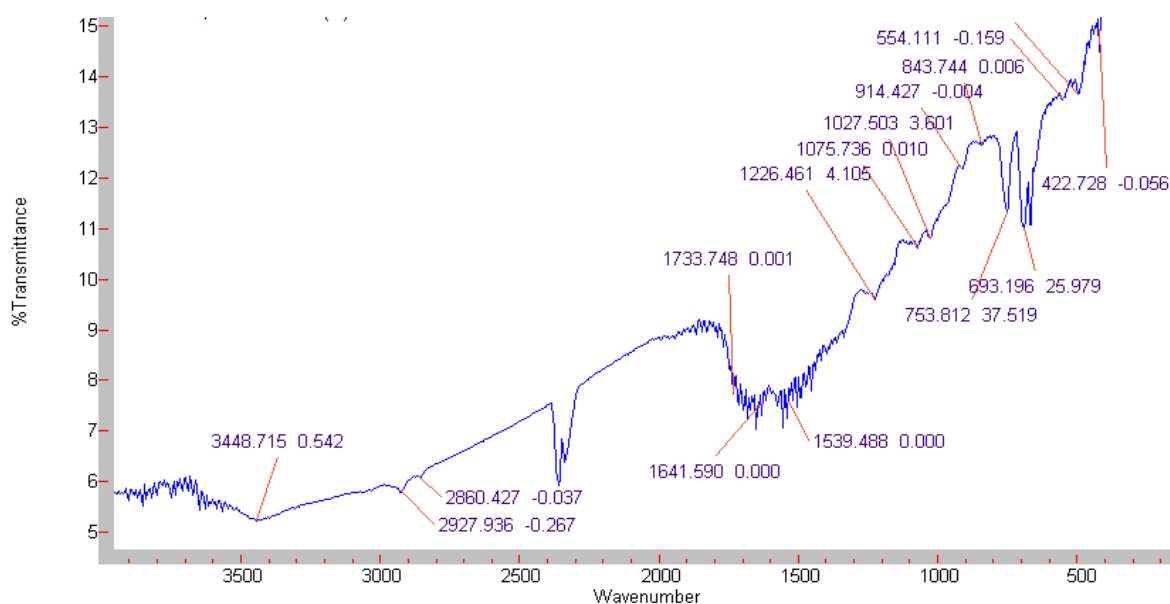

Figure 3. The FT-IR spectroscopy of the sorbent

The FT-IR spectroscopy of the sorbent has been studied. In IR spectrum of sorbent are observed the following vibrations: –OH group valence vibrations of carboxyl group at 3600-3100 cm^{-1}, –NH group valence vibrations at 3400-3200 cm^{-1}, -C=O group valence vibrations of carboxyl group at 1750-1715 cm^{-1}, C-N valence vibrations and N-H deformation vibrations at 1570-1550 cm^{-1}, deformation C=C vibrations in benzene ring at 710-680 cm^{-1}.

3.2 The effect of pH
pH or medium acidity is one of the important experimental parameters affecting sorption process. The effect of pH on the removal or retention of silver (I) ions from aqueous solutions has been investigated. The appropriate pH of buffer solutions was adjusted using 0, 1 N CH_3COOH and NH_4OH to achieve the desired medium acidity (3–8). At pH=6 removal of silver (I) ions is the maximum and higher than at pH<6. According to results, after pH 6 the sorption of silver (I) ions will decreases. Therefore, the optimum pH value for quantitative adsorption of the silver (I) is pH=6. Fig. 2 shows the dependence of the sorption capacity on the medium acidity.

3.3 Influence of contact time

Contact time is also an important parameter that determines the diffusion of molecules of the absorbed substance into the pores of the sorbent. 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 analyses were averaged. By the results, the sorbent is fully saturated with silver (I) ions during 150 minutes. After 150 min, the adsorption rate becomes constant, the adsorption process reach equilibrium and further increasing in saturation time wasn't significantly change the adsorption of metal ions. Therefore, saturation time of 150 minutes was chosen for further experiments.

3.4 The effect of initial silver (I) solution concentration

The effect of initial silver (I) solution concentration on the adsorption capacity of modified synthetic chelating polymeric sorbent was determined using solutions of concentrations ranging from 0.2 to 8.0 M. The amount of the sorbed silver (I) from aqueous solutions was determined. The mass of the sorbent is 500 mg. The results of the experiments show, that the amount of silver(I) adsorbed onto the surface of modified synthetic chelating polymeric sorbent increases with increasing initial silver(I) ions concentration and reaches maximum at $6 \cdot 10^{-2}$ mol L^{-1}. The sorption capacity of the sorbent toward silver (I) calculated by the equation:

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

where Q- is the sorption capacity of sorbent($mg \cdot g^{-1}$), V-volume of solution, C_0- is the initial concentration of silver ions ($mg \cdot l^{-1}$), C is the concentration of silver ions after the sorption process ($mg \ l^{-1}$) and m-mass of the sorbent (mg). The maximum sorption capacity of sorbent with respect to silver ions is 462,8 $mg \cdot g^{-1}$.

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:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where R is the percentage recovery, C_o 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 1,2,3-triphenylguanidine was 92%.

3.5 Influence of ionic strength

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 μ=1.0. Further, there is a significant decrease in metal (I) sorption from solutions with a concentration of more than 1.0 M. Therefore, all further experiments were carried out in aqueous solutions with an ionic strength of 1.0 M.

3.6. Desorption process

From the point of view of analytical chemistry 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 silver (I) 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;2 M solutions of H₂SO₄ and HNO₃. The best elution properties toward silver (I) ions possessed the 0, 5 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 1,2,3-triphenylguanidine can be used several times for the preconcentration of silver(I) process without changing its qualities.

4. Conclusion

Study of sorption behavior of silver (I) on synthetic chelating sorbent modified with 1,2,3-triphenylguanidine show that the highest sorption achieved at value of pH 6. Sorption capacity of Ag (I) onto the synthetic polymer modified sorbent was studied and found to be 462,8 mg g^{-1}. By the results of analysis period of 3 hours was selected as time to reaching the sorption equilibrium or contact time.

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