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**SEPARATION OF CADMIUM BY CHELATING POLIMERIC SORBENTS AND
APPLYING PRECONCENTRATION****E.H.Aliyev, *F.N.Bahmanova, *S.Z.Hamidov, *F.M.Chiragov***"Azersu" OJSC Central Laboratory***Baku State University**ciraqov@mail.ru*

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Copolymer of maleic anhydride with styrene is modified and two new chelating sorbents are synthesized. These sorbents contains fragments of *m*-phenylenediamine (S1) and diaminobenzidine (S2). The sorption conditions of cadmium with these sorbents were investigated for the first time (pH=5, $C_{Cd^{2+}}=6 \cdot 10^{-2}$ mol/l, $V_{liquid}=20$ ml, $m_{sorbent}=0.05$ g, CE=487 mg/g (for S1) and CE=509 mg/g (for S2).

Sorption was studied in static and dynamic modes. The results of the study showed that the maximum sorption of sorbents S1 and S2 is observed at pH 5. The effect of metal concentration on sorption was also studied. The developed methodology has been applied to isolate cadmium(II) from the water of the river Agstafa and the river Jogaz of the Kazakh region of the Azerbaijan Republic.

Keywords: copolymer, sorbent, *m*-phenylenediamine, diaminobenzidine, concentration, determination of cadmium, desorption, method.

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A heavy metal, such as cadmium(II), which enters the environment as a result of human activity, is a dangerous pollutant of nature. To separate this metal from various natural and industrial objects, spectrophotometric, chromatographic, and sorption methods [1–3] are used. The basic methods for determining ions do not always satisfy current requirements of the detection limit and require their separation from related elements. Combined methods, including pre-concentration are more preferable for increasing the sensitivity.

Pre-concentration methods allow you to isolate trace elements from a large volume of complex composition and lower the detection limit. By proposed method, you can also eliminate or significantly reduce the influence of macro-components, and this improves the accuracy and accuracy of the analysis [4, 5]. Many previously known sorbents have certain disadvantages: low sorption capacity [6–12], unsatisfactory degree of sorption [8]. The synthesis of sorbents with higher sorption properties with respect to cadmium(II) always remains an important problem. The aim of the present work is the study of the cadmium sorption by chelating sorbents based on the matrix of maleic anhydride with styrene.

Experimental part

In the present work only chemical grade reagents are used for experiment. Solution of cad-

mium (10^{-2} M) was prepared by dissolving an sample of $Cd(NO_3)_2 \cdot 4H_2O$ [13] in distilled water. Working solutions were prepared by diluting the initial one. The sorbents containing *m*-phenylenediamine (S1) and diaminobenzidine (S2) fragments which are used for experiment were synthesized according to the procedure [14].

Synthesis of sorbents based on a copolymer of maleic anhydride with styrene. The radical copolymerization of maleic anhydride with styrene is carried out on a benzene solution in a water bath at 75–80°C for 140 minutes. Azo-*bis*-isobutyronitrile which is recrystallized in ethanol was used as an initiator. The synthesized copolymer is washed by benzene and dried oven at 50°C until constant mass is obtained. The output of the copolymer is 95–97%. From the literature it is known that maleic anhydride forms a linear sequential copolymer with styrene with a molar ratio of 1:1. The calculated amount of formaldehyde and the corresponding amine is added to the synthesized copolymer. The reaction is carried out in a sand bath with continuous stirring. Due to the fact that the reaction is carried out in an aqueous medium, the anhydride groups in the copolymer composition undergo hydrolysis.

As a result of the interaction of formaldehyde and amine, unstable carbonylamine is formed in the system. Obtained carbonylamine

interacts with the carboxyl groups of the macromolecule and the introduced amine fragment enters the macromolecule. Granules of sorbent of plant grounded in the agate stage and sieved through a sieve (0.14 mm) in order to use it in the analysis.

The identification of sorbents was carried out by IR spectroscopy.

Cadmium sorption was studied in static and dynamic conditions. The required acidity of the medium was created (maintained) with solutions of HCl, NaOH, and ammonium-acetate buffer solutions. The equilibrium time in the system was determined during preliminary kinetic experiments. The concentration of cadmium in equilibrium solutions was determined by the spectrophotometric method. The initial concentration of the reagents in the sorption experiments was 10^{-3} mol/l. The magnitude of sorption, expressed as mg/g, was calculated by the formula:

$$\Gamma = \frac{(C_0 - C_{\text{equil}}) \cdot V}{m},$$

where C_0 – initial concentration of metal in solution, mol/l; C_{equil} – concentration of solution at equilibrium after sorption, mol/l; V – volume of solution from which sorption is carried, l; m – mass of sorbent, g. Sorption level (in %) is calculated by formula:

$$\Gamma(\%) = \frac{C_0 - C_{\text{equil}}}{C_0} \cdot 100$$

Equipment. The pH of the solutions was measured using a PHS-25 ionomer with a glass electrode. The concentration of absorbed cadmium was determined on the device ICP-OES Thermo ICAP 7400 Duo. The concentration of cadmium(II) was calculated using a calibration curve, the results obtained were processed by mathematical and statistical methods [15].

Results and discussion

1. *Static conditions.* We have investigated the sorption of cadmium on the surface of the sorbent. One of the main factors influencing the degree of sorption of cadmium is the acidity of the medium. The effect of pH on the concentration of cadmium(II) with a chelateforming sorbent in the pH range of 1–10 was studied.

The sorption capacity of the sorbent is investigated in static conditions. 2 ml of 10^{-2} M cadmium solution is added to 50 mg of sorbent and left in the buffer medium at pH = 1–8. The mixture is filtered and the optical density is measured at $\lambda = 490$ nm. The amount of the remaining metal in the solution is determined on the basis of the dependence of optical density on the concentration and the amount of sorbed ions is calculated accordingly. It is found that the maximum extraction of cadmium was at pH 6.

During the preliminary kinetic experiments, it was found that the maximum degree of cadmium sorption is reached in 2 hours and then practically does not change. For all further experiments, the time to establish the sorption equilibrium was 2 hours.

The influence of the ionic strength of the solution was studied by the photometric method. Cadmium (II) was sorbed from solutions containing 0.1–1.4 M KCl. The results of the study showed that a significant decrease in cadmium sorption occurs from KCl solutions with a concentration of more than 0.8 M.

One of the main criterias for assessing sorption processes is sorption isotherms, which determine the dependence of the magnitude of the sorption of a substance on its equilibrium concentration in solution. With an increase in the concentration of cadmium in the solution, the amount of sorbed metal increases, and at a concentration of $6 \cdot 10^{-2}$ mol/l, it becomes maximum at (pH=5, $C_{\text{Cd}^{2+}} = 6 \cdot 10^{-2}$ mol/l, $V_{\text{liquid phase}} = 20$ ml, $m_{\text{sorbent}} = 0.05$ g, CE=487 mg/g (for S1) and CE=509 mg/g (for S2)).

The possibility and the conditions for desorption of cadmium with various mineral acids also was studied and determined after concentration on the proposed sorbents (HClO_4 , H_2SO_4 , HNO_3 , HCl) (Table 1).

The table 1 shows that cadmium(II) is quantitatively desorbed with 2 M HClO_4 . It is possible repeated use of the regenerated sorbent for concentration.

2. *Dynamic conditions.* **Influence flows rates solution of sample and eluent.** Cadmium(II) solution was passed through a minicolumn, containing 100 mg of sorbent at a rate of 1–5 ml/min.

Table 1. The effect of the concentration of different acids on the degree of extraction (%) of cadmium ($n^*=3$)

Acid	Concentration, mol/l	Degree of desorption, %	
		S1	S2
HCl	0.5	74	69
	1.5	83	77
	2.0	90	92
HClO ₄	0.5	87	89
	1.5	91	93
	2.0	96	98
HNO ₃	0.5	80	71
	1.5	87	74
	2.0	91	92
H ₂ SO ₄	0.5	81	80
	1.5	89	86
	2.0	90	91

n^* – number of experiments

As a result of the analysis, it was found that the optimal flow rate is 1.0 ml/min. The maximum desorption of absorbed cadmium(II) ions occurs at a flow rate of eluent of 1 ml/min. In further studies, 5.0 ml of 2.0 M HClO₄ was used as eluent at a flow rate of 1.0 ml/min.

The developed methodology has been applied to isolate cadmium(II) from the water of the rivers Agstafa and Jogaz of the Kazakh region of the Azerbaijan Republic.

The experiment. In order to extract cadmium(II) ions from river waters, 100 ml of the filtered sample is acidified with 5.0 ml of HNO₃ (1:1) and passed through a mini column at a flow rate of 1.0 ml/min. Sorbed ions are eluted with 5.0 ml of 1.0 M HClO₄. The concentration of cadmium(II) in the solution of the eluate is determined by using the device "ICP-OES thermo ICAP 7400 Duo". The results are presented in Table 2.

Table 2. Results of cadmium(II) determination, µg/l in rivers waters ($n=5$, $P=0.95$)

Water sample	Method EPA 20071	Photometric method
Agstafa river	10.4±0.024	10.27±0.031
Jogaz river	1.11±0.035	0.996±0.027

The results of the analysis showed the possibility of using the synthesized sorbent for the sorption-spectrophotometric determination of cadmium(II). The developed method is more economical, faster and environmentally safer than [6, 7] (Table 3).

Table 3. Optimal conditions for the concentration of cadmium (II) ions under static conditions

Sorption volume, mg/g	Reference
487	S1 [our]
509	S2 [our]
162.4	[6]
31.95	[9]

Thus, the current study showed the possibility of using the matrix of a copolymer of maleic anhydride by styrene, modified with amines, for the sorption-photometric determination of cadmium. It can be reused after regeneration. The developed method is applied to the determination of cadmium trace amounts in various natural and industrial objects.

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İLKİN QATILAŞDIRMA YOLU İLƏ KADMIUMUN XELATƏMƏLƏGƏTİRİCİ POLİMER SORBENTLƏRLƏ AYRILMASI

E.H.Əliyev, F.N.Bəhmənova, S.Z.Həmidov, F.M.Çıraqov

Malein anhidridinin stiroil ilə sopolimerinin modifikasiyası yolu ilə tərkibində *m*-fenilendiamin (S1) və diaminobenzidin (S2) fraqmentlərini saxlayan iki xelatəmələgətirici sorbent sintez edilmişdir. İlk dəfə olaraq kadmiyumun bu sorbentlərlə sorbsiya şəraiti tədqiq edilmişdir ($\text{pH}=5$, $C_{\text{Cd}^{2+}}=6 \cdot 10^{-2}$ mol/l, $V_{\text{m.f.}}=20$ ml, $m_{\text{sorb.}}=0.05$ q, $\text{ST}=487$ mq/q (S1 üçün) və $\text{ST}=509$ mq/q (S2 üçün)). Sorbsiya statik və dinamik şəraitdə öyrənilmişdir. Tədqiqatın nəticələri göstərdi ki, S1 və S2 sorbentlərinin maksimal sorbsiyası pH 5-də müşahidə olunur. Eyni zamanda metalın qatılığının sorbsiyaya təsiri də tədqiq edilmişdir. İşlənmiş metodika kadmiyum(II) Azərbaycan Respublikasının Qazax rayonunun Akstafa və Coqaz çaylarının suyundan ayrılması məqsədi ilə tətbiq edilib.

Açar sözlər: sopolimer, sorbent, *m*-fenilendiamin, diaminobenzidin, qatılaşıdırma, kadmiyumun təyini, desorbsiya, metodika.

ВЫДЕЛЕНИЕ КАДМИЯ ХЕЛАТООБРАЗУЮЩИМИ ПОЛИМЕРНЫМИ СОРБЕНТАМИ С ПРИМЕНЕНИЕМ ПРЕДВАРИТЕЛЬНОГО КОНЦЕНТРИРОВАНИЯ

Э.Г.Алиев, Ф.Н.Бахманова, С.З.Гамидов, Ф.М.Чырагов

Модификацией сополимера малеинового ангидрида со стиролом синтезированы два хелатообразующих сорбента, содержащие фрагменты *m*-фенилендиамина (S1) и диаминобензидина (S2). Впервые определены сорбционные условия кадмия этими сорбентами ($\text{pH}=5$, $C_{\text{Cd}^{2+}}=6 \cdot 10^{-2}$ моль/л, $V_{\text{ж.ф.}}=20$ мл, $m_{\text{сорб.}}=0.05$ г, $\text{CE}=487$ мг/г (для S1) и $\text{CE}=509$ мг/г (для S2). Сорбция изучалась в статическом и динамическом режимах. Результаты исследования показали, что максимальная сорбция сорбентов S1 и S2 наблюдается при pH 5. Также было исследовано влияние концентрации металла на сорбцию. Разработана методика для выделения кадмия(II), которая применяется с целью его извлечения из рек Акстафа и Джозаг Казахского района Азербайджанской Республики.

Ключевые слова: сополимер, сорбент, *m*-фенилендиамин, диаминобензидин, концентрирование, определение кадмия, десорбция, методика.