

SORPTION EXTRACTION OF LEAD(II) USING A CHELATING SORBENT BASED ON MALEIC ANHYDRIDE-STYRENE

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A new sorbent has been synthesized based on a maleic anhydride-styrene copolymer modified with 2-allyl phenol ether. The conditions for the preliminary concentration of Pb(II) using the synthesized sorbent have been investigated. The adsorption isotherm for lead(II) ions with the sorbent has been constructed. It has been established that as the concentration of lead in the solution increases, the amount of adsorbed metal also increases, reaching a maximum at a concentration of 6×10^{-2} mol/L (pH=5, $C_{\text{Pb}^{2+}} = 6 \times 10^{-3}$ mol/L, adsorption capacity=420 mg/g). The influence of different mineral acids (HClO₄, H₂SO₄, HNO₃, HCl) at equal concentrations on the desorption of lead(II) from the sorbent has also been studied. Maximum desorption of lead(II) is observed in hydrochloric acid. The degree of extraction of lead(II) ions under optimal conditions exceeds 95%.

Keywords: lead, sorbent, concentration, desorption, river water

INTRODUCTION

Lead is one of the most toxic metals, and its levels must be monitored when assessing the quality of drinking water, food products, raw materials, pharmaceuticals, and more. Several methods exist for extracting lead from natural and industrial sources, particularly through sorption; however, many known sorbents have certain drawbacks [1-4]. These include low sorption efficiency [1], with some sorbents failing to adsorb the metal at room temperature and requiring heating to a specific temperature [3]. Additionally, many sorbents exhibit low adsorption capacity [2, 4].

To determine and extract lead from natural and industrial sources, both natural and synthetic sorbents are often used for concentration. Currently, chelating sorbents [5-7] are most commonly employed as synthetic sorbents for the concentration and determination of lead(II).

The sorption properties of polymeric sorbents primarily depend on the nature, position within the chain, and the number of functional analytical groups present in the polymer, as well as the physicochemical properties of the polymer matrix [8].

The aim of this study is to investigate the sorption of lead(II) using a chelating sorbent synthesized from a maleic anhydride-styrene copolymer modified with 2-allyl phenol ether. Additionally, the development of a method for its extraction from river water will be explored.

EXPERIMENTAL

Reagents and Solutions: In this study, a polymeric chelating sorbent based on a maleic anhydride-styrene copolymer was used. The sorbent was synthesized by modifying the copolymer with 2-allyl phenol ether according to a known methodology [9].

A standard Pb(II) solution with a concentration of 100 mg/L, produced by Merck with a purity of 99.99%, was utilized. To achieve the required acidity, hydrochloric acid (pH 1-2) and ammonium acetate buffer solutions (pH 3-11) were employed. The ionic strength of the solution was maintained constant by using potassium chloride (analytical grade).

Apparatus: The pH of the solutions was measured using a pH meter of the “HANNA edge” brand. The concentration of Pb(II) ions in the initial solution was determined using an “Agilent ICP MS 7700e” instrument with Mass Hunter software, while the concentration of adsorbed lead was measured using an “ICP-OES Thermo ICAP 7400 Duo” instrument. The sorption studies were conducted under static conditions.

RESULTS AND DISCUSSION

To determine microquantities of lead(II) ions, the conditions for preliminary concentration using the synthesized chelating sorbent were investigated, and the optimal concentration conditions were established.

Measurement of Pb Concentration in the Initial Solution: The concentration of Pb in the initial solution was determined using an Agilent ICP MS 7700e instrument with Mass Hunter software. A calibration curve was constructed from 9 points using a standard Pb solution (100 mg/L) produced by Merck with a purity of 99.99%. Each point was calibrated with 3 replicates. All calibration solutions were prepared in 2% nitric acid using deionized water.

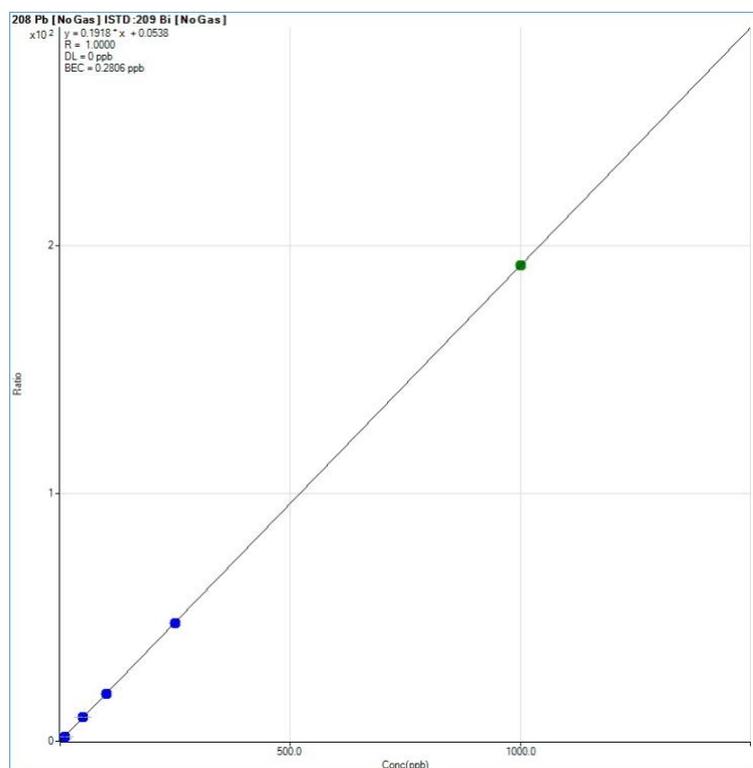


Figure 1. Calibration curve for Pb constructed using the ICP MS 7700e instrument

Calibration								
Level	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD	
1	<input type="checkbox"/>	0.000	0.000	5410.45	0.0538	P	0.0	
2	<input type="checkbox"/>	0.200	0.232	9237.87	0.0984	P	0.4	
3	<input type="checkbox"/>	1.000	1.008	23806.44	0.2471	P	1.3	
4	<input type="checkbox"/>	5.000	4.919	93209.96	0.9973	P	0.9	
5	<input type="checkbox"/>	10.000	9.905	183391.92	1.9538	P	2.0	
6	<input type="checkbox"/>	50.000	50.404	918400.62	9.7221	P	0.9	
7	<input type="checkbox"/>	100.000	98.674	1845216.36	18.9810	P	0.0	
8	<input type="checkbox"/>	250.000	248.677	4484884.09	47.7536	P	0.0	
9	<input type="checkbox"/>	1000.000	1000.445	18083083.44	191.9537	A	0.0	

Figure 2. Calibration results

Influence of pH on Sorption: The effect of pH on the concentration of Pb(II) using a chelating sorbent was studied in the pH range of 1.0 to 10.0. The results indicated that quantitative extraction is achieved at pH 5.0. At pH < 4, the low extraction efficiency may be attributed to the protonation of the sorbent's functional groups and the low degree of swelling of the polymer. As the pH of the liquid phase increases, the swelling of such polymeric sorbents also increases, creating favorable conditions for the interaction of Pb(II) ions with the coordination-active groups in the macromolecule. In aqueous solutions at pH ≥ 8, Pb(II) ions undergo hydrolysis, and alongside the cationic form, they may also exist as hydroxocomplexes [10]. At higher pH values, hydrolysis accelerates, leading to a gradual decrease in the sorption of Pb(II).

The sorption capacity of the sorbent was investigated under static conditions. To 50 mg of the sorbent, a lead solution was added and left in a buffered environment at pH 1.0-10.0. The mixture was filtered, and the concentration of Pb(II) ions in the solution after sorption was determined using a calibration curve previously constructed with the "ThermoFisher ICP OES 7400" instrument, allowing for the calculation of the sorbent's sorption capacity. The results at various pH values are presented in Table 1.

Table 1. Influence of pH on the sorption of Pb(II) using a chelating sorbent.

pH	1	2	3	4	5	6	7	8
CE, мг/г	243	267	284	314	420	351	314	245

All further studies were conducted at pH 5.0.

Influence of Lead(II) Concentration on the Sorption Process: To determine the optimal conditions for the sorption of lead(II) ions using the synthesized sorbent, an investigation was carried out to examine the dependence of sorption capacity on lead(II) concentration. The results are presented in Table 2. A sorption isotherm was constructed (see Fig. 1).

Table 2. Results of the study on the dependence of sorption capacity on lead(II) concentration.

C ₀ , моль/л	2·10 ⁻⁴	4·10 ⁻⁴	8·10 ⁻⁴	1·10 ⁻³	2·10 ⁻³	4·10 ⁻³	6·10 ⁻³	8·10 ⁻³
CE, мг/г	51	126	215	255	324	391	420	420

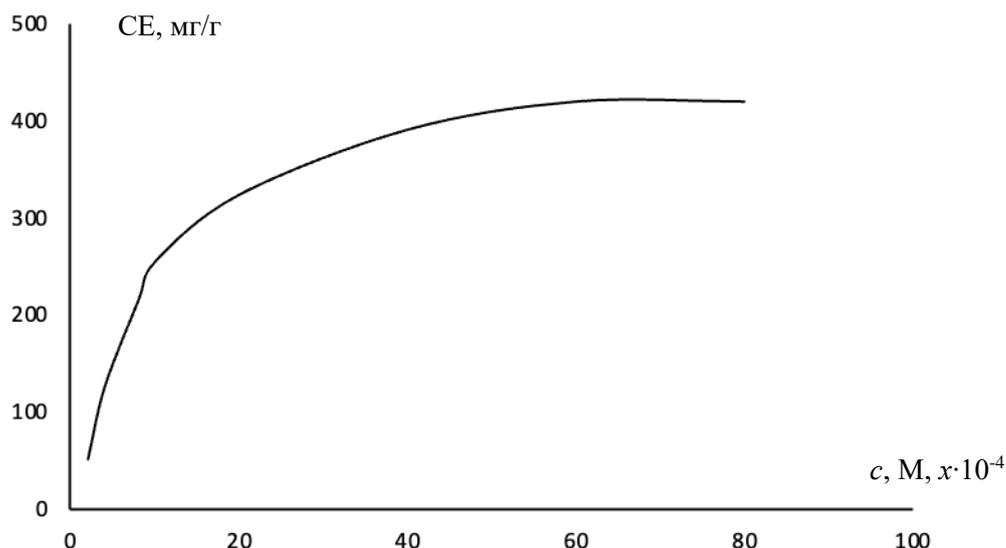


Fig. 3. Sorption isotherm of lead(II) using the chelating sorbent.
 $m = 50 \text{ mg}$, $V = 20 \text{ mL}$, $\text{pH } 5.0$

As the concentration of lead in the solution increases, the amount of adsorbed metal also increases, reaching a maximum at a concentration of $6 \times 10^{-2} \text{ mol/L}$ ($\text{pH}=5$, $C_{(\text{Pb}^{2+})}=6 \times 10^{-2} \text{ mol/L}$, $V=20 \text{ mL}$, $m_{\text{sor}}=0.05 \text{ g}$, $C_e=420 \text{ mg/g}$).

Influence of Ionic Strength: The effect of ionic strength on sorption was studied. Increasing the ionic strength to 0.8 mol/L does not significantly affect sorption; however, further increases lead to a substantial decrease in sorption. This reduction is attributed to the diminished ability for lead(II) complex formation as the ionic environment surrounding the functional groups increases. The dependence of sorption on time was also investigated. Complete sorption of lead(II) occurs after 2 hours under static conditions.

Study of Desorption: The influence of various mineral acids (HClO_4 , H_2SO_4 , HNO_3 , HCl) at the same concentrations on the desorption of lead(II) ions from the sorbent was investigated. It was found that maximum desorption of lead(II) occurs in 2.0 M hydrochloric acid.

Influence of Flow Rate of Sample Solutions and Eluents: A lead solution was passed through a mini-column containing 100 mg of sorbent at a flow rate of $1\text{-}5 \text{ mL/min}$. The analysis revealed that the optimal flow rate is 1.0 mL/min . Maximum desorption of the adsorbed Pb(II) ions occurs at an eluent flow rate of $1\text{-}3 \text{ mL/min}$. In further studies, 5.0 mL of 1.0 M HClO_4 was used as the eluent at a flow rate of 1.0 mL/min .

The developed method was applied to isolate lead(II) from the waters of the Akstafa and Djogaza rivers in the Kazakh region of the Republic of Azerbaijan.

Analysis Procedure: To extract lead(II) ions from river water, 100 mL of filtered sample is acidified with 5.0 mL of HNO_3 ($1:1$) and passed through a mini-column at a flow rate of 1.0 mL/min . The adsorbed ions are eluted with 5.0 mL of 1.0 M HClO_4 . The concentration of Pb(II) in the eluate is determined using a calibration curve previously constructed with the "ICP-OES Thermo ICAP 7400 Duo" instrument. The obtained results are presented in Table 3.

Table 3. Results of lead(II) determination in river water ($n=5$, $P=0.95$).

Water Sample	Pb Found, $\mu\text{g/L}$ (ICP-OES thermo ICAP 7400 DUO)	Detected by Photometric Method, Pb, $\mu\text{g/L}$	S_r
Akstafa River	$3,757 \pm 0,075$	$3,744 \pm 0,050$	0,015
Djogaz River	$0,835 \pm 0,052$	$0,819 \pm 0,025$	0,021

Optimal conditions for the concentration of lead(II) ions using the polymeric sorbent have been established. The study demonstrated that under these optimal conditions, lead ions are quantitatively adsorbed ($R > 95\%$).

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