UDC 544.77
DOI: 10.15587/1729-4061.2025.337919

DEVELOPMENT OF POLYADSORBENTS BASED ON POLYETHYLENIMINE AND LOW MOLECULAR WEIGHT LIGANDS FOR THE EXTRACTION OF GROUP II METAL IONS FROM WASTEWATER

Nazgul Ashimkhan
Candidate of Chemical Sciences, Associate Professor*
Manshuk Murzagaliyeva
Corresponding author
Candidate of Chemical Sciences, Associate Professor*
E-mail: m_murzagalieva@mail.ru
Gulnur Daribayeva
PhD
Research Institute of Food Safety
Almaty Technological University
Raiymbek ave., 348/5, Almaty,
Republic of Kazakhstan, 050061
Ardak Sapiyeva
Candidate of Chemical Sciences
Department of General and Biological Chemistry
Astana Medical University
Beybitshilik str., 49a, Astana, Republic of Kazakhstan, 010000
*Department of Chemistry
Kazakh National Medical University
named after S. D. Asfendiyarov
Tole Bi str., 94, Almaty, Republic of Kazakhstan, 050000

The object of this study is the physicochemical processes of interaction between Group II metal ions and polyethyleneimine (PEI) and low-molecular-weight ligands (salicylic acid, sulfosalicylic acid, EDTA) with the aim of developing polyadsorbents for the selective extraction of toxic ions from aqueous media. The problem to be solved is the development of effective and selective polyadsorbents for removing toxic metal ions from wastewater.

Potentiometric, conductometric, and viscometric analysis methods have established that in binary PEI-M^{2+} systems, coordination complexes are formed with a molar ratio of PEI:M^{2+} = 2:1. For systems with Sr^{2+} and Ba^{2+} ions, stepwise complexation was identified, with particles of composition 6:1 and 4:1 being formed at the initial stage, respectively. The stability of the complexes formed was established in the following order: $Be^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+}$.

Thermodynamic parameters showed that the complexation processes are spontaneous and exothermic, with the decrease in entropy being associated with an increase in order within the system. Stability constants ($lg\beta_0$) range from 5.4 (Mg^{2+}) to 10.16 (Be^{2+}).

Quantum chemical calculations have shown that the reaction centers in the ligand molecules are: the oxygen atoms of the carbonyl group (H_2Sal), the sulfonate group (H_3Ssal), and the carboxyl group (H_2edta^{2-}). It has been established that donor-acceptor interactions predominate in PEI-M^{2+}-H_2Sal/H_3Ssal ternary systems, while electrostatic interactions dominate in PEI-Zn^{2+}/Cd^{2+}-H_2Sal and PEI-Be^{2+}-H_2edta^{2-} systems.

In sorption tests in model solutions, the ternary complexes PEI-Be^{2+}-H_3Ssal and PEI-Hg^{2+}-H_3Ssal demonstrated the highest efficiency: the degree of removal of Be^{2+} reached 97.1%, Hg^{2+} – 93.4%, while for Mg^{2+} and Ba^{2+} it was less than 70%. Modified PEI with H_3sal proved to be the most effective adsorbent among those studied. In industrial trials, the developed adsorbents reduced the concentrations of Be^{2+} and Hg^{2+} in wastewater to 0.004 and 0.002 mg/l, respectively, which meets the maximum permissible concentrations for discharge into water bodies

Keywords: metal, ion, complexation, polyethyleneimine, ligand, wastewater, titration, thermodynamics, adsorption

Received 06.06.2025
Received in revised form 14.07.2025
Accepted 18.08.2025
Published 28.08.2025

How to Cite: *Ashimkhan, N., Murzagaliyeva, M., Daribayeva, G., Sapiyeva, A. (2025). Development of polyadsorbents based on polyethylenimine and low molecular weight ligands for the extraction of group II metal ions from wastewater. Eastern-European Journal of Enterprise Technologies, 4 (10 (136)), 37–46. https://doi.org/10.15587/1729-4061.2025.337919*

1. Introduction

The removal of metal ions from wastewater remains one of the most pressing challenges in modern ecology due to their high toxicity, persistence, and ability to accumulate in living organisms. Heavy metal ions, such as beryllium, cadmium, and mercury, are one of the most common pollutants found in industrial and municipal wastewater. These metals pose a serious threat to both human health and aquatic ecosystems. It has been established that such pollutants can persist in the environment for a long time, disrupting food chains and reducing biodiversity.

In recent years, polyethyleneimine (PEI) has been considered a promising polymer for developing heavy metal adsorbents due to its high density of amino groups, hydrophilicity, and ability to form stable chelate complexes. A systematic review shows that functionalization and composite formation of PEI-based materials significantly enhance their effectiveness in removing heavy metals from wastewater [1]. The study presents PEI derivatives encapsulated in an alginate matrix, which provided improved sorption capacity and stability for the extraction of Cd(II), Cu(II), and Zn(II) ions from multicomponent solutions [2]. Additionally, the successful synthesis of PEI-SiO_2 nanocomposite microparticles with high stability and efficiency in binding copper ions has been demonstrated [3]. These studies confirm that directed modification and composite integration of PEI open up possibilities for creating highly efficient and regenerable wastewater treatment systems for removing toxic heavy metal ions.

Recently, the polymer polyethyleneimine (PEI) has been used for chelating heavy metal ions due to its strong chelating properties, hydrophilicity, and the large number of amino groups in its macromolecular chain. The synthesis of composite materials based on PEI is attracting significant attention in the context of toxic heavy metal removal due to their unique properties, such as high water affinity, metal binding, thermal stability, mechanical strength, and reusability. Furthermore, the amino group in PEI contributes significantly to the effective adsorption of heavy metal cations and anions [1–3].

Recent advancements have once again highlighted that PEI is a multifunctional adsorbent. Its ability to interact with various metal ions thru ion exchange, coordination bonding, and hydrogen bond formation has been extensively studied. The development of polymer ligands based on PEI continues to show great potential for the selective capture of metal ions in wastewater systems [4, 5]. The resulting polymer-metal complex can be used to remove hardness and heavy metals from water, which contributes to limiting the exploitation of natural resources and reducing the amount of waste discharged into the environment [6]. In addition to polymer sorbents, the use of low molecular weight ligands such as organic acids and amino acids has demonstrated improved complexation and metal ion removal characteristics. These ligands promote the formation of soluble and bioavailable complexes, thereby increasing extraction efficiency. A systematic comparison of different types of ligands showed that their structural features critically influence their metal binding affinity and selectivity [7, 8].

Further improvement of sorption processes was achieved thru functional modifications of biopolymers, such as chitosan grafted with EDTA, which significantly enhance their adsorption properties [9]. Studies on the use of functionalized polymers have confirmed the importance of molecular design for enhancing heavy metal binding efficiency, as demonstrated by the example of a chitosan/polyacrylamide double-network hydrogel modified with EDTA [10]. In turn, a comprehensive review of modern methods for removing heavy metal ions from wastewater highlights that the key factors for successful application are the rational modification of adsorbents, their regeneration capacity, and their stability under real operating conditions [11].

Collectively, these studies suggest that complexes based on polyethyleneimine and low-molecular-weight ligands hold significant potential for modern water purification technologies.

Thus, research on the development of polymer-metal complexation systems for the targeted removal of Group II metal ions is highly relevant for improving modern wastewater treatment methods.

2. Literature review and problem statement

The papers [12, 13] present the results of research on the application of cellulose-based materials as effective and environmentally friendly alternatives for water purification. It is shown that regenerated cellulose, cellulose acetate, nanocellulose, as well as hydrogels and aerogels derived from cellulose, have high adsorption potential for removing heavy metals, oils, salts, and dyes from water. Various modification methods, including the incorporation of nanoparticles and polymer grafting, are discussed as ways to enhance performance. The findings emphasize the unique properties of cellulose-based materials – such as biodegradability, low toxicity, high surface area, and the presence of functional groups – that make them promising for filtration and adsorption. However, questions related to the mechanical strength of these materials, the scalability of production methods, and their performance under real-world conditions remain unresolved. The reason for this may be the complexity of balancing biodegradability with long-term stability, as well as the high cost and technical difficulty of producing such materials on an industrial scale. These limitations make the large-scale deployment of cellulose-based systems currently less feasible.

An option for overcoming these difficulties may be the use of composite or hybrid materials combining cellulose with more robust polymers or functional nanomaterials, which can preserve the environmental benefits while enhancing mechanical and functional properties. This is the approach used in the papers [14, 15], where the authors examine carbon-based, biological, and inorganic adsorbents for the removal of toxic metal ions such as Pb^{2+}, Cr^{6+}, As^{3+}, As^{5+}, Hg^{2+}, and Cd^{2+}. These studies emphasize the importance of adsorption kinetics, sorption mechanisms, and material uniformity in designing effective regenerable adsorbents. Despite this, unresolved questions remain regarding the selectivity and specificity of adsorption mechanisms, especially in multicomponent wastewater systems. Objective difficulties arise from the complex competitive interactions among different pollutants, as well as the limitations of current analytical methods for accurately monitoring these interactions in real-time.

The papers [16, 17] present the results of research on the fabrication of a TiO_2-decorated PVDF membrane using a mussel-inspired method for oil/water separation. It is shown that the resulting superhydrophilic membrane demonstrates high separation efficiency. However, questions related to the selectivity of such membranes toward metal ions and their regeneration under industrial conditions remain unresolved. The reason for this may be the limited applicability of oil/water separation membranes for ionic contaminants and a lack of data on their long-term operation in real wastewater systems.

In the work [18], the development of a composite membrane based on PVDF/graphene is considered, obtained by electrospinning a nanofiber film, which was used for oil/water emulsion separation. Despite the improved mechanical properties and stability of the material, questions remain open regarding the mechanisms of metal ion adsorption and the environmental cost of graphene production. This highlights the challenge of finding a balance between improving performance and cost-effectiveness in the use of advanced nanomaterials. Complementing these results, study [19] focuses on VIPS-fabricated graphene oxide/PVDF membranes, which exhibit versatile and controllable properties in oil/water separation systems.

The paper [20] provides a broad review of polymeric adsorbents used for wastewater treatment, highlighting the promise of materials such as polysaccharides, nanomagnetic polymers, and covalent organic frameworks. However, a comprehensive analysis of their long-term adsorption efficiency, regeneration capabilities, and environmental safety is still lacking. This is likely due to objective difficulties in simulating long-term operational conditions and scaling up these systems while preserving economic and environmental feasibility.

One possible strategy to overcome these difficulties is the systematic evaluation of the physicochemical behavior of such adsorbents under realistic conditions, combined with the optimization of their structure thru functional modifications. As noted in the work [21] dedicated to modified biochars, the presence and nature of functional groups on the surface directly determine the adsorption mechanisms and the overall efficiency of heavy metal ion removal. This approach highlights the importance of molecular architecture in increasing adsorption capacity. However, without rigorous experimental verification under real wastewater treatment conditions, these findings remain largely theoretical and require further confirmation.

All this allows to state that it is appropriate to conduct a study devoted to the physicochemical processes of complex formation between group II metal ions and polyethyleneimines in combination with low-molecular-weight ligands. Such research will address current knowledge gaps, improve the understanding of coordination mechanisms in multicomponent systems, and contribute to the development of next-generation materials for wastewater treatment.

3. The aim and objectives of the study

The aim of this study is to develop effective polyadsorbents for wastewater treatment. This will improve the efficiency of water purification to meet regulatory standards for heavy metal content, reduce the environmental impact, and expand the application of modified polymer materials in water treatment technologies.

To achieve this aim, the following objectives were accomplished:

– to study the complexation process of group II metal ions with polyethyleneimine, determine the composition of the double complex, its stability, and the effect of ionic strength on the complexation process;

– to calculate the main thermodynamic characteristics of the complexation process and establish the influence of temperature and the nature of the metal ion on the parameters ΔG, ΔH, and ΔS;

– to perform quantum-chemical calculations using the PM3 method with the MOPAC 7.0 program to determine the reaction centers in low-molecular-weight ligand molecules;

– to study the interaction processes in ternary systems containing group II metal ions, PEI, and low-molecular-weight ligands, and to identify the competitive influence of ligands on the formation of ternary complexes.

4. Methods and materials

The object of this study is the physicochemical processes of interaction between Group II metal ions and polyethyleneimine (PEI) and low-molecular-weight ligands (salicylic acid, sulfosalicylic acid, EDTA) with the aim of developing polyadsorbents for the selective extraction of toxic ions from aqueous media.

The main hypothesis of the study: it is assumed that due to its polyfunctionality and cationic nature, branched PEI forms stable coordination complexes with group II metal ions, and the introduction of low-molecular-weight ligands allows for an increase in the stability, selectivity, and sorption capacity of these complexes.

Assumptions underlying the study:

– the interaction of metals with ligands occurs according to the laws of coordination chemistry and is realized through donor-acceptor mechanisms;

– PEI maintains its chemical stability under experimental conditions;

– complexation processes reach equilibrium during measurements using potentiometric and spectroscopic methods.

Simplifications made:

– the influence of competing ions typical of natural waters is not considered at this stage;

– PEI is treated as a statistically homogeneous polymer, despite possible polydispersity;

– the calculations only take into account complexes with a 1:1 and 2:1 composition (ligand:metal).

In the study of the interaction processes of metal ions with macromolecular and low-molecular ligands, a set of physicochemical methods was applied. These include potentiometry, conductometry, viscosimetry, and IR spectroscopy.

To determine the coordination number of metal-complexing ions and the stability constants of the obtained polymer-metal complexes, we used a modified Bjerrum method. Potentiometric studies were conducted under thermostatic conditions on the ionomer I-500 using silver chloride and glass electrodes with a pH measurement accuracy of ± 0.02.

Viscometric research aimed at studying the conformational state of macromolecules was conducted using a Ubbelode viscometer, with distilled water used as the solvent. Viscosity measurements were also conducted under thermostatic conditions, and the liquid flow time (τ) was recorded with a stopwatch.

For conducting conductometric studies, an AC bridge P-5010 with platinum electrodes was used. The correctness of the bridge operation was verified on standard samples by measuring their resistance. Conductometric and potentiometric titrations were performed simultaneously in a single cell with monitoring of pH and resistance changes in the studied systems.

Polymer-metal complexes were synthesized by mixing aqueous solutions of the starting components with control over their ratio and the pH of the medium.

One of the key methods for determining the structure of the compounds was IR spectroscopy. IR absorption spectra of the samples were obtained in KBr pellets on an FTIR-SATELLITE spectrometer (MATSON, USA).

For the quantum-chemical analysis of the geometric, energetic, and electronic characteristics of the reagents, the PM3 method was used, included in the software packages MORAS-7 and HYPERCHEM-6.0.

Objects of study. In the study, branched polyethyleneimine with a molecular weight of 10000 and a hydrolysis degree of 10% from the Japanese company "Hitachi" was used, as well as salicylic and sulfosalicylic acids and sodium salt of EDTA. To determine the stability constants of the complexes, a 0.1 N HCl solution prepared and salt NaCl for creating ionic strength. To study the processes of complex formation in binary and ternary systems, the following metal salts were used: $Be(SO_4)_2{\cdot}8H_2O$, $Hg_2(NO_3)_2{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}6H_2O$, $SrCl_2{\cdot}6H_2O$, $BaCl_2{\cdot}6H_2O$, $CdSO_4{\cdot}8H_2O$, $ZnSO_4{\cdot}7H_2O$, $Hg(NO_3)_2{\cdot}H_2O$.

5. Complexation of polyethyleneimine with metal ions and ligands for water purification

5. 1. Physicochemical study of the complexation process of Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} ions with polyethyleneimine

The mixing of an aqueous PEI solution with Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} ions is accompanied by a decrease in pH and an increase in the conductivity of the medium (Fig. 1, 2). The interaction process in the studied system can be explained by the release of a proton from the imine groups of PEI. The viscosity of the system decreases (Fig. 3) because the polymer chain shortens due to intrachain chelation. As the concentration of metal ions increases, the viscosity of the system also increases. This happens because metal ions affect the conformation of the polyelectrolyte chains. Under the influence of many metal ions, the polyelectrolyte becomes more extended. Uniformly charged segments of the polymer chain repel each other due to electrostatic forces. This repulsion leads to the unfolding of the macromolecule. As a result, its hydrodynamic size increases, which in turn causes the viscosity of the solution to rise.

For all the studied systems, the effective molar ratios of the components have been determined, i. e., for one metal-complexing ion, there are two constituent units of the polymer ligand. In the PEI-Sr^{2+} and PEI-Ba^{2+} systems, complex formation occurs in stages, with complex particles of compositions 6:1 and 4:1 forming in the first stage, respectively.

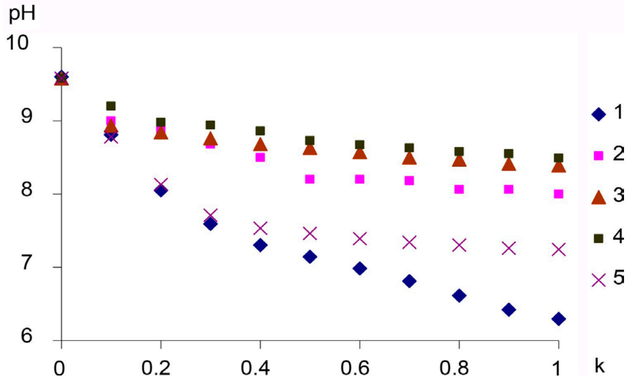

Fig. 1. Potentiometric titration: 1 – PEI-Be^{2+}; 2 – PEI-Mg^{2+}; 3 – PEI-Ca^{2+}; 4 – PEI-Sr^{2+}; 5 – PEI-Ba^{2+}

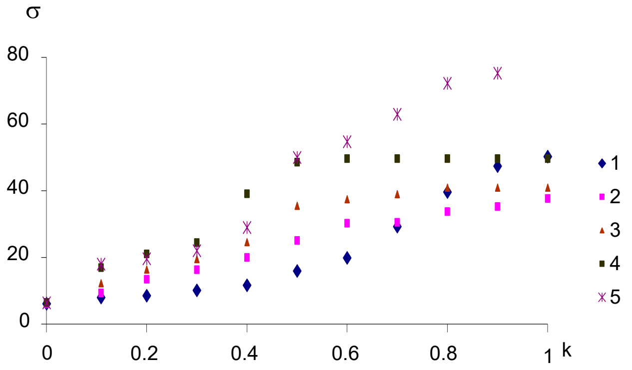

Fig. 2. Conductometric titration: 1 – PEI-Be^{2+}; 2 – PEI-Mg^{2+}; 3 – PEI-Ca^{2+}; 4 – PEI-Sr^{2+}; 5 – PEI-Ba^{2+}

Based on the results of the experiments, it can be assumed that the interaction of reagents in binary systems PEI-M^{2+} (Be, Mg, Ca) proceeds according to the following scheme

$$\left[-CH_2-CH_2-NH_2^+OH^- -\right]_n +$$
$$+nMAn\left[M(NH)_2\right]_n^{2+} + nAn + nOH^- + nH^+.$$

PEI:Sr^{2+} system.

At the first stage, six imine groups of PEI form a polymer-metal complex (PMC) with a central complexing ion (pH = 9.5 – 8.5)

$$6\left[-CH_2-CH_2-NH_2^+OH^- -\right]_n + nSrCl_2\left[Sr^{2+}(NH)_6\right]_n +$$
$$+6nOH^- + 2nCl^- + 6nH^+.$$

At the second stage, as the concentration of metal ions increases, a 2:1 polycation is formed (pH = 8,5–7)

$$\left[Sr^{2+}(NH)_6\right]_n\left[Sr^{2+}(NH)_2\right]_n.$$

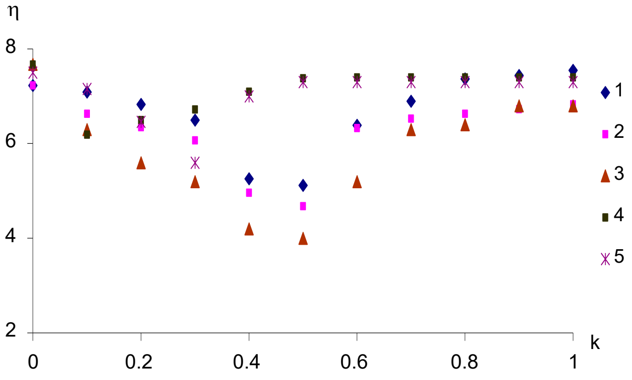

Fig. 3. Viscosimetric titration: 1 – PEI-Be^{2+}; 2 – PEI-Mg^{2+}; 3 – PEI-Ca^{2+}; 4 – PEI-Sr^{2+}; 5 – PEI-Ba^{2+}

In the PEI-Ba^{2+} system, at the first stage, four imine groups of PEI coordinate with the central complexing ion, forming a polymer-metal complex with a 4:1 ratio. As the concentration of metal ions increases, a 2:1 polycation is formed according to the scheme outlined above. In polyethyleneimine complexes with a 2:1 ratio according to the given scheme, the ligand number of the complexing ion is equal to two, while its primary coordination number remains unchanged due to the formation of donor-acceptor bonds between these metal ions and solvent ions or the corresponding anions of acids.

5. 2. Thermodynamics of the reaction of Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} ions with polyethyleneimine

The stepwise and overall stability constants ($\lg\beta$) of polyethyleneimine complexes were calculated using a modified Bjerrum method, while the standard thermodynamic constants ($\lg\beta_0$) were determined by extrapolating the experimentally obtained constants to zero ionic strength using Vasiliev's equation (Table 1).

When analyzing the stability constants of the obtained polymer-metallic complex, it was shown that the PEI – Be^{2+} complex is characterized by the highest stability. The Be^{2+} ion, which has the smallest size and the highest charge density in this series, exhibits the highest complexation properties and, due to its high polarizability and hydration energy, shows chemical activity in forming stable complexes with nitrogen-containing ligands. It has been established that the complexes of Ca^{2+}, Sr^{2+}, Ba^{2+} ions with polyethyleneimine are more stable than the complexes of Mg^{2+}. This is explained by the fact that the studied metal ions can form coordination compounds of varying stability depending on their nature and the characteristics of the functional groups of the polymer ligand, as well as on factors referred to as «structural similarity». For Mg^{2+} ions, the stability of the complexes is lower because the share of the structural similarity factor is small.

Such a regular change in the stability of polyethyleneimine complexes can be explained by differences in the chemical nature of the cations. More stable complexes are formed with ions that have a greater ability to interact with σ-donor ligands, which is related to their charge and radius. In the considered series $Be^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+}$, this ability increases, which determines the increase in the stability of coordination compounds with polyethyleneimine. Only for the Mg^{2+} ion, the stability of the PEI-Mg^{2+} complex is lower due to the dominance of "structural mismatch" of this polymer ligand.

The stability of polyethyleneimine complexes is determined by the ratio of the properties of ligands and metal ions, which affect the stability constants. The complex-forming ability of PEI is determined by the presence of nitrogen atoms in its structure-electron donors with high electronegativity, low polarizability, and resistance to oxidation. These characteristics make polyethyleneimine an effective ligand, especially when interacting with alkaline earth metal ions, which have high coordination ability. As a result, stable chelate complexes are formed.

According to the data in Table 1, the stability of the polymer-metal complex increases with the rise in ionic strength, which is due to several reasons. Firstly, inorganic electrolytes significantly affect the conformation of polyelectrolyte molecules, as they screen the charge of the chain, leading to the contraction of the polymer chain, an increase in local concentration, and enhanced availability of ionogenic groups for coordination with the macromolecule. Secondly, neutral salts are hydrated by water molecules. As the molar fraction of salt in the solution increases, the concentration of free water molecules not bound to salt ions decreases, leading to a reduction in the density of hydrated layers between the cations of complexing metals and the unprotonated imine group of PEI. Thirdly, the strength of hydrogen bonds decreases.

The work calculates the thermodynamic characteristics of the complexation process of group IIA ions with PEI, which are summarized in Table 2.

The negative values of the change in Gibbs energy indicate that the complexation reaction in this system proceeds spontaneously in the forward direction. The change in the Gibbs energy under consideration depends on enthalpic and entropic factors. The relative contribution of each factor depends on the nature of the ligand and the central metal ion. As seen from Table 2, the enthalpy factor has a significant impact on the change in total free energy with a small change in entropy. The formation of a donor-acceptor bond is accompanied by the release of a large amount of heat, which is the driving force of the reaction between the reagents, as evidenced by the values of the enthalpy change during the complexation process. Therefore, the increase in temperature during the exothermic reaction is a negative factor for the stability of the polymer-metal ion complex, which, as seen from Tables 1, 2, leads to a decrease in the stability constants of the complexes. The process of complex formation of Be^{2+} and Mg^{2+} ions with PEI is characterized by a negative change in entropy compared to the reactions of polymer-metal complex formation with Ca^{2+}, Sr^{2+}, and Mg^{2+} ions. The change in entropy of the complexation process varies depending on the disruption of the hydration layer in the ligand groups of PEI, the displacement of a water molecule from the first coordination sphere of the metal ion, and the formation of a chelate structure. As the order of the system decreases, the contribution of the previous two factors becomes less significant, as the functional groups of PEI enter the first coordination sphere of Be^{2+} and Mg^{2+} ions, and the formation of a stable polychelating structure increases the rigidity of the polymer chain, resulting in a decrease in the change in the system's entropy.

Table 1

Values of stability constants of polymer-metal complexes of Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} ions with polyethyleneimine $\left(k = \frac{\left[M^{n+}\right]}{PEI}\right)$

T, K	I	lg b				
		PEI-Be^{2+} ($k = 0.5$)	PEI-Mg^{2+} ($k = 0.5$)	PEI-Ca^{2+} ($k = 0.5$)	PEI-Sr^{2+} ($k = 0.5$)	PEI-Ba^{2+} ($k = 0.5$)
298	0	10.16 ± 0.10	5.40 ± 0.05	5.91 ± 0.06	5.89 ± 0.06	5.86 ± 0.06
	0.1	10.25 ± 0.09	5.80 ± 0.06	6.00 ± 0.06	5.91 ± 0.06	5.89 ± 0.06
	0.5	10.85 ± 0.10	5.95 ± 0.06	6.90 ± 0.07	5.95 ± 0.06	5.90 ± 0.06
	0.75	11.20 ± 0.11	6.70 ± 0.07	7.05 ± 0.07	5.97 ± 0.06	5.96 ± 0.07
	1.0	11.40 ± 0.11	6.85 ± 0.07	8.30 ± 0.08	6.02 ± 0.07	6.00 ± 0.07
308	0	9.26 ± 0.09	5.38 ± 0.05	5.86 ± 0.06	5.83 ± 0.06	5.81 ± 0.06
	0.1	9.40 ± 0.09	5.75 ± 0.06	5.95 ±0.06	5.84 ± 0.06	5.82 ± 0.06
	0.5	9.65 ± 0.10	5.90 ± 0.06	6.70 ± 0.07	5.86 ± 0.06	5.83 ± 0.07
	0.75	9.91 ± 0.10	6.25 ± 0.06	6.75 ± 0.07	5.88 ± 0.06	5.86 ± 0.07
	1.0	10.22 ± 0.10	6.75 ± 0.07	6.80 ± 0.07	5.90 ± 0.06	5.87 ± 0.08
318	0	7.85 ± 0.08	4.69 ± 0.05	5.77 ± 0.06	5.57 ± 0.06	5.55 ± 0.08
	0.1	7.88 ± 0.08	5.70 ± 0.06	5.80 ± 0.06	5.60 ± 0.06	5.58 ± 0.07
	0.5	8.70 ± 0.09	5.80 ± 0.06	5.82 ± 0.06	5.70 ± 0.07	5.68 ± 0.08
	0.75	8.88 ± 0.09	5.85 ± 0.06	5.90 ± 0.06	5.82 ± 0.07	5.81 ± 0.07
	1.0	9.10 ± 0.09	6.50 ± 0.07	6.40 ± 0.06	5.84 ± 0.07	5.82 ± 0.07

Table 2

Thermodynamic characteristics of the complexation process in the PEI-M^{2+} system

System	T, K	lgβ_0	$-\Delta_rG$, kJ/mol	$-\Delta_rH$, kJ/mol	Δ_rS, kJ/mol·K
PEI-Be^{2+} ($k = 0.5$)	298	10.16 ± 0.10	57.89 ± 0.58	210.45 ± 2.11	–509.95 ± 5.10
	308	9.26 ± 0.09	54.54 ± 0.55		
	318	7.85 ± 0.08	47.73 ± 0.48		
PEI-Mg^{2+} ($k = 0.5$)	298	5.40 ± 0.08	30.77 ± 0.31	65.69 ± 0.67	–114.82 ± 1.15
	308	5.38 ± 0.08	31.69 ± 0.32		
	318	4.69 ± 0.14	28.52 ± 0.29		
PEI-Ca^{2+} ($k = 0.5$)	298	5.91 ± 0.06	33.68 ± 0.34	12.90 ± 0.13	69.89 ± 0.70
	308	5.86 ± 0.06	34.51 ± 0.35		
	318	5.77 ± 0.06	35.09 ± 0.35		
PEI-Sr^{2+} ($k = 0.5$)	298	5.89 ± 0.06	33.56 ± 0.34	29.41 ± 0.30	13.45 ± 0.13
	308	5.83 ± 0.06	33.22 ± 0.33		
	318	5.57 ± 0.06	33.88 ± 0.34		
PEI-Sr^{2+} ($k = 0.5$)	298	26.92 ± 0.26	153.60 ± 1.53	607.90 ± 6.09	–1540 ± 15.40
	308	20.88 ± 0.20	123.14 ± 1.23		
	318	20.11 ± 0.20	122.45 ± 1.22		
PEI-Ba^{2+} ($k = 0.5$)	298	5.86 ± 0.06	33.39 ± 0.33	28.52 ± 0.29	17.10 ± 0.16
	308	5.81 ± 0.06	34.22 ± 0.34		
	318	5.82 ± 0.07	33.75 ± 0.34		
PEI-Ba^{2+} ($k = 0.25$)	298	11.68 ± 0.11	66.64 ± 0.66	82.89 ± 0.84	132.31 ± 1.32
	308	11.63 ± 0.11	68.59 ± 0.68		
	318	11.38 ± 0.10	69.29 ± 0.69		

Thus, in these systems, the formation of a stable coordination compound occurs depending both on the nature of the complexing agent – the metal ion – and on the conformational state of the polymer ligand and external (*I*, *T*) factors.

5. 3. Evaluation of the reactivity of some low-molecular-weight ligands for the modification of polyethyleneimine surfaces using quantum calculations

Quantum-chemical calculations to determine the reaction center in the molecules of salicylic, sulfosalicylic, and ethylenediaminetetraacetic acids were carried out using the semi-empirical PM3 method in the MOPAC 7 program. Graphical illustrations of the optimized geometric models were created using the graphic editor in the HYPERCHEM 6 program. When examining the geometric and electronic characteristics of the model molecules, the following conclusions were made:

– in the model molecule of salicylic acid, the reaction center is the oxygen atom of the carbonyl group. However, the oxygen atom of the hydroxyl group in the molecule can also participate in a donor-acceptor bond;

– in the molecule of sulfosalicylic acid, the reaction centers are primarily the oxygen atoms of the sulfonyl group, as well as the oxygen atoms of the carboxyl and hydroxyl groups;

– in the model molecule of ethylenediaminetetraacetic acid, the reaction center is the oxygen atom of the carboxyl group. The possibility of the arrival of acceptor electrons to the nitrogen atom is limited by the steric factor. In addition to atomic distances, charge characteristics, electron densities, and reaction orders of the given salicylic, sulfosalicylic, ethylenediaminetetraacetic acids, and Be^{2+}-H_3Ssal, electronic and energetic characteristics were calculated (Table 3).

Table 3

Electronic and energetic characteristics of salicylic, sulfosalicylic, ethylenediaminetetraacetic acids, and Be^{2+}-H_3Ssal

Compound	D_fH^o, kJ	*E*, eV	*IP*, eV	*m*, D
$C_7O_3H_6$	–477.65	–1803.20	9.40	2.09
$C_7O_5H_6S$	–978.85	–2870.50	10.14	2.47
$C_{10}O_8H_{16}N_2$	–1491.39	–4107.61	9.84	1.57
Be^{2+}-H_3Ssal (1)	–1001.19	–2884.26	8.23	2.73
Be^{2+}-H_3Ssal (2)	–990.98	–2884.15	8.32	3.41

Quantum-chemical modeling of the process of binding a beryllium ion with the sulfo- and carboxyl groups in the PEI-Be^{2+}-H3Ssal system was conducted. In the first model form, the hydrogen ion in the hydroxyl group, which is part of the sulfo group, is bound by the substitution of the beryllium atom; in the second model form, the reactive centers are the hydroxyl and carbonyl oxygen atoms in the carboxyl group. Comparing the calculated geometric, electronic, and energetic parameters of the two binding models, the following conclusions can be drawn about the binding of the beryllium ion with the oxygen atoms in the sulfonyl group in the model system Be^{2+}-H_3Ssal:

– then the Be^{2+} ion forms a new strong bond with the oxygen atoms in the sulfonyl group;

– this model system Be^{2+}-H_3Ssal is thermodynamically stable compared to the model system in which the oxygen atoms in the carboxyl group participate in the reaction;

– it is easy to extract electrons from it to form a donor-acceptor bond, as it has a low ionization potential.

5. 4. Triple systems consisting of group II metal ions, polyethyleneimine, and low-molecular-weight ligands

The study of ternary systems containing ions Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Hg_2^{2+}, polymer ligand – PEI, and these low molecular weight ligands is of great importance both theoretically and practically. From a scientific perspective, one of the important questions is determining the mutual influence of ligands of different natures on the process of forming ternary polymer-metal complexes. Moreover, the results of the study of ternary systems can serve as a basis for the development of polyadsorbents effective for many metal ions, with the aim of separating, concentrating metal ions, and purifying industrial wastewater, which is also relevant from an environmental perspective.

The results of potentiometric, conductometric, and viscometric studies of the ternary systems show that when low-molecular-weight ligands are added to the binary PEI-M^{n+} system, the interaction process in each system depends on the nature of the complexing agent, metal ion, and ligand, leading to the formation of ternary polymer-metal complexes (Fig. 4–6).

In systems consisting of PEI-Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+}, Hg_2^{2+}-H_2Sal (H_3Ssal), low-molecular ligands with coordination-bound metal ions are formed through donor-acceptor bonding, creating a triple polymer-metal complex with various ligands. And in the ternary systems PEI-Zn^{2+}(Cd^{2+})-H_2Sal (H_3Ssal), PEI-Be^{2+}-H_2edta^{2-}, the ternary polymer-metal complex is formed through electrostatic binding with positively charged polyelectrolytes and low-molecular-weight ligands.

To determine the coordination of ligands in the synthesized complex polymer-metallic complexes, their IR spectra were discussed. The main vibrational frequencies are presented in Table 4.

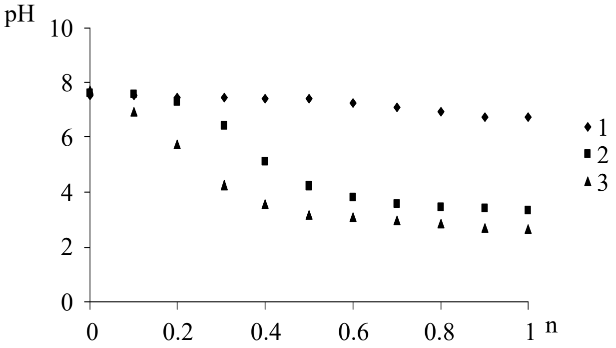

Fig. 4. Potentiometric titration of the PEI-Be^{2+} system: 1 — ethylenediaminetetraacetic acid (EDTA); 2 — salicylic acid; 3 — sulfosalicylic acid

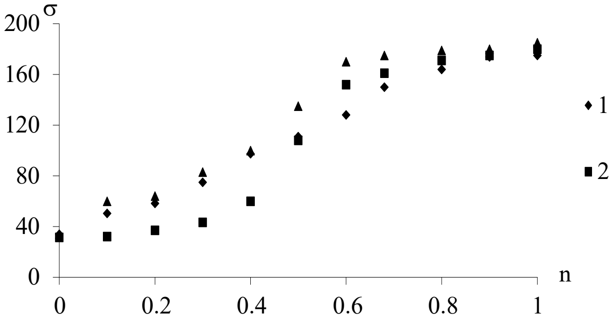

Fig. 5. Conductometric titration of the PEI-Be^{2+} system: 1 — ethylenediaminetetraacetic acid (EDTA); 2 — salicylic acid; 3 — sulfosalicylic acid

Table 4

Main frequencies of oscillations of polymer-metallic complexes in the IR Spectrum

Absorption bands	PEI	H_2edta^{2-}	H_2Sal	H_3Ssal	PEI-Be^{2+}-H_3Ssal	PEI-Hg^{2+}-H_3Ssal	PEI-Hg^{2+}-H_2Sal	PEI-Cd^{2+}-H_2edta^{2-}
n (OH)	3500	3526	3428	3112	3430	3436	3586	–
			3238				3526	
n (NH)	3300	3385	–	–	3065	3067	–	3427
	3282							
n(C=O) + d^{as} (CNH) +d (COH)	1651	1673	1659	1672	–	1670	1614	–
	1580							
n^{as} (SO_3^-) + n^{as} (CCN)	–	–	1190	1169	1158	1168	1124	–
			1156	1146	1124	1125		
				1123				
n^s (SO_3^-) + n (C-C)	–	–	1090	1083	1079	1093	–	–
						1084		
			1031	1041	1030	1039		
r (CNH) + n^{as} (CCN)	–	900	894	887	887	888	826	844
				842	835	837		
		817		803	811	803		
d^{as} (COO^-) +d (C-C-C)	–	653	699	667	670	666	–	645
			660	606		621		619

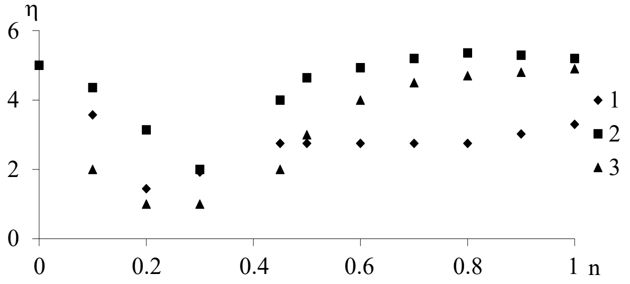

Fig. 6. Viscosimetric titration of the PEI — Be^{2+} system:
1 — ethylenediaminetetraacetic acid (EDTA); 2 — salicylic acid;
3 — sulfosalicylic acid

Analysis of the IR spectroscopy results shows that upon interaction of the aforementioned metal ions with PEI and a second ligand of a different nature (the molecules H_2Sal, H_3Ssal, and H_2edta^{2-}), a complex polymer-metal complex is formed. When coordinating with metal ions, the reaction center in the PEI molecule is the nitrogen atom of the imine group, as evidenced by the shift in the frequency of the valence vibration corresponding to this group to the range of 3200–3300 cm^{-1}, while H_2Sal, H_3Ssal, and H_2edta^{2-} are the oxygen atoms of the carbonyl group. Only in the PEI-Be^{2+}-H_3Ssal system does the beryllium ion form a coordination bond with the sulfonyl group of salicylic acid. Other heteroatoms in the ligand of these molecules participate in the formation of numerous hydrogen bonds.

6. Discussion of the results of the study on the wastewater purification from group II metal ions using polyethyleneimine and low-molecular-weight ligands

During the study of the physicochemical properties of complex formation of Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions with polyethyleneimine (PEI), important aspects of interactions between metal ions and the polymer were identified. The obtained data show that complex formation occurs through the release of protons from the imine groups of PEI (Fig. 1–3), leading to the formation of stable polymer-metal complexes. Especially interesting are the results related to the Be^{2+} ion, which showed maximum stability due to its small size and high charge density (Table 1).

The detected molar ratios between the components indicate the presence of stable structures, which is consistent with general notions about the acid-base nature of cations. The stability of the complexes also increases with the increase in the ionic strength of the solution due to charge screening and changes in the conformation of PEI molecules, which affects the availability of ionogenic groups (Table 1).

The discussion of the thermodynamics of complex formation of group IIA ions with polymeric ligands, such as polyethyleneimine (PEI), demonstrates the interplay of various factors affecting the stability of these complexes (Table 2). The spontaneous process, confirmed by the negative change in Gibbs energy, indicates that the formation of complexes is energetically favorable. Enthalpic factors play a key role, as exothermic reactions associated with the formation of donor-acceptor bonds are accompanied by the release of a significant amount of energy. However, high temperatures can negatively affect the stability of complexes, indicating the importance of controlling temperature regimes in experiments. At the same time, changes in entropy caused by the disruption of the hydration layer and the displacement of water affect the level of order in the system. This can either promote the formation of stable polychelate structures or, conversely, hinder it, depending on the properties of the ions used. The differences in entropic changes between Be^{2+} and Mg^{2+} ions compared to the heavier ions Ca^{2+} and Sr^{2+} highlight how important the nature of the ions is for the stability of the formed complexes.

Quantum-chemical calculations confirmed the key role of oxygen atoms in the reactivity of salicylic, sulfosalicylic, and ethylenediaminetetraacetic acids, especially in their interactions with ions such as beryllium (Table 3). In salicylic acid, the carbonyl oxygen and hydroxyl oxygen act as reaction centers, while sulfosalicylic acid demonstrates multiple reaction centers, indicating its ability to form donor-acceptor complexes. Ethylenediaminetetraacetic acid illustrates the influence of steric effects on binding with acceptors. The binding of beryllium ions with sulfonyl groups highlights the thermodynamic stability of such systems, opening new opportunities for the development of electrolytic systems and a deeper understanding of ionic interactions. These results highlight the importance of the electronic characteristics of molecules for predicting their chemical behavior, which has significant applications in the chemical and pharmaceutical industries.

The study of ternary polymer-metal complexes with Be^{2+}, Mg^{2+}, Ca^{2+} ions, and others confirms the significance of interactions between components for creating effective adsorbents (Fig. 3–5). The inclusion of low-molecular-weight ligands in systems with the polymer ligand PEI significantly affects the formation of stable complexes, which is important for wastewater treatment and the separation of metal ions. FTIR spectroscopy analysis revealed specific coordination bonds, particularly between the beryllium ion and the sulfonyl group of salicylic acid.

In contrast to [18], where the removal of heavy metals is achieved via biological mechanisms involving living microalgae – systems that are highly sensitive to fluctuations in pH and temperature – the triple polymer-metal complexes synthesized in this work demonstrate chemical and structural stability in a wide range of conditions. Specifically, the newly developed complexes such as PEI-Be^{2+}(Hg^{2+},Hg_2^{2+})-H_3Ssal, PEI-Hg^{2+}(Hg_2^{2+})-H_2Sal, and PEI-Zn^{2+}(Cd^{2+}, Hg^{2+}, Hg_2^{2+})-H_2edta^{2-} enable selective binding and removal of toxic metal ions, including beryllium and mercury, with efficiency reaching up to 97%. This result is made possible by the synergistic coordination mechanism involving both the polymer matrix (PEI) and low-molecular-weight ligands, which provide multidentate binding sites and stabilize complex formation through donor-acceptor and electrostatic interactions.

Unlike conventional polymeric adsorbents described in [21], which primarily rely on surface-level sorption and suffer from regeneration difficulties and low selectivity, the obtained polymer-metal complexes form inner-sphere coordination bonds, which significantly enhance selectivity toward small, high-charge-density ions such as Be^{2+} and Hg_2^{2+}. This structural feature allows the material to maintain its adsorption capacity in real wastewater matrices with competing ions and fluctuating composition.

Thus, compared to global analogs [15, 20], the synthesized ternary complexes are not only environmentally and economically advantageous, but also demonstrate high adsorption efficiency, reproducibility, and adaptability, making them highly promising for industrial applications in the post-treatment of wastewater contaminated with heavy metals.

The developed polymer-metal complexes allow for the selective extraction of toxic metal ions (Be^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Hg_2^{2+}) from various solutions. At the "Tospa Su" facility, laboratory tests of polymer compositions for purifying wastewater from car washes in Almaty from beryllium and mercury ions were conducted. The results of the research show the high efficiency of polymer compositions for the further purification of wastewater and the possibility of predicting their behavior based on thermodynamic characteristics. Thanks to complexation with polyethyleneimine and salicylic acid, 93–97% purification of wastewater from mercury and beryllium ions has been achieved.

In calculating the stability of polymer coordination compounds, a number of simplifying assumptions were made to ensure the applicability of the law of mass action in its concentration form. The polymer electrolyte was considered a homogeneous system, with the ionic strength regulated using aqueous solutions of NaCl. The reactive groups of polyethyleneimine were assumed to be chemically identical, with uniform dissociation constants that remain unchanged upon protonation and complexation. While these assumptions facilitated the modeling process, they impose several important limitations.

First, the applicability of the developed models is restricted to laboratory-controlled conditions. The behavior of the complexes in the presence of organic contaminants, hard water ions, or highly mineralized environments has not yet been evaluated. Second, the stability of the synthesized complexes decreases under extreme pH conditions and at elevated temperatures above 50°C, likely due to conformational changes in the polyethyleneimine backbone and disruption of coordination bonds. Third, the reproducibility of the results outside the tested pH range (4–8), temperature (20–25°C), and in the presence of competitive ionic species has not been confirmed and requires further validation through pilot-scale studies.

Among the disadvantages of the current study is the absence of kinetic data on the formation and dissociation of the polymer-metal complexes. This limits the ability to optimize contact times and predict sorption dynamics during scale-up. Additionally, the regeneration of the synthesized sorbents and their performance over multiple cycles was not examined. The selective behavior of the complexes in multicomponent solutions containing competing ions such as Ca^{2+}, Fe^{3+}, or Pb^{2+} was also not addressed.

Overcoming these limitations and disadvantages will improve the robustness and transferability of the developed approach for practical implementation in wastewater treatment systems targeting toxic heavy metal ions.

Future work may focus on kinetic studies, sorbent regeneration protocols, and competitive binding evaluations to enhance the practical applicability and industrial relevance of the proposed method.

7. Conclusions

1. The complexation behavior of group II metal ions (Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) with polyethyleneimine (PEI) was studied using potentiometric, conductometric, and viscosimetric methods. It was established that coordination compounds with a stoichiometry of PEI:M^{2+} = 2:1 are formed in binary systems. In PEI-Sr^{2+} and PEI-Ba^{2+} systems, stepwise complex formation was observed, with formation of polymer-metal particles of 6:1 and 4:1 composition, respectively, at the initial stage. The stability series of the resulting complexes was determined as: $Be^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+}$, which correlates with the acid-base character and ionic radius of the metal cations. The PEI–Mg^{2+} complex exhibited the lowest stability due to structural incompatibility between the small, highly hydrated Mg^{2+} ion and the flexible PEI ligand.

2. Thermodynamic analysis revealed that all studied complexation processes are spontaneous ($\Delta_r G^\circ < 0$) and exothermic ($\Delta_r H^\circ < 0$). For example, for the PEI-Be^{2+} system, the calculated parameters were: $\Delta_r G^\circ = -53.34$ kJ/mol, $\Delta_r H^\circ = -210.45$ kJ/mol, $\Delta_r S^\circ = -509.95$ J/mol·K. Negative entropy changes for Be^{2+} and Mg^{2+} indicate increased ordering within the complexes. The stability constants ($\lg\beta_0$) ranged from 5.4 for Mg^{2+} to 10.16 for Be^{2+}, confirming the high affinity of PEI for smaller, more polarizing cations.

3. Quantum chemical calculations identified the main reactive sites in low-molecular-weight ligands: carbonyl oxygen atoms in salicylic acid (H_2Sal), sulfonyl oxygens in sulfosalicylic acid (H_3Ssal), and carboxyl oxygen atoms in EDTA (H_2edta^{2-}). Due to steric hindrance, coordination through EDTA nitrogen atoms is limited.

4. In ternary systems, distinct interaction mechanisms were identified. For PEI–Me^{2+}-H_2Sal/H_3Ssal, complexation occurs predominantly via donor–acceptor interactions, forming stable polymer–metal–ligand complexes. In contrast, systems such as PEI-Zn^{2+}/Cd^{2+}-H_2Sal and PEI-Be^{2+}-H_2edta^{2-} form complexes stabilized primarily by electrostatic interactions between the positively charged PEI and the metal-ligand moiety. Sorption studies demonstrated that PEI-Be^{2+}-H_3Ssal and PEI-Hg^{2+}-H_3Ssal complexes were the most effective for ion removal. Be^{2+} was removed with 97.1% efficiency, and Hg^{2+} with 93.4%, whereas for Mg^{2+} and Ba^{2+}, removal efficiency remained below 70%. The PEI modified with sulfosalicylic acid was identified as the most efficient polymer-based sorbent. In pilot-scale wastewater treatment trials, this material reduced Be^{2+} and Hg^{2+} concentrations to 0.004 mg/L and 0.002 mg/L, respectively – both meeting regulatory discharge limits.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this study, whether financial, personal, authorship or otherwise, that could affect the study and its results presented in this paper.

Financing

The study was performed without financial support.

Data availability

Data will be made available on reasonable request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

References

1. Ayalew, Z. M., Guo, X., Zhang, X. (2022). Synthesis and application of polyethyleneimine (PEI)-based composite/nanocomposite material for heavy metals removal from wastewater: A critical review. Journal of Hazardous Materials Advances, 8, 100158. https://doi.org/10.1016/j.hazadv.2022.100158
2. Bertagnolli, C., Grishin, A., Vincent, T., Guibal, E. (2016). Recovering Heavy Metal Ions from Complex Solutions Using Polyethylenimine Derivatives Encapsulated in Alginate Matrix. Industrial & Engineering Chemistry Research, 55 (8), 2461–2470. https://doi.org/10.1021/acs.iecr.5b04683
3. Semenova, A., Vidallon, M. L. P., Follink, B., Brown, P. L., Tabor, R. F. (2021). Synthesis and Characterization of Polyethylenimine–Silica Nanocomposite Microparticles. Langmuir, 38 (1), 191–202. https://doi.org/10.1021/acs.langmuir.1c02393
4. Yoo, S.-H., Lee, S.-C., Ko, M., Yoon, S., Lee, J., Park, J.-A., Kim, S.-B. (2023). Adsorption of Hg(II) on polyethyleneimine-functionalized carboxymethylcellulose beads: Characterization, toxicity tests, and adsorption experiments. International Journal of Biological Macromolecules, 241, 124516. https://doi.org/10.1016/j.ijbiomac.2023.124516
5. Larsson, M., Nosrati, A., Kaur, S., Wagner, J., Baus, U., Nydén, M. (2018). Copper removal from acid mine drainage-polluted water using glutaraldehyde-polyethyleneimine modified diatomaceous earth particles. Heliyon, 4 (2), e00520. https://doi.org/10.1016/j.heliyon.2018.e00520
6. Tran, A. T.-K., Hoang, N. T.-T., Nguyen, P. T. (2023). Optimizing sulfonation process of polystyrene waste for hardness and heavy metal removal. Case Studies in Chemical and Environmental Engineering, 8, 100396. https://doi.org/10.1016/j.cscee.2023.100396
7. Houari, B., Louhibi, S., Tizaoui, K., Boukli-hacene, L., Benguella, B., Roisnel, T., Dorcet, V. (2019). New synthetic material removing heavy metals from aqueous solutions and wastewater. Arabian Journal of Chemistry, 12 (8), 5040–5048. https://doi.org/10.1016/j.arabjc.2016.11.010
8. Zhang, D., Wu, B., Wang, T., Yılmaz, M., Sharma, G., Kumar, A., Shi, H. (2025). Multi-mechanism synergistic adsorption of lead and cadmium in water by structure-functionally adapted modified biochar: A review. Desalination and Water Treatment, 322, 101156. https://doi.org/10.1016/j.dwt.2025.101156
9. Verma, M., Ahmad, W., Park, J.-H., Kumar, V., Vlaskin, M. S., Vaya, D., Kim, H. (2022). One-step functionalization of chitosan using EDTA: Kinetics and isotherms modeling for multiple heavy metals adsorption and their mechanism. Journal of Water Process Engineering, 49, 102989. https://doi.org/10.1016/j.jwpe.2022.102989
10. Ma, J., Zhou, G., Chu, L., Liu, Y., Liu, C., Luo, S., Wei, Y. (2016). Efficient Removal of Heavy Metal Ions with An EDTA Functionalized Chitosan/Polyacrylamide Double Network Hydrogel. ACS Sustainable Chemistry & Engineering, 5 (1), 843–851. https://doi.org/10.1021/acssuschemeng.6b02181
11. Qasem, N. A. A., Mohammed, R. H., Lawal, D. U. (2021). Removal of heavy metal ions from wastewater: a comprehensive and critical review. Npj Clean Water, 4 (1). https://doi.org/10.1038/s41545-021-00127-0
12. Sharma, K., Choudhary, P., Majeed, A., Guleria, S., Kumar, M., Rana, A. K., Rajauria, G. (2025). Cellulose based membranes, hydrogels and aerogels for water treatment application. Industrial Crops and Products, 225, 120474. https://doi.org/10.1016/j.indcrop.2025.120474

13. López-Maldonado, E. A., Abdellaoui, Y., Abu Elella, M. H., Abdallah, H. M., Pandey, M., Anthony, E. T. et al. (2024). Innovative biopolyelectrolytes-based technologies for wastewater treatment. International Journal of Biological Macromolecules, 273, 132895. https://doi.org/10.1016/j.ijbiomac.2024.132895
14. Sheraz, N., Shah, A., Haleem, A., Iftikhar, F. J. (2024). Comprehensive assessment of carbon-, biomaterial- and inorganic-based adsorbents for the removal of the most hazardous heavy metal ions from wastewater. RSC Advances, 14 (16), 11284–11310. https://doi.org/10.1039/d4ra00976b
15. Danouche, M., El Ghachtouli, N., El Arroussi, H. (2021). Phycoremediation mechanisms of heavy metals using living green microalgae: physicochemical and molecular approaches for enhancing selectivity and removal capacity. Heliyon, 7 (7), e07609. https://doi.org/10.1016/j.heliyon.2021.e07609
16. Shi, H., He, Y., Pan, Y., Di, H., Zeng, G., Zhang, L., Zhang, C. (2016). A modified mussel-inspired method to fabricate TiO_2 decorated superhydrophilic PVDF membrane for oil/water separation. Journal of Membrane Science, 506, 60–70. https://doi.org/10.1016/j.memsci.2016.01.053
17. Zhu, Y., Xie, W., Li, J., Xing, T., Jin, J. (2015). pH-Induced non-fouling membrane for effective separation of oil-in-water emulsion. Journal of Membrane Science, 477, 131–138. https://doi.org/10.1016/j.memsci.2014.12.026
18. Yuan, X., Li, W., Liu, H., Han, N., Zhang, X. (2016). A novel PVDF/graphene composite membrane based on electrospun nanofibrous film for oil/water emulsion separation. Composites Communications, 2, 5–8. https://doi.org/10.1016/j.coco.2016.10.001
19. Venault, A., Chiang, C.-H., Chang, H.-Y., Hung, W.-S., Chang, Y. (2018). Graphene oxide/PVDF VIPS membranes for switchable, versatile and gravity-driven separation of oil and water. Journal of Membrane Science, 565, 131–144. https://doi.org/10.1016/j.memsci.2018.08.018
20. Alaba, P. A., Oladoja, N. A., Sani, Y. M., Ayodele, O. B., Mohammed, I. Y., Olupinla, S. F., Daud, W. M. W. (2018). Insight into wastewater decontamination using polymeric adsorbents. Journal of Environmental Chemical Engineering, 6 (2), 1651–1672. https://doi.org/10.1016/j.jece.2018.02.019
21. Liu, C., Zhang, H.-X. (2022). Modified-biochar adsorbents (MBAs) for heavy-metal ions adsorption: A critical review. Journal of Environmental Chemical Engineering, 10 (2), 107393. https://doi.org/10.1016/j.jece.2022.107393