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Synthesis, Characterization and Application of New Polymers Imprinted with Zinc (II) Ions

In this work, molecularly imprinted polymers with zinc imprints and their comparison polymers without imprints were synthesized. A comparative characterization of the physical parameters of the synthesized zinc-imprinted (ZnIP) and non-imprinted (NIP) polymers was carried out using the methods of elemental analysis, conductometry, scanning electron microscopy, and IR-Fourier spectroscopy. The ability of the resulting polymers to molecularly recognize zinc was evaluated. Based on experimental data on static adsorption, the adsorption capacity of ZnIP and NIP was determined using an atomic emission spectrometer. It was found that ZnIP is characterized by better physical parameters and a higher ability for molecular recognition of zinc compared to NIP. ZnIP with zinc imprints were found to have better sorption capacity for zinc than their reference polymers. The sorption of zinc by molecular imprinted ZnIP is mainly due to the complex formation and pores of the initial carbon product. The synthesized ZnIP have increased porosity. The presence of pores with a diameter <50 nm in ZnIP is associated with voids formed after acid hydrolysis, which is clearly visible in images recorded by scanning electron microscopy. Thus, the possibility of using ZnIP as a selective sorbent has been established.

Keywords: molecularly imprinted polymers, comparison polymer, sodium humate, polyvinyl alcohol, template, zinc, sorption, adsorbent.

Introduction

Currently, water pollution with heavy metals is constantly increasing and poses a great threat to the environment. Therefore, the analysis of environmental objects for the content of heavy metals and the development of appropriate detoxifiers are of great importance.

With the development of modern technologies, the interest of researchers in the problems of synthesis of molecularly imprinted polymers (MIP) in the field of molecular recognition is steadily growing. Due to the unique properties and the ability of MIP to molecular recognition, these polymers are finding new applications. To create new polymer materials with improved performance characteristics, it is possible to control the process of template formation during the formation of MIP and after its removal from the polymer matrix, the formation of a selective recognition cavity for the template of the molecule. Such polymers, which recognize target molecules with high selectivity, are relevant and are attracting increasing attention [1–10].

The use of molecularly imprinted polymers in the development of sorption materials is based on their ability to remove contaminants, including trace levels, in a highly selective manner, and the exceptional stability of polymer materials under harsh conditions makes it possible to simplify the process of water purification in general.

In recent years, researchers have made extensive use of the rapidly developing molecular imprinting technology to create new polymeric sorption materials [16–25]. The polymeric materials produced by molecular imprinting are widely and successfully used in industries such as chemical, pharmaceutical, biotechnological, and especially at the stages of purification of the final product [26–30].

As you know, zinc (Zn) is one of the most common heavy metals that is most often found in wastewater. Zinc compounds penetrate into natural water treatment from industrial wastewater. Dangerous forms of zinc in water are sulfates and chlorides, which belong to heavy metal salts. Both their excess and deficiency can cause damage to the systems of all living organisms [11–15]. Therefore, water purification from such a heavy metal as zinc is an important component of the water treatment system in production and industry.

Previously, molecular imprinted polymers have been synthesized and used for water purification from heavy metals [16, 20, 31, 32]. Continuing the research on the development of MIP, in this work zinc-imprinted polymers (ZnIP) and non-imprinted polymers (NIP) were synthesized based on the product of processing oxidized coal mining waste — humic acids (HA) and a functional monomer.

Humic acids are known to be a complex mixture of high-molecular and multifunctional compounds of aromatic, heterocyclic and alicyclic nature, replaced by alkyl chains of different lengths with limiting and unsaturated bonds. Humic acids are natural detoxifiers. The aromatic nuclei of humic acids contain a large number of carboxyl, hydroxyl, and quinoid groups, which allow them to participate in a variety of redox reactions. In this regard, it is of interest to create a MIP based on functionalized humic acids with zinc imprints using the molecular imprinting method for the selective isolation of zinc ions from an aqueous medium.

As an analogue of the structural fragments of sodium humate (HNa), we considered a functional monomer — polyvinyl alcohol (PVA), copolymerization with which should lead to enrichment of the imprinted polymer product with sites designed for molecular recognition of target zinc molecules.

The purpose of the study. On the basis of sodium humate, polyvinyl alcohol, to synthesize molecular imprinted polymers capable of molecular recognition of zinc and to conduct a comparative analysis of the textural properties of synthesized polymers.

Experimental

Materials

In this study the following materials were used: sodium humate (HNa), isolated from oxidized coal from the Shubarkol deposit (Karaganda, Kazakhstan); polyvinyl alcohol ($(C_2H_4O)_x$, M = 1–15·10^4, produced by Sigma-Aldrich); template — zinc acetate ($(Zn(CH_3CO_2)_2 \cdot 2H_2O$, M=219.50 g/mol, produced by Sigma-Aldrich)); crosslinking monomer — formaldehyde (CH_2O, 37 % aqueous solution, produced by Sigma-Aldrich); initiator of free radical polymerization — benzoyl peroxide (BPO) ($C_{14}H_{10}O_4$, M=242.23 g/mol, produced by Sigma-Aldrich); solvent — distilled water.

Synthesis of Sodium humate (HNa)

Sodium humate was isolated from samples of oxidized coal from the Shubarkol deposit during alkaline impregnation caused by intercalation of sodium hydroxide into it. The alkaline impregnation method included the following stages: mixing dried coal with an aqueous alkali solution with a concentration providing a given NaOH/substrate mass ratio (1:10); heating (100 °C, 2 hours) with stirring and holding at room temperature; separation of the liquid phase from the residual coal. The residual coal was further treated with water, and the mixture was heated with stirring and the boiling point of a water bath for further 30 minutes. The first and second filtrates of sodium humate solutions were combined, poured into a crystallizer and dried at room temperature to a dry state. Dry sodium humate was weighed and the yield was determined. The yield of sodium humate is 76.00–82.00 % by weight of dry coal.

Synthesis of molecular imprinted polymers with Zn^{2+}

The synthesis of a molecular imprinted polymer with zinc was carried out according to a previously developed and modified method [20] as follows: a solution of $Zn(CH_3COO)_2$ was prepared, where the content of zinc ions introduced during tuning was 4.50 mg-eq. Then this solution was introduced into a solution of sodium humate. The mixture was kept for 3 hours with stirring until a stable prepolymerization complex was formed between the polymer molecules and the template. Next, a functional monomer (polyvinyl alcohol), a crosslinking agent (formaldehyde) and an initiator (benzoyl peroxide) were added to the prepolymerization complex. Benzoyl peroxide is an initiator of the oxidative process, which allows for the oxidative destruction of polyvinyl alcohol macromolecules with the formation of oligomers with an additional number of ketone, aldehyde and carboxyl groups. The oxidation process proceeds by a radical mechanism. Metals with variable valence contained in the mineral part of HNa act as catalysts for this process [33]. Next, the mixture was subjected to heat treatment at 70 °C for 180 minutes. At the end of the copolymerization process, the resulting product was centrifuged (Hermle Labortechnik GmbH, Wehingen, Germany) at a speed of 4000 rpm, washed with water to a neutral medium, dried, crushed and sieved. The template was removed from the polymer mesh by acid hydrolysis with 0.1 N HCl solution, heated to 50–60 °C and kept for 30 minutes. The resulting product was filtered and the precipitate was washed with water until the Cl^- ions disappeared. The comparison polymers (non-printed polymers) were synthesized using a similar technique without the participation of a template, all other participants in the polymerization reaction remained the same.

Investigation of the obtained results of zinc-imprinted and non-imprinted polymers

A complexometric analysis based on the titration of zinc ions with a solution of Trilon B in an acetate buffer with xylene orange as indicator, after binding of interfering elements with complexing agents, was used to determine the content of zinc ions in zinc-imprinted polymers (ZnIP). The content of zinc ions introduced during tuning was 4.50 mg-eq per gram of imprinted polymer.

The reaction in zinc-impregnated and non-imprinted (NIP) polymers was monitored by reverse titration, according to the content of oxygen-containing groups using the laboratory conductometer Anion-4100 (Infraspak-Analyte, Novosibirsk, Russia).

The number of carboxyl groups was determined by the acetate method. The measurements were carried out sequentially on three hitches, and the average value of the three experiments was taken as the final value.

The elemental analysis of ZnIP and NIP for the content of carbon, hydrogen, nitrogen and oxygen was carried out on an elemental analyzer (Elementar Unicube, Langenselbold, Germany).

The composition of the zinc-imprinted and non-imprinted polymers obtained was confirmed by IR spectroscopy data performed on the FSM-1201 IR Fourier spectrometer (Infraspec Company, St. Petersburg, Russia). The range of wave numbers was 4000-400 cm^{-1}, the error in the determination of the wave numbers did not exceed 2 cm^{-1}.

A MIRA 3 scanning electron microscope (Tescan Orsay Holding, Brno-Kohoutovice, Czech Republic) equipped with a system of detectors registering different signals was used to estimate the particle size and surface morphology of the obtained ZnIP and NIP. Images with topographic contrast were obtained using secondary electron detectors. The elemental composition on the ZnIP and NIP surfaces was determined by X-ray energy dispersive microanalysis.

The sorption properties of synthesized zinc-imprinted ZnIP and non-imprinted polymers (NIP) were studied using the method described in [16]. To do this, 1 g of composite samples were mixed with a solution of zinc salt. The mixture was stirred at 120 rpm in a thermostatically controlled rocking chair at 25 °C for 24 hours. The solutions were then centrifuged and filtered to determine the concentration of free zinc in them using an inductively coupled plasma atomic emission spectrometer ICAR6500 DUOLA (SPECTRO ARCOS EOP SPECTRO Analytical instruments GmbH, Germany).

Results and Discussion

Zinc-imprinted polymers (ZnIP) based on functionalized sodium humate capable of recognizing template molecules were obtained using the molecular imprinting method. Their composition and physicochemical properties have been studied. The scheme for the preparation of ZnIP is shown in Figure 1.

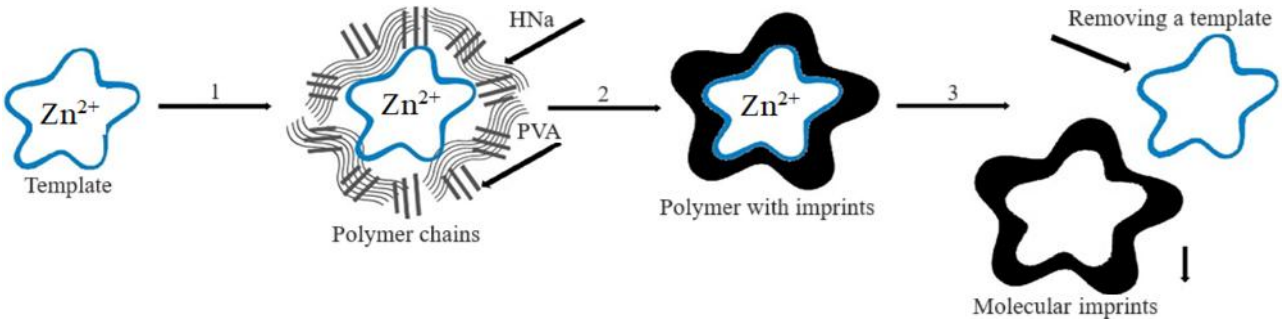

Figure 1. The scheme of obtaining a zinc-imprinted polymer

The results of the chemical studies of synthesized zinc-imprinted polymers are confirmed by data from elemental analysis, IR spectroscopy, complexometry, conductometry and electron microscope. The physicochemical characteristics of zinc-imprinted polymers (ZnIP) in comparison with non-imprinted polymers (NIP) are shown in Table.

As can be seen in Table, the oxygen content decreases by 4.54–6.41 % with the introduction of imprinted zinc polymers. This indicates the possibility of binding zinc ions by carboxyl and hydroxyl groups. A decrease in the content of oxygen-containing groups in zinc-imprinted polymers also makes it possible to assume their binding to zinc ions by the mechanism of complexation. Thus, in zinc-imprinted polymers, their content is 4.21–4.98 mg-eq/g, and in non-imprinted polymers — 4.82–5.75 mg-eq/g. The ZnIP yield is 78.42–80.69 %, and NIP yield is 77.26–79.84 %.

T a b l e

Characteristics of imprinted polymers

№	Sample	Component Ratio (HNa:PVA)	C^g, %	H^g, %	O^g, %	Σ(COOH+OH) mg-eq/g	Yield, %
1	NIP_1	1:1	56.30±0.2	3.83±0.1	39.22±0.4	4.82±0.2	77.26
2	$ZnIP_1$		60.74±0.2	3.95±0.1	34.68±0.4	4.21±0.2	78.42
3	NIP_2	5:1	57.20±0.2	3.86±0.1	38.29±0.4	5.75±0.2	79.84
4	$ZnIP_2$		63.52±0.2	3.97±0.1	31.88±0.2	4.98±0.2	80.69

The IR spectra of non-imprinted and zinc-imprinted polymers are shown in Figure 2.

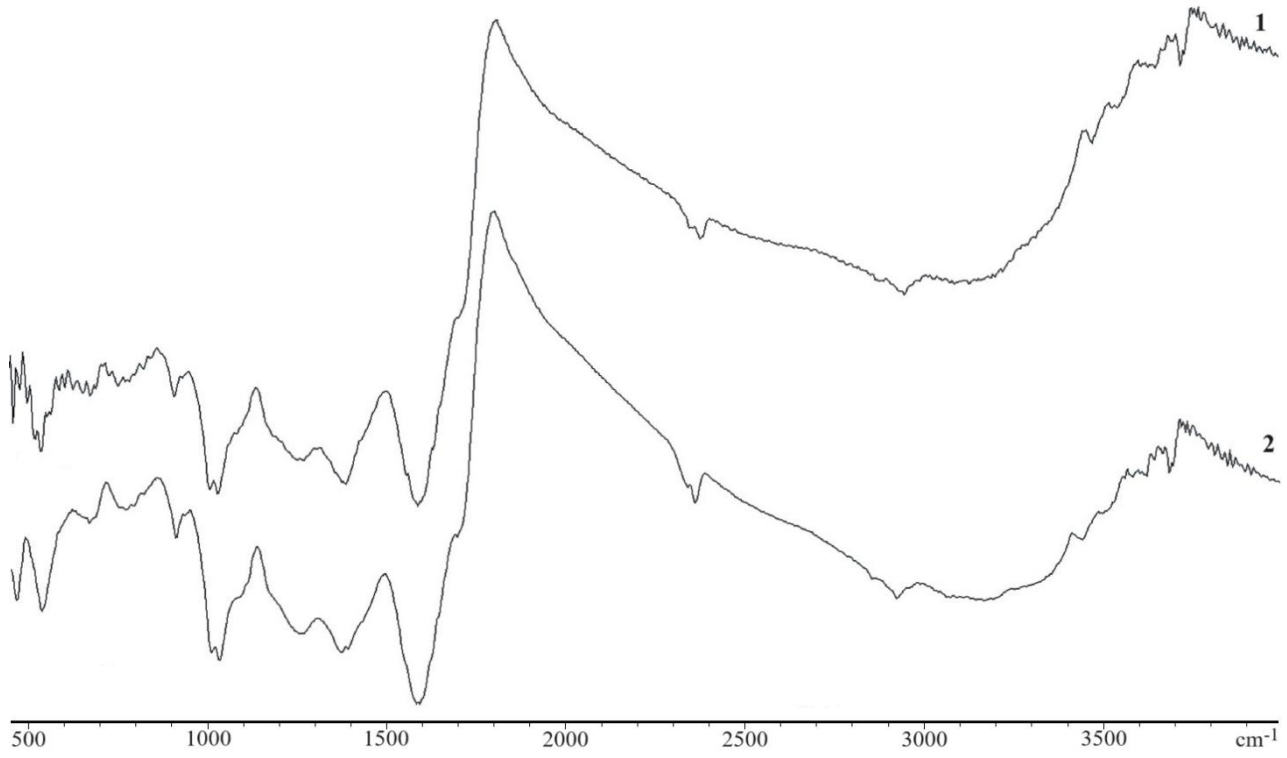

Figure 2. IR spectra: 1 –$ZnIP_1$, 2 — NIP_1

Analysis of the IR spectra of the zinc-imprinted polymers shows that the stretching peak characteristic of both the carboxylic groups at 1713 cm^{-1} and the hydroxyl groups at 3443 cm^{-1} suggest the possibility of zinc ions binding by the ion exchange and complexation mechanisms. There is a significant increase in absorption in the region of valence vibrations of methylene and methyl C–H at 2923 and 2857 cm^{-1}, as well as deformation of C–CH_3 groups at 1385 cm^{-1}. The observed facts can be explained by destructive processes leading to a reduction in the length of the aliphatic chain and an increase in the number of ring –CH_3 groups. The stretching peaks in the region of 1695–1713 cm^{-1} are attributed to the carboxyl and ketocarbonyl (C=O) groups, whereas peaks 1130–1190 cm^{-1} and 1150 cm^{-1} are associated with the stretching of C–O molecules of carbohydrates, alcohol and ether groups, respectively. An increase in the intensity of the band with a maximum at 915–933 cm^{-1} is associated with an increase in the content of substituted aromatic structures. The absence of absorption of the characteristic band of the COOH-group 1713 cm^{-1} and the appearance of new bands characteristic of the carboxylate grouping 1585 and 1385 cm^{-1} in zinc-imprinted polymers suggests that part of the zinc ions is bound by the carboxyl group to the chelate complex. The bond between Zn–O is in the range from 400 to 600 cm^{-1}. This means that peaks 467 and 485 cm^{-1} clearly represent Zn–O bonds. The evidence of the presence of coordination nodes with the participation of C–O on the surface and in the volume of composites is the absorption in the region of 600–800 cm^{-1}, which relate to the valence vibrations of carboxyls. The absence of absorption bands characterizing the valence oscillations of the Zn–O bond in the spectra of non-imprinted polymers indicates the decay of these bonds.

The textural characteristics of ZnIP and NIP with topographic contrast were obtained using a TESCAN MIRA 3 scanning electron microscope (Fig. 3-4). The elemental composition of the samples was determined by quartering in different areas of the sample surface using X-ray energy dispersive microanalysis X-Act (Oxford Instruments).

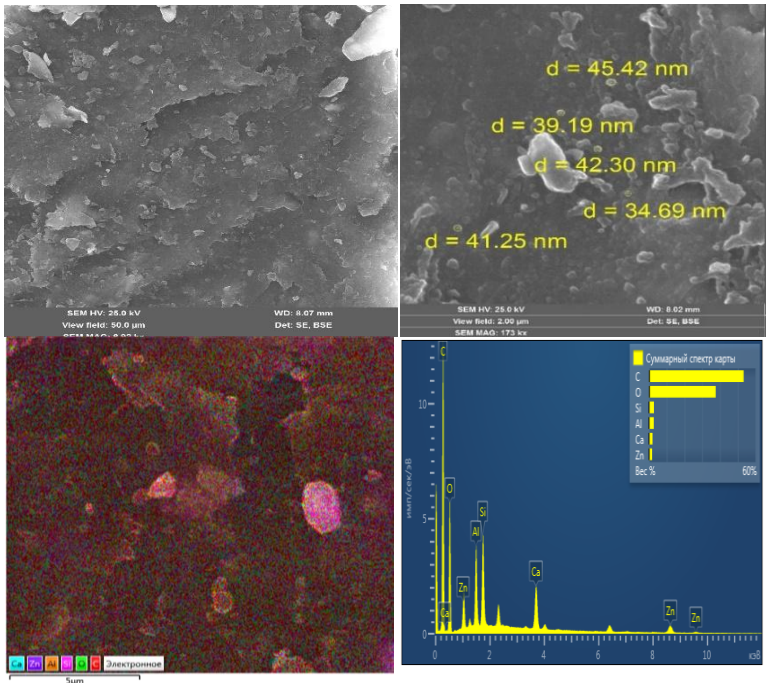

Figure 3. $ZnIP_1$ microstructure with elemental analysis

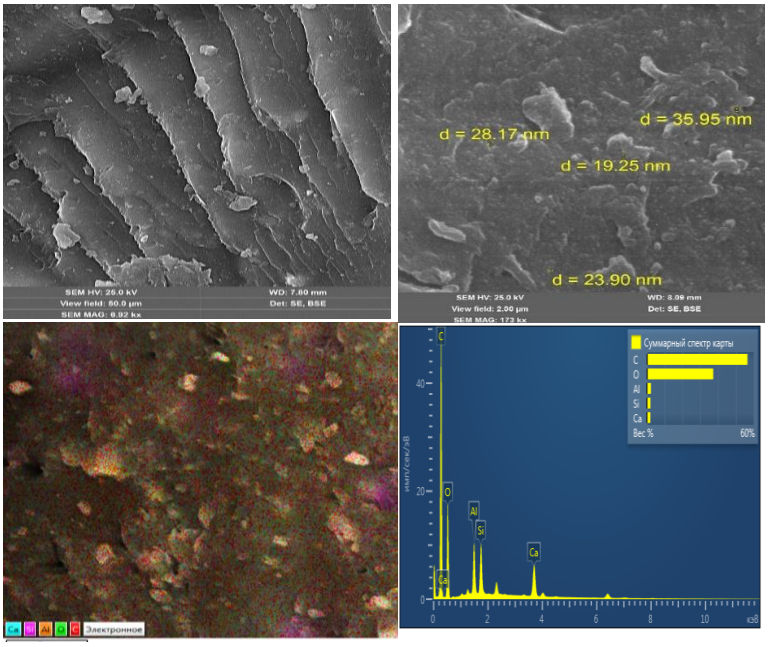

Figure 4. NIP_1 microstructure with elemental analysis

A comparative analysis of micrographs obtained of zinc-imprinted and non-imprinted polymers indicates a difference in their surface morphology and particle size. The $ZnIP_1$ electron micrographs (Fig. 3) show spherical and cubic formations and are characterized by increased porosity compared to NIP_1. It should be noted that removing the template from the polymer mesh uncorks additional pores, which is clearly visible in the images recorded by scanning electron microscopy (Fig. 3). The elemental composition and multilayer EDS-map confirm the composition of the products obtained, and the distribution of chemical elements

on the microstructure confirms the presence of elements that make up both zinc-imprinted and non-imprinted polymers.

To study the binding capacity of the zinc-imprinted and non-imprinted obtained, experiments on static adsorption of zinc were carried out (Fig. 5).

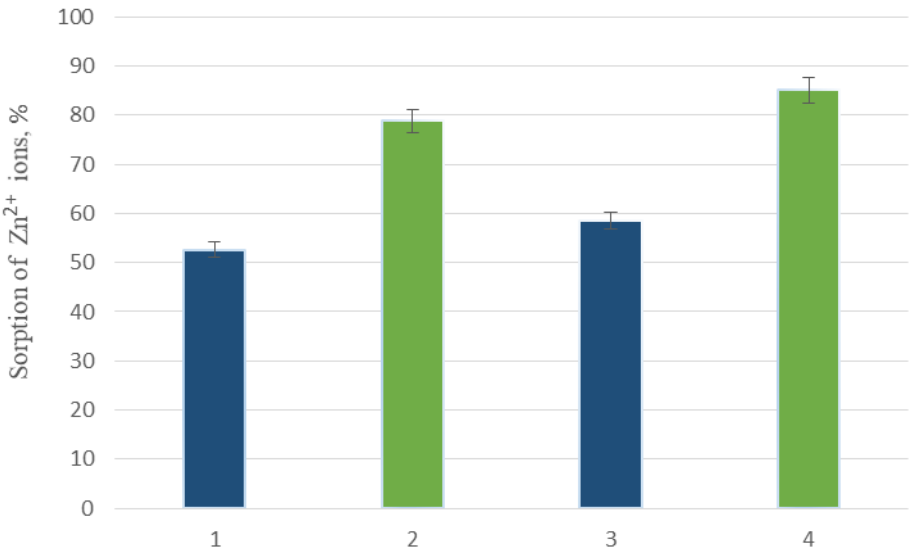

Figure 5. Results of sorption properties of synthesized polymers: 1 — NIP_2; 2 — $ZnIP_2$, 3 — NIP_1; 4 — $ZnIP_1$

A study of the adsorption properties of imprinted polymers pre-tuned to zinc ions showed a sharp increase in sorption capacity compared to non-imprinted polymers. The effect of improving sorption properties for Zn^{2+} is 78.90 % and 85.07 % for $ZnIP_2$ and $ZnIP_1$ samples, respectively. This confirms the assumption that there are pores in the system that corresponding to the ionic radius of the hydrolyzed metal and the effectiveness of the polymer selectively tuned to the sorbed ion.

Conclusions

Thus, two types of polymer sorbents were synthesized: zinc-imprinted polymers (ZnIP) and non-imprinted polymers (NIP). Synthesized zinc-imprinted and non-imprinted polymers were obtained with different ratios of sodium humate and polyvinyl alcohol. It was found that increasing the content of the functional polymer did not affect the yield of zinc-imprinted polymers. The decrease in oxygen-containing groups in the composition of the zinc-imprinted polymers indicates the possible binding of the template via the complexation mechanism. In this case, the sequential cross-linking of the prepolymerization complex with the functional monomer creates an imprinted sorption layer. An analysis of zinc-imprinted and non-imprinted polymers was carried out using modern physicochemical methods. The results of the evaluation the sorption properties of zinc-imprinted polymers and comparison polymers showed that imprinted polymers synthesized on the basis of sodium humate and polyvinyl alcohol at a ratio of 1:1 have the highest affinity for zinc. The obtained zinc-imprinted polymers using molecular imprinting technology can be recommended as sorption materials, the operating principle of which is based on the effect of molecular recognition and selective extraction.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Alma Khassenovna Zhakina** conceptualization, data curation, methodology, project administration, resources, software, writing — original draft, writing — review & editing; **Oxana Vasilievna Arnt** formal analysis, investigation, visualization; **Yevgeniy Petrovich Vassilets** formal analysis, investigation, visualization; **Arailym Alzhankyzy** formal analysis, investigation; **Almat Maulenuly Zhakin** formal analysis, investigation.

Conflicts of Interest

The authors declare no conflict of interest.

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