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Виконані дослідження продуктів взаємодії іонів важких металів (Pb(II), Cd(II), Cu(II), Zn(II)) з полігексаметиленгуанидином у водних розчинах. Методом полярографічного відновлення встановлено вплив концентрації поліелектроліту на процес зв'язування іонів політантів у Me-ПГМГ-асоціати. З використанням ІЧ-спектроскопії підтверджено утворення асоціатів іонів металів з полігексаметиленгуанидином

Ключові слова: полігексаметиленгуанидин, важкі метали, гідроксополуки, Me-ПГМГ-асоціати, полярографія, ІЧ-спектроскопія, аквакомплекс, флокулянт, поліелектроліт

Выполнены исследования продуктов взаимодействия ионов тяжелых металлов (Pb(II), Cd(II), Cu(II), Zn(II)) с полигексаметиленгуанидином в водных растворах. Методом полярографического восстановления установлено влияние концентрации полиэлектролита на процесс связывания ионов полютантов в Me-ПГМГ-ассоциаты. С использованием ИК-спектроскопии подтверждено образование ассоциатов ионов металлов с полигексаметиленгуанидином

Ключевые слова: полигексаметиленгуанидин, тяжелые металлы, гидроксо соединения, Me-ПГМГ-ассоциаты, полярография, ИК-спектроскопия, аквакомплекс, флокулянт, полиэлектролит

FEATURES OF FORMATION AND IDENTIFICATION OF SPARINGLY SOLUBLE AND COORDINATION COMPOUNDS OF POLYHEXAMETHYLENEGUANIDINE WITH Pb(II), Cd(II), Cu(II), Zn(II) IN AQUEOUS SOLUTIONS

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1. Introduction

At present, the anthropogenic impact on water resources is becoming more active. Noncompliance with sanitary norms by enterprises, outdated treatment technologies of waste water discharged into surface waters cause a high content of toxic substances in the environment. Along with insufficiently treated water, pollutants migrate to water bodies, soil, plants and animals, creating an imminent threat to human health. The relevance of the search of new, more advanced water treatment methods is due to the fact that the existing technologies for heavy metals removal from the treated water are bulky, expensive, sensitive to acidity and not effective enough. Widespread methods of reactant purification and coagulation do not provide sufficient purity and introduce the secondary pollution to the treated water. Hence, the studies of the reaction of heavy metal compounds with multifunctional flocculants, including polyhexamethyleneguanidine hydrochloride (PHMG HC) for improving water treatment technologies are relevant.

2. Literature review and problem statement

In the analysis of the methods of heavy metal ions removal from solutions, we should note two main trends: the metal ion transfer to a sparingly soluble state [1], and the consolidation of the pollutant ion binding associates [2]. The fulfillment of these conditions greatly facilitates the process of coagulation, flocculation, filtering and precipitation. Given the above, it is of interest to study the formation features of compounds of ions of the investigated metals with PHMG and choose the optimum conditions for the selected reactant.

At the same time, it is well known that the guanidine compounds are highly effective and much less toxic to humans compared with other biocidal agents. Such a low toxicity of guanidine is due to the fact that warm-blooded organisms have enzyme systems, which can cause polymer degradation [3, 4].

The presence of rather high positive surface charge gives the properties of cationic polyelectrolyte, flocculant and

surfactant to PHMG. The high reactivity enables the use of PHMG for obtaining composites with biocidal properties. The $[\text{Al}_2(\text{SO}_4)_3\text{:PHMG}]$ composition with the mass ratio of the first and second components in the range from 10:1 to 150:1, proposed to be used [5] for the clarification, disinfection and decoloration of water in the process cycle simplifies significantly not only the chemical feed plant, but also the units for injecting reactants into water.

Interesting results have been obtained during the study of complexing abilities of PHMG with ions of metals, in particular, Mg, Al, Cr, Fe, Co, Ni, Cu, Pb, Pt [4, 6, 2].

An important advantage of PHMG as a flocculant is the ability to significantly reduce the dose of the coagulant used in the water treatment technology by 2–4 times [7]. The coagulant dose reduction allows improving the chemical safety of water by reducing the content of residual aluminum.

There are a large number of works of Ukrainian and foreign scientists dealing with the study of physical and chemical properties, synthesis methods and antiseptic characteristics of PHMG [8, 9]. Careful attention is paid to the study of properties of PHMG chemically sealed on the surface of sorption materials. Thus, the research [10] shows the use of the modified adsorbent which is PHMG chemically sealed on the surface of amine-containing silica gel. The authors use this adsorbent for removal of V(V), Mo(VI), W(VI), Cr(VI) ions from aqueous solutions. The research [11] presents the results of investigating the polyhexamethyleneguanidine-modified natural zeolite for removal of Cr(VI) ions. At the same time, insufficient attention is paid to the study of the promising use of PHMG as a flocculant, possessing biocidal properties.

Thus, polyhexamethyleneguanidine hydrochloride is a high molecular weight cationic polyelectrolyte exhibiting the properties of flocculant, biocide and organic base. In the guanidine polymer group, the protonation of which forms guanidinium cation in aqueous solution, the positive charge distribution among three nitrogen atoms is relatively uniform and thus guanidinium compounds are relatively stable [12]. However, the products of its reaction with heavy metal ions a priori cannot be identified without experimental research.

3. Research goal and objectives

The goal of the research is to investigate the reaction of heavy metal ions (Pb(II), Cd(II), Cu(II), Zn(II)) with PHMG in aqueous solutions and identify the associates of the Me (II)-PHMG type.

To achieve this goal, the following studies were conducted:

- polarography of salt solutions of the studied metals in the presence of PHMG using the dropping mercury electrode to reveal the reaction of the Me(II)-PHMG system;
- determination of bonds present in the products of the reaction of ions of the above metals with PHMG using IR spectroscopy.

4. Materials and methods of the study of the metal ions-PHMG reaction

4.1. Materials and equipment used in the experiment

The following salts were used in the studies: – $\text{Cu}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$, GOST 4163-68, “reagent grade”; $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$,

GOST 6262-79, “reagent grade”; $\text{Pb}(\text{NO}_3)_2$, GOST 4236-77, “reagent grade”; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, GOST 4174-77, “reagent grade”; PHMG HC, TU 10-09-41-90.

Polarography of the solutions was conducted using the PU-1 universal polarograph, with the dropping mercury electrode in an automatic two-electrode mode [13].

To identify the heavy metal ions-PHMG reaction products, the IR spectroscopy method was used, analyses were performed on the Varian Scimitar 1000 FT-IR spectrograph.

4.2. The method of the study of the reaction of the investigated metals with PHMG

Polarography of the solutions of Me(II)-PHMG systems (where Me(II) is Pb(II), Cd(II), Cu(II), Zn(II)) was carried out in an electrolytic cell. To eliminate the interference of dissolved oxygen, measurements were made after the preliminary deaeration of the polarographic cell with high-purity argon while continuous feeding of it using the hydraulic lock. The polarograms of solutions of Me(II)-PHMG systems were studied in a series of solutions with a constant metal concentration and a variable PHMG content ($C_{\text{Me(II)}} = (1.5 \div 1.9) \text{ mmol/dm}^3$, $S_{\text{PHMG}} = (0.23 \div 201.0) \text{ mmol/dm}^3$).

Preparation of samples to IR spectroscopy was carried out by mixing salt solutions of Cd(II), Pb(II), Cu(II) and Zn(II) ($C_{\text{Pb(II)}} = C_{\text{Cd(II)}} = C_{\text{Cu(II)}} = C_{\text{Zn(II)}} = 0.024 \text{ mol/dm}^3$) with the PHMG solution ($C_{\text{PHMG}} = 0.024 \text{ mol/dm}^3$), pH of the PHMG solution was previously brought by the HCl solution to pH=5.0. The resulting precipitate was washed with bidistilled water of the same pH value up to a negative response to Cd(II), Pb(II), Zn(II), Cu(II) ions using the dithizone solution in carbon tetrachloride [14], then dried at $t = 70^\circ \text{C}$ for 3 days. The resulting powder was tabletted with KBr and analyzed.

5. The results of the studies of Me(II)-PHMG systems

Polarography of Me(II)-PHMG systems revealed that the reaction of Pb(II), Cd(II), Zn(II) and Cu(II) with the polymer in all cases causes the decrease of the limiting current of reduction in the polarograms.

However, the reduction of Zn(II) and Cu(II) in the presence of PHMG occurs in two stages with a significant cathode bias of the half-wave potential. The first stage refers to the cathode metal reduction from the aquo complex, the second – the metal reduction from the complex Me-PHMG-associate.

The polarograms of soluble Zn(II)-PHMG compounds and determination of the coordination number with their use are shown in Fig. 1, 2.

The IR spectra of the reaction products are shown in Fig. 3–7. According to the results of IR-spectroscopy, the absorption bands were determined in the following frequency ranges: $(3650 \div 3500) \text{ cm}^{-1}$, $(2930 \div 2860) \text{ cm}^{-1}$, $(1200 \div 600) \text{ cm}^{-1}$, $(500 \div 300) \text{ cm}^{-1}$, which correspond to: stretching vibrations of hydroxyl groups OH; methylene groups; deformation vibrations δ (Me-OH); stretching vibrations ν (Me-N).

More attention was paid to the absorption bands corresponding to the vibrations of the hydroxyl groups bound with the metal ions and the vibrations of the Me-N bonds, as well as changes in the IR spectra, which can be attributed to the probable redistribution of the electron density of the guanidine ring in the range of $(1500 \div 1200) \text{ cm}^{-1}$.

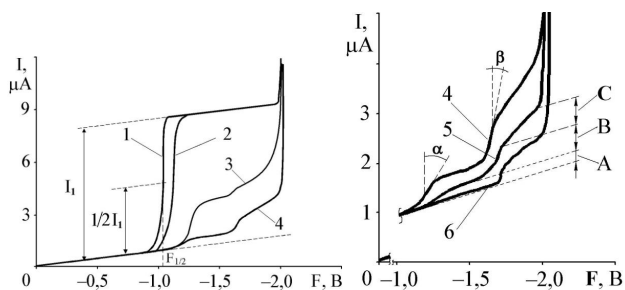


Fig. 1. The polarograms of Zn(II) reduction in the presence of PHMG: 1 – $C_{\text{PHMG}}=0 \text{ mmol/dm}^3$; 2 – 0.23 mmol/dm^3 ; 3 – 4.8 mmol/dm^3 ; 4 – 15 mmol/dm^3 ; 5 – 48 mmol/dm^3 ; 6 – 201 mmol/dm^3 . A – the Zn(II) aquo complex reduction wave, complicated by the PHMG adsorption on the mercury drop; B – the Zn(II)-PHMG complex reduction wave; C – the blurred part of the reduction wave of the Zn(II)-PHMG complex of variable composition; $E_{1/2}$ – an example of determination of the half-wave potential; α and β – the angles of the tangents of the polarographic wave at the respective half-wave potentials for the sections A and B

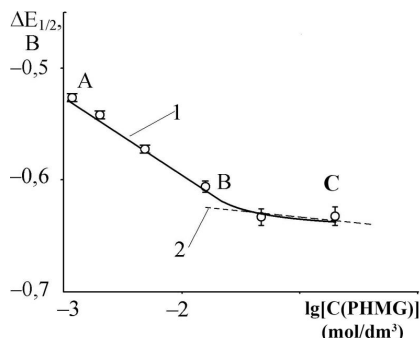


Fig. 2. The dependence of the bias of the half-wave potential of zinc reduction on the dropping mercury electrode on the PHMG concentration (1) and the linear approximation (2) of the formation area of the Zn(II)-PHMG complex in the absence of the Zn(II) aquo complex

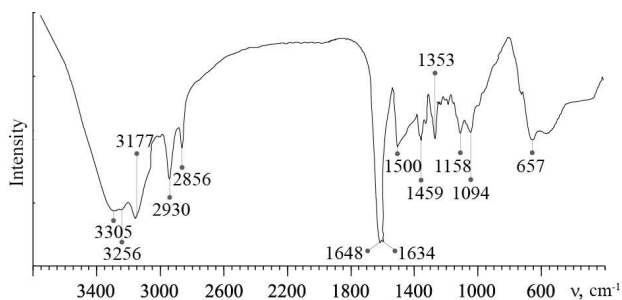


Fig. 3. The IR spectrum of PHMG

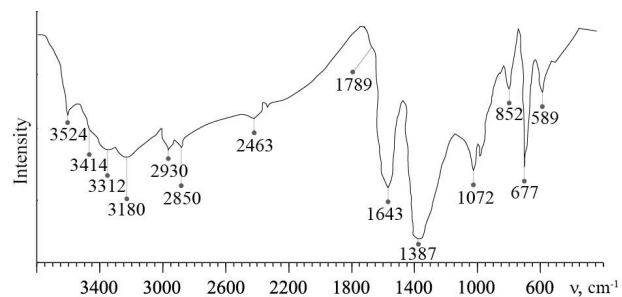


Fig. 4. The IR spectrum of the reaction products of the Pb(II)-PHMG system

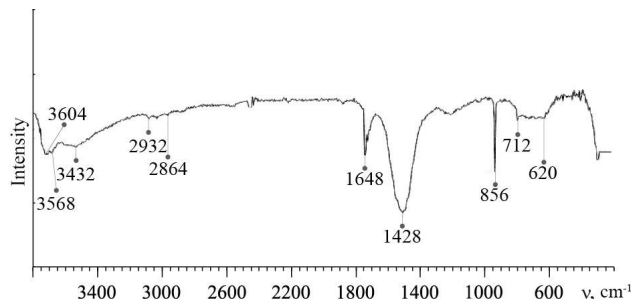


Fig. 5. The IR spectrum of the reaction products of the Cd(II)-PHMG system

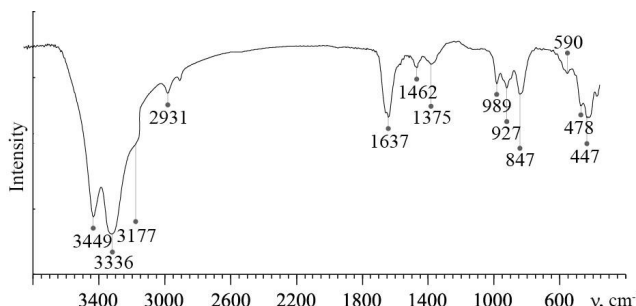


Fig. 6. The IR spectrum of the reaction products of the Cu(II)-PHMG system

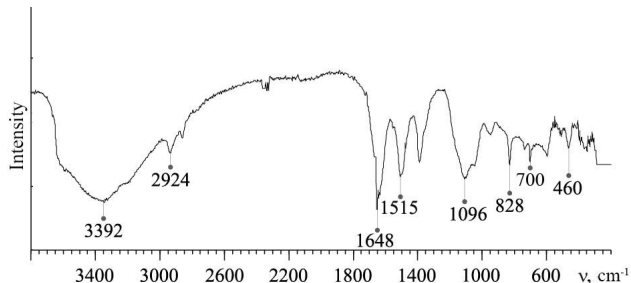


Fig. 7. The IR spectrum of the reaction products of the Zn(II)-PHMG system

6. Discussion of the results of the studies of the nature of the metal ions-PHMG reaction

Analysis of the IR spectrograms revealed significant differences in the number and intensity of the absorption bands of pure PHMG HC and its compounds with metals, which may indicate clear changes in the frequencies of the stretching and deformation vibrations of the macromolecules formed. Similarity was also observed in the IR spectra of the PHMG compounds with Cd(II) and Pb(II) ions, in contrast to the IR spectra of Zn(II)-PHMG and Cu(II)-PHMG.

The above data (Fig. 4, 5) show that in the presence of Cd(II) and Pb(II) ions, the absorption bands of methylene groups ($2930, 2860 \text{ cm}^{-1}$) disappear. Instead, in the range corresponding to the absorption bands of hydroxide ions of adsorbed water ($3650\text{--}3500 \text{ cm}^{-1}$ [15]), weak absorption bands ($3604, 3568, 3432 \text{ cm}^{-1}$) appear for the PHMG compound with Cd(II) and (3524 cm^{-1}) for a similar compound with Pb(II). Furthermore, in the literature [15, 16] there is evidence that the bands corresponding to the deformation vibrations δ (Me-OH) are in the range from 1200 cm^{-1} to 600 cm^{-1} . Their frequency depends on the atomic mass of the metal, the strength of the hydrogen bonds created by the

OH group and the Me–O bond covalence. Therefore, the absorption bands (1112,856,716) cm^{-1} for Cd(II)-PHMG and (1072,852,677,589) cm^{-1} for Pb(II)-PHMG may indicate the emergence of bonds between PHMG and hydrolyzed metal ions. The fact of the increasing number and intensity of absorption bands favors the formation of metal aggregates with PHMG due to hydroxy compounds, including due to the appearance of bridges of OH groups with metal ions [17]. It is known [17] that for hydroxy complexes, unlike aquo complexes, there are no absorption bands in the IR spectra corresponding to the deformation vibration $\delta_s(\text{Me-OH})$ in the range of (1700÷1600) cm^{-1} (Fig. 4, 5). On this basis, we can assume a high probability of formation of hydroxide salts of metals (Cd(II), Pb(II)) with PHMG by substitution of H^+ of the protonated guanidine group with CdOH^+ and PbOH^+ cations. The emergence of fairly strong absorption bands with the frequency of (1428) cm^{-1} for Cd(II)-PHMG and (1387) cm^{-1} for Pb(II)-PHMG, and along with it, a significant reduction in the band intensity of the guanidine group (1648) cm^{-1} may indicate a considerable redistribution of the electron density among the nitrogen atoms of the guanidine ring, as well as a decrease in the C=N (1570) cm^{-1} bond strength in the formation of PHMG compounds with hydrolyzed Cd(II) and Pb(II) involving the donor-acceptor mechanism.

The data of IR spectroscopy of Cu(II)-PHMG and Zn(II)-PHMG systems (Fig. 6, 7) indicate a slight decrease in the intensity of the absorption bands of the methylene group and the absence of changes in the frequency range in which there may be the absorption bands of ions of hydroxyls and adsorbed water (3650÷3500) cm^{-1} . At the same time, in the frequency range of (500÷300) cm^{-1} , absorption bands (592,460,350) cm^{-1} for Zn(II)-PHMG and (590,478,447) cm^{-1} for Cu(II)-PHMG appear, which according to the data analysis [17] correspond to the stretching vibrations $\nu(\text{Me-N})$. The intensity of the absorption band of the guanidine group (1648) cm^{-1} for Zn(II)-PHMG changes slightly to suggest a considerable redistribution of the electron density in the ring. The narrow intense absorption bands (700.828) cm^{-1} may indicate the occurrence of deformation vibrations $\delta(\text{Me-OH})$ in hydroxy complexes. The absorption bands (1096.944) cm^{-1} have a more diffuse configuration and confirm the assumption that the Zn(II) cation enters the Zn(II)-PHMG associate in the hydrolyzed form. A similar conclusion about the presence of hydroxy copper in the Cu(II)-PHMG reaction products can be made based on the presence of the absorption bands (989,927,847) cm^{-1} in the IR spectrum of the Cu(II)-PHMG system. Besides, for Cu(II)-PHMG, there is a noticeable decrease in the intensity of the absorption band of the guanidine group (1648) cm^{-1} , which may indicate its involvement in the donor-acceptor interaction (Me-N). This behavior of the guanidine group nitrogen may indicate that not all of the polymer units (PHMG) are involved in the formation of donor-acceptor bonds with the metal, but their interaction energy varies due to the coordination bond (Me-N) in the adjacent units.

The reproducible feature of the polarographic reduction of zinc in the Zn(II)-PHMG system is a significant negative bias of the half-wave potential (Fig. 1, *curve 2*) compared with the reduction of Zn(II) from the aquo complex (Fig. 1, *curve 1*). The PHMG concentration of 0.23 mmol/dm^3 is not enough for substantial displacement of the equilibrium of the formation of complexes with 0.16 mmol/dm^3 Zn(II), thereby the decrease in the limiting current of Zn(II) reduction in

the presence of PHMG (Fig. 1, *curve 2*) does not occur, and a noticeable cathode bias of the half-wave potential $E_{1/2}$ is due to the complication of the Zn(II) discharge by polyhexamethyleneguanidine adsorbed on the mercury drop. A significant excess in the surface concentration of PHMG on the growing mercury drop, compared with the volume of the solution is confirmed by the fact of suppression of the polarographic maxima that are present in the reduction of aquo complexes of metal ions from solutions without PHMG or other organic surfactants.

An increase in the PHMG concentration to 4.8 mmol/dm^3 causes further cathode bias $E_{1/2}$ and is accompanied by a decrease in the limiting current of zinc reduction (Fig. 1, *curves 3–6*). The reduction of Zn(II) consists of two stages: the first one (Fig. 2, *section A*) apparently corresponds to the reduction of the residual aquo complex of Zn(II), in spite of more than 3-fold excess of PHMG. This may indicate that only a part of guanidine groups are available for the reaction with Zn(II). The second wave (Fig. 1, *sections B, C*) corresponds to the zinc reduction from the Zn(II)-PHMG compound. The presence of two waves on the polarogram for Zn(II) in the presence of PHMG (Fig. 1, *curves 3, 4*) suggests the one-electron mechanism of Zn(II) reduction through Zn(I) to Zn^0 . However, the angle (Fig. 1, α, β) of the polarographic wave at respective potentials $E_{1/2}$ is functionally related to the number of electrons in the unit process of discharge. Consequently, a significant difference in the angles of the tangents α and β to the polarographic wave on the sections A and B most likely corresponds not to the one-electron mechanism of Zn(II) discharge through the Zn(I) to Zn^0 , but consistent reduction of the Zn(II) aquo complex (*section A*, Fig. 1) and the Zn(II)-PHMG complex (Fig. 1, *section B-C*). The Zn(II) reduction from the complex is irreversible, so the given values of instability constants are approximate.

The wave blur (Fig. 1, *sections B-C*) may indicate the reaction of Zn(II) with the PHMG molecule under a significant impact of its coiling [18] and decrease in the amount of reaction-available guanidine groups.

This is indicated by the dependence of the half-wave potential bias on the log PHMG concentration shown in Fig. 2 by the curve with a decreasing angle and the non-compliant straightforwardness of the approximating equation [19]:

$$\Delta E_{1/2} = a + b \cdot \lg[\text{PHMG}]. \quad (1)$$

The subsequent calculation of the coordination number by the equation (2) [19]

$$p = -zb / 0,059, \quad (2)$$

with determination of b by the angle of the tangent to the curve $E_{1/2} - \lg[\text{PHMG}]$ points to the variable value of the coordination number p and decrease of it to $p < 1$, indicating the primary influence of the PHMG molecule coiling [18, 20] on the formation of Me(II)-PHMG-associates at concentrations of (0.23÷201) mmol/dm^3 .

It should be noted that the reaction of Pb(II) and Cd(II) with PHMG causes only the decrease in the limiting current of reduction of the corresponding aquo complexes on the polarograms, i. e. it can be assumed that these metals form sparingly soluble compounds with PHMG and pass to the colloidal state, visualized by the characteristic opalescence. This is consistent with the presence of a more pronounced

absorption band (856) cm^{-1} for Cd(II) and (677) cm^{-1} for Pb(II) in the IR spectra characterizing the bond of the metal ion with the OH group, which suggests the reaction of Pb(II) and Cd(II) with PHMG to form insoluble hydroxy compounds.

The polarographic reduction of C(II) is similar to the reduction of Zn(II), i. e. with a significant cathode bias of the half-wave potential in the presence of PHMG and with two distinct phases of the polarographic wave.

7. Conclusions

1. Polarography and IR spectroscopy revealed the reaction of polyhexamethyleneguanidine to form sparingly soluble basic salts for Pb(II) and Cd(II), metal compounds for Cu(II) and Zn(II) through the reaction of its ion with the PHMG amino group to form fairly soluble compounds.

It was found that the Zn(II)-PHMG complex with a variable coordination number $p=(1\div 3)$, determined by polarography, may indicate the impact of the PHMG adsorbed on the cathode and the effect of the PHMG molecule coiling on the formation of associates.

2. Using the method of IR spectroscopy, identification of Me-PHMG-associates was carried out, the types of bonds involved in the formation of the studied compounds were identified. It was found that the data of IR spectroscopy confirm the assumptions about the nature of the Me-PHMG associates resulting from polarography of solutions. It was concluded that the formation of Me-PHMG-associates defines the prospects for the PHMG use in water purification from heavy metals. Taking into account the revealed features of its reaction with metal ions, it can be recommended as a flocculant in water treatment technologies.

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