WATER PURIFICATION FROM HEAVY METAL IONS USING LIME AND PHMG

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The method of metal ions' chemical precipitation using polyhexamethylene guanidine (PHMG) and calcium oxide (CaO) was employed for extracting metal ions from concentrated solutions. The order of reagent introduction was found to be crucial in the extraction process, with the best extraction efficiency observed when PHMG was added to water before CaO. This order of addition facilitated the polyelectrolyte effect, resulting in the unfolded conformation of macromolecules and enhancing their interaction with metal ions in solution. Optimal dosage ranges were determined, coinciding with the concentration interval of the polyelectrolyte effect, which maximized the flocculation ability and complex formation of PHMG. The combined use of PHMG and CaO, along with variations in pH, achieved high degrees of metal ion removal (>99%) in a single stage of solution treatment, except for chromium (Cr^{3+}) and cobalt (Co^{2+}). The surface activity of PHMG and ability to transfer metal ions as metal-polymer complexes supported its use in the flotation method for extracting heavy metal ions from low-concentration aqueous solutions. The kinetics of PHMG and metal ion removal by flotation showed rapid binding of metal ions to polymer macromolecules, and regression equations were established to describe the kinetics. The residual concentrations of metal ions after flotation met regulatory sanitary and environmental requirements for wastewater and drinking water.
A two-stage scheme for heavy metal ion extraction was developed, involving chemical precipitation and flotation extraction, with a pilot plant designed and manufactured for testing. During wastewater treatment in an electroplating production setting, metal ion concentrations that complied with regulatory standards were achieved.

Keywords: *flotation, lime, heavy metal extraction, PHMG, polyhexamethylene guanidine, precipitation*

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1. Introduction

The presence of heavy metals in wastewater poses a significant threat to both human health and the environment. Various industrial activities, such as plating and electroplating, mining, petrochemicals, and metal smelting, contribute to the contamination of wastewater with heavy metals. These non-biodegradable pollutants can be carcinogenic and have detrimental effects on living organisms, even at trace concentrations. Therefore, the development of efficient methods for the removal of heavy metal ions from wastewater is of utmost importance.

Numerous studies have focused on different approaches for heavy metal removal, including electrocoagulation, adsorption using synthetic and natural adsorbents, magnetic field implementation, advanced oxidation processes, and membrane technologies (Fig.1).

Among the different methods, chemical precipitation, specifically coagulation precipitation, is widely employed in industrial applications and is considered one of the most mature and effective approaches. This technique involves converting dissolved metal ions into solid particles, facilitating their sedimentation.

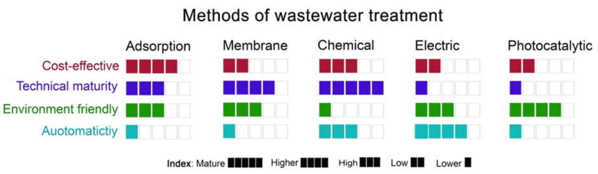

Fig. 1. *A general comparison between the typical methods used for heavy metals removal from wastewater (Qasem, 2021)*

Reagent coagulation precipitates metal ions through pH adjustment, electro-oxidizing potential modification, or co-precipitation (Ojovan, 2019). Hydroxide precipitation, a common form of coagulation precipitation, is cost-effective and allows for pH adjustment (Yadav, 2019). It involves the addition of calcium hydroxide (lime) to the wastewater, resulting in the formation of insoluble metal hydroxide precipitates:

$$Metal^{n+} + Ca(OH)_2 \rightarrow Metal(OH)_n\downarrow + Ca^{2+}.$$

However, hydroxide precipitation requires high pH values and substantial amounts of precipitants, which can be a disadvantage (Park, 2014).

While hydroxide precipitation has been effective for the removal of metals such as Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Cr^{3+}, challenges such as the generation of large volumes of sludge, dewatering difficulties, disposal concerns, and the interference of complexing agents with metal hydroxide precipitation need to be addressed.

Polyhexamethylene guanidine (PHMG) is a cationic polymer with a high affinity for heavy metal ions. It possesses strong chelation capabilities due to the presence of guanidine functional groups along its polymer chain. PHMG demonstrates excellent stability, solubility, and a relatively low cost.

The antibacterial properties of PHMG are well known and, moreover, this substance is being investigated as a wound-healing agent (Dias, 2021).

The effectiveness of PHMG in heavy metals removal has been extensively investigated in laboratory and pilot-scale studies. The polymer's mechanism of action involves the formation of stable complexes with heavy metal ions, leading to their sequestration and subsequent removal from aqueous solutions.

Moreover, the use of PHMG for heavy metals removal offers additional advantages, including pH stability, resistance to microbial degradation, and compatibility with various water treatment processes (Liu, 2021).

2. Materials and Methods

The mass concentration of PHMG salts is measured by the spectrometric method according to the procedure that has a Metrological Certification.

The measurement method is based on the measurement at an analytical wavelength of 540 nm and at pH = 3 of the difference in optical density between the solution of the PHMG-eosin association formed in a water sample and the solution without PHMG (zero solution).

Concentrations of heavy metal ions in the water were determined by methods certified in Ukraine.

The precipitation process in a laboratory was carried out in a test coagulation unit (Jar testing equipment) with the possibility of controlling the speed of the agitator in each reactor.

The scheme of the installation for testing the methodology on real wastewater is shown in Figure 4.

3. Results and Discussion

The method of metal ions' chemical precipitation using PHMG and CaO was used to extract metal ions from concentrated solutions. The order of reagent introduction plays a crucial role in the extraction process.

Table 1 presents data on the Recovery rate of metal ion extraction depending on the sequence of CaO and PHMG adding. The results indicate that adding PHMG to water before CaO leads to the best extraction efficiency. This order of adding creates favorable conditions for the manifestation of the polyelectrolyte effect, resulting in the unfolded conformation of macromolecules, which enhances their interaction with metal ions in solution.

Table 1. *Influence of the sequence of reagent injection on the extraction rate. The initial concentration (mmol/L) of metal ions - 1.0, CaO - 5.0, PHMG - 0.014*

Reagent dosing sequence	Extraction rate, %					
	Cu^{2+}	Ni^{2+}	Co^{2+}	Cr^{3+}	Fe^{3+}	Zn^{2+}
1 – CaO 2 – PHMG	98.3	97.8	93.7	87.8	97.5	98.4
1 – PHMG 2 – CaO	99.9	99.9	96.9	91.0	99.8	99.9

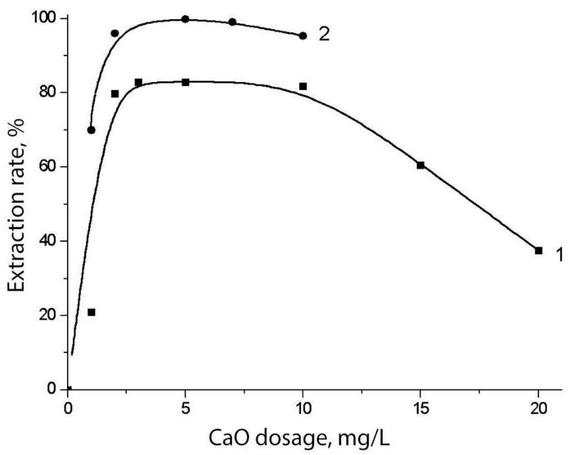

Fig. 2. *Zn^{2+} Extraction Rate on CaO Dosage: 1 - Without PHMG; 2 - With 2.5 mg/L PHMG*

Figure 2 illustrates the dependence of Zn^{2+} ion removal on the dosage of CaO (curve 1) and under the combined action of PHMG and CaO (curve 2). The use of PHMG significantly enhances the extraction of zinc ions, and similar results were observed for other metals.

Figure 3 demonstrates the effect of different doses of PHMG on the extraction of Zn^{2+} ions at a constant dose of CaO. The results indicate that increasing the dose of PHMG within the range of 1-5 mg/L enhances the extraction efficiency, while further increasing the dose to 10-15 mg/L reduces the degree of ion extraction. Similar trends were observed for other metals.

The investigation of heavy metal ion extraction from aqueous solutions using PHMG has enabled the determination of the optimal dosage range where maximum extraction efficiency is achieved. This range coincides with the concentration interval of the polyelectrolyte effect, which facilitates the complex formation and maximizes the flocculation ability of PHMG. The combined use of PHMG and CaO, along with variations in pH, has resulted in high degrees of metal ion removal (> 99 %) in a single stage of solution treatment, except for Cr^{3+} and Co^{2+}.

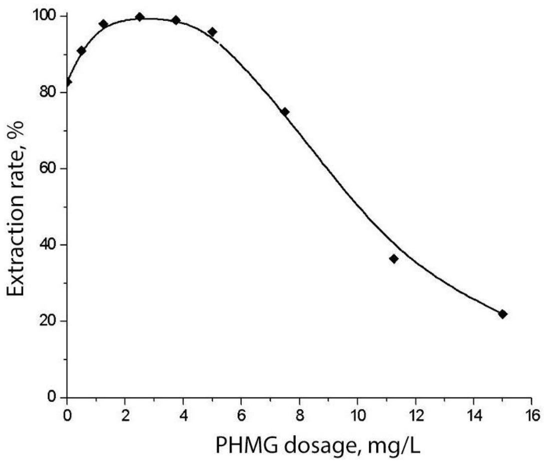

Fig. 3. *Zn^{2+} Extraction Rate on PHMG Dosage (with CaO)*

The obtained results establish the optimal technological parameters for metal ion extraction from aqueous solutions using PHMG and confirm its effectiveness as a substance for achieving high extraction efficiencies. The surface activity of PHMG and the ability to transfer metal ions as metal-polymer complexes to the surface layer support its use in the flotation method for extracting heavy metal ions from low-concentrated aqueous solutions, including further purification after chemical precipitation.

The kinetics of PHMG and metal ion removal from aqueous solutions in the presence of PHMG by flotation were studied (Fig. 4). The results indicate that the kinetics of metal ion removal aligns with that of PHMG, indicating rapid binding of metal ions to polymer macromolecules. This process does not limit the flotation method of metal ion removal. Similar findings were observed for all studied metals.

A computer program was employed to analyze the kinetic curves and establish regression equations describing the kinetics of PHMG and metal ion extraction by flotation, and determine the coefficients in the regression equations.

The residual concentrations of metal ions after flotation demonstrate the efficacy of the method in reducing the content of heavy metal ions in solutions to levels that comply with regulatory sanitary and environmental requirements for wastewater and drinking water.

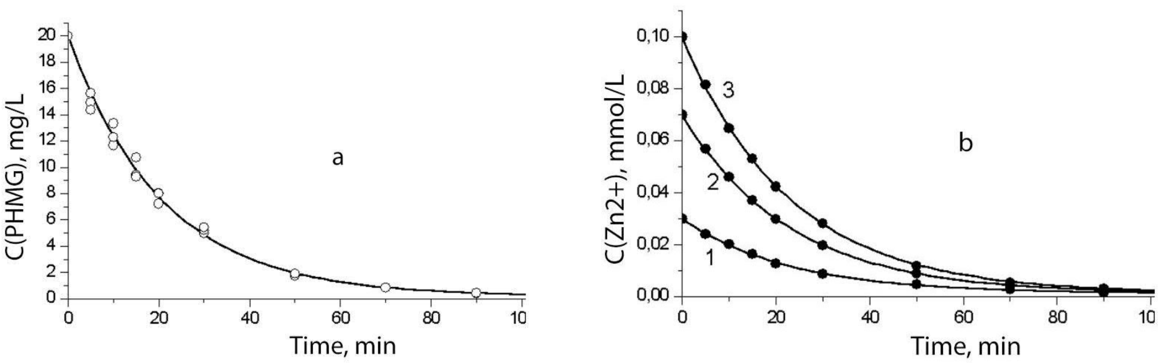

Fig. 4. *Kinetics of PHMG (a) and Zn^{2+} Ion (b) Removal by Flotation at Different Initial Concentrations of Zn^{2+} Ions: 1 - 0.03; 2 - 0.07; 3 - 0.1 mmol/L.*

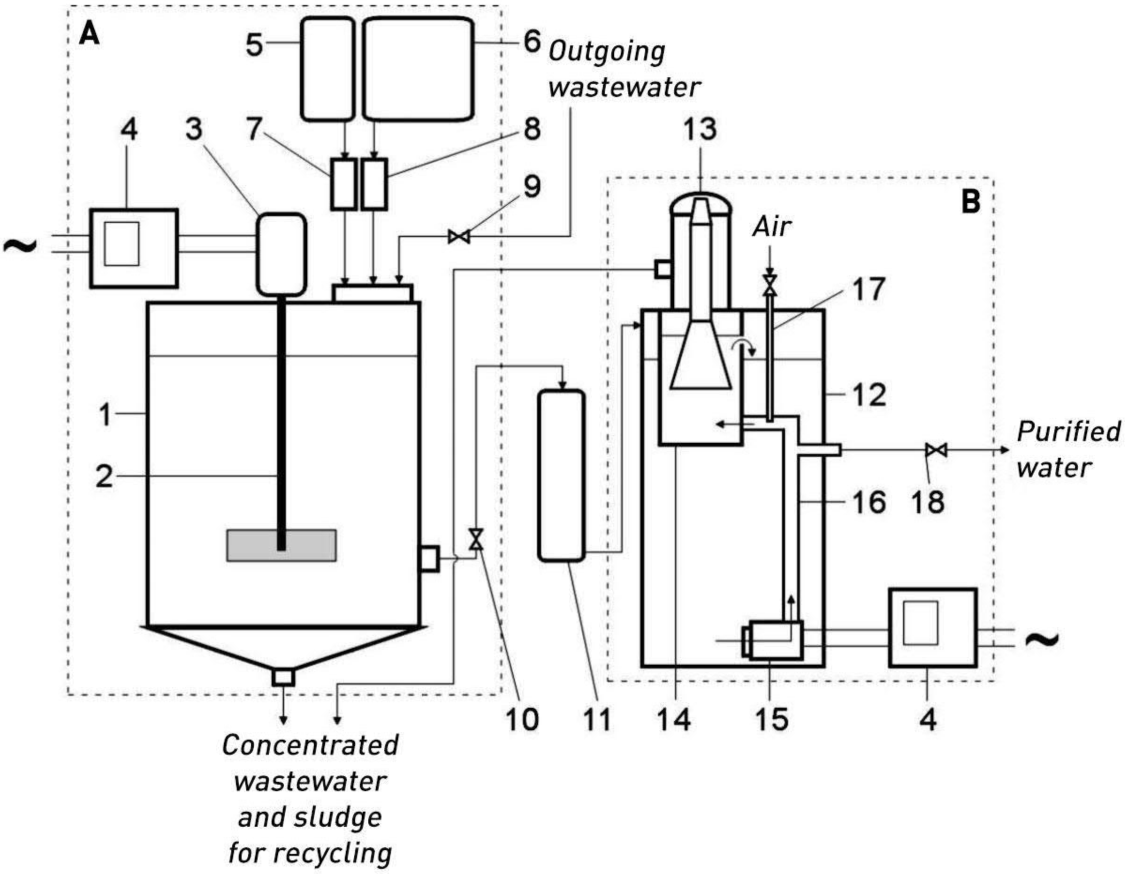

***Fig. 5.** Pilot plant for water purification from heavy metal ions:*
A - Precipitation Unit, B - Flotation Unit. 1, 12 - Tanks, 2 - Stirrer, 3 - Electric Motor, 4 - Control Unit, 5, 6 - Reagent Tanks, 7, 8 - Dispensers, 9, 10, 18 - Taps, 11 - Sand Filter, 13 - Extractor Nozzle, 14 - Constant Level Tank, 15 - Submersible Pump, 16 - Pipe, 17 - Air Injector.

***Table 2.** Results of electroplating production's wastewater treatment at the pilot plant*

Metal ion, mg/L	Wastewater		MPC for wastewater	MPC for drinking water
	before treatment	after treatment		
Fe^{3+}	9.0	0.1	2.5	0.3
Cr(VI)	0.58	0.01	0.1	0.05
Cu^{2+}	2.4	0.1	0.5	0.1
Ni^{2+}	12.5	0.08	0.5	0.1
Zn^{2+}	14.74	0.03	1.0	0.01
Hg^{2+}	0.02	<0.0001	0.005	0.0005
Pb^{2+}	0.15	<0.0001	0.1	0.03

Based on the established technological parameters, a two-stage scheme for the extraction of heavy metal ions from aqueous solutions using PHMG is developed. The scheme includes a stage of chemical precipitation and flotation extraction of heavy metal ions. The necessity of the second stage is caused by the necessity of water purification from the main pollutant as well as from the excess of PHMG (Fig. 4).

To implement this scheme, a pilot plant comprising a chemical precipitation unit and a flotation unit (Fig. 5) was designed and manufactured. During the testing of the pilot plant for wastewater treatment in electroplating production, metal ion concentrations that meet the regulatory standards were achieved (Table 2).

4. Conclusions

This study substantiates the main technological parameters for the effective extraction of metal ions from aqueous solutions using PHMG and proposes a two-stage technological scheme comprising chemical precipitation and flotation extraction. The technology has been successfully tested at a pilot plant for the treatment of industrial metal-containing wastewater, demonstrating its high efficiency in reducing heavy metal ion concentrations below the standard levels using PHMG with lime at 1st stage. The treatment cost is comparable to the CaO-based chemical precipitation technology, but the extraction efficiency is significantly higher.

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ОЧИЩЕННЯ ВОДИ ВІД ІОНІВ ВАЖКИХ МЕТАЛІВ З ВИКОРИСТАННЯМ ВАПНА ТА ПГМГ

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Метод хімічного осадження іонів металів з використанням полігексаметиленгуанідину (ПГМГ) та оксиду кальцію (CaO) було застосовано для вилучення іонів металів з концентрованих розчинів. Було виявлено, що порядок введення реагентів має вирішальне значення для процесу вилучення, причому найкраща ефективність вилучення спостерігалася, коли ПГМГ додавали у воду перед CaO. Такий порядок додавання сприяє поліелектролітному ефекту, що призводить до розгорнутої конформації макромолекул і посилює їхню взаємодію з іонами металів у розчині. Визначено оптимальні діапазони дозування, що збігаються з концентраційним інтервалом прояву поліелектролітного ефекту, в яких максимально проявляється флокуляційна здатність та комплексоутворення ПГМГ. Комбіноване використання ПГМГ і CaO, поряд з варіюванням pH, дозволило досягти високих ступенів видалення іонів металів (>99%) за одну стадію обробки розчину, за винятком хрому (Cr^{3+}) і кобальту (Co^{2+}). Поверхнева активність ПГМГ та здатність переносити іони металів у вигляді металополімерних комплексів сприяли його використанню у флотаційному методі для вилучення іонів важких металів з низькоконцентрованих водних розчинів. Кінетика флотації ПГМГ та вилучення іонів металів показала швидке зв'язування іонів металів з макромолекулами полімеру, а для опису кінетики були отримані рівняння регресії. Залишкові концентрації іонів металів після флотації відповідали нормативним санітарно-екологічним вимогам до стічних вод та питної води. Розроблено двоступеневу схему вилучення іонів важких металів, що включає хімічне осадження та флотаційне вилучення, а також спроектовано та виготовлено пілотну установку для проведення випробувань. Під час очищення стічних вод в умовах гальванічного виробництва було досягнуто концентрацій іонів металів, що відповідають нормативним стандартам.

Ключові слова: *вапно, вилучення важких металів, осадження, ПГМГ, полігексаметиленгуанідин, флотація*