

STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF FULVIC ACID SOLUTIONS

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The article examines the extraction and purification process of fulvic acids derived from oxidized brown coal from the Maikuben deposit using the Forsyth method. The purification process includes stages such as adsorption, ion exchange purification, and dialysis, with activated carbon (Coconut) serving as the adsorbent. The physicochemical properties of fulvic acid and its neutral dilute solutions were analyzed using infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. The study focused on the unique composition of fulvic acid, determining the content of trace elements and essential organic compounds functioning as nutrients. The reliability of the results is confirmed by the consistency of repeated experiments and the application of alternative analytical methods. In addition, antioxidant properties of fulvic acid were determined, which opens up new prospects as biologically active additives and pharmaceuticals. Forsyth's method has demonstrated its effectiveness, allowing to obtain a purer product with fewer losses compared to traditional purification methods. This approach demonstrates the potential for developing environmentally friendly technologies for extracting valuable substances from domestic coal resources. Further research in this area will substantiate the specific properties and patterns in the interaction of fulvic acid with other inorganic compounds, and expand the potential for application.

Keywords: coal, fulvic acid, membrane purification, dialysis, adsorption, organic acids

ФУЛЬВОҚЫШҚЫЛЫ ЕРІТІНДІЛЕРІНІҢ ФИЗИКА-ХИМИЯЛЫҚ ҚАСИЕТТЕРІН ЗЕРТТЕУ

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Мақалада Майкөбен кен орнының тотыққан қоңыр көмірлерінен алынған фульвоқышқылын Форсит әдісімен алу және тазарту қарастырылады. Тазарту кезеңдері: адсорбция, иондық тазарту және диализ, мұнда адсорбент ретінде «Кокосты» белсендірілген көмір қолданылды. Фульвоқышқылының және оның бейтарап сұйылтылған ерітінділерінің физика-химиялық қасиеттері ИҚ және ЯМР спектроскопиясының көмегімен талданды. Фульвоқышқылының бірегей құрамы зерттелді, қоректік зат ретінде әрекет ететін микроэлементтер мен маңызды органикалық қосылыстардың құрамы анықталды. Нәтижелердің сенімділігі қайталанатын тәжірибелер мен талдаудың балама әдістерінің ұқсастықтары кезінде қанағаттанарлық. Сонымен қатар, фульвоқышқылының антиоксиданттық сипаттамалары анықталды, бұл биологиялық белсенді қоспалар мен фармацевтикалық препараттар ретінде жаңа перспективаларды ашады. Форсит әдісі дәстүрлі тазарту әдістерімен салыстырғанда аз шығынмен таза өнім алуда өзінің тиімділігін көрсетті. Бұл тәсіл отандық көмір ресурстарынан бағалы заттарды алудың экологиялық таза технологияларын әзірлеудің әлеуетін көрсетеді. Бұл бағыттағы зерттеулерді одан әрі жүргізу фульвоқышқылының басқа бейорганикалық қосылыстармен әрекеттесуінің ерекше қасиеттері мен заңдылықтарын негіздеуге және пайдалану мүмкіндіктерін кеңейтуге мүмкіндік береді.

Түйін сөздер: көмір, фульвоқышқылы, мембраналы тазарту, диализ, адсорбция, органикалық қышқылдар

ИЗУЧЕНИЕ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ РАСТВОРОВ ФУЛЬВОВОЙ КИСЛОТЫ

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В статье рассмотрены извлечение и очистка методом Форсита фульвовой кислоты, полученной из окисленных из бурых углей месторождения Майкубен. Проведены стадии очистки: адсорбция, ионная очистка и диализ, где в качестве адсорбента использовали активированный уголь «Кокосовый». Проанализированы физико-химические свойства методами ИК- и ЯМР-спектроскопии фульвовой кислоты и её нейтральных разбавленных растворов. Исследован уникальный состав фульвовой кислоты, определены содержание основных микроэлементов, важных органических соединений, выступающих в качестве питательных веществ. Достоверность результатов удовлетворительная при сходимости повторных опытов и альтернативных методов анализа. Наряду с этим, были определены антиоксидантные характеристики фульвокислоты, что открывает новые перспективы в качестве биологически активных добавок и фармацевтических препаратов. Метод Форсита продемонстрировал свою эффективность, позволяя получить более чистый продукт с меньшими потерями по сравнению с традиционными методами очистки. Данный подход демонстрирует потенциал для разработки экологически чистых технологий извлечения ценных веществ из отечественных угольных ресурсов. Дальнейшие исследования в этой области позволят обосновать специфические свойства и закономерности при взаимодействии фульвокислоты с другими неорганическими соединениями, расширить потенциал применения.

Ключевые слова: уголь, фульвокислота, мембранная очистка, диализ, адсорбция, органические кислоты

Introduction. Currently, humic substances are in demand and are widely produced naturally, as well as synthetically by radical polymerization, abiotic oxidation and enzymatic methods [1-3].

The ability of fulvic acids to enhance solubility creates potential for the development of novel drug delivery systems and the improvement of various pharmacological effects, such as antioxidant activity [4,5], anti-inflammatory properties, and benefits for gastric health [5,6]. The influence of fulvic acid on metal ion mobility in various media has been established due to the abundance of oxygen-containing functional groups. Water-soluble salts of fulvic acid with alkali and alkaline earth metal cations promote their release, as well as precipitation, dissolution, or complex formation with trivalent ions [7-9].

Fulvic acid is an essential fraction of the organic composition of soil, demonstrating higher chemical and physicochemical activity compared to humic acid. The molecule of fulvic acid is small enough to overcome any barriers in its path and contains approximately 14 quadrillion electrons, which act as free radical scavengers. When introduced into a biological environment, fulvic acid molecules convert accumulated waste into nutrients and neutralize free radical waste products [9,10].

Additionally, fulvic acid serves as a transport system capable of delivering nutrients while binding toxins, pesticides, heavy metals, chemical pollutants, mercury, and radionuclides into complexes [8].

Furthermore, fulvic acids play a significant role in the acid-base buffering capacity of soil, contributing to the retention, release, and biological mobility of metal ions and organic chemicals within soil matrices [10].

Depending on their methods of extraction, fulvic acids find applications ranging from dietary supplements to pharmaceuticals. Incorporating fulvic acids into dietary supplements supports immune system enhancement and protection against diseases associated with oxidative cell damage, such as cardiovascular and oncological disorders. Due to their antioxidant properties, fulvic acids can provide protective effects on the cardiovascular system by neutralizing free radicals that may damage vascular and cardiac cells. Including fulvic acids in dietary supplements may lower the risk of atherosclerosis and inflammatory vascular processes, making them promising for the prevention of cardiovascular diseases such as hypertension and ischemic heart disease [11-13].

Materials and methods. The Forsyth method was employed to purify fulvic acid extracted from domestic brown coal from the Maikuben deposit. Through a three-stage purification process, a high purity level of 99% was achieved. Commercially available coconut-based sorbents were used as adsorbents, specifically the activated coconut charcoal Extrasorb GAC (12x40) from India. With its high specific surface area and sorption capacity, this charcoal effectively captured and removed impurities, contributing to the successful purification of fulvic acids. The characteristics of the adsorbent are presented in Table 1.

Table 1 - Characteristics of coconut-based activated charcoal Extrasorb GAC (12x40)

Parameter	Value
Particle Size	12x40 mesh
Specific Surface Area	~1100 m ² /g
Iodine Number	1000 mg/g
Bulk Density	0.48 g/cm ³
Hardness	98%
Moisture Content	≤ 5%
Ash Content	≤ 3%
pH	6-8
Pore Volume	0.55 cm ³ /g

The final purification stage was conducted using a membrane method (dialysis) until a pH of 4-5 was achieved in distilled water, ensuring complete removal of accompanying ions. By diluting the fulvic acid with distilled water to a neutral medium, a 1.5% model solution was prepared.

Results and discussion. The IR spectra of fulvic acids were obtained in the Laboratory of Organometallic Chemistry and Catalysis at Nazarbayev University (Kazakhstan) using a Nicolet iS10 FT-IR spectrometer.

In the IR spectrum of the initial sample, distinct peaks for C=O groups in saturated fatty acids, carboxyl, aldehyde, and ketone groups are absent. A weak band is observed at 1635 cm⁻¹, which may indicate the presence of C=C bonds. This suggests a low concentration of carbonyl compounds or their strong association with other functional groups. The broad band at 3000–3500 cm⁻¹ corresponds to OH group stretching vibrations associated with hydrogen bonding, but it is poorly defined. This could be due to the presence of strong intramolecular hydrogen bonds that obscure the characteristic bands of OH groups. In the IR spectrum of purified fulvic acid obtained using sorbent, the following bands are clearly observed: 3600–3000 cm⁻¹, representing various OH stretching vibrations, with sharp peaks identified approximately at 3035, 2945, and 2880 cm⁻¹. These peaks are characteristic of CH stretching vibrations. The peak at 3035 cm⁻¹ suggests the

potential presence of aromatic CH, whereas the peaks at 2945 and 2880 cm^{-1} indicate aliphatic CH bonds found in alkanes or alkyl groups. A relatively small and sharp peak was detected at 2185 cm^{-1} , which falls within the region associated with nitriles ($\text{C}\equiv\text{N}$) or cumulenes. A moderately intense peak around 1693 cm^{-1} indicates the presence of a carbonyl group ($\text{C}=\text{O}$), which could signify ketones, aldehydes, carboxylic acids, esters, or amides. A sharp peak at approximately 1401 cm^{-1} suggests the presence of CH bending, likely due to CH_2 bending. The obtained spectral data confirm the presence and changes in the functional groups of fulvic acid after purification. The observation of distinct $\text{C}=\text{O}$ and OH group bands indicates the removal of impurities and the improvement of the composition of the purified sample (Figure 1).

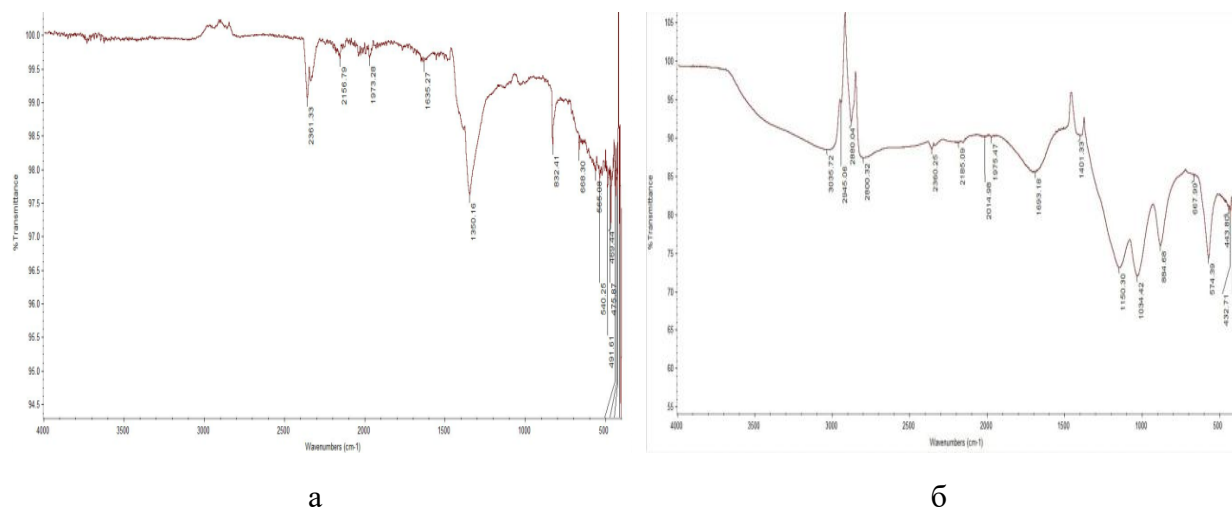


Fig. 1- IR Spectra Analysis:
(a) Original fulvic acid derived from potassium humate; (b) Purified fulvic acid

The NMR analysis of fulvic acid was performed using a JEOL ECA-500 MHz NMR spectrometer. Both the unpurified and purified samples exhibit characteristic aromatic signals in the range of approximately 6.9 to 8.2 ppm, indicating the presence of aromatic rings in the fulvic acid structure. The shifts of aromatic protons (7.0-8.2 ppm) correspond to substituted benzene or polycyclic aromatic systems. The complex multiplets observed in both spectra suggest that the substitution in the aromatic ring systems varies, with nonequivalent aromatic protons displaying spin-spin coupling. Relative integrations imply the presence of similar aromatic components in the two samples. The change in relative integration suggests a modification in the chemical environment of the aromatic protons. These shift changes likely occur as molecules alter their interactions with one another.

The most significant difference between the spectra is observed in the aliphatic region. The first spectrum (unpurified sample) exhibits a broader range of signals between δ -0.1 and 3.0 ppm, indicating a higher complexity of aliphatic components in the unpurified fulvic acid. These signals likely correspond to varying chain lengths, branching, and substitution patterns in the aliphatic components of the raw sample, which probably contains other biomolecules. After purification, a noticeable reduction in the number of signals in the aliphatic region is observed.

The second spectrum shows a pronounced singlet at δ 2.17 and a multiplet at δ 1.36, suggesting that some aliphatic components were removed or altered during purification. A large peak at 4.7 ppm in the unpurified sample implies a higher content of water or residual solvent. The inverted peak in the purified sample suggests that the sample was saturated to suppress the signal and improve its clarity. The simplified aliphatic region in the purified fulvic acid sample implies that the purification process was effective in removing or altering many of the original aliphatic components. This simplification may include the removal of free fatty acids, carbohydrates, or other small molecular contaminants. (Figure 2).

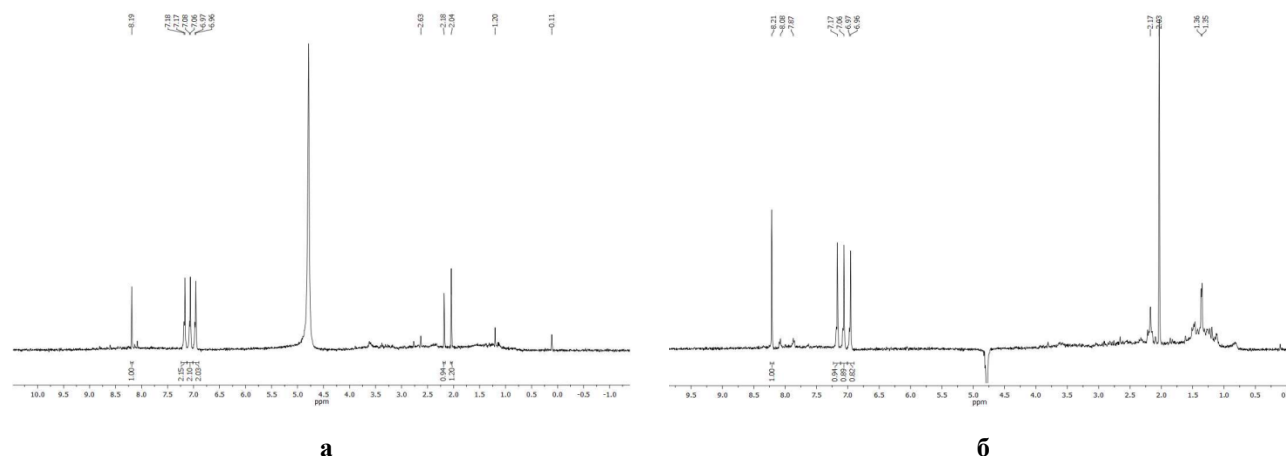


Fig. 2 - NMR Spectra Analysis:
(a) Original fulvic acid derived from potassium humate; (b) Purified fulvic acid

The results of the spectral analysis reveal significant changes in the composition and structure of fulvic acid before and after purification. The IR spectra indicate improved clarity of bands associated with functional groups such as C=O and OH in the purified sample. The NMR spectra confirm an increase in the concentration of saturated hydrocarbon chains and a decrease in ester and alcohol groups. These changes highlight the effectiveness of sorbents in purifying fulvic acid and enhancing its properties.

The chemical analysis of the concentrated fulvic acid solution was conducted using atomic absorption spectrometry to determine the levels of toxic metals, such as lead, cadmium, mercury, and arsenic. High-performance liquid chromatography (HPLC) methods were applied to analyze the model solution to detect the presence of antioxidants (Tables 2–3). The results indicated the absence of toxic elements in the solutions and a substantial presence of antioxidants in the fulvic acid solution, in line with the regulatory requirements of GOST 26932–86, "Raw Materials and Food Products. Methods for Determining Toxic Element Content." The parameters of the model solution fully meet the established standards, confirming its safety and compliance with regulations.

Table 2 - Chemical indicators of purified fulvic acid solution with "Coconut" sorbent

Name of indicators, units of measurement	Permissible concentrations	Results
1	2	3
- antioxidant content, mg/dm ³		1356.0±0.058
- toxic elements, mg/dm ³ :		
-Lead (Pb)	0.3	Not found
- Arsenic (As)	0.1	Not found
- Cadmium (Cd)	0.03	Not found
- Mercury (Hg)	0.005	Not found

Table 3 - Chemical Indicators of the Model Solution

Name of indicators, units of measurement	Norm according to the regulatory document	Results
1	2	3
toxic elements, mg/dm ³ :		
-Lead (Pb)	0.3	Not found
- Arsenic (As)	0.1	Not found
- Cadmium (Cd)	0.03	Not found
- Mercury (Hg)	0.005	Not found
- antioxidant content, mg/dm ³		138.16±0.042
- dry matter content. %		Not found
- aflatoxin B ₁ , mg/l	1.0-3.5	Not found
- titratable acidity, %	0.7-3.8	0.24±0.02
Pesticides, mg/kg, not more than:		
- Hexachlorocyclohexane (alpha, beta, gamma isomers)	0.01	Not found
- 4,4 - dichlorodiphenyltrichloromethylmethane and its metabates	0.005	Not found
Amino acid composition, %		Not found
- water soluble, mg/100 g		
- B ₁ (thiamine chloride)		Not found
-B ₃ (pantothenic acid)		Not found
- B ₆ (pyridoxine)		Not found
- B ₉ (folic acid)		Not found

The organic composition of the samples was thoroughly investigated, with results presented in Figures 3–4. High-performance liquid chromatography (HPLC) identified the presence of oxalic, formic, tartaric, and malic acids in the sorption-purified fulvic acid solution. Additionally, a small amount of vitamin B2 (riboflavin) was detected.

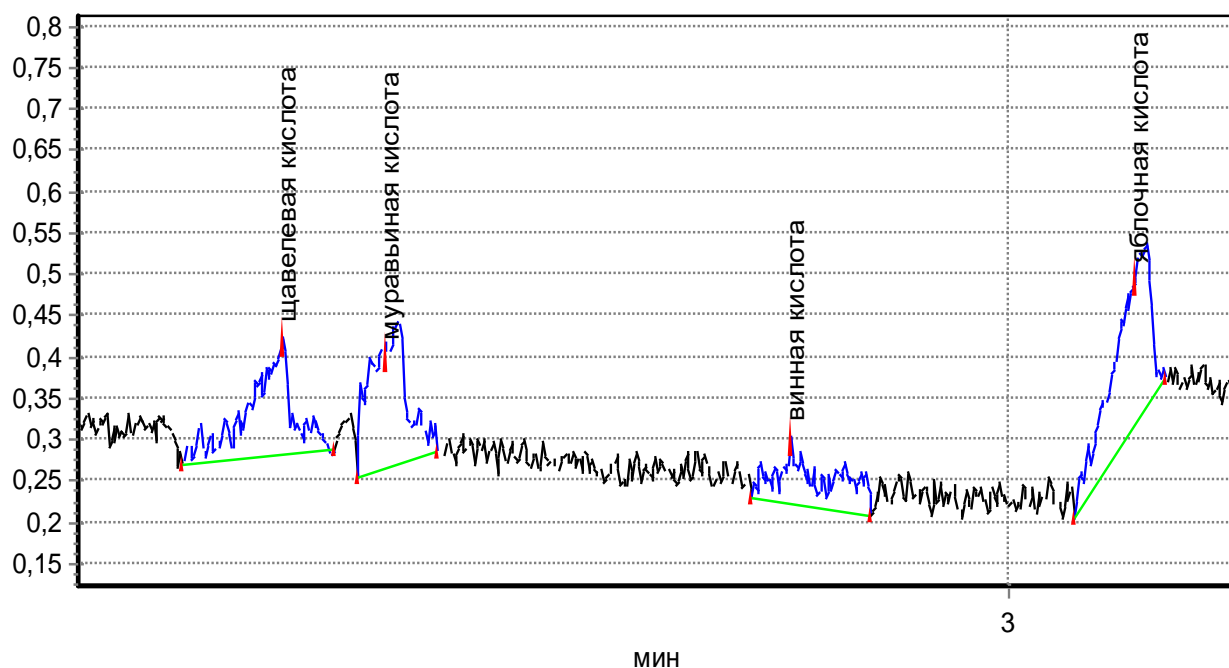


Fig. 3 - Chromatograms of organic acid content in the model fulvic acid solution

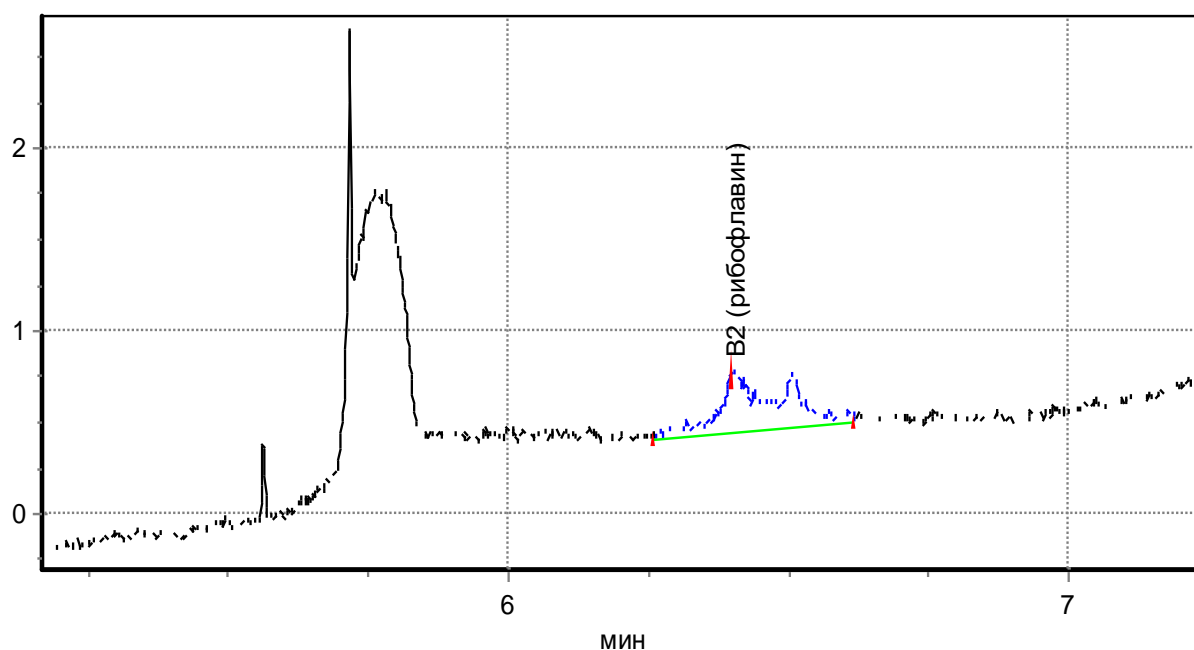


Fig. 4 - Chromatograms of amino acid content in the model fulvic acid solution

Thus, the obtained results of the component analysis and chemical composition of fulvic acid and its neutral solutions contribute to the development of sources for the production of beneficial products. The processing of carbon-containing raw materials and the extraction of valuable substances will significantly enhance the advancement of efficient methods for obtaining competitive components for useful products.

Conclusion. The results indicated that the neutral solution based on fulvic acid contains a significant amount of particularly important organic compounds with high potential for the production of beneficial food products.

In the future, additional physicochemical analysis of the composition of fulvic acid extracted from coal feedstock under various conditions will be conducted, along with a detailed examination of its antioxidant properties.

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ТЕХНОЛОГИЯ ПОЛУЧЕНИЯ МОДИФИЦИРОВАННОГО АКТИВИРОВАННОГО УГЛЯ И ИССЛЕДОВАНИЕ И ЕГО СОРБЦИОННЫХ СВОЙСТВ

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В данной статье представлены результаты исследований по технологии получения модифицированного активированного угля и исследование его сорбционных свойств по отношению к фосфатным ионам. Процесс химической модификации активированного угля заключался в нанесении на его поверхность активных центров, которые обеспечивают избирательное связывание целевых ионов, в данном случае фосфатов. Для этого использована пропитка угля растворами солей железа (FeCl_3) с дальнейшей термической обработкой. В результате на поверхности угля образуются оксиды, которые играют ключевую роль в формировании активных центров для адсорбции. Образующиеся на поверхности угля оксиды железа, такие как Fe_2O_3 и Fe_3O_4 , вступают в координационные взаимодействия с фосфатными ионами, что значительно увеличивает сорбционную емкость материала. Структурные изменения модифицированного угля были подтверждены методами ИК спектроскопии и СЭМ-анализа. Исследование сорбционных свойств полученного модифицированного активированного угля проводилось в различных условиях, включая варьирование pH, температуры и дозировки адсорбента. Эксперименты показали, что наибольшая эффективность адсорбции (85%) достигнута при pH 7, температуре 30 °C и дозировке адсорбента 0,5 г/л. Также проведен сравнительный анализ сорбционных свойств модифицированного и немодифицированного углей. Модифицированный активированный уголь продемонстрировал значительно более высокую эффективность адсорбции (85%) по сравнению с немодифицированным углем (62%).

Ключевые слова: модифицированный активированный уголь, оксиды железа, фосфаты, сорбционные свойства, водоочистка.

МОДИФИКАЦИЯЛАНҒАН БЕЛСЕНДІРІЛГЕН КӨМІРДІ АЛУ ТЕХНОЛОГИЯСЫ ЖӘНЕ ОНЫҢ СОРБЦИЯЛЫҚ ҚАСИЕТТЕРІН ЗЕРТТЕУ

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Бұл мақалада модификацияланған активтендірілген көмір алу технологиясы және оның фосфат иондарымен сорбциялық қасиеттерін зерттеу нәтижелері ұсынылған. Активтендірілген көмірді химиялық модификациялау процесі оның бетіне мақсатты иондарды тандап байланыстыратын активті орталықтарды орналастырудан тұрады, бұл жағдайда фосфаттар. Осы мақсатта көмірді темір тұздарының (FeCl_3) ерітінділерімен сіңдіру және кейіннен термиялық өңдеу әдісі қолданылды. Нәтижесінде көмір бетінде оксидтер пайда болып, олар адсорбция үшін активті орталықтарды қалыптастыруда маңызды рөл атқарады. Көмір бетінде пайда болатын темір оксидтері, мысалы, Fe_2O_3 және Fe_3O_4 , фосфат иондарымен координациялық өзара әрекеттесуге түсуі нәтижесінде материалдың сорбциялық сыйымдылығы едәуір артады. Модификацияланған көмірдің

құрылымдық өзгерістері ИҚ спектроскопиясы және СЭМ талдау әдістерімен расталды. Алынған модификацияланған активтендірілген көмірдің сорбциялық қасиеттері әртүрлі жағдайларда, соның ішінде рН, температура және адсорбент дозасын өзгерту арқылы зерттелді. Эксперименттер көрсеткендей, ең жоғары адсорбция тиімділігі (85%) рН 7, температура 30 °С және адсорбент дозасы 0,5 г/л болғанда қол жеткізілді. Сондай-ақ, модификацияланған және модификацияланбаған көмірдің сорбциялық қасиеттерін салыстырмалы түрде талдау жүргізілді. Модификацияланған активтендірілген көмір адсорбция тиімділігінің едәуір жоғары екенін көрсетті (85%), ал модификацияланбаған көмір үшін бұл көрсеткіш 62% болды.

Түйін сөздер: модификацияланған активтелген көмір, темір оксидтері, фосфаттар, сорбциялық қасиеттері, су тазарту

TECHNOLOGY FOR THE PRODUCTION OF MODIFIED ACTIVATED CARBON AND THE STUDY OF ITS SORPTION PROPERTIES

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This article presents the results of research on the technology for obtaining modified activated carbon and its sorption properties concerning phosphate ions. The process of chemical modification of activated carbon involved applying active sites to its surface, which enable selective binding of target ions, in this case, phosphates. For this, the carbon was impregnated with iron salt solutions (FeCl_3) followed by thermal treatment. As a result, oxides formed on the carbon surface, which play a key role in the formation of active sites for adsorption. The iron oxides formed on the carbon surface, such as Fe_2O_3 and Fe_3O_4 , engage in coordination interactions with phosphate ions, significantly increasing the sorption capacity of the material. The structural changes in the modified carbon were confirmed using FTIR spectroscopy and SEM analysis. The sorption properties of the obtained modified activated carbon were studied under various conditions, including variations in pH, temperature, and adsorbent dosage. The experiments showed that the highest adsorption efficiency (85%) was achieved at pH 7, a temperature of 30°C, and an adsorbent dosage of 0.5 g/L. A comparative analysis of the sorption properties of modified and unmodified carbon was also conducted. The modified activated carbon demonstrated significantly higher adsorption efficiency (85%) compared to the unmodified carbon (62%).

Keywords: modified activated carbon, iron oxides, phosphates, sorption properties, water purification.

Введение. Активированный уголь является наиболее предпочтительным адсорбентом для различных промышленных применений благодаря превосходным сорбционным свойствам, таким как большая площадь поверхности, превосходная пористость, высокая физико-химическая стабильность и поверхностные функциональные группы [1].

Согласно химической науке, активированный уголь представляет собой разновидность углерода с несовершенной структурой, практически не содержащий примесей. По своей химической структуре он схож с графитом [2]. Он может быть синтезирован из различной биомассы или неорганического сырья путем пиролиза с последующей физической или химической активацией [3]. Несмотря на различные преимущества активированного угля в качестве адсорбента, все еще существуют ограничения в производственном процессе, препятствия для повторного роста, способность к вторичной переработке и избирательность по отношению к загрязняющим веществам, которые ограничивают его использование при существенной очистке сточных вод [4]. Важно отметить, что существует множество исследований, в которых изучаются возможные варианты использования

углеродных материалов, в частности, активированного угля в качестве адсорбента тяжелых металлов, для адсорбции CO_2 и удаления красителей [5, 6, 7, 8].

Литературный обзор показывает, что активированный уголь благодаря развитой пористой структуре и высокой удельной поверхности широко применяется как сорбент, но его эффективность для удаления специфических ионов, включая фосфаты, ограничена [9]. Для решения этой проблемы активно разрабатываются методы химической модификации угля с использованием переходных металлов, в частности ионов железа. Введение ионов железа на поверхность угля формирует активные центры, способные образовывать координационные связи с фосфатными ионами, что увеличивает сорбционную емкость материала [10].

Целью настоящего исследования является разработка технологии получения модифицированного активированного угля и изучение его адсорбционных свойств по отношению к фосфатам. На основе проведенных экспериментов будут определены оптимальные условия для использования данного материала в системах водоочистки, что обеспечит повышение эффективности удаления загрязнителей и устойчивое управление водными ресурсами.

Для достижения поставленной цели определены следующие задачи исследования:

1. разработка методики модификации активированного угля с использованием железа для улучшения его адсорбционных свойств в отношении фосфатов;
2. оценка эффективности полученного материала в различных условиях, включая варьирование pH, температуры и дозировки адсорбента;
3. исследование изменений в структуре угля до и после модификации с помощью анализа сканирующей электронной микроскопией (СЭМ) и инфракрасной (ИК) спектроскопии;
4. сравнительный анализ эффективности модифицированного и немодифицированного активированного угля с помощью ионной хроматографии.

Новизна данного исследования состоит в разработке технологии получения модифицированного активированного угля, являющимся ценным компонентом систем очистки сточных вод от вредных примесей.

Таким образом, предлагаемая технология получения модифицированного активированного угля представляет собой перспективное направление в химической технологии для создания высокоэффективных материалов для водоочистки.

Материалы и методы. Для проведения данного исследования был использован активированный уголь, модифицированный ионами железа, а также разработаны экспериментальные методики, направленные на изучение его адсорбционных свойств. Основная цель методологии заключалась в оптимизации условий получения модифицированного активированного угля и исследовании его эффективности для удаления фосфатов из сточных вод. Описание материалов, процедуры модификации, а также методов анализа представлено ниже.

Исходные материалы.

Активированный уголь. Для проведения экспериментов был использован активированный уголь с размером гранул от 0,5 до 2,5 мм и насыпной плотностью 0,49–0,53 г/см³. Пористость угля составляла 0,07 см³/г.

Железосодержащие реагенты. Для модификации угля применялся 1 М раствор хлорида железа (FeCl_3). Этот реагент обеспечивает ионы железа (Fe^{3+}), которые, при дальнейшей термической обработке, превращаются в оксиды железа (Fe_2O_3 и Fe_3O_4), создавая активные центры для адсорбции фосфатов.

Растворы фосфатов. Модельные растворы фосфатов с концентрацией 50 мг/л были приготовлены с использованием Na_3PO_4 . Эти растворы использовались для изучения сорбционных свойств модифицированного угля в условиях варьирования параметров эксперимента [11].

Модификация активированного угля.

Модификация активированного угля проводилась по следующей методике:

1. Пропитка угля ионами железа. Активированный уголь был погружен в 1М раствор FeCl_3 и выдержан при комнатной температуре в течение 24 часов для адсорбции ионов железа на его поверхности. В ходе этого процесса ионы железа связывались с активными центрами угля, образуя предварительные комплексы.

2. Сушка и термическая обработка. После пропитки уголь подвергался сушке при температуре 105 °С в течение 12 часов для удаления лишней влаги. Затем материал был прокален при 350°С в инертной атмосфере (азот), что способствовало образованию оксидов железа (Fe_2O_3 и Fe_3O_4) на поверхности угля. Эта стадия критична для создания активных центров, способных к адсорбции фосфатов.

3. Охлаждение и хранение. После термической обработки модифицированный уголь охлаждали до комнатной температуры и хранили в герметичной емкости для предотвращения контакта с воздухом и влаги, что могло бы снизить его адсорбционную активность.

Экспериментальные условия.

Для исследования эффективности модифицированного активированного угля проводились адсорбционные эксперименты, направленные на удаление фосфатов из модельных растворов. Эксперименты проводились при различных условиях pH, температуре и дозировке угля для определения оптимальных параметров адсорбции.

1. Варьирование pH. Для оценки влияния кислотно-щелочного баланса раствора использовались буферные растворы, чтобы поддерживать pH в диапазоне от 5 до 9. Известно, что pH раствора существенно влияет на диссоциацию фосфатных ионов и, соответственно, на эффективность их адсорбции на поверхности модифицированного угля [12].

2. Варьирование температуры. Эксперименты проводились при двух температурных режимах: 25 °С и 30 °С. Температура влияет на кинетику адсорбции и возможность образования координационных комплексов между фосфатами и железом [12].

3. Дозировка угля. Для каждого эксперимента варьировалась дозировка модифицированного активированного угля в диапазоне от 0,1 до 0,5 г/л. Это позволило изучить зависимость адсорбции от количества угля, присутствующего в растворе, и найти оптимальную дозировку для достижения наибольшей сорбционной емкости.

Методики анализа.

Для количественного определения концентрации фосфатов и оценки эффективности адсорбции использовались следующие методы.

1. Спектрофотометрический метод. Остаточная концентрация фосфатов в растворах после адсорбции измерялась спектрофотометрически с использованием метода молибдата аммония. Метод молибдата аммония используется для количественного определения концентрации фосфатов в растворе. В ходе анализа фосфат-ион взаимодействует с молибдатом аммония, образуя комплексное соединение, которое можно обнаружить спектрофотометрически. Этот метод подходит для измерения концентраций фосфатов после адсорбции [13]. Образцы фильтровались через мембранные фильтры перед измерениями, что позволяло исключить влияние твердых частиц.

2. ИК-спектроскопия. Изменения в структуре угля до и после модификации оценивались с помощью анализа сканирующей электронной микроскопией (СЭМ) и инфракрасной (ИК) спектроскопии. ИК-спектроскопия позволяет выявить присутствие оксидов железа на поверхности угля и изменение химической структуры после модификации, как видно на рисунке 1.

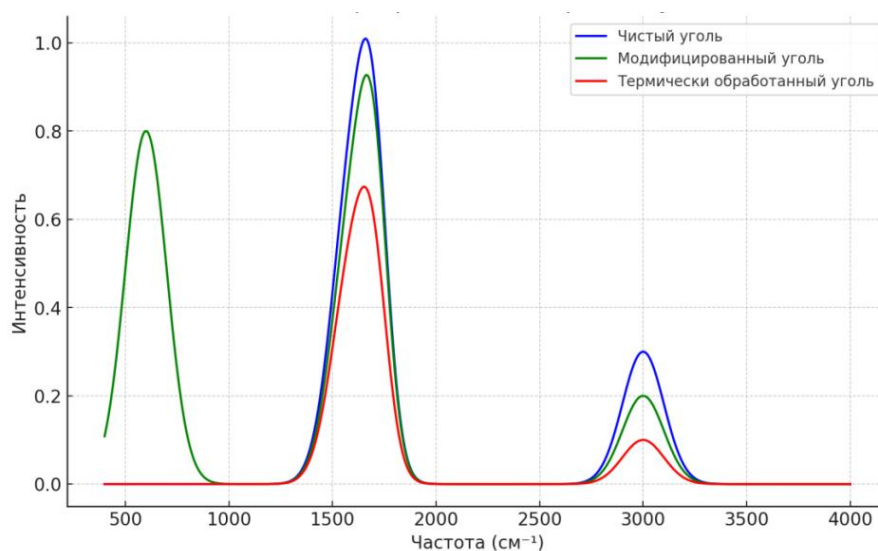


Рис. 1 - Результаты ИК-спектроскопии различных образцов угля

На рисунке приведены ИК-спектры трех различных образцов угля: чистого угля, модифицированного угля с оксидами железа и угля, подвергнутого термической обработке.

Для чистого угля характерны интенсивные полосы поглощения в диапазоне 1500–1800 см^{-1} , которые соответствуют валентным колебаниям $\text{C}=\text{C}$ (около 1600 см^{-1}) в ароматических кольцах и $\text{C}=\text{O}$ (около 1700 см^{-1}) в карбонильных группах [14]. Наблюдается также слабая полоса около 3000 см^{-1} , связанная с валентными колебаниями $\text{C}-\text{H}$, что указывает на наличие алкановых групп в структуре угля.

Модифицированный уголь демонстрирует новые полосы поглощения в области около 600 см^{-1} , которые можно отнести к колебаниям $\text{Fe}-\text{O}$, что подтверждает наличие оксидов железа в образце. При этом основные углеродные полосы сохраняются, но их интенсивность несколько изменяется, что свидетельствует о взаимодействии между органической матрицей угля и оксидами железа [15].

Для угля, подвергнутого термической обработке, наблюдается уменьшение интенсивности полос в области $\text{C}-\text{H}$ (3000 см^{-1}), что указывает на деградацию углеводородных цепей. Также видны изменения в интенсивности полос $\text{C}=\text{C}$ и $\text{C}=\text{O}$, что свидетельствует о термической модификации ароматических и карбонильных структур.

3. Анализ pH и температуры. Значения pH контролировались с помощью pH-метра с точностью до 0,01, а температура поддерживалась с использованием термостатируемых реакционных сосудов для стабильности экспериментальных условий.

Расчет эффективности адсорбции. Эффективность адсорбции фосфатов рассчитывалась по следующей формуле:

$$\text{Эффективность адсорбции (\%)} = C_0(C_0 - C_t) \times 100,$$

где: C_0 - начальная концентрация фосфатов в растворе (мг/л);

C_t - остаточная концентрация фосфатов в растворе после адсорбции (мг/л).

Этот расчет позволил количественно оценить эффективность модифицированного активированного угля при различных условиях эксперимента.

Для подтверждения достоверности результатов все эксперименты проводились в трехкратной повторности, а результаты выражались как среднее значение с указанием стандартного отклонения.

Таким образом, выбранные материалы и методы позволили провести всесторонний анализ сорбционных свойств модифицированного активированного угля и оптимизировать условия его получения и применения в системах водоочистки.

Результаты и обсуждение. В ходе исследования была проведена оценка адсорбционных свойств модифицированного активированного угля для удаления фосфатов из модельных растворов. Результаты показали, что модификация угля ионами железа существенно увеличивает его адсорбционную емкость по сравнению с немодифицированным углем. Ниже представлены детализированные результаты экспериментов и их обсуждение.

Влияние pH на адсорбцию фосфатов

Равновесие адсорбции зависит от кислотно-щелочного баланса раствора. При pH около 6–7 наблюдается максимальная адсорбция фосфатов, поскольку в этом диапазоне pH оксиды железа на поверхности активированного угля сохраняют свои координационные свойства, необходимые для связывания с фосфат-ионами. В щелочной среде (pH > 8) сорбционная способность оксидов железа снижается из-за их перехода в менее реакционноспособные формы, а также из-за повышения концентрации конкурирующих гидроксид-ионов, что приводит к конкуренции за активные центры. Эксперименты показали, что оптимальные результаты по адсорбции достигались при pH 7, что подтверждается данными, представленными в таблице 1.

Таблица 1. Влияние pH на эффективность адсорбции фосфатов (дозировка угля 0,5 г/л, температура 30 °C)

pH	Эффективность адсорбции, %
5	75
7	85
9	78

Наибольшая адсорбционная способность модифицированного активированного угля наблюдалась при нейтральном значении pH (85%), что связано с оптимальной диссоциацией фосфатных ионов при pH 7. При более высоком pH (9) эффективность адсорбции несколько снижается до 78%, что объясняется снижением координационной активности оксидов железа в щелочной среде. В кислой среде (pH 5) адсорбция также оказывается менее эффективной (75%), что связано с протонированием активных центров на поверхности угля, что мешает взаимодействию с фосфатами.

Этот результат подтверждает, что модифицированный активированный уголь демонстрирует наилучшие сорбционные свойства в слабощелочной и нейтральной среде, что делает его перспективным материалом для использования в системах водоочистки с естественным диапазоном pH.

Влияние температуры на адсорбцию.

Температурная зависимость адсорбции фосфатов на модифицированном угле показывает, что повышение температуры увеличивает скорость реакции, что может объясняться улучшением диффузии фосфатов к активным центрам. В условиях температурного диапазона 25–35 °C кинетика адсорбции соответствует псевдо-второму порядку, однако при более высоких температурах возможно снижение прочности координационных связей между фосфатами и железом вследствие тепловой десорбции. Энтальпия адсорбции фосфатов на оксидах железа свидетельствует о том, что процесс носит экзотермический характер, и чрезмерное повышение температуры может вызывать разрыв координационных связей. Результаты экспериментов при различных температурах представлены в таблице 2.

Таблица 2. Влияние температуры на эффективность адсорбции фосфатов (рН 7, дозировка угля 0,5 г/л)

Температура, °С	Эффективность адсорбции, %
25	81
30	85

Данные таблицы показывают, что увеличение температуры от 25°С до 30°С приводит к увеличению эффективности адсорбции с 82% до 85%. Это связано с тем, что при повышенной температуре увеличивается подвижность фосфатных ионов, что способствует их более быстрому взаимодействию с активными центрами на поверхности угля. При этом температура 30°С представляется оптимальной для сорбционных процессов, так как дальнейшее увеличение температуры может вызвать десорбцию адсорбированных фосфатов и снижение эффективности процесса.

Таким образом, для обеспечения максимальной сорбционной активности модифицированного активированного угля рекомендуется поддерживать температуру на уровне 30 °С, что соответствует реальным условиям очистки сточных вод в промышленных системах.

Влияние дозировки угля на адсорбцию.

Важным аспектом адсорбционного процесса является начальная концентрация фосфатов в растворе. Исследования показывают, что при низких концентрациях фосфатов (до 50 мг/л) процесс адсорбции ограничен количеством доступных активных центров, и адсорбционная емкость близка к максимальной. При повышении концентрации фосфатов (> 100 мг/л) наступает насыщение адсорбента, и скорость адсорбции начинает снижаться. Оптимальная дозировка модифицированного активированного угля составляет 0,5 г/л, так как дальнейшее увеличение дозировки незначительно повышает эффективность адсорбции, что связано с равновесной адсорбционной способностью поверхности угля. Результаты представлены в таблице 3.

Таблица 3- Влияние дозировки модифицированного активированного угля на адсорбцию фосфатов (рН 7, температура 30 °С)

Дозировка угля, г/л	Эффективность адсорбции, %
0,1	65
0,5	85

При увеличении дозировки активированного угля с 0,1 г/л до 0,5 г/л эффективность адсорбции фосфатов возросла с 65% до 85%. Это связано с увеличением числа активных центров для взаимодействия с фосфатными ионами. Однако дальнейшее увеличение дозировки угля может быть экономически неоправданным, так как при этом эффективность адсорбции увеличивается незначительно.

Данный результат позволяет оптимизировать дозировку адсорбента для систем водоочистки, при которой достигается максимальная эффективность при минимальных затратах на материал.

4. Сравнительный анализ эффективности модифицированного и немодифицированного активированного угля с использованием ионной хроматографии.

Анализ эффективности адсорбции фосфатов на модифицированном и немодифицированном активированном угле проводился методом ионной хроматографии

при комнатной температуре (25 °C) и pH 7. Образцы контактировали с углем в течение 24 часов при начальной концентрации фосфатов 50 мг/л и дозировке адсорбента 0,5 г/л.

Для анализа использовалась анионная колонка с элюентом 3,5 mM Na₂CO₃ и 1 mM NaHCO₃, что обеспечивало разделение фосфатов и стабильный поток 1,0 мл/мин. Подавление фоновой проводимости элюента осуществлялось при помощи подавителя с ионообменной мембраной в форме капилляра, позволяющей заменять ионы Na⁺ в элюенте на H⁺.

Применение мембранного подавителя снижало фон проводимости, позволяя детектировать низкие концентрации анионов с высокой точностью. Результаты представлены в таблице 4.

Таблица 4 -Сравнительный анализ эффективности модифицированного и немодифицированного активированного угля с использованием ионной хроматографии

Тип угля	Время удерживания (мин)	Площадь пика	Высота пика	Остаточная концентрация фосфатов (мг/л)
Модифицированный	3,5	500	120	10
Немодифицированный	3,5	800	180	30

Полученные хроматограммы показывали более низкий пик для модифицированного угля, что подтверждает его большую сорбционную способность по сравнению с немодифицированным углем. Данные ионной хроматографии позволяют заключить, что модифицированный уголь с оксидами железа имеет значительно более высокую эффективность в удалении фосфатов из раствора.

Выводы. Получен модифицированный активированный уголь и исследованы его сорбционные свойства по отношению к фосфатным ионам.

Результаты исследования демонстрируют, что модифицированный активированный уголь обладает высокими сорбционными свойствами по отношению к фосфатам, что делает его перспективным материалом для использования в системах водоочистки. Модификация угля ионами железа привела к увеличению числа активных центров на его поверхности, что позволило значительно повысить его адсорбционную емкость.

Проведенная оценка эффективности полученного реагента показала, что наиболее высокая адсорбционная способность угля наблюдалась при pH 7 и температуре 30 °C, что связано с оптимальными условиями для образования устойчивых комплексов между фосфатами и железом. Эффективность удаления фосфатов достигла 85% при дозировке 0,5 г/л, что подтверждает возможность применения данного материала в системах очистки сточных вод с высокой степенью загрязнения.

По сравнению с немодифицированным углем, модифицированный уголь продемонстрировал значительно более высокую эффективность адсорбции, что подтверждает необходимость его химической обработки для повышения сорбционных свойств.

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OVERVIEW OF MECHANISMS FOR ENSURING SAFE WORK IN CHEMICAL PRODUCTION

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This article presents the results of the review of scientific and technical information on the use of a risk-based approach (RBA) in providing personal protective equipment (PPE) at an enterprise. Regulatory documents, scientific works and developments of domestic and foreign scientists on the use of PPE against industrial health and safety hazards and their selection based on RBA were used as the theoretical and methodological basis for the study.

Scientific works are considered in the Science Direct, Dergi Park, Web of Science (Publon), Elsevier, Google Scholar databases, on professional industry platforms on labor protection ILO, EU-OSHA, NEBOSH, IOSH.

The study contains information retrieval, descriptive, experimental and effective research stages. The information retrieval stage includes the study of scientific and methodological literature, national and interstate standards. This article covers the entire range of theoretical and methodological substantiation of the use of PPE in the provision of RBA, including regulatory standards for the use of PPE, in force in the Republic of Kazakhstan in comparison with international practice

Keywords: personal protective equipment (PPE), labor protection, Labor Code, collective agreement, industrial safety, harmful production factors, professional risks, regulatory and technical framework.

ХИМИЯЛЫҚ ӨНДІРІСТЕГІ ҚАУІПСІЗ ЖҰМЫСТЫ ҚАМТАМАСЫЗ ЕТУ МЕХАНИЗМДЕРІНЕ ШОЛУ

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¹Қазақстан Республикасы Еңбек және халықты әлеуметтік қорғау министрлігінің еңбек қауіпсіздігі және еңбекті қорғау жөніндегі республикалық ғылыми-зерттеу институты, Астана қ., Қазақстан,

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Бұл мақалада кәсіпорында жеке қорғаныс құралдары (ЖҚҚ) қамтамасыз етуде тәуекелге бағытталған тәсілді (ТБТ) қолдану туралы ғылыми-техникалық ақпаратты қарау нәтижелері келтірілген. Зерттеудің теориялық және әдістемелік негізі ретінде нормативтік құжаттар, ғылыми еңбектер мен отандық және шетелдік ғалымдардың ЖҚҚ-ны өнеркәсіптік денсаулық пен қауіпсіздік қатерлеріне қарсы қолдану және оларды ТБТ негізінде тандау бойынша әзірлемелері пайдаланылды.

Ғылыми жұмыстар Science Direct, Dergi Park, Web Of Science (Publon), Elsevier, Google Scholar дерекқорларында, ХЕҰ, ЕО-OSHA, NEBOSH, IOSH еңбекті қорғау бойынша кәсіби салалық платформаларда қарастырылады.

Зерттеу ақпаратты іздеу, сипаттамалық, эксперименттік және тиімді зерттеу кезеңдерін қамтиды. Ақпаратты іздеу кезеңі ғылыми-әдістемелік әдебиеттерді, ұлттық және мемлекетаралық стандарттарды зерттеуді қамтиды. Бұл мақала Қазақстан Республикасында

халықаралық практикамен салыстырғанда қолданыстағы ЖҚК пайдалану жөніндегі нормативтік стандарттарды қоса алғанда, ЖҚК көрсету кезінде ЖҚК пайдаланудың теориялық және әдіснамалық негіздемелерінің барлық спектрін қамтиды.

Түйін сөздер: жеке қорғаныс құралдары (ЖҚК), еңбекті қорғау, Еңбек Кодексі, ұжымдық шарт, өнеркәсіптік қауіпсіздік, зиянды өндірістік факторлар, кәсіби тәуекелдер, нормативтік-техникалық база.

ОБЗОР МЕХАНИЗМОВ ОБЕСПЕЧЕНИЯ БЕЗОПАСНОГО ТРУДА НА ХИМИЧЕСКОМ ПРОИЗВОДСТВЕ

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В данной статье представлены результаты обзора научно-технической информации об использовании риск-ориентированного подхода (РОП) при обеспечении средствами индивидуальной защиты (СИЗ) на предприятии. В качестве теоретико-методологической основы исследования были использованы нормативные документы, научные труды и разработки отечественных и зарубежных ученых по применению средств индивидуальной защиты от производственных рисков для здоровья и техники безопасности и их подбору на основе РОП.

Научные работы рассматриваются в базах данных Science Direct, Dergi Park, Web of Science (Publon), Elsevier, Google Scholar, на профессиональных отраслевых платформах по охране труда ILO, EU-OSHA, NEBOSH, IOSH.

Исследование содержит информационно-поисковый, описательный, экспериментальный и результативный этапы исследования. Информационно-поисковый этап включает в себя изучение научно-методической литературы, национальных и межгосударственных стандартов. Данная статья охватывает весь спектр теоретических и методологических обоснований использования СИЗ при оказании РСА, включая нормативные стандарты по использованию СИЗ, действующие в Республике Казахстан в сравнении с международной практикой.

Ключевые слова: средства индивидуальной защиты (СИЗ), охрана труда, Трудовой кодекс, коллективный договор, промышленная безопасность, вредные производственные факторы, профессиональные риски, нормативно-техническая база.

Introduction. As is known, occupational safety and health requirements are established by regulatory legal acts of the Republic of Kazakhstan and must contain rules, procedures and standards aimed at preserving the life and health of workers in the course of their work.

Occupational safety and health requirements are mandatory for employers and employees when they carry out their activities in the territory of the Republic of Kazakhstan [1].

In the system of measures aimed at ensuring safe working conditions, PPE of workers plays an important role. Ensuring safe working conditions is one of the main tasks of the International Labour Organization (ILO). According to Article 16 of the ILO Occupational Safety and Health Convention, 1981 (No. 155), employers are obliged to ensure the safety of workplaces, machinery, equipment and processes under their control, as well as the use of PPE to prevent accidents or harmful effects on the health of their workers. In all the sources studied, four distinctive approaches to the selection of PPE were found:

- approaches related to the provision of PPE and their proper use (information, training in the correct use of PPE);

- collective, personal disciplinary responsibility for failure to use PPE;
- unification and modernization of protective equipment;
- factor approach [2].

New threats are emerging, principles and approaches to providing PPE during a pandemic are changing, including poorly studied biological threats [3-7].

However, at present there are no works that would cover the entire broad range of theoretical and methodological justification for the use of PPE in the provision of RBA with an analysis of regulatory standards for the use of PPE in force in the Republic of Kazakhstan in accordance with international practice.

Materials and methods. The theoretical and methodological basis of the study was based on regulatory documents, scientific works and developments of domestic and foreign scientists on the use of PPE against the impact of harmful and hazardous production factors and their selection based on RBA [8].

The results of the review revealed that in the post-Soviet countries (RF, RB, RK) PPE and its components must comply with the requirements of the Technical Regulations of the Customs Union "On the safety of personal protective equipment" (hereinafter - TR CU019/2011) [9].

In the Russian Federation, there are currently standard standards for the issuance of PPE for 195 professions in accordance with the Order of the Ministry of Labor of Russia dated December 9, 2014 "On approval of standard standards for the free issuance of special clothing, special footwear and other personal protective equipment to workers of cross-cutting professions and positions of all types of economic activity engaged in work with harmful and (or) hazardous working conditions, as well as in work performed in special temperature conditions or associated with pollution" [10], which specifies the standards, rules for the issuance, storage and use of PPE. In the Republic of Belarus, the procedure for providing workers with PPE is regulated by the Instructions for Providing Workers with PPE. Figures 1 and 2 show the mechanisms for providing and issuing PPE in Russia and the Republic of Belarus, respectively.

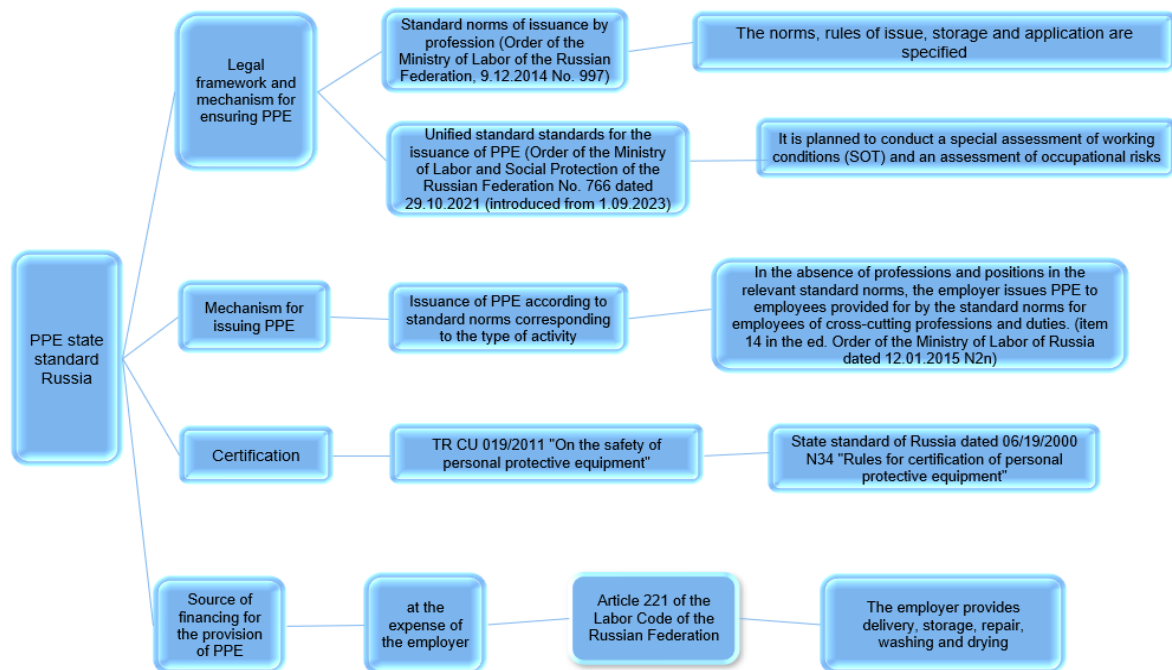


Fig. 1- Mechanism for Providing and Issuing PPE in Russia

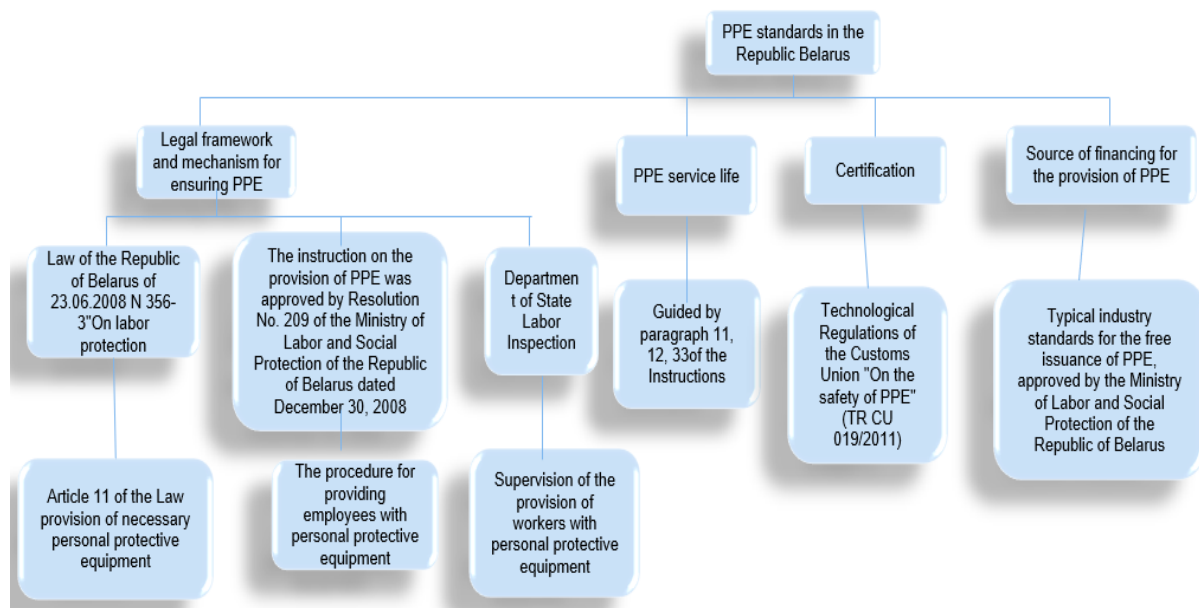


Fig. 2 - Mechanism for Providing and Issuing PPE in the Republic of Belarus

Based on the results of the review of best practices in PPE provision mechanisms using the example of Canada, the USA, Great Britain, Poland, and Japan [11-17], two countries from the North American continent were identified as leaders.

The priority in ensuring occupational safety in Canada is the organization of preventive measures, i.e., the reduction and elimination of hazards. PPE is designed to protect against safety and/or health threats. For example, helmets, safety glasses, and safety boots are designed to prevent or reduce the severity of injury in case of emergency (Figure 3).

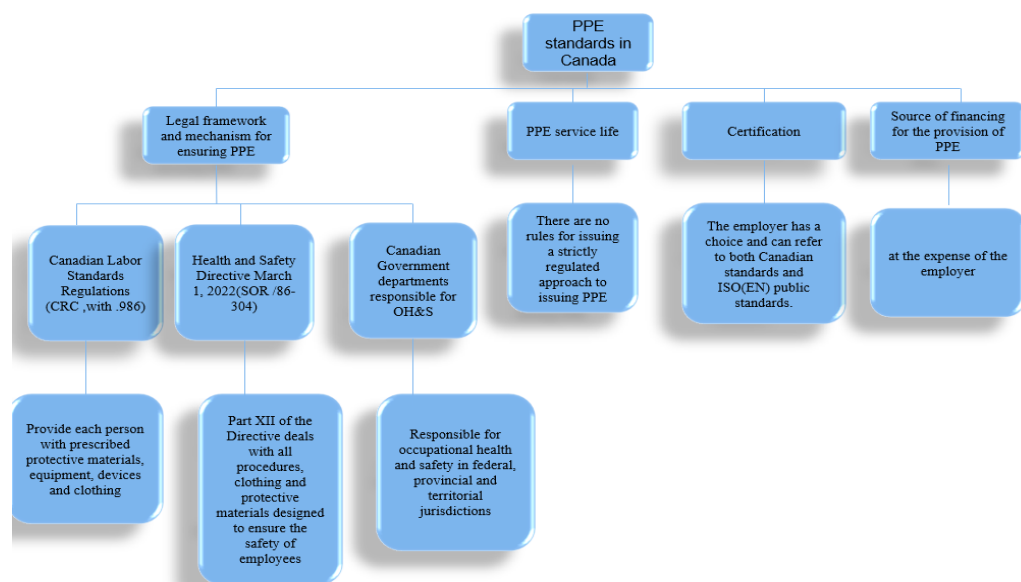


Fig. 3- Mechanism for providing and issuing PPE in Canada

The type and nature of hazards in the workplace in the USA are the main indicators of the correct choice of PPE purchased at the employer's expense [12]. At the same time, employees are given instructions on the risks that can be avoided or limited by using PPE, the reasons for using PPE, how to use it safely and effectively, and the actions to maintain it in good condition, such as cleaning, replacing, storing (Figure 4).

In the UK, eliminating the hazard is the most effective way to manage risks. According to the PPE provision policy (Figure 5), after conducting a risk assessment using various control levels, the employer is obliged to provide PPE to its employees at its own expense [13].

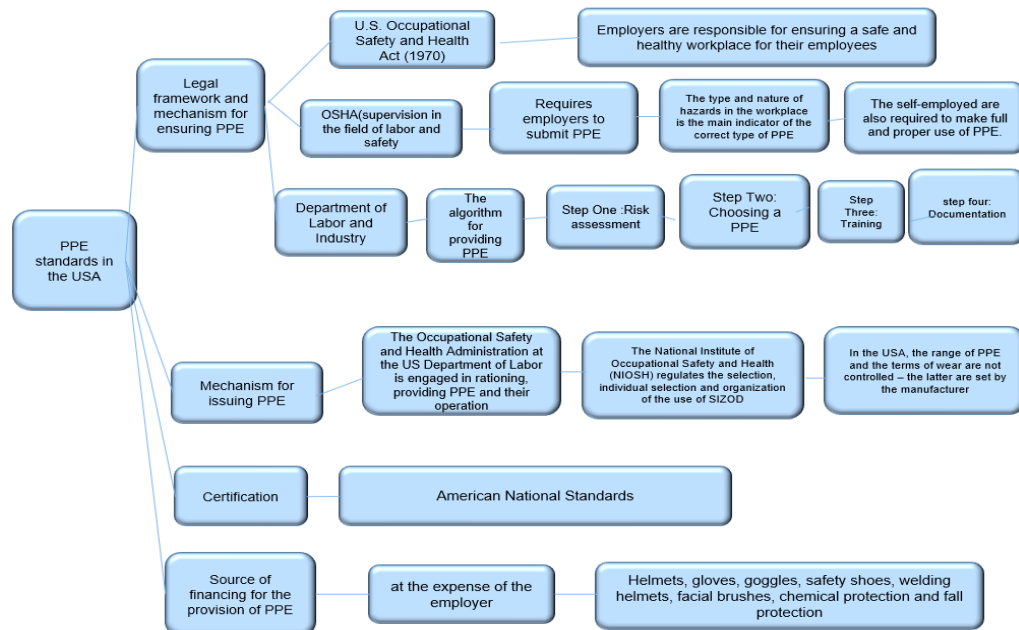


Fig. 4 - PPE provision and issue mechanism in the USA

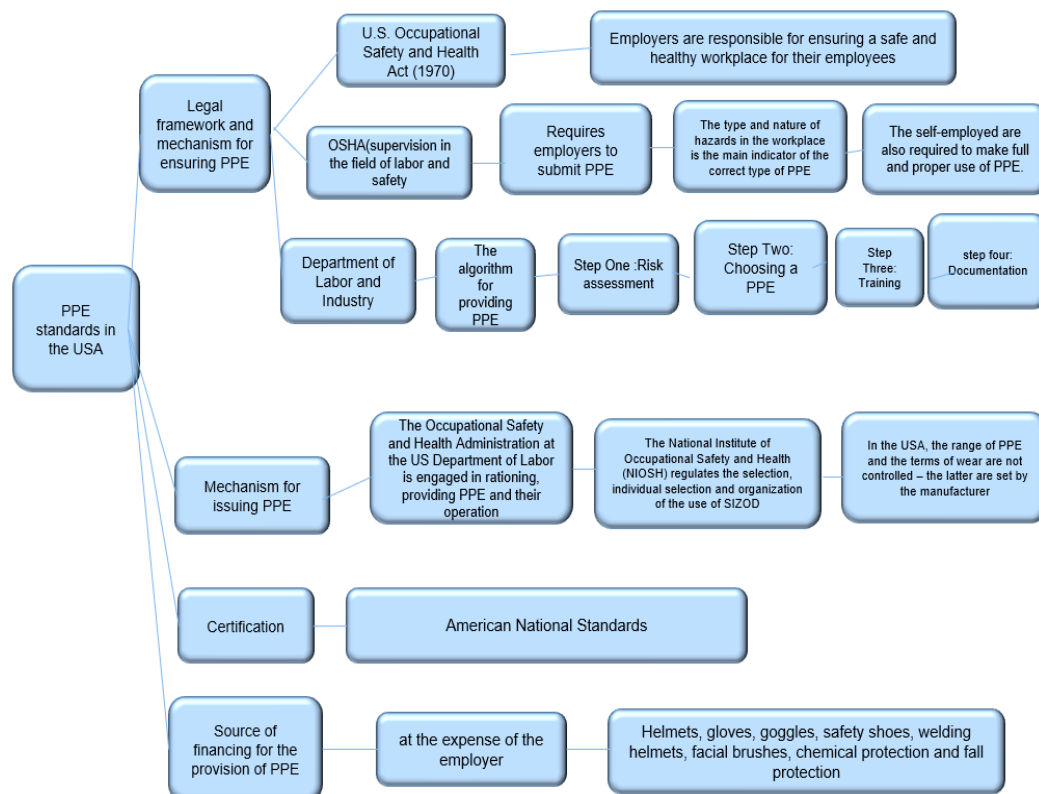


Fig. 5 - PPE provision and issue mechanism in the UK

In the EU countries, the conformity assessment processes for personal protective equipment are carried out only in accordance with the EU Regulation 2016/425. Thus, in Poland they must also comply with the requirements specified in the Act dated August 30, 2002 "On the Conformity Assessment System" [14]. In Japan, the regulations on the provision of PPE are based on risk

assessment (Figure 6). According to the requirements of the Occupational Safety and Health Act, Japanese employers are required to independently develop accident prevention programs at work and determine what protective equipment they will use to prevent accidents [16].

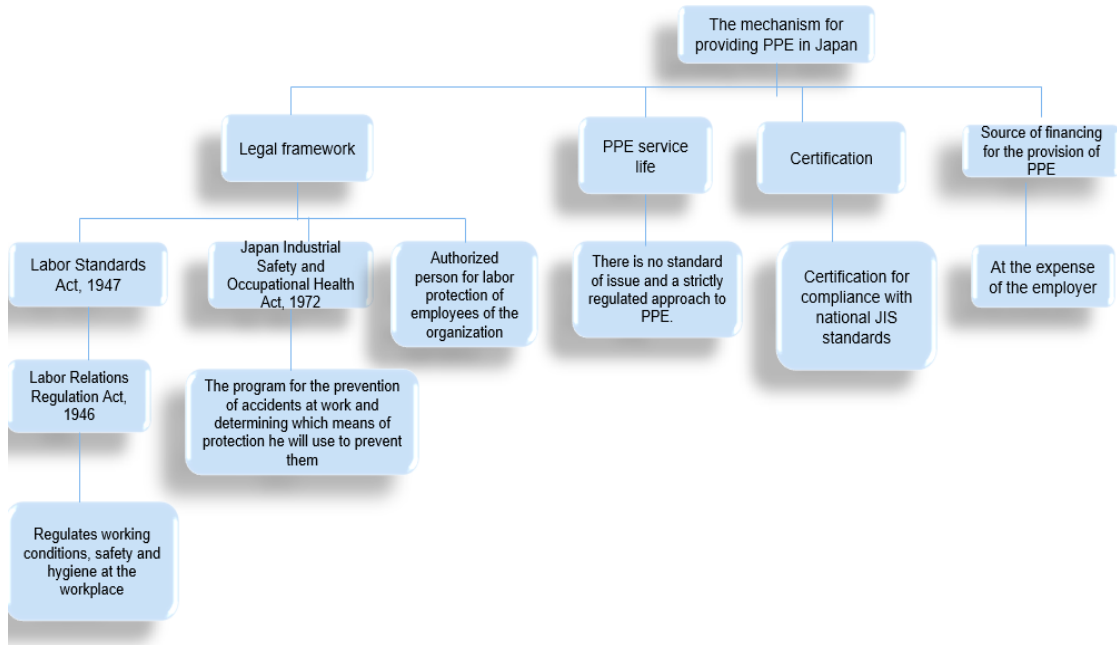


Fig. 6 - Mechanism for providing and issuing PPE in Japan

Mixed/hybrid approach – is currently typical for providing PPE in Poland (Figure 7) and Russia. In Poland [14], according to the Labor Code, the employer determines the types of personal protective equipment, as well as work clothes and footwear, the use of which is required in certain positions. At the same time, this is done on the basis of the Resolution of the Minister of Labor and Social Policy of September 26, 1997 "On General Rules for Occupational Health and Safety", which contains detailed rules for the use of PPE, including a list of risks that require personal protective equipment ("Types of work requiring the use of personal protective equipment with an indication and decoding of the types of personal protective equipment"). At the same time, the period of wear and operation is determined based on the manufacturer's requirements provided in the documentation for the PPE. Accordingly, the regulatory framework for the list of risks imposes on the employer an obligation to assess the professional risk of each employee, which is provided for by the Labor Code.

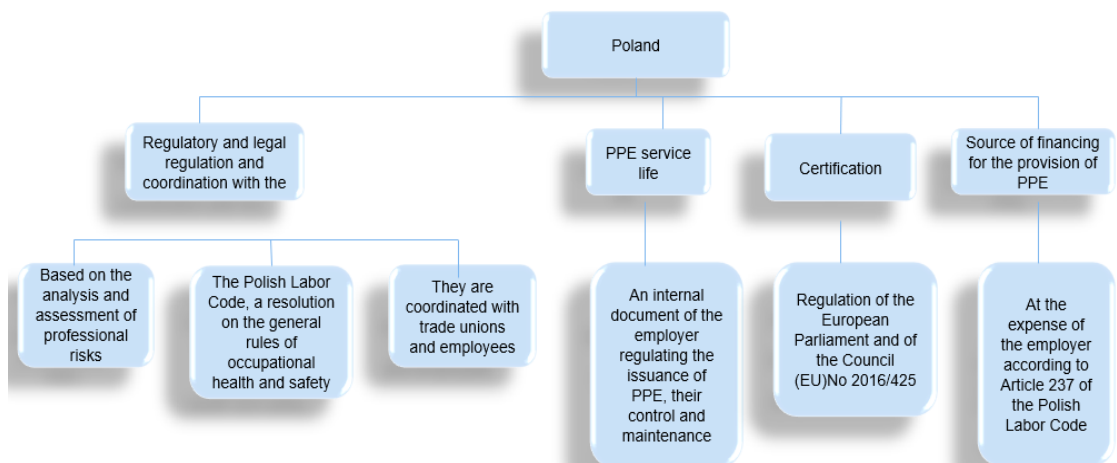


Fig. 7 - Mechanism for providing and issuing PPE in Poland

Thus, the employer of any enterprise must develop and approve by a local act the standards for the free issuance of PPE to employees, based on the Unified Standard Standards, taking into account the results of the special assessment of working conditions, the results of the assessment of professional risks, the opinion of the representative body of employees. These standards can be developed by the enterprise itself, as well as by involving third-party organizations or specialists [14].

Based on the results of the analysis, the mechanisms and features of the legal regulation of the provision of PPE were grouped as follows:

The list approach, which is based on strict regulatory consolidation of the list of professions and types of work, for which PPE is provided, sets and wearing periods are regulated, in some cases, provision in excess of standards is prohibited. Regulation is carried out on an industry basis, equalizing the working conditions of employees without taking into account the actual state and measures taken by the employer to improve working conditions (change in technology, technical re-equipment, use of collective protective equipment, exclusion of employee employment directly in the zone of exposure to harmful factors, etc.). Approval of standards by an act of the employer is formal in nature, the assessment of the provision of PPE consists in comparing it with uniform/industry standards. This approach is observed in post-Soviet countries such as Russia, Belarus, Kazakhstan.

Risk-oriented approach, which is based on mandatory assessment of the professional risk of a specific employee. The provision of PPE is not standardized at the legislative level, but the employer's responsibilities to ensure the protection of employees are legislatively established. However, there are certain PPE that are presented in the standards for specific works (helmet and high-visibility vest for loading and unloading works without the obligation to provide special clothing against contamination, etc.) [18-21]. The standards for issuing and the terms of wearing/operation of PPE are tied to the information contained in the technical documentation for a specific product. The role of employee representatives in this aspect is very important, since the formation of the PPE register by the employer is carried out with their participation/agreement, often with the agreement of the employee himself. This approach is used in Canada, the USA, Great Britain, and Japan.

A mixed/hybrid approach, which is currently typical for providing PPE in Poland and Russia. In Poland, according to the Labor Code, the employer determines the types of personal protective equipment, as well as work clothes and footwear, the use of which is required in certain positions. At the same time, this is done on the basis of the Resolution of the Minister of Labor and Social Policy of September 26, 1997 "On General Rules for Occupational Health and Safety" [15], which contains detailed rules for the use of PPE, including a list of risks that require personal protective equipment ("Types of work requiring the use of personal protective equipment with an indication and decoding of the types of personal protective equipment"). At the same time, the period of wear and operation is determined based on the manufacturer's requirements, given in the documentation for the PPE. Accordingly, the regulatory framework for the list of risks imposes on the employer an obligation to assess the professional risk of each employee, which is provided for by the Labor Code.

Russia is in a transitional stage from the list approach and the hybrid approach used alongside it, characterized by legislative regulation of the procedure for providing PPE (Rules, Standard Standards) without taking into account the industry focus. The key reform provides for the transition from Standard Industry Standards for the Issuance of PPE (more than 60 documents) in favor of Uniform Standard Standards acceptable for all industries and sectors of the economy, which indicate the names of professions, names and types of PPE, their quantities per year. Risk-focused approach consists in introducing standards for the issuance of PPE depending on the hazards that pose a threat to the life and health of workers. A separate appendix provides the names

of hazards identified based on the results of the assessment of professional risks, PPE that must be issued with a possible design, additional elements and quantity per year. The approved standards serve as the basis for local regulations at enterprises.

Results and discussion. At the same time, the employer's obligation to use certified PPE remains a single regulated requirement for all approaches. There is a significant regulatory and technical framework, standards, bodies for confirming product compliance with safety and quality requirements, and state control is carried out.

The study found that to ensure occupational safety, it is necessary to identify hazards, subsequently assess the risk of their impact, and provide protective equipment taking into account the risk. The basis for identifying hazards is the classification of hazardous and harmful production factors. It is necessary to highlight those features that will allow the best identification of hazardous and harmful production factors, assess the risks of their impact on the worker's body, develop protective measures and implement them in practice, thereby preventing injuries and diseases associated with the employee's work and the employer's production activities. Based on the classification, it is possible to fully and reliably identify hazards in the workplace [21-24].

In this regard, in the course of scientific work, a classifier of risks associated with the impact of production factors on the worker's body was developed (Table 1-2) [25,26].

Table 1 – Classifier of harmful and hazardous production factors

No.	Fact or code	Name of risks associated with factors of the production environment	Need to provide PPE (+/-)
1	1	Impact of industrial factors of mechanical nature	
2	1.1	Fall in the work area	
3	1.1.1	Fall from a height or to a depth	+
4	1.1.2	Fall when slipping on slippery surfaces	+
5	1.1.3	Fall, collapse, avalanche of objects (solid, liquid or gaseous objects)	+
6	1.1.4	Fall, destruction of buildings, structures and their elements	+
7	1.2	Road accident	
8	1.2.1	Vehicle collision	+
9	1.2.2	Transport accidents	-
10	1.3	Impact of production equipment	
11	1.3.1	Moving and rotating parts of equipment, mechanisms, machines, tools (impacts, grips, crushing)	+
12	1.3.2	Stationary cutting parts of production equipment, mechanisms, machines, tools (cuts, scratches)	+
13	1.3.3	Impact of high surface temperatures of equipment, mechanisms, machines, tools, liquids, gases, vapors	+
14	1.3.4	Impact of low surface temperatures of equipment, mechanisms, machines, tools	+
15	2	Impact of production factors of a physical nature	
16	2.1	Impact of electric current	
17	2.1.1	Electric shock from equipment, mechanisms, machines, tools	+
18	2.1.	Impact of an electric arc	+

	2		
19	2.2	Risk of fire or explosion	
20	2.2.1	Ignition of flammable substances	+
21	2.2.2	Static electricity	+
22	2.2.3	Exposure to smoke, steam, harmful gases and dust	+
23	2.2.4	Working with pressure vessels	+
24	2.3	<i>Climate/microclimate</i>	
25	2.3.1	Increased air temperature in open areas	+
26	2.3.2	Decreased air temperature in open areas	+
27	2.3.3	Increased air velocity in open areas	+
28	2.3.4	Increased air humidity in open areas	+
29	2.3.4	Increased air temperature indoors	+
30	2.3.4	Decreased air temperature indoors	+
31	2.3.4	Increased air velocity indoors	+
32	2.3.4	Increased air humidity indoors	+
33	2.3.4	Increased thermal radiation	+
34	2.3.4	Increased atmospheric pressure	-
35	2.4	<i>Ionizing radiation</i>	
36	2.4.1	Alpha radiation	+
37	2.4.2	Beta radiation	+
38	2.4.3	Gamma radiation (expository)	+
39	2.4.4	X-ray radiation	+
40	2.4.5	Electrically charged air particles - aeroions	+

The proposed classifier consists of 6 main groups, 19 names, and 55 subgroups of production factors, and its application is substantiated using examples.

Table 2 - Classifier of harmful and hazardous production factors

No.	Factor code	Name of risks associated with factors of the production environment	Need to provide PPE (+/-)
1	2.5	<i>Non-ionizing radiation</i>	
2	2.5.1	Electrostatic field	+
3	2.5.2	Permanent magnetic field (including hypogeomagnetic)	+
4	2.5.3	Industrial frequency electric and magnetic fields	+

5	2.5.4	Broadband electromagnetic fields generated by personal computers	-
6	2.5.5	Infrared radiation	+
7	2.5.6	Ultraviolet radiation	+
8	2.5.7	Laser radiation	+
9	2.6	<i>Vibroacoustic factors</i>	
10	2.6.1	Continuous noise	+
11	2.6.2	Pulsed noise	+
12	2.6.3	General vibration	+
13	2.6.4	Local vibration	+
14	2.6.5	Infrasound	+
15	2.6.6	Ultrasound	+
16	2.7	<i>Light environment</i>	
17	2.7.1	Insufficient illumination of the work area	+
18	2.7.2	Increased illumination of the work area (brightness of light, direct and reflected, increased pulsation of the light flux)	+
19	2.8	<i>Aerosol composition of air</i>	
20	2.8.1	Highly and moderately fibrogenic aerosols	+
21	2.8.2	Low-fibrogenic aerosols	+
22	3	Impact of industrial factors of chemical nature	
23	3.1	<i>Chemical substances contained in the air of the working area (aerosols, vapors, gases, fumes)</i>	
24	3.1.1	Acute toxicity substances	+
25	3.1.2	Irritant substances	+
26	3.1.3	Carcinogenic substances	+
27	3.1.4	Allergenic substances	+
28	3.1.5	Substances hazardous to reproductive health	+
29	3.1.6	Substances prohibited for inhalation and skin contact (antitumor drugs, estrogen hormones, narcotic analgesics)	+
30	3.1.7	Solutions of acids, alkalis, etc., solid and bulk substances that affect the skin and mucous membranes	+
31	4	Impact of production factors of biological nature	
32	4.1	Microorganisms-producers, preparations containing living cells and spores of microorganisms	+
33	4.2	Pathogenic microorganisms and viruses (causative agents of especially dangerous and other infectious diseases)	+
34	4.3	Getting of poisons, waste products and plants themselves, insects, arachnids, animals on the skin and inside the body	+
35	5	Impact of production factors of psychophysiological nature	
36	5.1	Difficulty of labor	-
37	5.2	Intensity of labor	-
38	6	Exposure to general industrial contaminants	
39	6.1	Water (including contaminated) and solutions of non-toxic substances (dyes, adhesives, oily and other substances) and labor products	+
40	6.2	Non-toxic dust (fine chips, small fragments, coarse dust)	+

The classifier contains the following main names of risks associated with the impact of factors of the production environment and the work process on the worker's body:

- impact of production factors of a mechanical nature (fall in the work area, road traffic

accident, impact of production equipment);

- impact of production factors of a physical nature (electric current, threat of fire or explosion, climate/microclimate, ionizing radiation, non-ionizing radiation, vibroacoustic factors, light environment, aerosol composition of air);

- impact of production factors of a chemical nature (chemical substances contained in the air of the working area (aerosols, vapors, gases, fumes);

- impact of production factors of a biological nature (microorganisms - producers, pathogenic microorganisms and viruses, waste products of plants, insects, arachnids, animals);

- impact of production factors of a psychophysiological nature (severity of work, labor intensity);

- impact of general industrial pollutants (water and solutions of non-toxic substances, non-toxic dust)

Conclusions. Analysis of the current mechanisms for providing PPE in the Republic of Kazakhstan has established that regulation is determined by 22 industries and 3,544 professions based on approved standards for issuing special clothing and other personal protective equipment to employees of organizations of various types of economic activity.

Compliance with the established standards in practice puts the employer in a strict framework, on the one hand, with the need to purchase PPE that is inadequate for working conditions, on the other hand, with the impossibility of increasing/decreasing the wearing period and quantity, changing the completeness, etc. The domestic mechanism for providing PPE is characterized by a “list” approach and strict regulation of the types of PPE depending on the profession or position of the employee, which in some cases leads to the creation of barriers in ensuring safe work at enterprises. At the same time, the experience of developed countries shows the effectiveness of using RBA in providing PPE.

Thus, developed foreign countries use models for providing PPE based on an assessment of professional risks, analyzing specific hazards and providing relevant means of protection against them. The introduction of risk assessment into the labor legislation of the Republic of Kazakhstan and the existing regulatory mechanism for the provision of PPE, which does not take into account the specifics of the labor process and the presence/absence of harmful production factors and professional risks, requires revision. It is assumed that based on the results of the assessment of professional risks, as well as taking into account the physical, chemical, biological factors of the production environment and factors of the labor process, employers should be able to independently develop and approve standards for providing PPE to employees of the enterprise [2].

In this regard, it is necessary to improve the current regulatory mechanism for providing special clothing, footwear and other PPE with increased flexibility in determining the contingent of employees, choosing protective equipment, assigning additional sets, replacement and complex PPE, service life.

Thus, the employer of any enterprise must develop and approve by a local act the standards for the free issuance of PPE to employees, based on the unified standard guidelines, taking into account the results of the special assessment of working conditions, the results of the assessment of professional risks, the opinion of the representative body of employees. These standards can be developed by the enterprise itself, or by involving third-party organizations or specialists.

Considering that the range of modern PPE fully covers protection against all possible factors of the production environment and professional risks, a methodology for providing PPE based on RBA will be developed and implemented, as well as a nomenclature of PPE corresponding to the degree and type of exposure to harmful and (or) hazardous production factors [2].

Also, based on the results of the study, a classifier of risks associated with the impact of production factors on the worker's body, as well as a classifier of harmful and hazardous production factors were developed.

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




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IMPORTANCE OF MXENE NANOCOMPOSITES IN THE DETECTION OF HEAVY METALS

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


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One of the strongest and most common chemical pollution is its environmental pollution with heavy metals. Heavy metals are actively involved in biological processes, which are part of many enzymes. The toxicity of heavy metal ions causes a number of harm to environmental components and human health. That is why the detection of heavy metals is so important. The creation of a reliable and effective system for detecting heavy metals is crucial. And traditional detection methods are often not enough to meet the current needs. Therefore, the use of electrochemical sensors in the detection of heavy metals is currently taking an important place. Electrochemical sensors have become a promising area of research due to their unique capabilities. Improving the detection efficiency of electrochemical sensors is the main area of research. The leading strategy for significantly improving detection performance involves adding nanomaterials to electrochemical sensors. This review compares MXene nanocomposites with the achievements of nanomaterials in the field of electrochemical sensors in recent years. This makes it possible to obtain new ideas for the manufacture of electrochemical sensors with high sensitivity and low detection threshold. We believe that knowing and combining the benefits of different nanomaterials to produce innovative electrode modification materials can eliminate the risk of heavy metal ions in many food, environmental and other industries.

Keywords: heavy metals, electrochemical sensors, nanomaterials, modification, MXene nanocomposites.

АУЫР МЕТАЛДАРДЫ АНЫҚТАУДА MXENE НАНОКОМПОЗИТТЕРДІҢ МАҢЫЗЫ

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Ең күшті және ең көп таралған химиялық ластанудың бірі - ол қоршаған ортаның ауыр металдармен ластануы. Ауыр металдар көптеген ферменттердің құрамына кіретін биологиялық процестерге белсенді қатысады. Ауыр металл иондарының уыттылығы қоршаған орта компоненттеріне және адам денсаулығына бірқатар зиянын келтіреді. Сондықтан да ауыр металдарды анықтау өте маңызды болып табылады. Ауыр металдарды анықтау үшін сенімді және тиімді жүйені құру қажет. Ал дәстүрлі анықтау әдістері көбінесе қазіргі қажеттіліктерді қанағаттандыру үшін жеткіліксіз. Сондықтанда қазіргі кезде ауыр металдарды анықтауда электрохимиялық сенсорларды қолдану маңызды орын алып отыр. Электрохимиялық сенсорлар өзінің ерекше мүмкіндіктерінің арқасында зерттеудің перспективалық бағытына айналды. Электрохимиялық сенсорларды анықтау тиімділігін арттыру зерттеудің негізгі бағыты болып табылады. Анықтау өнімділігін айтарлықтай жақсартудың жетекші стратегиясы наноматериалдарды электрохимиялық сенсорларға қосуды қамтиды. Бұл шолу MXene нанокөмірлерін соңғы жылдардағы электрохимиялық сенсорлар саласындағы наноматериалдардың жетістіктерін салыстырады. Бұл жоғары сезімталдығы бар және анықтау шегі төмен электрохимиялық сенсорларды дайындау үшін жаңа идеялар алуға мүмкіндік береді. Электродтарды

модификациялау үшін инновациялық материалдар алу үшін әртүрлі наноматериалдардың артықшылықтарын білу және біріктіру көптеген азық-түлік, экологиялық және де басқа салалардағы ауыр металл иондарының қаупін жоя алады деген ойдамыз.

Түйін сөздер: Ауыр металдар, электрохимиялық сенсорлар, наноматериалдар, модификация, MXene нанокөміртер.

ВАЖНОСТЬ НАНОКОМПОЗИТОВ MXENE ДЛЯ ОПРЕДЕЛЕНИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ

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Одним из самых сильных и распространенных химических загрязнений является загрязнение окружающей среды тяжелыми металлами. Тяжелые металлы активно участвуют в биологических процессах, входя в состав многих ферментов. Токсичность ионов тяжелых металлов наносит ряд повреждений компонентам окружающей среды и здоровью человека. Именно поэтому обнаружение тяжелых металлов так важно. Необходимо создать надежную и эффективную систему для обнаружения тяжелых металлов. А традиционных методов обнаружения зачастую недостаточно для удовлетворения современных потребностей. Поэтому использование электрохимических сенсоров для обнаружения тяжелых металлов в настоящее время занимает важное место. Электрохимические сенсоры стали перспективным направлением исследований благодаря своим уникальным возможностям. Повышение эффективности обнаружения электрохимических сенсоров является основным направлением исследований. Ведущей стратегией для значительного повышения эффективности обнаружения является добавление наноматериалов в электрохимические сенсоры. В данном обзоре сравниваются нанокөміртер MXene с достижениями наноматериалов в области электрохимических сенсоров за последние годы. Это позволяет получить новые идеи для изготовления электрохимических сенсоров с высокой чувствительностью и низким порогом обнаружения. Мы считаем, что знание и комбинирование преимуществ различных наноматериалов для создания инновационных материалов для модификации электродов может устранить опасность ионов тяжелых металлов во многих пищевых, экологических и других отраслях промышленности.

Ключевые слова: тяжелые металлы, электрохимические сенсоры, наноматериалы, модификация, нанокөміртер MXene.

Introduction. Heavy metals are particularly biodegradable pollutants. They enter aquatic ecosystems, enter water and sediment phases, accumulate in organisms, and even at low levels cause a number of serious diseases and disorders [1-4]. For example, neurological, cardiovascular, respiratory and reproductive diseases [5]. Heavy metals in the environment pose a serious threat to wildlife and human health because they are bioavailable and can be absorbed and enriched in food [6]. Toxic metals are largely distributed into the environment. The distribution of heavy metals by wind in the form of particles or vapor depends on their physical state. The metal components move from the atmosphere to the soil or water surface, resulting in environmental pollution. Industrial wastewater is a major source of metal pollution in the hydrosphere. Wastewater containing toxic heavy metals like nickel, lead, copper, chromium, cadmium, and arsenic poses environmental and health hazards [7]. Heavy metals affecting human health include elements such as mercury, nickel, lead, chromium, cadmium, aluminum and copper [8]. Heavy metals in water, air and soil can be transferred to plants, aquatic organisms and organisms and then enter the food chain and pose a threat to human health [9].

Year after year, the population around the world is growing. As the world's population grows, the demand for food, drinking water and many other industries increases. Due to the

increased demand, the quality requirements for food and drinking water are increasing. To ensure consumer safety, we must detect harmful substances present in very low concentrations. One of the most commonly used methods today is the use of electrochemical sensors.

Electrochemical sensors are tools for detecting and counting heavy metals because they tend to be highly specific, sensitive, inexpensive and portable. This makes them valuable for small and mobile remote applications. Since complete elimination of food and drinking water contamination may not seem possible in the near future, assessment of legal limits should always be considered in the context of general nutrition, especially in the case of children. Ongoing research continues to improve sensor performance, enhance detection capabilities, and address calibration, interference, and sample preparation issues, further advancing the development of electrochemical sensors in food safety applications [10].

The world of sensors is diverse and due to this, it is developing at a rapid pace. Due to continuous technological improvement it is becoming more and more in demand. Electrochemical sensors are a convenient solution for variable analyzer detection due to their low cost and availability and are widely used in agriculture, food and oil industry as well as in environmental and biomedical fields. Electrochemical sensors have long been required for the study of biological substances. The sensors are characterized not only by their durability, high sensitivity and accuracy, but also by their low cost, speed and simplicity. Many nanomaterials have been obtained in more than two decades. Specific metals, conducting polymers, metal oxides and organometallic and carbon-based nanomaterial structures. Nanomaterials contribute to the analytical performance included in electrochemical analysis. This modification increases the payload capacity by utilizing recognition molecules such as enzymes, antibodies and aptamers as well as bioinspired receptors that can accurately and efficiently capture the target, thereby increasing the specificity of electrochemical sensors [11].

Electrochemistry-an important quantitative analysis strategy for testing various biochemical entities such as proteins, metabolites, neurotransmitters, electrolytes, heavy metals, etc. Further, demonstrating wide applications in the fields of private health care, public health, clinical diagnostics, food safety and environmental analysis [12-14]. Generally, a complete electrochemical conversion system usually consists of two parts: sensing electrodes and electrochemically sensitive circuits. The former is used to convert biochemical signals into electrical signals. The latter uses various electrochemical test methods to excite the electrodes with voltage, collect, process, analyze the data and transmit them as electrical signals [15,16].

MXenes' electrical conductivity, rich surface chemistry and high aspect ratio are attractive characteristics for sensor processing . The ideal sensor has high performance, low detection , low production cost, low hysteresis, fast and efficient processing reaction, as well as fast recovery properties during reuse . Pressure and deformation sensors are production responsible in a wide pressure range and require high performance in thousands of deformation cycles. The cycles require high resistance in thousands of deformation cycles. The sensors demonstrated this product when made from MXenes, mxen/polymer nanocomposites, and mixed two-dimensional (2D) mxen-based heterostructures. Examples: silver nanoparticles, carbon nanotubes, and graphene oxide nanoparticles are 0D, 1D, and 2D nanoparticles that were combined with MXene and used to create Mxene-based 2D heterostructures [17].The latter includes mxen and heterostructure of 0D, 1D or 2D nanomaterials. These are heterostructures, as well as the detection of pure MXene and MXene /polymer nanocomposites and toxic compounds in food, monitoring of human movements and health status, gas and condition measurement, voice recognition and other input in sensory systems. appropriateness, voice recognition and other aspects [18].

Table 1- Lists many MXene-based sensors and their corresponding applications [19]

Nanocomposite components	Application
Ti₃C₂ / reduced graphene oxide	Pressure sensor
Ti₃C₂/ Ag nanowire	Strain sensor

Ti₃C₂ / chitosan	Biosensor for detecting pesticides
Ti₃C₂ / Nafion	Detecting nitrile ions
Ti₃C₂ / PANI	Ethanol, methanol, ammonia, and acetone detection
Ti₃C₂ / polyurethane	Stretchable strain sensing fabric
Ti₃C₂/ poly(vinylidene fluoride-trifluoroethylene)	Capacitive pressure sensor
Ti₃C₂ / natural microcapsules	Epidermal flexible pressure sensors
Ti₃C₂ / poly(dimethylsiloxane)	Skin conformal sensors for health monitoring
Ti₃C₂ / gold nanoparticles	Glucose detection biosensor
Ti₃C₂ and TiO₂	H ₂ O ₂ detection
hollow MXene spheres/ reduced graphene	Piezoresistive pressure sensor
Ti₃C₂ / ink	Strain sensor for health monitoring

MXene performance in sensor systems depends on the type and concentration of surface functional groups (hydroxyl, oxygen, fluorine, chlorine). For example, the simulation results showed that oxygen-ending MXene has excellent performance for ammonia detection, while hydroxyl-ending MXene has better performance for ethanol detection. To further improve the electrochemical performance of electrochemical sensors, sensitive Nanomaterials and 2D materials have been introduced due to high electrocatalytic effect and high electrical conductivity [20].

MXene is a novel 2D material with a rare combination of properties such as electrical and metallic conductivity, hydrophilicity, biocompatibility and large surface area, convenient size customization, rich surface chemistry, flexibility, and layered structure. Due to its versatile properties, MXene is considered as a building material for future materials and devices [21].

As an electrode material, MXene is a potential candidate for synthesis for various energy storage devices such as supercapacitors and batteries. Composites based on metal oxides and metal sulfides are the most effective electrode materials for supercapacitor electrodes. Research was carried out to improve the properties of MXene-based composites [22].

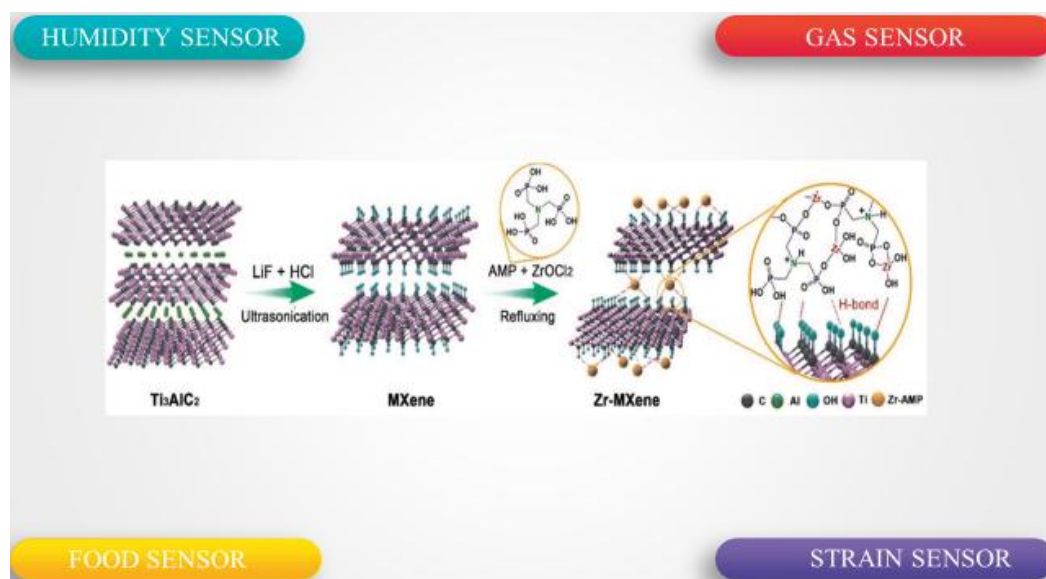


Figure 1 - Types of Mxene-based sensors [19]

Table 2 - Advantages and disadvantages of MXene materials

	Advantages	Disadvantages
MXene	<ul style="list-style-type: none"> -Stability - Optical properties - Good hydrophilicity - Conductivity -Outstanding mechanical properties - Thermal effect - Excellent biocompatibility - High electrical conductivity 	<ul style="list-style-type: none"> -The preparation process of MXene sensitive materials must be further developed - The abundant functional groups on the surface of MXene materials endow them with customizable optical and electrical properties, but also bring new challenge

Materials and methods. Nanocomposite WO_3 /MXene

Al-Zoha Wapsi and others [23] used a hydrothermal method for the synthesis of tungsten oxide nanorods. The synthesis of WO_3 /MXene by a simple ultrasound method was carried out. The samples obtained were characterized by structural, spectral, morphological and elemental analysis. The photocatalytic and antibacterial activity of synthesized samples, these aspects are discussed in detail. Max (Ti_3AlC_2) powder was used in a 50 ml Teflon container to synthesize MXene with the formula Ti_3C_2Tx used. To synthesize MXene with the formula Ti_3C_2Tx in a 50 ml Teflon container. For MXene synthesis, 10 ml of HF is poured into a Teflon container and then released into a suction cup. Then, instead of low HF, MAX 0.5 g powder and a pinch were added. The mixture was equipped with magnetic instruments for an hour at room temperature.

The combustion optimization of the mixture was carried out at the installation temperature for 24 hours with magnetic power. Deionized (DI) water was added to dilute the product, and MXene was obtained by centrifugation at more than 5000 rpm. The washing of these deposits was performed until the PH reached 6. The Aqueous Dispersion was carried out using a PTFE membrane by vacuum filtration. Filtrate is here.

For FESEM analysis, samples were sprayed with gold for 120 seconds at a current of 15 ma. Figure-2 A, B WO_3 and WO_3 /MXene nanocomposite morphology control. Figure-2 - (a) illustrates the block/stick pattern morphology of WO_3 . Figure-2 (b) MXene WO_3 is defined as impregnated with nano wires. MXene Nano sample structure formation in Figure 2 - (c). The size of the WO_3 was about 13 nm, after the reduction of FESEM. The MXene layer was estimated at ~175 nm on an additional micro-image. For FESEM analysis, the samples were subjected to gold spraying for 120 seconds at a current of 15 ma. Figure-2 A,B WO_3 and WO_3 /MXene nanocomposite morphology control. Figure 1 shows the morphology of WO_3 with a block or stick inscription. Figure - 2 (b) MXene WO_3 is detected in an impregnated manner with nano wires. Figure 2 (c) shows the MXene formation of the nanoscale structure. The size of the WO_3 volume was about 13 nm, which is after the reduction of FESEM. In the micrograph, the size of the mxen layer was 175 nm.

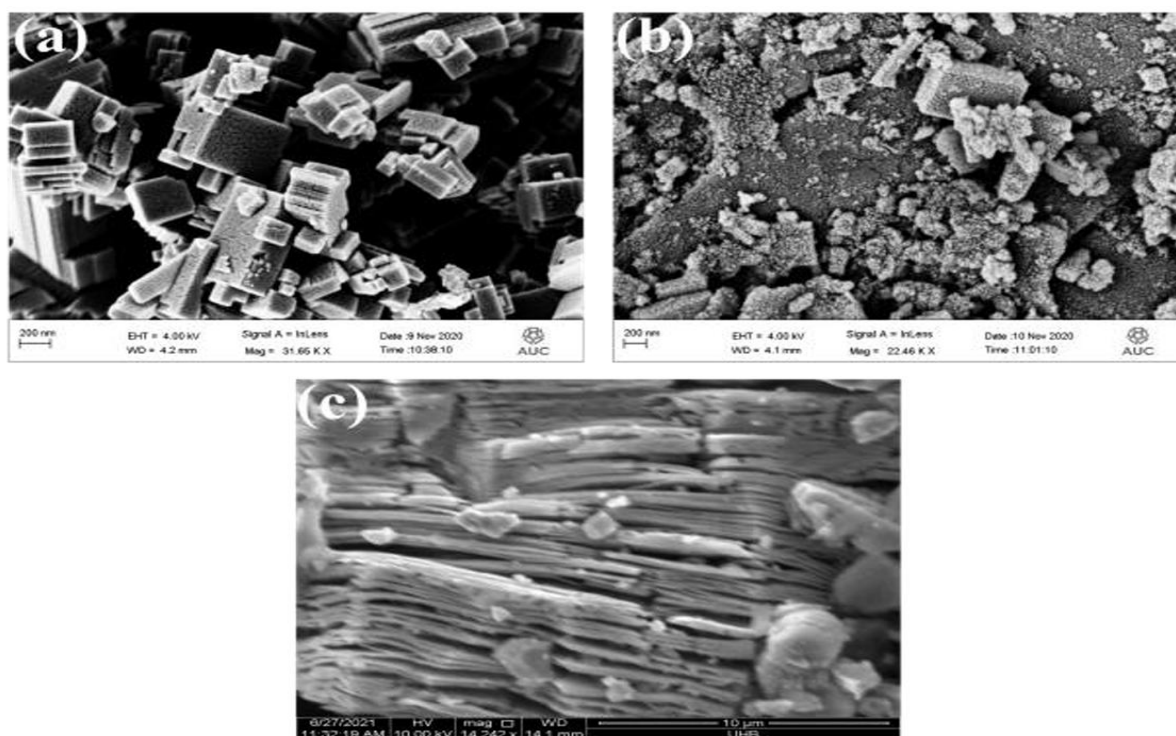


Figure 2 - FESEM images (A) WO_3 , (b) WO_3/MXene nanocomposite and (c) MXene [23]

In this paper, A.Z. Warsi, Aziz, F. Zulfiqar et al. prepared WO_3 , MXene and WO_3/MXene nanocomposite which showed potential applications in biological and environmental remediation. WO_3 , MXene and WO_3/MXene nanocomposite were synthesized by hydrothermal method, wet chemical etching and sonication, respectively. XRD, XRD, FTIR, EDX and FESEM were used to determine the structural, spectral, elemental and morphological characteristics of the synthesized samples, respectively. BET analysis was performed to determine the surface area. The photocatalytic degradation of methylene blue using WO_3 , MXene and WO_3/MXene nanocomposites was 99%, 54% and 89%, respectively. The photocatalytic activity of WO_3 was significant. MXene is a two-dimensional material with very low photocatalytic activity, which acts only as an auxiliary material to enhance the photocatalytic ability of the composite with WO_3 .

The prepared samples also showed good antibacterial activity against bacteria of positive strain; in case of negative strains, WO_3 , MXene and WO_3/MXene nanocomposite showed antibacterial activity at high concentrations [23].

$\text{Bi}_2\text{S}_3/\text{MXene}$ nanocomposite

In a study [24] by S. Sinha, A. Raucci et al. developed a novel electrochemical sensing platform using $\text{Bi}_2\text{S}_3/\text{MXene}$ nanocomposite. The modified shape, composition and electrical characteristics of the prepared composites and their electrodes were studied by various electrochemical methods SEM, XRD, XPS and others. A 1 mg/ml solution of $\text{Bi}_2\text{S}_3/\text{MXene}$ nanocomposite was prepared by dispersing DI (deionized) in water. This standard solution was the base of the electrode modification process. This initial solution base served as the electrode modification process. An 8 μL dispersion of $\text{Bi}_2\text{S}_3/\text{MXene}$ nanocomposites was carefully placed on the surface of SPE to modify the electrode. $\text{Bi}_2\text{S}_3/\text{MXene}$ nanocomposites were synthesized directly by microwave-assisted hydrothermal method. The figure below shows the accumulation of 3 - (A) [24] Bi_2S_3 nanoparticles. These are granular nanoparticles with diameters ranging from 70 to 100 nm. And figure 3 - (B) shows the MXene SPE image. This figure shows the complex layered lamellar structure of MXene after removing the Al layers from the MAX phase. SEM image of Bi_2S_3 -MXene nanocomposites are shown in Fig.3C and 3D (small and large scale).

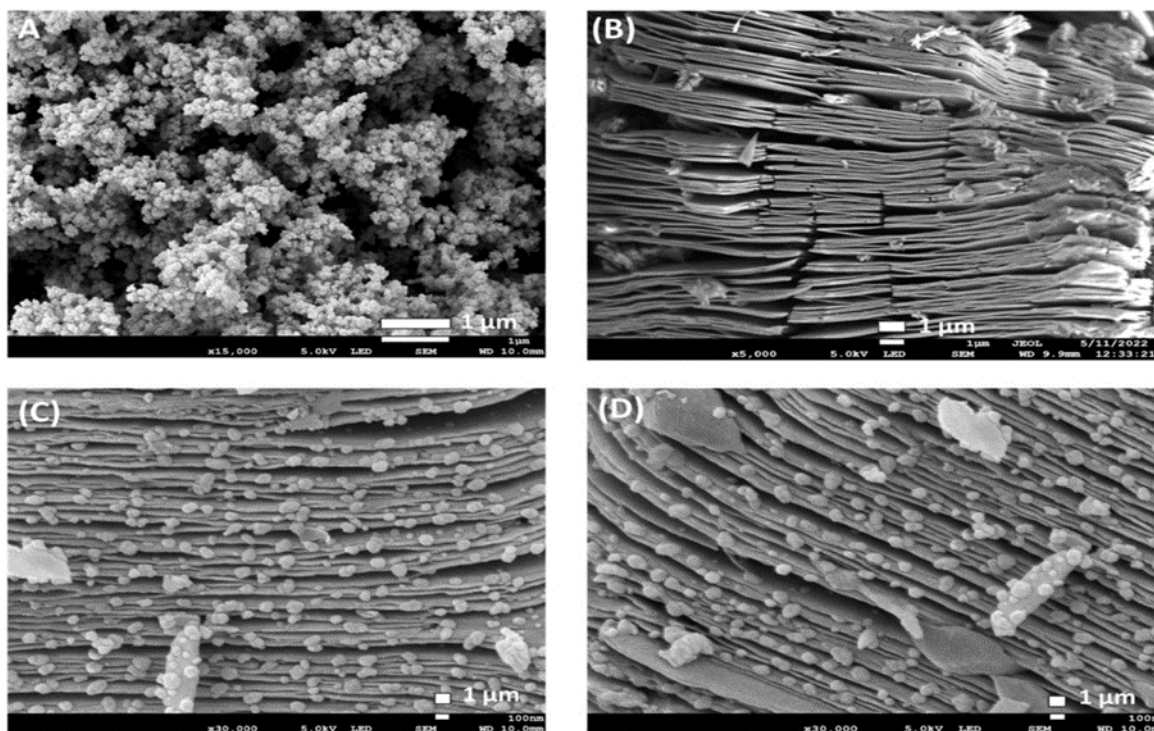


Figure 3 - Structural characteristics of (A) Bi_2S_3 ; (B) MXene; (C) Bi_2S_3 -MXene nanocomposite at low magnification; (D) Bi_2S_3 -MXene nanocomposite at high magnification [24]

The uniform growth of Bi_2S_3 nanoparticles in MXene layers growth of Bi_2S_3 nanoparticles (F and OH) was due to the presence of electronegative functional groups. The synergistic effect of Bi_2S_3 nanoparticles and MXene can improve the electrochemical performance. First, MXene provides a highly conductive platform for the uniform growth of Bi_2S_3 nanoparticles. This leads to reduced agglomeration of Bi_2S_3 nanoparticles and increased number of detection sites for the target analyte [25]. Secondly, MXene is highly conductive, which leads to an increase in charge between Bi_2S_3 nanoparticles and the electrolyte [26]. In addition, the oxidation resistance property demonstrated by MXene plays an important role in protecting Bi_2S_3 nanoparticles from corrosion [27]. The binding of MXene and Bi_2S_3 nanoparticles can lead to improved performance in Zn(II) detection.

The study focuses on the synthesis of a composite made of $\text{MoO}_2@ \text{Mo}_2\text{C}$ -MXene.

This article discusses the new CdS/MoO_2 photocatalyst @ Mo_2C -MXene developed by You Jin, Huizhuan Jing, Libo Wang, Qianku Hu and Aigo Zhou. 0.2 g of NaBF_4 (99.9%, McLean, China) was used as a guiding reagent, dissolved in 15 ml of 1.0 m HCl solution (36-38% C/a , Yantai Shuangshuang Chemical, China) and stirred for 30 minutes. The temperature of the hydraulic system is maintained at 180 °C for 24 hours every day. The temperature of the hydraulic system is kept at 180 °C for 24 hours every day. Subsequently, $\text{MoO}_2@ \text{Mo}_2\text{C}$ -MXene Composite powders were collected, subjected to washing with deionized water and ethanol to achieve a neutral reaction, and then dried for 12 hours at 60 °C for 12 hours under vacuum conditions.

$\text{CdS} / \text{MoO}_2@ \text{Mo}_2\text{C}$ photocatalysts were effectively synthesized by a two-stage hydrothermal method . In this system, a sediment formed on the surface of the $\text{CdS} / \text{MoO}_2@ \text{Mo}_2\text{C}$ -MXene Composite, forming an acanthospheric structure. $\text{CdS} / \text{MoO}_2@ \text{Mo}_2\text{C}$ (CMM5) showed an exceptional H_2 generation rate of 22,672 $\mu\text{mol}/(\text{g}\cdot\text{h})$ in visible light under optimal conditions, which is 11.8 times higher than CdS . full row, $\text{MoO}_2@ \text{Mo}_2\text{C}$ -MXene binary co-catalyst using CdS using high photocatalytic activity of productive H_2 generation with Mo_2C MXene as the only co-catalyst. Experimental effects the $\text{CdS}/\text{Mo}_2\text{C}$ system effects work with $\text{CdS} / \text{Mo}_2\text{C}$ with high photophysical and photoelectrochemical properties to serve as an electronic bridge between CdS and Mo_2C MXene with improved electrical conductivity . "no," he said. In addition to the $\text{CdS}/\text{Mo}_2\text{C}$ script, the CdS conduction band (CB) is a place to charge when $\text{MoO}_2@ \text{Mo}_2\text{C}$ is

MXene bound. This effectively limits the re - diffusion of Altered electrons into CdS , thus facilitating the operation of recombination. The band forbidden to control over CdS/MoO₂@Mo₂C makes it easy to absorb visible light. This CdS/Mo₂C [28] element restored a new photocatalytic system with the formation of a binary H₂ co-catalyst.

The process of preparing Ti₃C₂ involves the use of various chemical and physical methods to create a highly durable and efficient material: The crude powder (50 g) was weighed in the following ratio TiC:Ti:Al = 3.6:1.4:1 and then placed in a Teflon ball mill. Anhydrous ethanol was then added to the ball mill tank as a ball grinding aid and zirconium dioxide (5 nm diameter) as a grinding medium. The mass ratio of raw material powder, anhydrous ethanol and pellets should be 1:1:3. The ball was placed in a grinding vessel and the powder mixture was pulverized at 300 rpm for 4 hours. Next, a ball mill was used to obtain a homogeneous mixture and then it was transferred into a petri dish. The mixture was dried in an oven at 40°C for 24 hours, then sintered in a corundum crucible without pressure.

After the reaction was completely completed, the sintering furnace was allowed to cool down naturally to room temperature and a Ti₃AlC₂ ceramic block was obtained by pressureless sintering. A high-energy ball mill was used to completely pulverize the Ti₃AlC₂ ceramic block obtained by pressureless sintering in the previous step; finally, the desired Ti₃AlC₂ powder was successfully obtained. At room temperature, 5 g of Ti₃AlC₂ powder was slowly added to 80 mL of 40 wt% HF and left to react for 24 h under magnetic stirring at 1200 rpm. The above corrosion products were purified with deionized water until the pH of the supernatant became > 6 after centrifugation. The substrate was lyophilized to obtain Ti₃C₂ powder.

Preparation of the PANI-Ti₃C₂ composite: first, 0.2 g of Ti₃C₂ powder was dispersed in 30 mL of 1M hydrochloric acid solution, then ultrasonic dispersion was carried out for 1 h until a homogeneous suspension was obtained. Second, 100 μ L of pure aniline (ANI) obtained by distillation was added to the suspension and dispersed by ultrasonic dispersion for 1h. Then, 0.335 g of ammonium persulfate (APS) was dissolved in 30 mL of 1 M hydrochloric acid solution and added dropwise to the above solution. Finally, the solution was placed in an ice bath and stirred at 0°C for 6 hours. After reaction, the reaction product was washed with ultrapure water 5 times. After purification, the reaction product was lyophilized to obtain PANI-Ti₃C₂ nanocomposite [29].

Figure 1A shows the X-ray diffraction patterns of the obtained PANI, Ti₃C₂ and PANI-Ti₃C₂. The figure shows that the X-ray diffraction peak of PANI at 2 theta=20.5° corresponds to the surface (020) of the PANI crystal. The diffraction peak of Ti₃C₂ on the crystal plane (002) is shifted to the left along the x-axis from that of the original phase Ti₃AlC₂, which makes the characteristic peak of Ti₃C₂ weaker and wider.

This X-ray diffraction pattern can show that the degree of crystallinity and the degree of structural order of Ti₃C₂ are greatly reduced. In the X-ray radiograph of Ti₃C₂, the diffraction peaks at 2 theta =7.1°, 17°, 28°, 35°, 41° and 61° correspond to the crystal planes (002), (006), (008), (0010), (0012) and (110), respectively. Compared with the Ti₃C₂ XRD, the PANI-Ti₃C₂ XRD shows a new diffraction peak at 2 theta =20.7° corresponding to (020) crystal surface of PANI. The XRD peak of PANI-Ti₃C₂ at 2 theta =26° corresponds to TiO₂. This value is due to the fact that a small amount of Ti₃C₂ is oxidized by the addition of ammonium persulfate, an oxidizing agent, during the preparation of the PANI-Ti₃C₂ composite material. Thus, the phase analysis shows the successful preparation of PANI-Ti₃C₂ nanocomposite. Ti₃C₂ can easily immobilize enzymes/proteins on its surface, thus acting as a promising support to achieve DET with accelerated electrode kinetics, low detection limits, and high sensitivity and selectivity [30].

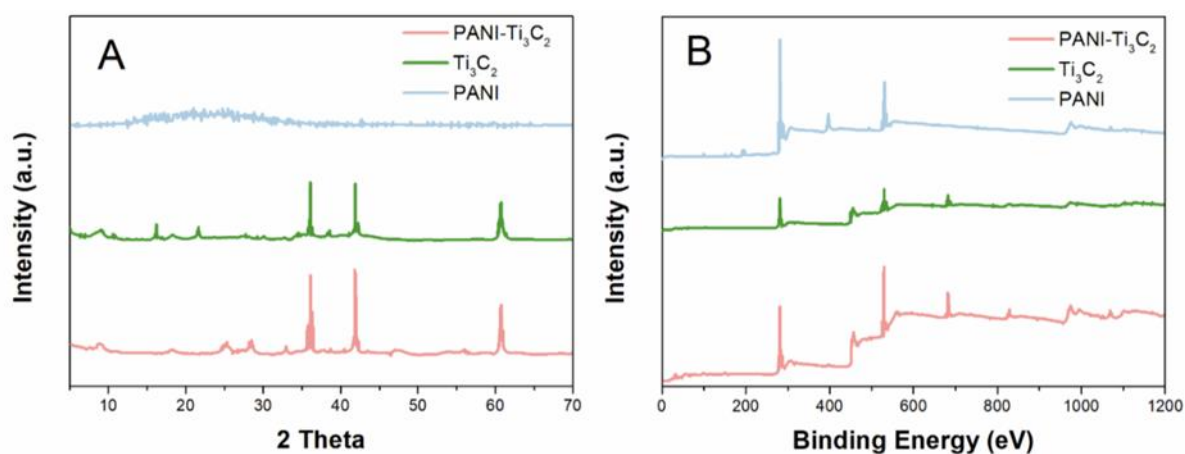


Figure 4 - (A) XRD patterns of PANI, Ti₃C₂ and PANI-Ti₃C₂. (B) XPS spectras of PANI, Ti₃C₂ and PANI-Ti₃C₂ [30]

Figure 1B shows the XRD spectra of the obtained PANI, Ti₃C₂ and PANI-Ti₃C₂. As can be seen from the figure, characteristic peaks C1s, O1s, F1s and Ti₂p appear, proving the existence of Ti₃C₂. At the same time, the appearance of characteristic peaks O1s and F1s proves the existence of functional groups -O, -OH and -F on the laminates of Ti₃C₂. The appearance of C1s and N1s peaks indicates the successful obtaining of PANI. Compared with Ti₃C₂, the broad XPS spectrum of PANI-Ti₃C₂ shows N1s peak, which further proves the successful preparation of PANI-Ti₃C₂ nanocomposites under low temperature stirring conditions. The above results are in agreement with the results of X-ray diffraction analysis. By the integral approximation method, N1s -analysis of the RFES spectra of the PANI-Ti₃C₂ nanocomposite showed four characteristic peaks at 397.1 eV, 398.2 eV, 400.1 eV and 400.5 eV corresponding to the imine structure (=NH-), amino group (-NH-), N atom (N++) with positron and protonated amino group, respectively. The results show that the PANI-Ti₃C₂ nanocomposite was successfully obtained by low-temperature oxidation reaction between Ti₃C₂ and aniline.

Ti₃C₂/TiO₂/CuO nanocomposites

In experiments, researchers Li, Wang, and Sun dissolved copper nitrate in deionized water and added Ti₃C₂ powder. The mixture was incubated for 24 hours, dried, and then synthesized into Ti₃C₂/TiO₂/CuO nanocomposites by annealing in an argon atmosphere at 500C for 30 minutes at a heating rate of 100C/min [31].

The fabrication of Ti₃C₂/TiO₂/CuO ternary nanocomposites, consisting of Ti₃C₂ nanosheets, TiO₂, and CuO nanoparticles, was enhanced by higher electron and hole separation efficiency compared to TiO₂, thereby improving their photocatalytic activity [32].

Discussion and results. In this research, a series of MXene-based nanocomposites including WO₃/MXene, Bi₂S₃/MXene, and Ti₃C₂/TiO₂/CuO were synthesized and characterized. The obtained materials showed high efficiency in various applications including photocatalytic decomposition of organic pollutants and electrochemical detection of heavy metals.

WO₃/MXene:

- The morphology of the nanocomposite determined by FESEM revealed the presence of nanowires and layered structure.
- The photocatalytic activity for methylene blue degradation reach-ed 89%, which is higher than that of pure WO₃ (99%) and significantly superior to that of MXene (54%).
- The nanocomposite demonstrated antibacterial activity against both positive and negative bacterial strains at high concentrations.

Bi₂S₃/MXene:

- The synergistic effect of Bi₂S₃ and MXene was found to improve electrochemical performance, increase the number of active sites for analytical detection, and improve corrosion resistance.
- The nanocomposite was successfully used for Zn(II) detection with high sensitivity.

Ti₃C₂/TiO₂/CuO:

- The ternary nanocomposite showed enhanced photocatalytic activity due to the improved electron-hole separation ability.
- The enhanced photocatalytic efficiency was attributed to the presence of TiO₂ and CuO, which enhanced the interaction with Ti₃C₂.

These results confirm the potential of MXene-based nanomaterials in applications related to ecological remediation, biosensing and environmental monitoring.

The results confirm the significant contribution of MXene-based nanocomposites in improving the properties of sensors and catalysts.

Photocatalytic activity:

The high efficiency of WO₃/MXene in the photocatalytic decomposition of methylene blue can be explained by the combination of MXene (high conductivity) and WO₃ (active catalytic ability) properties. This supports the hypothesis of a synergistic effect in the creation of hybrid nanomaterials. Similarly, Ti₃C₂/TiO₂/CuO nanocomposite demonstrates that the addition of CuO enhances the charge separation ability, which is critical for photocatalysis.

Electrochemical detection:

Bi₂S₃/MXene showed high sensitivity to Zn(II), which is attributed to the increase of active centers on the surface of MXene and its interaction with Bi₂S₃. This result is in line with current research in electrochemistry, where MXene is used as a basic structure to improve the sensor response.

Limitations and prospects:

Despite significant advances, difficulties in scaling up the production of MXene nanocomposites should be considered. Additional research is required to optimize synthesis methods and material stability. Prospects for the use of these materials include expanding their applications in environmental monitoring, biomedicine, and water quality control.

Thus, the results of this study confirm the relevance and promise of MXene-based nanocomposites for the development of high-performance sensors and catalysts. Future research should focus on improving the stability and fabrication processes of these materials.

Conclusion. This literature review is devoted to the detection of heavy metals. Heavy metals are found in many substances. There are many methods for detecting heavy metals. Despite the large number of methods, we must use the most effective of them. The article is written about the detection of heavy metals using a sensor. In order to improve the sensor, various nanomaterials are used. As a material, MXene-based nanocomposites were considered. Focused on MXene-based nanocomposites and sensor research methods developed on their basis. MXene materials are a stable single-phase structure consisting of five or more atoms, and its elemental ratio can be adjusted. MXene contains more transition metals, which greatly optimizes material properties such as conductivity, hardness, chemical stability, and bulk capacity.

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TESTING A NEW TECHNOLOGY OF PROCESSING COPPER ELECTROLYTE TO OBTAIN NICKEL SULFATE

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Complex processing of electrolyte is one of the priority tasks of copper producers. In this work, in order to obtain high-quality copper products and nickel sulfate, the following methods were used: neutralization, demineralization, extraction of impurities (As, Sb, Bi) with pseudo-brookite, additional oxidation of iron to trivalent, neutralization of the solution with nickel carbonate with the release of insoluble compounds of copper, iron and zinc and crystallization of nickel sulfate. The advantage of using basic copper sulfate as a neutralizing agent is the prevention of contamination of the electrolyte with foreign components, as well as its high chemical activity. The quantities required of basic copper sulfate for the implementation of the technology are formed at subsequent stages of processing. High-quality copper sulfate is obtained. Basic copper sulfate is also a raw material for obtaining copper oxide. The removal of such impurities as arsenic, antimony and bismuth is carried out using pseudo-brookite as their extractant. To prevent the ingress of divalent iron into the products, it was oxidized to trivalent by introducing calculated amounts of hydrogen peroxide. The working solution was purified from iron, zinc and residual copper by introducing phosphoric acid and nickel carbonate. Nickel sulfate was isolated from the solution by crystallization, its average yield was 71.6%. Identification of intermediate and target products was carried out by IR spectroscopy and laser atomic emission spectroscopy. The test results showed the efficiency of this method of processing copper electrolyte, aimed at expanding the range of products based on copper and nickel.

Keywords: copper electrolyte, pseudobrookite, nickel sulfate, deep decontamination, copper sulfate, neutralization, crystallization

НИКЕЛЬ СУЛЬФАТЫН АЛУ ҮШІН МЫС ЭЛЕКТРОЛИТІН ҚАЙТА ӨНДЕУДІҢ ЖАҢА ТЕХНОЛОГИЯСЫН СЫНАУ

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Электролитті кешенді өңдеу мыс өндірушілердің басым міндеттерінің бірі болып табылады. Бұл жұмыста жоғары сапалы мыс өнімдері мен никель сульфатын алу үшін келесі әдістер қолданылды: бейтараптандыру, мыссыздандыру, қоспаларды (As, Sb, Bi) псевдобрукитпен экстракциялау, темірді үш валентті темірге дейін тотықтыру, темір, мырыш және мысты ерімейтін қосылыстар түрінде шығару үшін ерітіндіні никель карбонатымен бейтараптандыру және никель сульфатын кристалдандыру. Бейтараптандырушы реагент ретінде негізгі мыс сульфатын пайдаланудың артықшылығы

электролиттің бөгде компоненттермен ластануын болдырмау, сонымен қатар оның жоғары химиялық белсенділігі болып табылады. Технологияны жүзеге асыруға оның қажетті мөлшерлері өндеудің келесі кезеңдерінде қалыптасады. Жоғары сапалы мыс купоросын өндіруді қамтамасыз етеді. Негізгі мыс сульфаты да мыс оксидін алу үшін шикізат болып табылады. Мышьяк, сурьма және висмут сияқты қоспаларды жою үшін экстрагент ретінде псевдобрукит қолданылды. Екі валентті темірдің өнімдерге енуіне жол бермеу үшін оны сутегі асқын тотығының есептік мөлшерін енгізу арқылы үш валентті темірге дейін тотықтырдық. Жұмыс ерітіндісін темірден, мырыштан және мыс қалдықтарынан тазартуға фосфор қышқылы мен никель карбонатын енгізу арқылы қол жеткізілді. Никель сульфаты ерітіндіден кристалдану арқылы бөлініп алынды, оның орташа шығымы 71,6% құрады. Аралық және мақсатты өнімдерді анықтау ИҚ-спектроскопия және лазерлік атомдық эмиссиялық спектроскопия көмегімен жүзеге асырылды. Сынақ нәтижелері мыс пен никель негізіндегі өнімдердің ассортиментін кеңейтуге бағытталған мыс электролитін өндеудің бұл әдісінің тиімділігін көрсетті.

Түйін сөздер: мыс электролиті, псевдобрукит, никель сульфаты, мыс электролитін терең мыссыздандыру, мыс купоросы, бейтараптау, кристаллдау.

ИСПЫТАНИЕ НОВОЙ ТЕХНОЛОГИИ ПЕРЕРАБОТКИ МЕДНОГО ЭЛЕКТРОЛИТА ДЛЯ ПОЛУЧЕНИЯ СУЛЬФАТА НИКЕЛЯ

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Комплексная переработка электролита одна из приоритетных задач производителей меди. В данной работе с целью получения качественной медной продукции и сульфата никеля использованы метод нейтрализации, обезмеживание, экстракция примесей (As, Sb, Bi) псевдобрукитом, доокисление железа до трехвалентного, нейтрализация раствора карбонатом никеля с выделением нерастворимых соединений меди, железа и цинка и кристаллизации сульфата никеля. Преимуществом использования основного сульфата меди в качестве нейтрализующего реагента является недопущение загрязнения электролита посторонними компонентами, а также его высокая химическая активность. Необходимые его количества для реализации технологии образуются на последующих стадиях переработки. Обеспечивается получение качественного медного купороса. Основным сульфат меди является также сырьем для получения оксида меди. Вывод таких примесей, как мышьяк, сурьма и висмут осуществлен применением псевдобрукита в качестве их экстрагента. Для предупреждения попадания двухвалентного железа в продукты, его окисляли до трехвалентного введением расчетных количеств пероксида водорода. Очистка рабочего раствора от железа, цинка и остаточного содержания меди достигалась введением фосфорной кислоты и карбоната никеля. Сульфат никеля выделен из раствора методом кристаллизации, его средний выход составил 71,6%. Идентификация промежуточных и целевого продуктов проведена методами ИК-спектроскопии и лазерной атомно-эмиссионной спектроскопии. Результаты испытаний показали эффективность данного способа переработки медного электролита, направленной на расширение ассортимента продукции на основе меди и никеля.

Ключевые слова: медный электролит, псевдобрукит, сульфат никеля, глубокое обезмеживание, медный купорос, нейтрализация, кристаллизация

Introduction. Processed technological solutions of electrolytic refining of copper contain significant amounts of copper and nickel sulfates, sulfuric acid, arsenic and other components of

copper electrolyte. To avoid the concentration of impurities in the electrolyte, part of the working solution is removed from the process for processing. The process of processing copper electrolyte is aimed at creating conditions for the selective release of harmful and undesirable impurities and ensuring the effective separation of valuable components for their further use in the technological cycle of copper production and obtaining marketable products. Analysis of existing developments [1-11] indicates a number of significant shortcomings in the known technological developments for the removal of arsenic from copper electrolyte and further processing of the solution, such as contamination of the electrolyte with foreign components, loss of copper in the form of copper-arsenate cakes, etc., due to which some of the proposed technologies have not been implemented.

To eliminate copper losses and obtain nickel sulfate, we have developed a new method for processing copper electrolyte [12]. The electrolyte processing process consists of four main stages, followed by vacuum filtration and crystallization of the final product:

- neutralization and deep de-copperization of copper electrolyte;
- extraction of arsenic, antimony and bismuth into the solid phase with pseudobrookite;
- additional oxidation of ferrous iron to ferric;
- deep neutralization of the working solution of carbon nickel with the release of insoluble compounds, iron and zinc, and crystallization of nickel sulfate.

According to the technological scheme, the process of processing copper electrolyte with obtaining nickel sulfate as a target product consists of four main stages:

This stage is carried out under the conditions accurately determined by the authors [12, 13]. The copper electrolyte is preliminarily diluted with water by two times. The latter neutralization is carried out by introducing a copper (II) oxide weighed portion in a molar ratio of $\text{CuO} : \text{Cu} = 3:1$ with constant stirring for four hours at a temperature of 98°C . The basic copper sulphate formed after separation is used to neutralize the electrolyte following portions. This operation is carried out at a temperature of 85°C with constant stirring for 15 minutes until the pH 1.3-1.5 reached. The basic copper sulfate is taken in a molar ratio to sulfuric acid of 2:1. Electrolyte samples are taken throughout the experiment and the solution pH is determined until the required value is reached.

The resulting copper-nickel mother liquors are re-diluted with water 2 times and subjected to deep de-curing with copper (II) oxide ($\text{CuO}:\text{Cu} = 3:1$) at 98°C for four hours with constant stirring.

2. The arsenic, antimony and bismuth extraction into the solid phase with the help of pseudobrookite is carried out in accordance with the method developed by us earlier [14].

The process is carried out in a thermostated cell at a temperature of 60°C with a given sulfuric acid concentration at constant stirring for one hour. A pseudobrookite weighed portion is taken equal to the ratio of the precipitant to arsenic 1:1 and served in two portions (the precipitant (DRP) dosage ratio is equal to 2). The hot solutions are then filtered out. The precipitate is separated from the resulting solution.

3. Additional oxidation of ferrous iron to ferric iron is carried out according to the conditions strictly specified by the authors [15]: a 50% solution of hydrogen peroxide is used as an oxidizing reagent, which is introduced into solutions at a temperature of 55°C , the oxidation process takes 1 hour with constant stirring. The amount of hydrogen peroxide required to oxidize all Fe^{2+} ions to Fe^{3+} is calculated from the reaction equation:

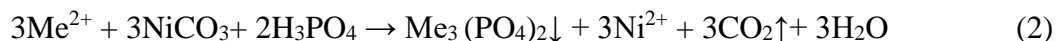


4. Deep neutralization of the working solution with nickel carbonate with the release of insoluble compounds of copper, iron and zinc, and crystallization of nickel sulfate.

Before deep neutralization of the electrolyte with nickel carbonate, it is necessary to transfer iron, zinc and the residual content of copper in solutions into a solid phase.

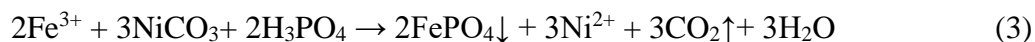
For this purpose, an 87% solution of orthophosphoric acid in a predetermined amount is injected into the working solutions. Orthophosphoric acid in a stoichiometric ratio is injected to

bind impurities into sparingly soluble phosphates according to the reaction equation:



whereas – Me^{2+} - ions Cu^{2+} and Zn^{2+} .

With the participation of the Fe^{3+} ion, the reaction proceeds according to the following equation:



Then the solutions are heated to 85⁰C with stirring. Water is added in an amount calculated from the reaction equation and heated further to 90⁰C. A nickel carbonate predetermined amount is added to the heated solutions in portions.

The solutions are constantly stirred and maintained at a temperature of 90⁰C for one and a half hours. When adding each portion, it is necessary to take a sample and measure the solutions pH. Measurements of pH are carried out until the value of 5.5-5.9 is set. With each pH measurement, the samples are cooled to a temperature of 23-25⁰C. Then the solutions are maintained at a temperature of 90⁰C. The authors of [15] found required conditions under which precipitates of iron, copper and zinc insoluble salts are formed, namely pH = 5.5-5.9.

At the process end, the solutions are subjected to vacuum filtration in a hot state. Unreacted nickel carbonate as well as copper, iron and zinc salts insoluble precipitates remain on the filter. The solutions pH is brought to values of ≈ 1.99 -2.02 with the help of adding the calculated amounts of concentrated sulfuric acid. The authors of [15] established that this pH limit is the conditions under which the nickel sulfate crystallization occurs. Further, the investigated solutions are cooled to a temperature of 20-23⁰C and left to stay aside for the nickel sulfate crystallization.

The purpose of this work is to test a new technology of processing of copper electrolyte with the removal of copper in the form of products assalts and hydroxides in large-scale laboratory conditions, and obtain a new product - nickel sulfate in accordance with the technological scheme developed by us (Figure 1).

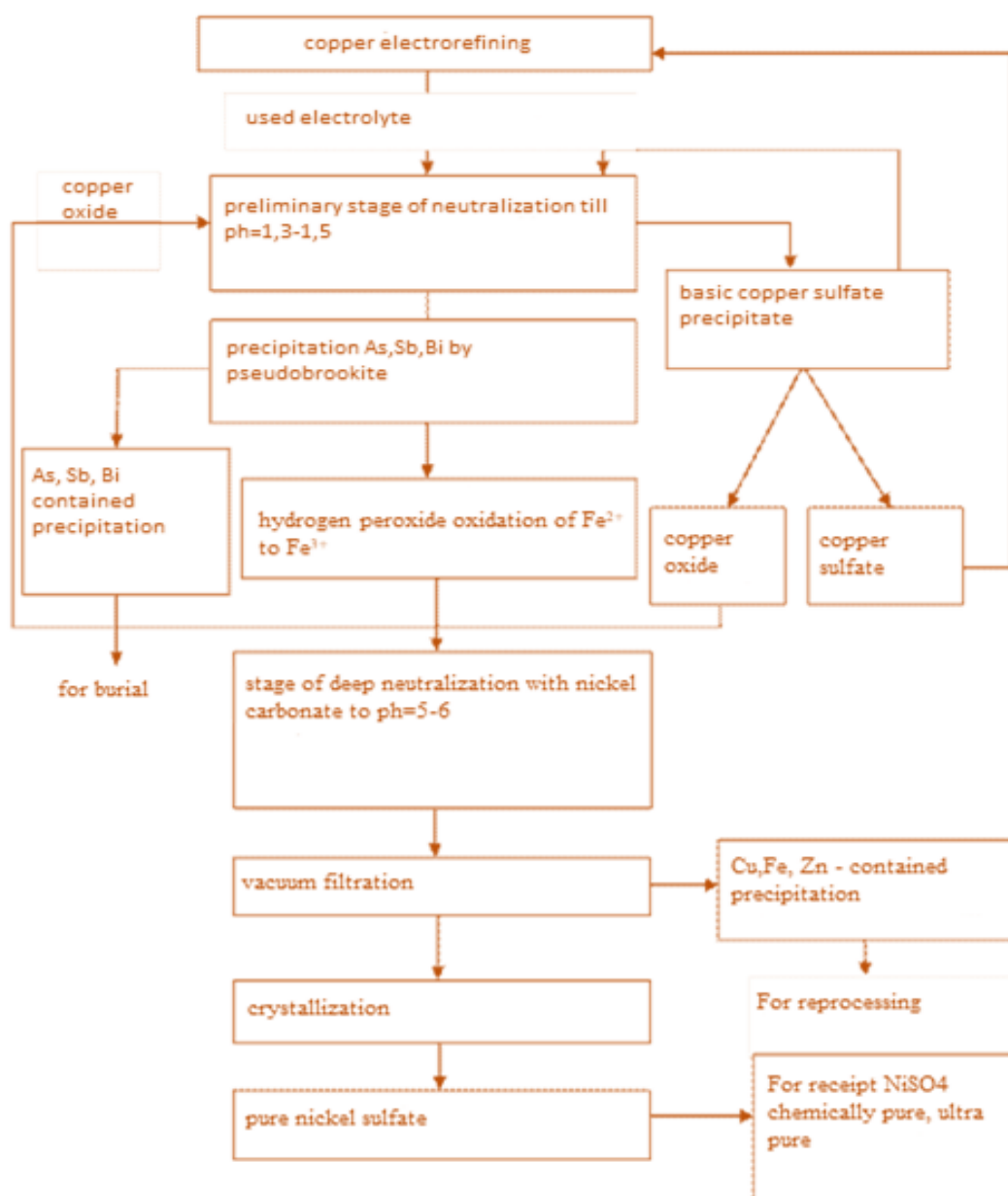


Fig. 1 -Technological scheme of the integrated processing of copper electrolyte to obtain nickel sulfate

Materials and methods. The object of large-scale laboratory tests is the technological copper-containing sulfuric solution of the corporation "KAZAKHMYS SMELTING" (Republic of Kazakhstan, city of Balkhash). The quantitative content of the main components of the process solution (Cu, Ni, H₂SO₄, As, Sb, Bi, Fe, Zn) was determined on a SPEKS SSP-705-4 scanning spectrophotometer, as well as on a laser atomic emission spectrometer SPEKS LAES MATRIX CONTINUUM (Closed Joint Stock «Company Spectroscopic Systems» Russian Federation, 2016) , the results of which are presented in Table 1.

Large-scale laboratory tests were carried out with a volume of the working solution equal to 500 ml.

Table 1 - Electrolytecomposition

Component	Cu	Ni	H ₂ SO ₄	As	Sb	Bi	Fe	Zn
g/l	51.20	16.98	95.88	14.04	8.63	5.78	9.42	9.17

Results and discussion. Based on known methods for processing copper electrolyte [12,14], 500 ml of water was added to a copper electrolyte with a volume of 500 ml, and treated with 96 g of copper (II) oxide in a molar ratio $\text{CuO}:\text{Cu} = 3:1$. The reaction mass was heated in a thermostated cell to 98°C with constant stirring for four hours. The solution volume was decreased by 2 times at the end of the neutralizing process. The solution was filtered in a hot state, resulting in a precipitate of basic dark green copper sulfate weighing 406.59 g on the filter. Further, basic copper sulfate obtained in an amount of 348.3 g was used for subsequent neutralization of copper electrolyte with a volume of 500 ml for each experiment.

The neutralization of free sulfuric acid was carried out for 15 min in a thermostated cell at a temperature of 85°C . The solution pH was monitored during the experiment until its values reached 1.31. Hot solutions were subjected to vacuum filtration, and then cooled to a temperature of 20°C . Copper sulfate weighing ≈ 43.8 g was obtained in each experiment. The solutions were analyzed for the residual content of sulfuric acid, copper, nickel, and arsenic. The average values of the investigation results are shown in Table 2.

Table 2 - Results of the copper electrolyte neutralization process
($\text{Cu}_3(\text{OH})_4\text{SO}_4:\text{H}_2\text{SO}_4 = 2:1$; $t = 85^{\circ}\text{C}$; $\tau = 15$ min)

pH of working solution		$\text{H}_2\text{SO}_4(\text{g/l})$	$\text{Cu}(\text{g/l})$	$\text{Ni}(\text{g/l})$	$\text{As}(\text{g/l})$
Before experiment	After experiment				
0.08	1.31	2.79	31.0	16.70	14.03

The obtained copper-nickel mother liquors were re-diluted with water 2 times and subjected to de-curing with copper (II) oxide. Width of the confidence interval according to the Cochran criterion for copper content $\Delta = 0.18\delta = 2\Delta$.

The resulting basic copper sulfate weighing 24.99 g was used to neutralize the next portion of the electrolyte. The main copper sulfate is also a raw material for the production of copper oxide, copper sulfate. The resulting solutions, after neutralization and de-curing of the electrolyte, were analyzed for the residual content of sulfuric acid, copper, nickel, and arsenic. The average values of the analysis results are shown in Table 3.

Table 3 - Copper electrolyte dressing from copper results
($\text{CuO}:\text{Cu} = 3:1$; $t = 98^{\circ}\text{C}$; $\tau = 4$ hour)

pH of working solution		$\text{H}_2\text{SO}_4(\text{g/l})$	$\text{Cu}(\text{g/l})$		$\text{Ni}(\text{g/l})$	$\text{As}(\text{g/l})$
Before experiment	After experiment		Before experiment	After experiment		
1.31	2.37	0.21	31.0	0.79	16.5	14.01

Copper-bearing sediments were identified by IR spectroscopic analysis (Figure 2). According to reference data [15], intense absorption bands at $1106\text{-}1366\text{ cm}^{-1}$ and $451\text{-}621\text{ cm}^{-1}$ are related to the sulfate ion. Also, a band in the region of $3140\text{ - }3433\text{ cm}^{-1}$ is characteristic of stretching vibrations of OH-groups, and absorption bands at $1340\text{-}1627\text{ cm}^{-1}$ associated with the presence of water molecules in a highly hydrated sediment. Based on the data of the IR spectra of the precipitate and the results of photometric analysis for copper, it was established that the resulting precipitate is the main copper sulfate $\text{Cu}_3(\text{OH})_4\text{SO}_4$.

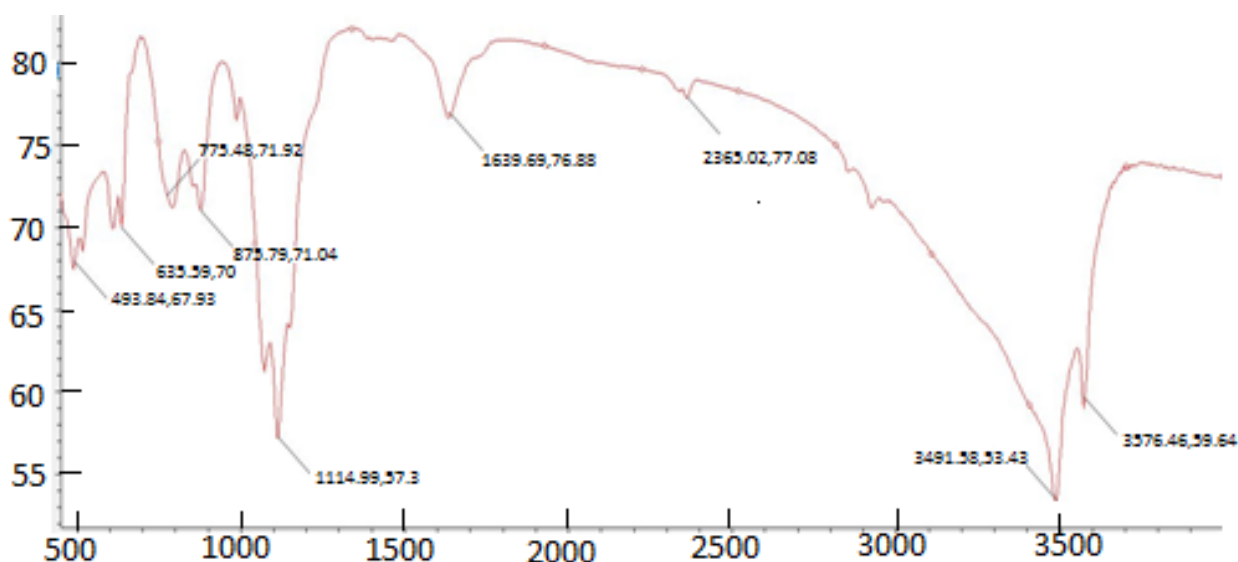


Fig. 2 - IR spectrogram of a copper-bearing precipitate

Additionally, the analysis for the content of impurities in the resulting sediment was carried out on a laser atomic emission spectrometer SPEX LAES MATRIX CONTINUUM (Figure 3). As can be seen from the spectrogram, intense green peaks are observed, which correspond to copper ions. The presence of such impurities as iron, zinc, arsenic, antimony, bismuth in the composition of the precipitate is not observed on the spectrogram. Thus, the resulting basic copper sulfate does not contain foreign impurities of other metals and is a chemically pure compound.

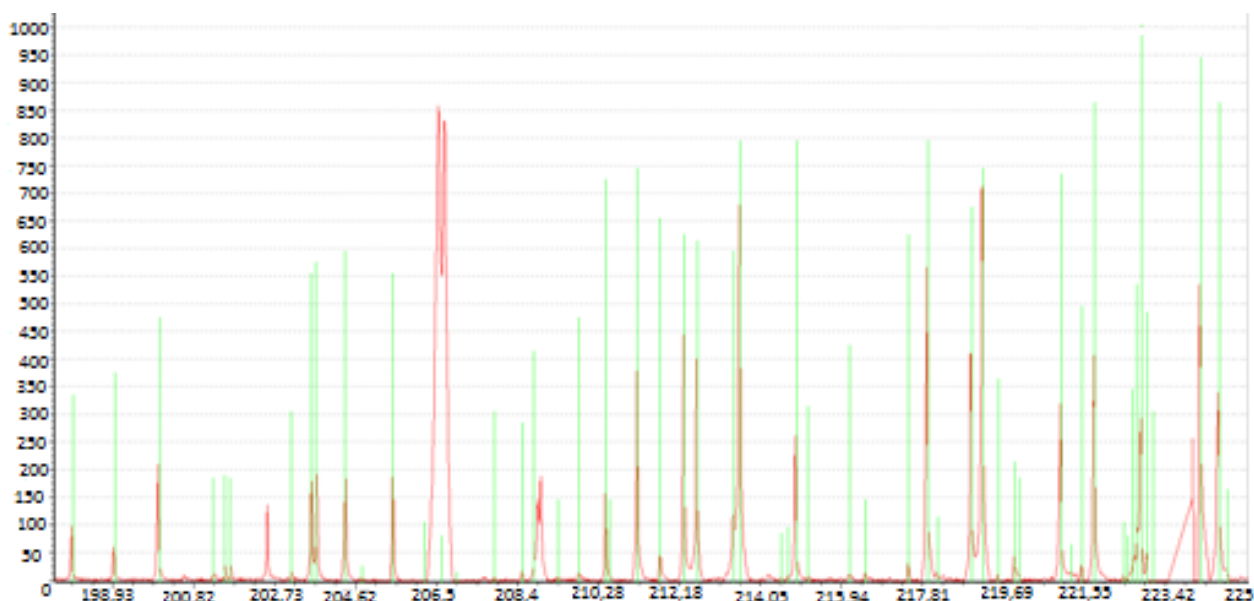


Fig. 3 – Laser spectrogram of copper-bearing sediment

The deposition of arsenic, antimony and bismuth with pseudobrookite was carried out in a thermostated cell at a temperature of 60°C, with a given concentration of sulfuric acid with constant stirring for one hour. We used the resulting solutions with a volume of 182 ml each. A weighed portion of pseudobrookite was taken equal to the ratio of the precipitant to arsenic 1:1 in the amount of 14.01 g and fed in two portions (DRP= 2). Then the solution was filtered while hot, the resulting filtrates with a volume of 165 ml were analyzed for the residual arsenic content, antimony and bismuth in them. The results of analyzes for the residual content of antimony, bismuth arsenic, shown in Table 4, showed that their content in solutions is reduced to trace amounts, i.e., the resulting solutions are almost completely purified from them.

For the oxidation of Fe^{2+} ions to Fe^{3+} , 3.1 ml of hydrogen peroxide was introduced into solutions with a volume of 158 ml of each experiment. Then the solutions were stirred for one hour in a thermostated cell at a temperature of 50-55°C. At the end of the experiments, the solutions were cooled and analyzes were carried out for the total iron content and for Fe^{3+} , the results of all analyzes of the experiments were averaged (g/l): $C(\text{Fe}_{\text{tot}}) = 6,035$; $C(\text{Fe}^{3+}) = 6,030$. Under these conditions, complete oxidation of Fe^{2+} to Fe^{3+} ions is achieved.

In order to purify working solutions from ions of copper, iron, zinc ($C(\text{Zn}^{2+}) = 6.7$ g/l; $C(\text{Fe}^{3+}) = 6.03$ g/l; $C(\text{Cu}^{2+}) = 0.79$ g/l) a solution of phosphoric acid in the amount of 13.8 ml were added in them.

Then the solutions were heated with stirring to 85°C, added H_2O in an amount of 25.5 ml, and the solutions were heated to 90°C. Nickel carbonate weighing 12.62 g was added to the heated solution in portions. The solutions were constantly stirred and kept at a temperature of 90°C for 1.5 hours. With the addition of each portion of nickel carbonate, a sample was taken and the pH of the solutions was measured. Nickel carbonate was added until a pH of about 5.98 was reached.

Insoluble precipitates and unreacted nickel carbonate were separated by vacuum filtration. 0.1 ml of concentrated sulfuric acid was added to the filtrate, after the addition of which the pH of the solutions reached a value of ≈ 2.39 .

At the end of the process, the solution was subjected to vacuum filtration while hot. Insoluble sediments weighing 2.19 g remained on the filter. Then the test solution was cooled to a temperature of 20-23°C. Crystals of nickel sulfate began to grow in the solution on the seventh day. The crystals were separated from the working solution by filtration, washed with distilled water, dried, and weighed. As a result, we got 66.35 g heptahydrate nickel sulfate, on average in each experiment.

Table 4 – The results of the precipitation of arsenic, antimony and bismuth by pseudobrookite ($t = 60^\circ\text{C}$; $\tau = 1$ hour; $\text{DRP} = 2$)

№ Experiment	$\text{Fe}_2\text{TiO}_5\text{:As}$	Concentration after experiment, (g/l)			Degree of precipitation, %		
		As	Sb	Bi	As	Sb	Bi
1	0.5:1	0.070	0.0023	0.0011	99.15	99.85	99.88
2	0.8:1	0.032	0.0016	0.0005	99.67	99.89	99.90
3	1:1	Traces	Traces	Traces	99.99	99.99	99.99
4	1.2:1	Traces	Traces	Traces	99.99	99.99	99.99
5	1.5:1	Traces	Traces	Traces	99.99	99.99	99.99

Calculated the average yield of the target product of nickel sulfate. The theoretical mass of the target product according to calculations from the reaction equations:



was 92.59 g. The average yield of the target product of nickel sulfate was 71.66% of the theoretically possible.

Analysis of the obtained IR spectra of nickel sulfate crystals (Figure 4) confirmed the absence of copper, iron and zinc impurities in nickel sulfate crystals. In the figure, one can see intense bands at 1106-1366 cm^{-1} and 451-621 cm^{-1} , which corresponds to the absorption bands of sulfate ions; in addition, bands are observed in the region of 1340-1670 cm^{-1} , characteristic of the presence of crystallized water in a highly hydrated sediment. It is also possible to observe low-intensity absorption bands in the region of 3440-3470 cm^{-1} characteristic of stretching vibrations of OH-groups, and an insignificant absorption band at 2830-2850 cm^{-1} related to the carbonate ion [15]. That is, the obtained crystals were confirmed to be nickel sulfate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$).

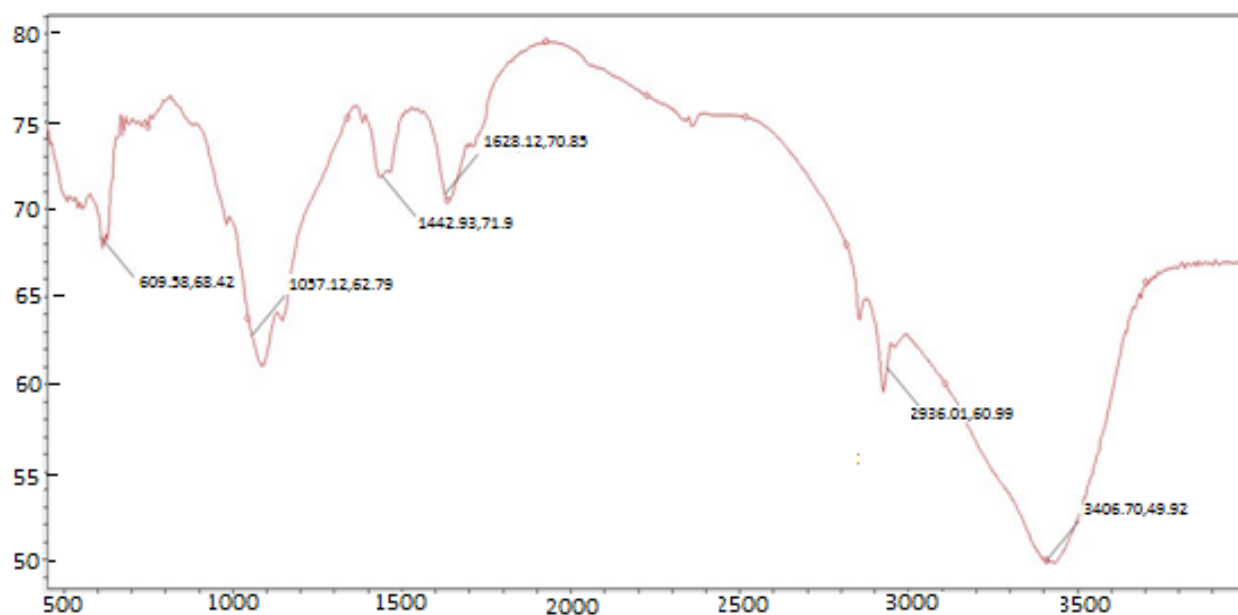


Fig. 4 - IR spectra of crystals of the obtained nickel sulfate

The nickel sulfate obtained as a result of large-scale laboratory tests, as noted earlier, does not contain metal impurities, and can be used as a raw material for obtaining nickel sulfate of reagent grade, special grade, which in turn confirms the technological significance of the tests carried out and the effectiveness of the technological scheme of the new technology for processing copper electrolyte (Figure 1).

Conclusion. The large-scale laboratory tests have shown the efficiency of the new technology of processing copper electrolyte and the possibility, along with obtaining marketable copper products: basic copper sulfate, copper oxide, copper sulfate, to expand the range of products of vitriol processing based on nickel - nickel sulfate. The results of large-scale laboratory tests can serve as initial data for planning and conducting subsequent production tests of a new technology of processing copper electrolyte.

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