IRSTI 31.23.99 **https://doi.org/10.58805/kazutb.v.1.26-660**

STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF FULVIC ACID SOLUTIONS

[1,2]M.K. Kazankapova, [1]B.T. Yermagambet, [1,2]A.B. Malgazhdarova, [1]Zh.M. Kassenova, [2]Zh.E. Jakupova

[1] «Institute of Coal Chemistry and Technology» LLP, Astana, Kazakhstan,
[2] L.N. Gumilyov Eurasian National University, Astana, Kazakhstan,
Correspondent-author: malgazhdarova.ab@mail.ru

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

[1]М.Қ. Қазанқапова, [1]Б.Т. Ермағамбет, [1,2]А.Б. Малғаждарова, [1]Ж.М. Касенова, [2]Ж.Е. Джакупова[2]

[1] «Көмір химиясы және технология институты» ЖШС, Астана, Қазақстан,
[2] Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Астана, Қазақстан,
e-mail: malgazhdarova.ab@mail.ru

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, коректік 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

[1]М.К. Казанкапова, [1]Б.Т. Ермағамбет, [1,2]А.Б. Малгаждарова ✉, [1]Ж.М.Касенова, [2]Ж.Е. Джакупова

[1]ТОО «Институт химии угля и технологии», Астана, Казахстан,
[2]Евразийский национальный университет им. Л.Н. Гумилева, Астана, Казахстан,
e-mail: malgazhdarova.ab@mail.ru

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.

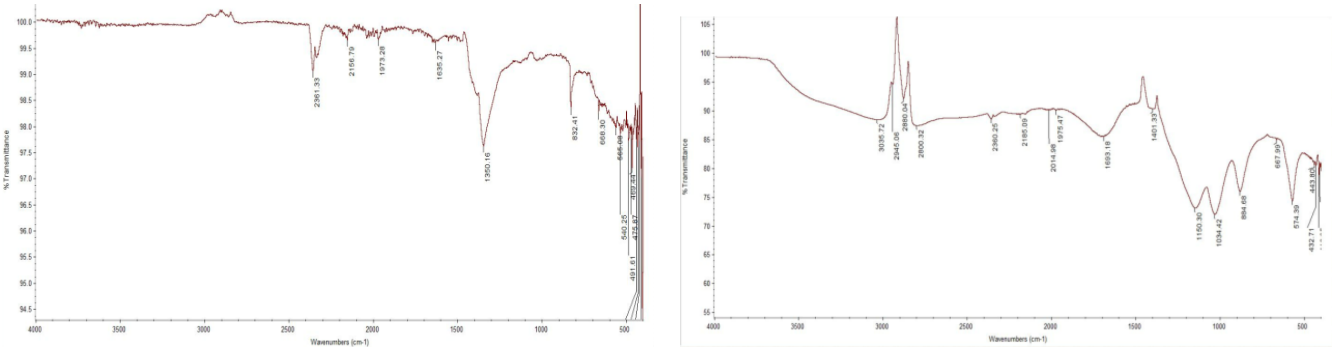
Table 1 - Characteristics of coconut-based activated charcoal Extrasorb GAC (12x40)

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.

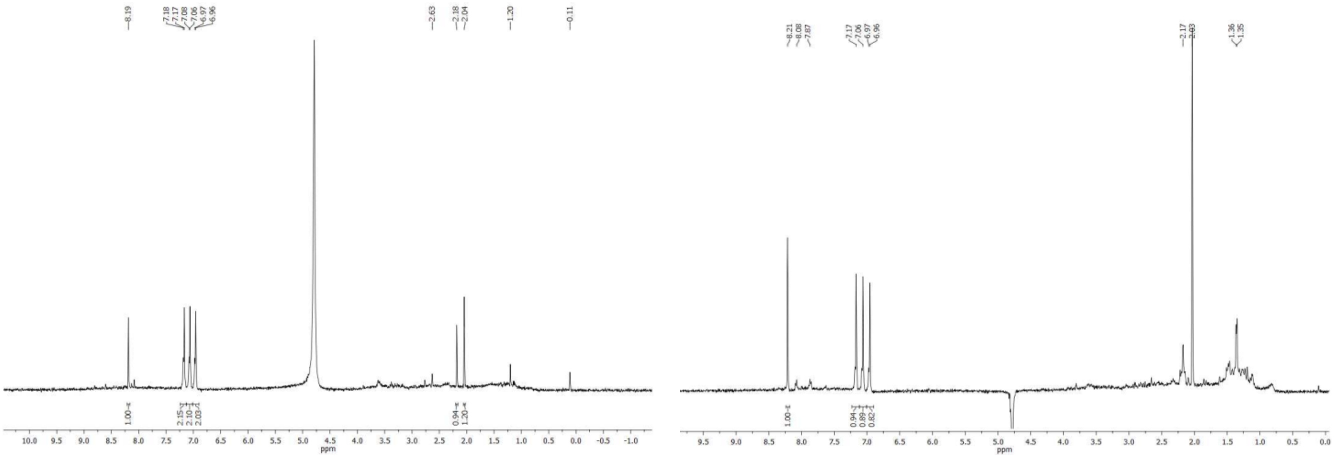
Results and discussion. The IR spectra of fulvic acids were obtained in the Laboratory of Organometallic Chemistry and Catalysis at Nazarbayev University (Kazakhstan) using a Nicolet iS10 FT-IR spectrometer.

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 (C≡N) or cumulenes. A moderately intense peak around 1693 cm^{-1} indicates the presence of a carbonyl group (C=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 C=O and OH group bands indicates the removal of impurities and the improvement of the composition of the purified sample (Figure 1).



Original fulvic acid derived from potassium humate **Purified fulvic acid**

Fig. 1 - IR Spectra Analysis



Original fulvic acid derived from potassium humate **Purified fulvic acid**

Fig. 2 - NMR Spectra Analysis

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.

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/dm3 - toxic elements, mg/dm3: - Lead (Pb) - Arsenic (As) - Cadmium (Cd) - Mercury (Hg)	 0.3 0.1 0.03 0.005	1356.0±0.058 Not found Not found Not found 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/dm3: - Lead (Pb) - Arsenic (As) - Cadmium (Cd) - Mercury (Hg)	 0.3 0.1 0.03 0.005	 Not found Not found Not found Not found
- antioxidant content, mg/dm3 - dry matter content. % - aflatoxin Bi. mg/l - titratable acidity, %	 1.0-3.5 0.7-3.8	138.16±0.042 Not found Not found 0.24±0.02
Pesticides, mg/kg, not more than: - Hexachlorocyclohexane (alpha, beta, gamma isomers) - 4,4 - dichlorodiphenyltrichloromethylmethane and its metabates	 0.01 0.005	 Not found Not found
Amino acid composition, % - water soluble, mg/100 g - B1 (thiamine chloride) - B3 (pantothenic acid) - B6 (pyridoxine) - Bc (folic acid)		Not found Not found Not found Not found Not found

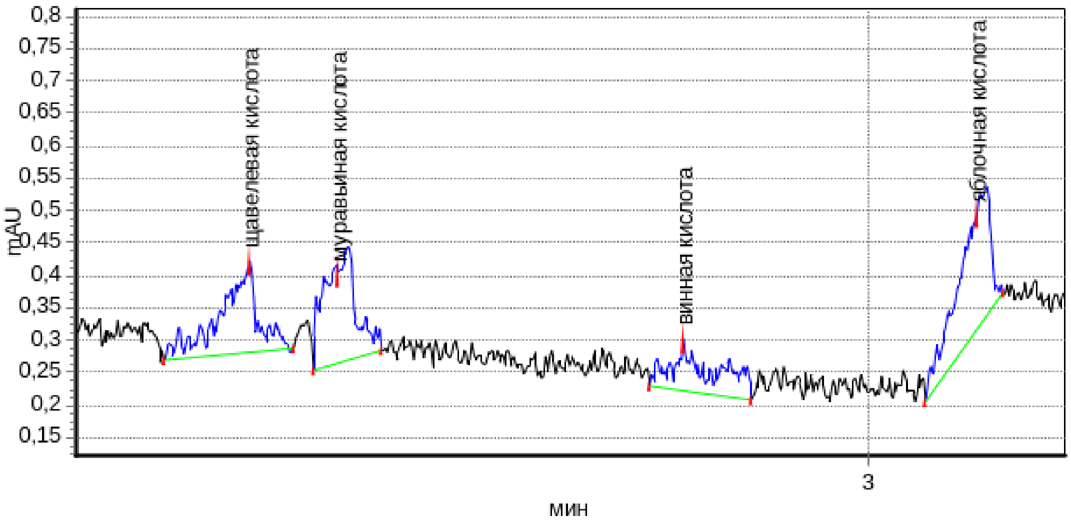


Fig. 3 - Chromatograms of organic acid content in the model fulvic acid solution

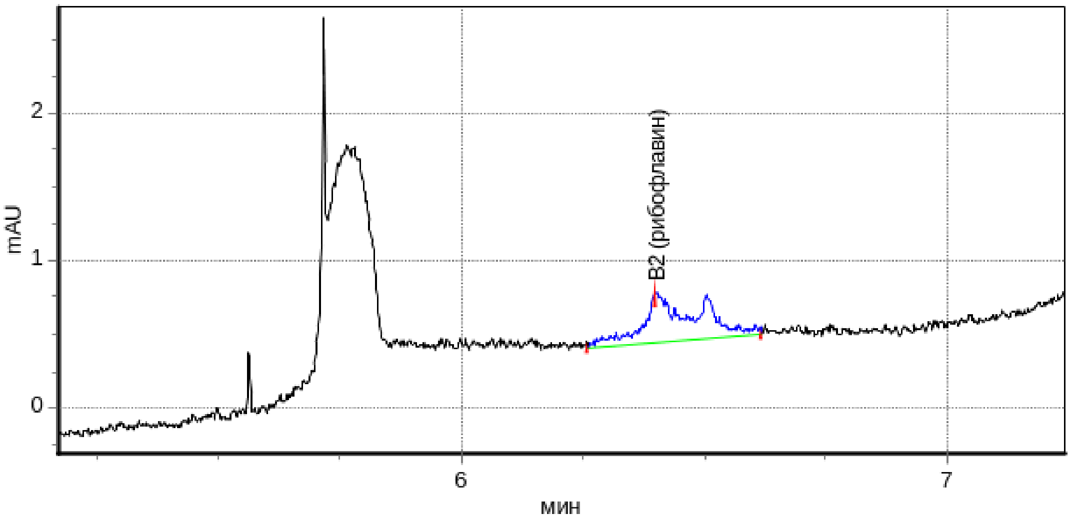


Fig. 4 - Chromatograms of amino acid content in the model fulvic acid solution

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).

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.

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.

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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Information about the authors

Kazankapova M.K. - PhD , assoc. professor, member correspondent of the KazNANS, Leading Researcher, Head of Laboratory of LLP «Institute of Coal Chemistry and Technology», Astana, Kazakhstan, e-mail: maira_1986@mail.ru;

Yermagambet B.T. - Doctor of Chemical Science, rofessor, Academician of the KazNANS, Project Manager, Chief Researcher, Director of LLP «Institute of Coal Chemistry and Technology», Astana, Kazakhstan, e-mail: bake.yer@mail.ru;

Malgazhdarova A.B.- master student Eurasian National University of L.N. Gumilyov, Junior Researcher «Institute of Coal Chemistry and Technology», Astana, Kazakhstan, e-mail: malgazhdarova.ab@mail.ru;

Kassenova Z.M.- Candidate of Technical Sciences (PhD), Leading Researcher LLP «Institute of Coal Chemistry and Technology», Astana, Kazakhstan, e-mail: zhanar_k_68@mail.ru;

Jakupova Zh.E. - Candidate of Chemical Sciences, associate Professor Eurasian National University of L.N. Gumilyov, Astana, Kazakhstan, e-mail: zhanereke@mail.ru

Сведения об авторах

Казанкапова М. К. -PhD, асс. профессор, чл.-корр. КазНАЕН, ведущий научный сотрудник, заведующий лабораторией ТОО «Институт химии угля и технологии», Астана, Казахстан, e-mail: maira_1986@mail.ru;

Ермагамбет Б.Т.-доктор химических наук, профессор, академик КазНАЕН, руководитель проекта, главный научный сотрудник, директор ТОО «Институт химии угля и технологии», Астана, Казахстан, e-mail: bake.yer@mail.ru;

Малгаждарова А. Б.- магистрант Евразийского национального университета им. Л.Н. Гумилева, младший научный сотрудник ТОО «Институт химии угля и технологии», Астана, Казахстан, e-mail: malgazhdarova.ab@mail.ru;

Касенова Ж. М.- кандидат технических наук (PhD), ведущий научный сотрудник ТОО «Институт химии угля и технологии», Астана, Казахстан, e-mail: zhanar_k_68@mail.ru;

Джакупова Ж.Е. - кандидат химических наук, доцент кафедры химии Евразийский национальный университета им. Л.Н. Гумилева, Астана, Казахстан, e-mail: zhanereke@mail.ru