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CONTENTS

PHYSICS

U.A. Ualikhanova, Y.Y. Kurban, A.M. Syzdykova, A.B. Altaibayeva, G.S. Altayeva
Dynamical systems analysis of the Starobinsky cosmological model.....11

M.B. Zhassybayeva, Z. Myrzakulova, M. Abeuova
Darboux transformation for the two-layer M-LXXII equation.....24

G.K. Beketova, N.N. Zhanturina, Z.K. Aimaganbetova
Cs₂AgBiBr₆ double halide perovskites as advanced materials for high-efficiency solar cells.....38

L.I. Shestakova, R.R. Spassyuk
Spectral studies of the k-f corona interface at 5000–6000 Å.....52

A.Khazhidinova, A. Khazhidinov
On the issue of fuel consumption of a thermal power plant.....66

T.B. Koshtybayev, K.K. Zhantleuov, M.E. Aliyeva
Greens function in the theory of quantum fluids.....77

A.V. Serebryanskiy, Ch.B. Akniyazov, Ch.T. Omarov, S. Sittykova, D. Kadyrova
Analysis of lunar impact flashes statistics.....91

G.T. Omarova, Zh.T. Omarova
The Lagrange - Jacobi equation and its application to the N - body problem.....105

Zh. Muratkhan, M. Khassanov
Methods for estimation of stellar wind parameters in high-mass X-ray binary systems with neutron stars.....113

V. Mukamedenkyzy, A. Izbasar, A. Aqikat
Investigation of structured flows induced by concentration-driven convection in ternary gases systems.....127

K. Saurova, S. Nysanbaeva, G. Turlybekova
Modeling of the optical system of a star tracker for accurate spacecraft attitude determination.....140

CHEMISTRY

- B.S. Serikbayeva, M.S. Satayev, N.K. Sarypbekova**
Study of the electroplating process on polypropylene using a conductive layer.....157
- A.P. Auyeshov, Ch.Z. Yeskibayeva, A.K. Dikanbayeva**
Resource-efficient utilization of serpentinite waste for magnesium sulfate production.....172
- A.K. Kozybaev, Zh.D. Alimkulova, S.O. Abilkasova**
Kinetic and thermodynamic studies of heavy metal adsorption onto water-washed Ca-montmorillonite clay.....184
- A.Abdрахmanova, V. Krivchenko, A. Sabitova1, B. Kuderina**
DOL-enhanced electrolytes as a route to stable anodes in Li–V₂O₅ systems.....196
- B.K. Massalimova, A.S. Shayakhmetova, A.S.Darmenbayeva**
Water resources of Northern Kazakhstan: environmental monitoring and sustainable anagement.....208
- A. Rakhimov, N. Zhanikulov, B. Taimasov, E. Potapova, A.K. Sviderskiy**
Investigation of lead slag processing waste as raw material for cement industry.....227
- L.M. Kalimoldina, K.Zh. Zhalgasbayev, A.S. Dauletbayev**
Comparative study of industrial wastewater treatment methods.....241
- A. Nurlan, S.R. Konuspayev, T.S. Abildin, K. Toshtay**
Transformations of hydrocarbons during the hydrogenation of gasoline containing benzene.....256
- G.J. Baisalova, B.K. Yertay, A.A. Taltenov, P. Kuzhatova, G. Saspugayeva**
A quantitative determination of the phenol compounds sum in the thallus of *Parmelia sulcata*.....274
- B.E. Myrzabekov, A.B. Makhanbetov, T.E. Gaipov, B.S. Abzhalov, N.N. Nurgaliyev**
Electrochemical reduction of manganese (II) ions on titanium and lead electrodes.....286
- A.S. Darmenbayeva, G.M. Zhussipnazarova, R. Reshmy, Zh.B. Mukazhanova, V.A. Rube**
Biocoatings based on flax stem cellulose and their properties.....298

МАЗМҰНЫ

ФИЗИКА

| | |
|--|-----|
| У.А. Уалиханова, Е.Е. Құрбан, А.М. Сыздыкова, А.Б. Алтайбаева, Г.С. Алтаева Старобинскийдің космологиялық моделін динамикалық жүйелер арқылы талдау..... | 11 |
| М.Б. Жасыбаева, Ж. Мырзақұлова, М. Абеуова Қос қабатты M-LXXII теңдеуі үшін дарбу түрлендіруі..... | 24 |
| Г.К. Бекетова, Н.Н. Жантурина, З.К. Аймағанбетова Cs ₂ AgBiBr ₆ қос галоидты перовскиттер: күн батареяларына арналған тиімділігі жоғары жаңа озық материалдары..... | 38 |
| Л.И. Шестакова, Р.Р. Спасюк 5000–6000 Å диапазонында k- және f-короналар арасындағы өтпелі аймақты спектрлік зерттеу..... | 52 |
| А. Хажидинова, А. Хажидинов Жылу электр станциясының отын тұтыну мәселесі..... | 66 |
| Т.Б. Қоштыбаев, К.Қ. Жантлеуов, М.Е. Алиева Кванттық сұйықтар теориясындағы Грин функциялары..... | 77 |
| А.В. Серебрянский, Ч.Б. Акниязов, Ч.Т. Омаров, С. Ситтыкова, Д. Кадырова Айдың беткі қабатына метеоридтардың соқтығысуын статистикалық тұрғыдазерттеу..... | 91 |
| Г.Т. Омарова, Ж.Т. Омарова Лагранж – Якоби тундеуі және оны N -денелі есепке қолдану..... | 105 |
| Ж. Мұратхан, М. Хасанов Нейтрон жұлдыздары бар массивті рентгендік екілік жүйелердегі жұлдыздық жел параметрлерін бағалау әдістері..... | 113 |
| В. Мукамеденқызы, А. Избасар, А. Ақиқат Үшкомпонентті газ жүйелеріндегі концентрациялық конвекцияның әсерінен құрылымдық ағындардың пайда болуын зерттеу..... | 127 |
| К. Саурова, С. Нысанбаева, Г. Турлыбекова Ғарыш аппараттарының ориентациясын нақты анықтау үшін жұлдыз сенсорының оптикалық жүйесін модельдеу..... | 140 |

ХИМИЯ

Б.С. Серикбаева, М.С. Сагаев, Н.К. Сарыпбекова

Электрөткізгіш қабатты қолданып, полипропиленге гальваникалық қаптама алу процесін зерттеу.....157

А.П. Ауешов, Ч.З. Ескибаева, А.К. Диканбаева

Серпентинит қалдығынан магний сульфатын алудың техникалық-экономикалық зерттеуі.....172

А.К. Қозыбаев, Ж.Д. Әлімқұлова, С.О. Әбілқасова

Сумен жуылған са-монтмориллонит сазында ауыр металдардың сорбциясының кинетикасы мен термодинамикасы.....184

А. Абдрахманова, В. Кривченко, А. Сабитова, Б. КудеринаLi–V₂O₅ жүйесіндегі тұрақты анодтарға қол жеткізуге арналған DOL-мен модификацияланған электролиттер.....196**Б.К. Масалимова, А.С. Шаяхметова, А.С. Дарменбаева**

Солтүстік Қазақстанның су ресурстары: экологиялық мониторинг және ұтымды басқару.....208

А. Рахимов, Н. Жаникулов, Б. Таймасов, Е. Потапова, А.К. Свидерский

Цемент өнеркәсібі үшін шикізат ретінде қорғасын қожын өңдеу қалдықтарын зерттеу.....227

Л.М. Калимолдина, Қ.Ж. Жалғасбаев, А.С. Даулетбаев

Өнеркәсіптік сарқынды суларды тазартудың әдістерін салыстырмалы түрде зерттеу.....241

Ә. Нұрлан, С.Р. Конуспаев, Т.С. Абильдин, К. Тоштай

Құрамында бензол бар бензинді гидрлеу кезінде көмірсутектердің өзгеруі.....256

Г.Ж. Байсалова, Б.К. Ертай, А.А.Талтенов, П. Кужатова, Г.Е. Саспугаева*PARMELIA SULCATA* талломындағы фенолды қосылыстардың жиынтық мөлшерін сандық анықтау.....274**Б.Э. Мырзабеков, А.Б. Маханбетов, Т.Э. Гаипов, Б.С. Абжалов, Н.Н. Нұрғалиев**

Марганец (II) ионының титан және қорғасын электродында электрохимиялық тотықсыздануы.....286

А.С. Дарменбаева, Г.М. Жусипназарова, Р. Решми, Ж.Б. Мукажанова, В.А. Рубе

Зығыр сабағынан алынған целлюлоза негізіндегі биожабындар және олардың қасиеттері.....298



СОДЕРЖАНИЕ

ФИЗИКА

| | |
|--|-----|
| У.А. Уалиханова, Е.Е. Курбан, А.М. Сыздыкова, А.Б. Алтайбаева, Г.С. Алтаева Анализ космологической модели старобинского с помощью динамических систем..... | 11 |
| М.Б. Жасыбаева, Ж. Мырзакулова, М. Абеуова Преобразование Дарбу для двухслойного уравнения M-LXXII..... | 24 |
| Г.К. Бекетова, Н.Н. Жантурина, З.К. Аймаганбетова Cs ₂ AgBiBr ₆ : двойные галоидные перовскиты как передовые материалы для высокоэффективных солнечных элементов | 38 |
| Л.И. Шестакова, Р.Р. Спасюк Спектральные исследования области перехода между К и F короной в диапазоне 5000–6000Å..... | 52 |
| А. Хажидинова, А. Хажидинов К вопросу о расходе топлива на тепловой электростанции..... | 66 |
| Т.Б. Коштыбаев, К.К. Жантлеуов, М.Е. Алиева Функции Грина в теории квантовых жидкостей | 77 |
| А.В. Серебрянский, Ч.Б. Акниязов, Ч.Т. Омаров, С. Ситтыкова, Д. Кадырова Исследование статистики ударов метеороидов о поверхность луны | 91 |
| Г.Т. Омарова, Ж.Т. Омарова Уравнение Лагранжа – Якоби и его применение к задаче N -тел..... | 105 |
| Ж. Муратхан, М. Хасанов Методы оценки параметров звездного ветра в массивных двойных рентгеновских системах с нейтронными звездами..... | 113 |
| В. Мукамеденкызы, А. Избасар, А. Акикат Исследование возникновения структурированных течений, обусловленных концентрационной конвекцией в трёхкомпонентных газовых системах..... | 127 |
| К. Саурова, С. Нысанбаева, Г. Турлыбекова Моделирование оптической системы звёздного датчика для точного определения ориентации космических аппаратов..... | 140 |

ХИМИЯ

Б.С. Серикбаева, М.С. Сатаев, Н.К. Сарыпбекова

Исследование процесса гальванопокрытия на полипропилене с использованием электропроводного слоя.....157

А.П. Ауешов, Ч.З. Ескибаева, А.К. Диканбаева

Технико-экономическое исследование получения сульфата магния из серпентинитового отхода.....172

А.К. Козыбаев, Ж.Д. Алимкулова, С.О. Абилкасова

Кинетика и термодинамика сорбции тяжелых металлов на промытой водой кальциево-монтмориллонитовой глине.....184

А. Абдрахманова, В. Кривченко, А. Сабитова, Б. КудеринаDOL – модифицированные электролиты как путь к стабильным анодам в системах $Li-V_2O_5$196**Б.К. Масалимова, А.С. Шаяхметова, А.С. Дарменбаева**

Водные ресурсы Северного Казахстана: экологический мониторинг и устойчивое управление.....208

А. Рахимов, Н. Жаникулов, Б. Таймасов, Е. Потапова, А.К. Свидерский

Исследование отходов переработки свинцового шлака в качестве сырья для цементной промышленности.....227

Л.М. Калимолдина, К.Ж. Жалгасбаев, А.С. Дәулетбаев

Сравнительное исследование методов очистки промышленных сточных вод.....241

А. Нурлан, С.Р. Конуспаев, Т.С. Абильдин, К. Тоштай

Превращения углеводов при гидрировании бензина, содержащего бензол.....256

Г.Ж. Байсалова, Б.К. Ертай, А.А.Талтенов, П. Кужатова, Г.Е. СаспугаеваКоличественное определение суммы фенольных соединений в талломе *PARMELIA SULCATA*.....274**Б.Э. Мырзабеков, А.Б. Маханбетов, Т.Э. Гайпов, Б.С. Абжалов, Н.Н. Нургалиев**

Электрохимическое восстановление ионов марганца (II) на титановом и свинцовом электродах.....286

А.С. Дарменбаева, Г.М. Жусипназарова, Р. Решми, Ж.Б. Мукажанова, В.А. Рубе

Биопокрытия на основе целлюлозы из стебля льна и их свойства.....298



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KINETIC AND THERMODYNAMIC STUDIES OF HEAVY METAL ADSORPTION ONTO WATER-WASHED CA-MONTMORILLONITE CLAY

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Abstract. Relevance. Pollution of water resources with heavy metal ions remains a major environmental problem. Wastewater from mining, metallurgical, and chemical industries often contains toxic Pb^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+} ions that bioaccumulate and threaten ecosystems and human health. Due to the limited effectiveness of traditional treatment methods, environmentally safe and cost-efficient adsorption technologies based on natural minerals are gaining importance.

Research objective. This study investigates the kinetics and thermodynamics of heavy metal ion adsorption on modified diatomite sorbents based on Ca-montmorillonite and determines diffusion, energy, and practical characteristics of the process.

Research methods. Adsorption of Pb^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+} was studied under static conditions at $pH = 5.5 \pm 0.5$ and 288–313 K. Kinetic parameters were determined using pseudo-second-order models, while equilibrium data used the Langmuir isotherms. IR spectroscopy evaluated structural and chemical changes in the sorbent surface.

Results. Heavy metal extraction reached 95–100% within 20–30 minutes and equilibrium achieved in 40–60 minutes. The kinetics follow a pseudo-second-order model ($R^2 \approx 0.99$), while equilibrium adsorption is described by the Langmuir isotherm, which indicates the monolayer nature of adsorption. Activation energies (kJ/mol) were: $Pb^{2+} - 75.5$; $Cd^{2+} - 51.1$; $Zn^{2+} - 45.6$; $Cu^{2+} - 26.1$. IR spectroscopy confirmed the



participation of $-\text{NH}_2$, $-\text{COOH}$, and $-\text{OH}$ groups in ion exchange and donor-acceptor interactions.

Practical significance. Modified diatomite sorbents demonstrate high efficiency in removing heavy metals from wastewater. The material is inexpensive, environmentally friendly, and suitable for use in industrial water treatment systems.

Keywords: heavy metals, Ca-montmorillonite, diatomite, polyethylenepolyamine, adsorption

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СУМЕН ЖУЫЛҒАН СА-МОНТМОРИЛЛОНИТ САЗЫНДА АУЫР МЕТАЛДАРДЫҢ СОРБЦИЯСЫНЫҢ КИНЕТИКАСЫ МЕН ТЕРМОДИНАМИКАСЫ

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Аннотация. Өзектілігі. Ауыр металл иондарымен судың ластануы қазіргі заманның ең өзекті экологиялық мәселелерінің бірі болып қала береді. Тау-кен, металлургия және химия өнеркәсібінен шығатын өнеркәсіптік ағынды суларда көбінесе биоаккумуляциялық және экожүйелер мен адам денсаулығына қауіп төндіретін Pb^{2+} , Cd^{2+} , Zn^{2+} және Cu^{2+} сияқты улы иондар болады. Дәстүрлі тазарту әдістерінің тиімділігі шектеулі болғандықтан, табиғи минералды материалдарға негізделген экологиялық таза және үнемді сорбциялық технологиялар ерекше маңызды.

Зерттеудің мақсаты. Бұл жұмыстың мақсаты — Са-монтмориллонит негізіндегі модификацияланған диатомды жер адсорбенттеріндегі ауыр металл иондарының сорбциясының кинетикасы мен термодинамикасын зерттеу, сондай-ақ процестің диффузиясын, энергиясын және практикалық сипаттамаларын анықтау.

Зерттеу әдістері. Pb^{2+} , Cd^{2+} , Zn^{2+} және Cu^{2+} сорбциясы тұрақты шайқалу жағдайында, $\text{pH} = 5,5 \pm 0,5$ және температурасы 288–313 К болғанда, статикалық жағдайда зерттелді. Кинетикалық параметрлер жалған екінші ретті модельдерді қолдану арқылы анықталды, ал тепе-теңдік деректері Ленгмюр изотермаларын қолдану арқылы талданды. Адсорбент бетіндегі құрылымдық және химиялық өзгерістер ИҚ спектроскопиясын қолдану арқылы бағаланды.

Нәтижелері. Ауыр металл иондарының экстракция жылдамдығы 20–30 минут ішінде 95–100%-ға жететіні, ал тепе-теңдікке 40–60 минут ішінде жететіні анықталды. Процесс кинетикасы жалған екінші ретті модельмен жақсы сипатталған ($R^2 \approx 0,99$), ал тепе-теңдік сорбциясы Ленгмюр изотермасымен сипатталады, бұл адсорбцияның моноқабатты сипатын көрсетеді. Белсенділік энергиялары (кДж/моль) анықталды: $Pb^{2+} - 75,5$; $Cd^{2+} - 51,1$; $Zn^{2+} - 45,6$; $Cu^{2+} - 26,1$. ИҚ-спектроскопия $-NH^+$, $-COOH$ және $-OH$ топтарының ион алмасу және донор-акцепторлық өзара әрекеттесулерге қатысуын растады.

Практикалық маңыздылығы. Нәтижелер модификацияланған диатомды жер сорбенттерінің ауыр металдарды ағынды суларды тазартуда жоғары тиімділігін растайды. Материал арзан, экологиялық таза және өнеркәсіптік су тазарту жүйелерінде енгізу үшін ұсынылуы мүмкін.

Түйін сөздер: ауыр металдар, Са-монтмориллонит, диатомит, полиэтиленполиамин, адсорбция

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КИНЕТИКА И ТЕРМОДИНАМИКА СОРБЦИИ ТЯЖЕЛЫХ МЕТАЛЛОВ НА ПРОМЫТОЙ ВОДОЙ КАЛЬЦИЕВО-МОНТМОРИЛЛОНИТОВОЙ ГЛИНЕ

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Аннотация. *Актуальность.* Загрязнение водных ресурсов ионами тяжёлых металлов остаётся одной из наиболее острых экологических проблем современности. Сточные воды горнодобывающей, металлургической и химической промышленности содержат токсичные ионы Pb^{2+} , Cd^{2+} , Zn^{2+} и Cu^{2+} , склонные к биоаккумуляции и представляющие серьёзную угрозу для экосистем и здоровья человека. В условиях низкой эффективности традиционных методов очистки возрастает значение экологически безопасных и экономичных сорбционных технологий на основе природных минералов.

Цель исследования. Изучение кинетических и термодинамических параметров сорбции ионов тяжёлых металлов на модифицированных адсорбентах на основе Са-монтмориллонита, а также определение диффузионных, энергетических и эксплуатационных характеристик процесса.



Методы исследования. Адсорбция Pb^{2+} , Cd^{2+} , Zn^{2+} и Cu^{2+} изучалась в статических условиях при постоянном встряхивании, $pH = 5,5 \pm 0,5$ и температуре 288—313 К. Кинетические параметры рассчитывались по модели псевдвторого порядка; равновесные данные анализировались по изотерме Ленгмюра. Структурно-химические изменения поверхностных групп оценивались методом ИК-спектроскопии.

Результаты. Показано, что степень извлечения ионов тяжёлых металлов составляет 95—100% в течение 20—30 минут, а равновесие достигается за 40—60 минут. Кинетика сорбции соответствует модели псевдвторого порядка ($R^2 \approx 0,99$), что свидетельствует о хемосорбционном механизме. Равновесная адсорбция хорошо описывается изотермой Ленгмюра, подтверждая монослойный характер процесса. Определены энергии активации (кДж/моль): Pb^{2+} — 75,5; Cd^{2+} — 51,1; Zn^{2+} — 45,6; Cu^{2+} — 26,1. ИК-спектроскопия выявила участие функциональных групп $-NH^+$, $-COOH$ и $-OH$ в ионообменных и донорно-акцепторных взаимодействиях с ионами металлов.

Практическое значение. Результаты демонстрируют высокую эффективность модифицированных диатомитовых сорбентов при очистке сточных вод от тяжёлых металлов. Материал отличается низкой стоимостью, экологической безопасностью и может быть рекомендован к использованию в промышленных системах водоочистки.

Ключевые слова: тяжёлые металлы, Са-монтмориллонит, диатомит, полиэтиленполиамин, адсорбция

Introduction. Environmental pollution with heavy metal ions is one of the pressing environmental issues of our time. Wastewater from industrial enterprises, including mining, metallurgical, and chemical industries, often contains toxic elements such as lead (Pb^{2+}), cadmium (Cd^{2+}), zinc (Zn^{2+}), and copper (Cu^{2+}). Since these elements are not biodegradable and tend to accumulate in living organisms, they pose a significant threat to ecosystems and human health (Iqbal, 2018).

Currently, various methods are used to remove heavy metals from aqueous environments: chemical precipitation, ion exchange, membrane and electrolytic technologies (Azimi et.al., 2017). However, most of these methods require high energy consumption, large amounts of reagents, and generate additional waste. Therefore, adsorption methods based on natural and inexpensive mineral materials are a more environmentally friendly and economically advantageous alternative (Ugwu et.al., 2019; Barakan et.al., 2021).

In recent years, natural diatomite and montmorillonite clays have been widely studied as effective sorbents for heavy metals due to their high specific surface area, porosity, and chemical stability. Modification of these materials with organic polymers, such as polyethylene polyamine, increases their adsorption capacity and enhances the activity of surface functional groups (ElSayed 2018; Zhao et.al., 2019).

The aim of this work is to study the kinetics and thermodynamics of heavy metal ion adsorption on modified diatomite sorbents based on Ca-montmorillonite, to determine

the diffusion and energy characteristics of the process, and to determine the practical significance of the results obtained in the field of environmental protection.

Materials and methods. Water-washed Ca-montmorillonite clay was used in the study. The adsorption of heavy metals from solutions was studied in a static mode with constant shaking. A sample of the sorbent-a solution with a specific sorbate concentration-was placed in a conical flask, maintained at a pH of 5.5 ± 0.5 for a specific time and at a specific temperature (Esmail et.al., 2013; Khachatryan 2014).

The components of the sorbent and metal solutions were determined depending on time and temperature. The kinetics and thermodynamics of the adsorption process were studied. Various temperatures (288, 293, 303, 313 K) were used to study the effect of temperature.

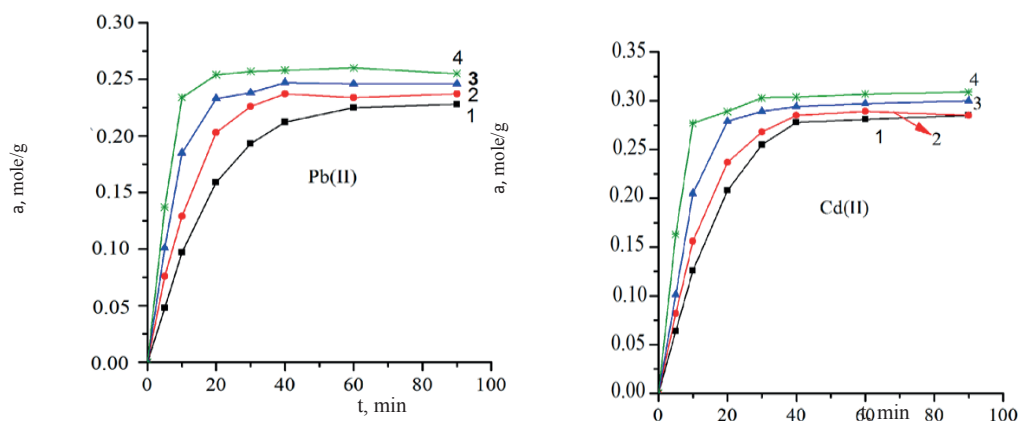
The following equations were used to describe the proportion of external diffusion into the environment: D_{external} is the external diffusion coefficient, and δ is the thickness of the solution film.

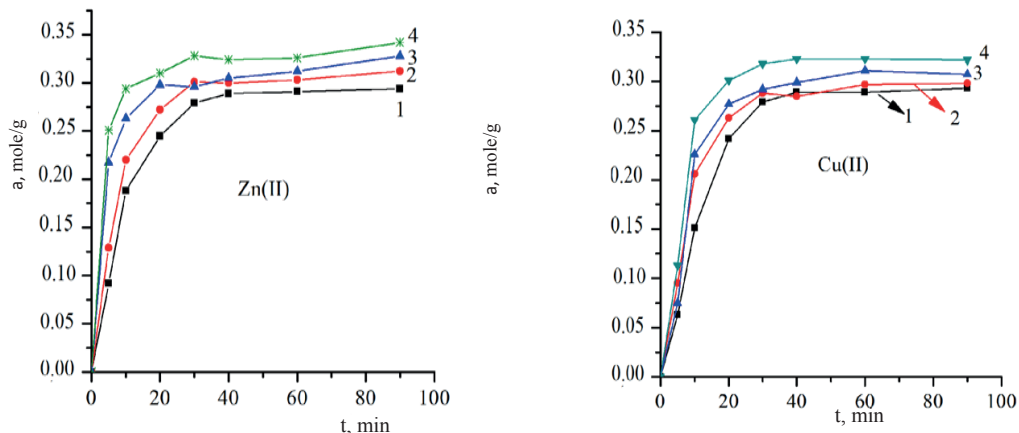
The Arrhenius equation was used to determine the activation energies (E_a) of the heavy metal adsorption process on diatomite sorbent. The Langmuir adsorption model was used to explain the experimental data.

Adsorbed metal ions are desorbed with a 1 M hydrochloric acid solution, with a desorption rate of 95–98%. The adsorbent purified in this way is treated with a 20–30% alkali solution for 2–3 hours and reused for further purification and extraction of metal ions.

To determine the mechanism of interaction of the modified diatomite sorbent with the surface, IR spectroscopy studies of samples were carried out before and after interaction with Cu^{2+} and Pb^{2+} ions.

Results and Discussion. *3.1 Kinetics.* The time dependencies of heavy metal adsorption studied in the temperature range of 288–293 K (Figure 1) show that for all studied systems, the adsorption values reach constant values after 40–60 minutes.





(C=100mg/dm³) at temperatures: 1-288K, 2-293K, 3-303K, 4-313K
 Figure 1 — Kinetic curves of heavy metal adsorption on diatomite sorbent

The degree of metal removal reaches 95-100% in about 20-30 minutes.

The contribution of external diffusion to the adsorption of heavy metals in the studied sorbent can be described (Wagner et.al., 2005; Godymchuk 2003) as follows (1):

$$\gamma = \frac{3D_{ext}}{r_0\sigma K_p} \quad (1)$$

Taking into account this equation, where $D_{external}$ is the external diffusion coefficient, r_0 is the radius of the sorbent particles, σ is the thickness of the solution shell around the sorbent particles, its value is taken to be equal to $5 \cdot 10^{-3}$ cm (Adebowale et.al., 2005), K_p is the distribution coefficient, determined by the equation (Lutsenko 2004; Vezentsev 2008): $K_p = a/C_p$, where a is the number of sorbed ions (mmol/g), and C_p is the equilibrium concentration of these ions in solution (mmol/cm³), $t D_{external}$ can be calculated from the tangent of the slope of the line $-\ln(1-F)$.

Processing of the kinetic adsorption curves of the studied heavy metals using equation (1) showed that the time of onset of the linear dependence of the function $-\ln(1-F)=f(t)$ depends primarily on the temperature of the experiment.

Thus, if at a temperature of 288–293 K a high linear dependence of this function is observed in the first 20–30 minutes, then at a temperature of 303–313 K this time is reduced to 5–10 minutes, which is due to a decrease in external diffusion resistance with increasing temperature. Consequently, the external diffusion coefficient also increases with increasing temperature.

In most cases, the dependence $a_t - t^{1/2}$ is polylinear, characterized by 2–3 sections and described by the following equation (2):

$$a_t = k_d \cdot t^{\frac{1}{2}} + A \quad (2)$$

where A is the segment cut off from the coordinate axis at $a_t=f(t^{1/2})$, dependence.

Diffusion parameters. 3.2. In equation (1), δ describes the thickness of the boundary layer. The first part describes the diffusion of the sorbate through the solution layer to the sorbent surface (Table 1).

Table 1. Diffusion parameters of heavy metal adsorption on diatomite sorbent.

| Ion | t, K | $D_{ext}, cm^2/sec.$ | $k_{d^2}, mole \cdot g^{-1} \cdot sec.^{-0.5}$ | $D_p, cm^2/sec.$ | B_i |
|------------------|--------|----------------------|--|----------------------|-------|
| Pb ²⁺ | 288 | $1.65 \cdot 10^{-5}$ | $4.60 \cdot 10^{-3}$ | $1.70 \cdot 10^{-8}$ | 5.00 |
| | 293 | $4.93 \cdot 10^{-5}$ | $5.60 \cdot 10^{-3}$ | $6.81 \cdot 10^{-8}$ | 3.37 |
| | 303 | $5.86 \cdot 10^{-5}$ | $6.90 \cdot 10^{-3}$ | $8.52 \cdot 10^{-8}$ | 3.00 |
| | 313 | $1.01 \cdot 10^{-4}$ | $9.30 \cdot 10^{-3}$ | $1.19 \cdot 10^{-7}$ | 3.10 |
| Cd ²⁺ | 288 | $2.07 \cdot 10^{-5}$ | $6.10 \cdot 10^{-3}$ | $5.96 \cdot 10^{-8}$ | 3.13 |
| | 293 | $2.80 \cdot 10^{-5}$ | $6.70 \cdot 10^{-3}$ | $7.24 \cdot 10^{-8}$ | 3.37 |
| | 303 | $3.20 \cdot 10^{-5}$ | $8.20 \cdot 10^{-3}$ | $8.94 \cdot 10^{-8}$ | 3.21 |
| | 313 | $5.85 \cdot 10^{-5}$ | $8.20 \cdot 10^{-3}$ | $2.26 \cdot 10^{-7}$ | 2.35 |
| Zn ²⁺ | 288 | $1.14 \cdot 10^{-5}$ | $6.30 \cdot 10^{-3}$ | $5.96 \cdot 10^{-8}$ | 3.37 |
| | 293 | $1.46 \cdot 10^{-5}$ | $7.40 \cdot 10^{-3}$ | $7.66 \cdot 10^{-8}$ | 3.19 |
| | 303 | $1.53 \cdot 10^{-5}$ | $8.90 \cdot 10^{-3}$ | $5.96 \cdot 10^{-8}$ | 4.35 |
| | 313 | $2.58 \cdot 10^{-5}$ | $1.25 \cdot 10^{-2}$ | $9.37 \cdot 10^{-8}$ | 4.74 |
| Cu ²⁺ | 288 | $1.18 \cdot 10^{-5}$ | $6.60 \cdot 10^{-3}$ | $6.39 \cdot 10^{-8}$ | 3.36 |
| | 293 | $1.41 \cdot 10^{-5}$ | $6.60 \cdot 10^{-3}$ | $8.09 \cdot 10^{-8}$ | 3.19 |
| | 303 | $1.68 \cdot 10^{-5}$ | $8.40 \cdot 10^{-3}$ | $6.81 \cdot 10^{-8}$ | 6.02 |
| | 313 | $1.81 \cdot 10^{-5}$ | $9.20 \cdot 10^{-3}$ | $8.52 \cdot 10^{-8}$ | 4.38 |

The second part, whose slope determines the internal diffusion rate constant, describes the internal diffusion process itself [3]. To calculate the internal diffusion coefficients (D_i), the classical equation for internal diffusion from a confined volume into a spherical body, proposed by Boyd and Adamson (Ivanov 2005; Byurnieva 2009; Neudachina 2004), was used (3):

$$F = 1 - \frac{6}{\pi^2} \exp\left(-\frac{D_i \pi^2 t}{r^2}\right) \quad (3)$$

where D_i is the internal diffusion coefficient, cm^2/s ; r is the radius of the sorbent grain, cm ; t is the time, s . $-\frac{D_i \pi^2 t}{r^2} = B_r$ — Fourier homochromy criterion.

Based on the determined t - B_t , the B_t — t dependence is constructed, the slope of which is determined by D_i .

The temperature dependence of the internal diffusion coefficient (Wax et al., 2001) is expressed by equation (4):

$$D_i = D_0 \exp\left(\frac{\Delta E_a}{RT}\right) \quad (4)$$

where ΔE_a is the activation energy of the overall diffusion process, and D_0 is the factor before the exponential factor.

The Biot coefficient is used to estimate the contributions of external and internal diffusion in the overall process (5):

$$B_i = \frac{D_{ext} r}{D_i \delta K_p} \quad (5)$$

As noted in (Kasani 2023), at $B_i \geq 20$ the adsorption process is limited by internal diffusion, at $B_i < 1$ — by external diffusion, intermediate values indicate mixed diffusion kinetics.

From Table 1, it can be seen that the external diffusion coefficients, being mainly single-order quantities, depend on the ion type and vary sequentially in the temperature range 293—313 K:

$$D_{ext} Pb^{2+} > D_{ext} Cd^{2+} > D_{ext} Zn^{2+} > D_{ext} Cu^{2+}.$$

The internal diffusion coefficients of Pb^{2+} and Cd^{2+} increase with increasing temperature, while for Zn^{2+} and Cu^{2+} , D_i does not show a clear temperature dependence. Studies have shown that the D_i values (and, consequently, the internal diffusion rate) of the ions under investigation depend on their crystallographic radii, decreasing as the latter increases; a similar dependence (Kostenko 2004).

The ions under study can be arranged in a row according to their crystallographic radii:

$$Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} \\ 0.1120.0990.0830.060$$

The results of the study indicate a mixed diffusion mechanism for the adsorption of heavy metals in the clay under investigation, with a slight predominance of the external diffusion mechanism, as also indicated by B_i criterion values ranging from 3.0 to 6.02.

It is assumed that the adsorption stage itself can make a significant contribution to the kinetics of the entire process. Therefore, to describe the patterns of this kinetic stage, pseudo-first-order and pseudo-second-order reaction models were used, which are linearly expressed by equations (6) and (7) (Lukaszczyk et.al., 2004):

$$\ln(a_\infty - a_t) = \ln a_\infty - k_1 t$$

$$\frac{t}{a_t} = \frac{1}{k_2 a_\infty^2} + \frac{1}{a_\infty} t \quad (6)$$

where a_∞ and a_t are the equilibrium adsorption quantity and adsorption quantity (mmol/g) at time t , respectively, and k_1 , k_2 are the adsorption rate constants of pseudo-first and pseudo-second order reactions, respectively.

t/a_t was calculated from the dependencies t , k_2 , and a_∞ using equation (6). A comparison of the results of using pseudo-first and pseudo-second-order models (Table 2) to describe the adsorption kinetics of the studied ions shows that in most cases the pseudo-second-order equation allows for the description of highly correlated experimental data. Coefficients are R_2 . Moreover, the values of a_∞ calculated by equation (1) give the best agreement with the experimental a_∞ . From Table 1, it can be seen that the values of the rate constants k_2 for all the ions studied increase with increasing temperature. From the dependences of $\ln k_2$.

$$\ln k_2 = -\frac{E_a}{RT} + \text{const} \quad (7)$$

According to the 1/T Arrhenius equation: the activation energies (E_a) of the adsorption process of heavy metals on diatomaceous sorbent were determined, kJ/mol: Pb^{2+} 75,5; Cd^{2+} 51,1; Zn^{2+} 45,6; Cu^{2+} 26,1.

Sufficiently high activation energy values may indicate reversely activated adsorption from subsequent ions on the modified sorbent.

Thus, in the case of Pb^{2+} , Cd^{2+} , Zn^{2+} and Cu^{2+} adsorption on modified diatomite, the adsorption kinetics are a combination of external and internal diffusion kinetics (with a slight predominance of external diffusion) and a pseudo-second-order reaction model is described.

The adsorption isotherms of Pb^{2+} , Cd^{2+} , Zn^{2+} and Cu^{2+} at 293 K are shown in Figure 2, which shows that the saturation process occurs during the adsorption of the studied ions in the concentration range of 0.8—1.2 mmol/dm³.

The results of the Langmuir isotherm equations based on experimental data are shown. The results obtained may be useful in developing a adsorption technology for the purification of natural wastewater from heavy metals using a modified sorbent based on diatomite.

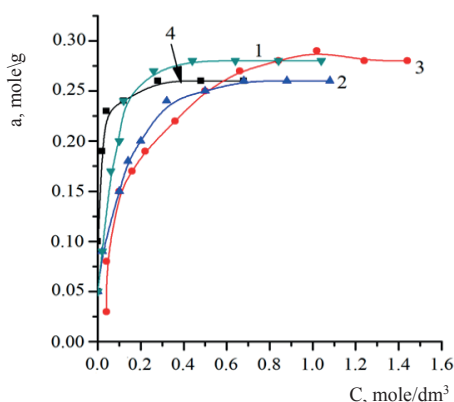
When describing experimental isotherms of heavy metal ions by mineral sorbents, the Langmuir adsorption model is often used in the literature (Vezentsev et.al., 2008).

$$A = \frac{A_{\infty} \cdot K \cdot C_p}{(1 + K \cdot C_p)} \quad (8)$$

where A_{∞} is the adsorption limit; K is the adsorption equilibrium concentration constant, which characterizes the intensity of the adsorption process, l/mol.

Linearization of adsorption isotherms according to the equation (Ivanov 2005):

$$\frac{1}{A} = \frac{1}{A_{\infty}} + \frac{1}{A_{\infty} \cdot K} \cdot \frac{1}{C_p} \quad (9)$$



Pb^{2+} (1), Cd^{2+} (2), Zn^{2+} (3) and Cu^{2+} (4) ($V = 50 \text{ cm}^3$; $m = 0,1 \text{ g}$; $\text{pH} = 5,5 \pm 0,5$; $\tau = 60 \text{ min}$; $t = 293\text{K}$)

Figure 2 - Adsorption isotherms of heavy metals on diatomite sorbent



The constants and correlation coefficients of the Langmuir equation are summarized in Table 2, which shows that the Langmuir isotherm is most suitable for describing the adsorption of the studied ions by the modified diatomite sorbent (see correlation R_2 and satisfactory agreement between experimental and calculated values according to equation (4) a_{∞} , which indicates a monolayer covering the surface of the heavy metal sorbent. It was also noted that the adsorption of heavy metals on diatomite sorbent is better described by the Langmuir equation and the pseudo-second-order reaction model.

Table 2. Equation constants.

| Cations | Langmuir equation | | | a_{exp} |
|------------------|-------------------|---------------------------|-------|------------------|
| | a, mmole/g | b, dm ³ /mmole | R^2 | |
| Pb ²⁺ | 0.26 | 135.795 | 0.999 | 0.26 |
| Cd ²⁺ | 0.31 | 8.405 | 0.997 | 0.28 |
| Zn ²⁺ | 0.28 | 15.489 | 0.998 | 0.26 |
| Cu ²⁺ | 0.29 | 28.851 | 0.999 | 0.28 |

It is known that the adsorption of heavy metals on the sorbent under study can occur through several mechanisms [5]: 1) ion exchange; 2) formation of chelate complexes with surface hydroxyl groups of the mineral; 3) “stacking” bonds on the edges and corners of valence attachment during the growth stages of montmorillonite crystals. In the case of the natural sorbent under study, the adsorption process proceeded by the mechanism of ion exchange with the replacement of heavy metal ions mainly by calcium, sodium, and magnesium cations.

The results of the study showed that the adsorption of Pb²⁺, Cd²⁺, Zn²⁺ and Cu²⁺ on modified diatomite occurs mainly by the ion exchange mechanism, is endothermic in nature and is well described by the Langmuir isotherm equation. The kinetics of this process is a combination of external and internal diffusion kinetics with the dominance of external diffusion kinetics and is best described by a pseudo-second-order reaction model.

The degree of deadsorption of adsorbed metal ions with hydrochloric acid solution reaches 95-98%. The purified adsorbent is reused for further purification and extraction of metal ions. This indicates that the diatomites modified in this way can be reused many times, and metals can be further concentrated and extracted by any physicochemical methods, which ensures the disposal of waste and the environmental and economic feasibility of using such a universal adsorbent.

3.3. IR spectra. In order to determine the mechanism of interaction of the modified diatomite sorbent with the surface, the IR spectra of the samples before and after interaction with Cu²⁺ and Pb²⁺ ions were studied.

On the surface of the sorbent, —NH₂, COOH, OH- groups were found, the corresponding vibrations were as follows: $\nu_2=1646.09-1408.53 \text{ cm}^{-1}$, $1079.29-589.31 \text{ cm}^{-1}$, $2926.75-3400 \text{ cm}^{-1}$ (Akhmedov et.al., 2001).

After contact with metal ions of the sorbents, a shift phenomenon is observed in all recorded peaks. The adsorption bands corresponding to amino groups at a frequency of 1408.53 cm^{-1} shifted to lower frequencies, while the band corresponding to the deformation vibrations of NH groups (at 799.52 cm^{-1}) shifted to higher frequencies. In addition, a peak at 1079.29 cm^{-1} sensitive to the influence of metal ions was detected. After interaction with Cu^{2+} and Pb^{2+} ions, this peak shifted to lower frequencies. A similar change occurred in the peak corresponding to carboxyl groups at 1243.82 cm^{-1} .

3.4. Sorption mechanism. Considering the above, it can be concluded that during the adsorption of Cu^{2+} and Pb^{2+} ions on the sorbent surface, their binding occurs mainly due to electrostatic, donor-acceptor interactions, and ion exchange mechanisms under the influence of —NH , —COO- , and OH- groups. Pb^{2+} and Cu^{2+} ions, as d-elements, tend to form donor-acceptor bonds with amino groups on the cell surface. In addition, both ions have the ability to interact with carboxyl and hydroxyl groups through ion exchange mechanisms.

Conclusion. The study showed that water-washed modified diatomite sorbents based on Ca-montmorillonite are capable of effectively removing heavy metal ions (Pb^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+}) from aqueous solutions. The adsorption process was studied under static conditions at $\text{pH} = 5.5 \pm 0.5$ and in the temperature range of $288\text{—}313\text{ K}$. The results showed that adsorption equilibrium is reached in $40\text{—}60$ minutes, and the degree of metal ion extraction is $95\text{—}100\%$.

The results of kinetic analysis showed that the adsorption process follows a pseudo-second-order reaction model, and the Langmuir isotherm is in good agreement with the experimental data. This confirms the monolayer nature of adsorption and the endothermicity of the process. An increase in temperature leads to an increase in the rate of external diffusion and a decrease in activation energy.

IR spectroscopy studies have shown that the functional groups —NH_2 , —COOH , and —OH on the sorbent surface interact with heavy metal ions, participating in ion exchange and the formation of donor-acceptor bonds, which, in turn, ensures high efficiency and selectivity of the sorbent.

The use of modified diatomite sorbents is an environmentally friendly and cost-effective method for treating natural and industrial water contaminated with heavy metals. The results of this study can serve as a scientific basis for the development of a new generation of adsorption materials for removing heavy metal ions.

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