

**ACADEMIC SCIENTIFIC
JOURNAL OF CHEMISTRY**

ISSN: 2224-5286 (Print)
ISSN: 2518-1491 (Online)

**№3
2026**

ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)



ACADEMIC SCIENTIFIC JOURNAL OF CHEMISTRY

3 (468)

JULY – SEPTEMBER 2026

PUBLISHED SINCE JANUARY 1947
PUBLISHED 4 TIMES A YEAR

ALMATY

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ACADEMIC SCIENTIFIC JOURNAL OF CHEMISTRY

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Owner: «Central Asian Academic Research Center» LLP (Almaty).

The certificate of registration of a periodical printed publication in the Committee of information of the Ministry of Information and Social Development of the Republic of Kazakhstan № KZ23VPY00121156, issued 05.06.2025

Thematic scope: *organic chemistry, inorganic chemistry, catalysis, electrochemistry and corrosion, pharmaceutical chemistry and technology.*

Periodicity: 4 times a year.

<http://chemistry-technology.kz/index.php/en/arhiv>

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«ACADEMIC SCIENTIFIC JOURNAL OF CHEMISTRY».

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Собственник: Республиканское общественное объединение ТОО «Центрально-азиатский академический научный центр» (г. Алматы).

Свидетельство о постановке на учет периодического печатного издания в Комитете информации Министерства информации и общественного развития Республики Казахстан № KZ23VPY00121156, выданное 05.06.2025 г.

Тематическая направленность: *органическая химия, неорганическая химия, катализ, электрохимия и коррозия, фармацевтическая химия и технологии.*

Периодичность: 4 раз в год.

<http://chemistry-technology.kz/index.php/en/arithv>

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«ACADEMIC SCIENTIFIC JOURNAL OF CHEMISTRY»

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Меншіктенуші: «Орталық Азия академиялық ғылыми орталығы» ЖШС (Алматы қ.).

Қазақстан Республикасының Ақпарат және қоғамдық даму министрлігінің Ақпарат комитетінде 05.06.2025 ж. берілген № KZ23VPY00121156 мерзімдік басылым тіркеуіне қойылу туралы куәлік.

Тақырыптық бағыты: *органикалық химия, бейорганикалық химия, катализ, электрохимия және коррозия, фармацевтикалық химия және технологиялар.*

Мерзімділігі: жылына 4 рет.

<http://chemistry-technology.kz/index.php/en/arhiv>

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RUBIDIUM SORPTION FROM AQUEOUS SOLUTIONS BY VEMEA–AGE–PEI ANION EXCHANGERS

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Abstract. Relevance. The recovery of rubidium from aqueous media is relevant because of the growing demand for rare alkali metals and the need for efficient sorption materials capable of operating under mildly acidic conditions. Purpose. The study aimed to evaluate the sorption characteristics of polyfunctional anion exchangers based on 2-aminoethyl vinyl ether (vinylether of monoethanolamine, VEMEA), allyl glycidyl ether (AGE), and polyethyleneimine (PEI) toward Rb^+ ions. Methods. The VEMEA–AGE–PEI anion exchanger was synthesized by polycondensation of pre-epoxidized VEMEA with AGE and PEI, followed by curing, fractionation, washing, and conversion to the OH^- form. The material was characterized by FTIR spectroscopy and physicochemical parameters. Rubidium sorption was studied under static conditions using Rb_2SO_4 model solutions. The effects of initial concentration, contact time, and solution pH were evaluated, and the equilibrium data were analyzed using the Langmuir and Freundlich models. Residual rubidium was determined by atomic emission spectrometry. Results. The maximum experimental sorption capacity reached 11.34 mg/g. Equilibrium was attained within 1 h. The Langmuir model gave $q_{\text{max}} = 8.78$ mg/g and $K_L = 0.313$ L/mg ($R^2 = 0.9993$), while the Freundlich model gave $K_f = 1.87$ and $n = 1.17$ ($R^2 = 0.9981$). Within the investigated pH range of 1.87–4.17, the highest sorption performance was observed at pH 4.17. FTIR spectral changes suggested the participation of amino and other donor groups in interactions with rubidium ions. Practical significance. The obtained results demonstrate the potential of VEMEA–AGE–PEI anion exchangers for

rubidium extraction and concentration from weakly acidic aqueous media and for the development of functional ion-exchange materials.

Keywords: rubidium, sorption, anion exchanger, polyethyleneimine, ion exchange, aqueous solution

Funding: *This research has been funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (BR27101179).*

For citations: Serikbayeva K.T., Chalov T.K., Sadykov K.A. Rubidium sorption from aqueous solutions by VEMEA–AGE–PEI anion exchangers. Academic Scientific Journal of Chemistry, 2026. — No.3. — P. 322–333. DOI: <https://doi.org/10.32014/2026.2518-1491.403>.

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СУЛЫ ЕРІТІНДІЛЕРДЕН РУБИДИЙДІ ВЭМЭА–АГЭ–ПЭИ АНИОНИТТЕРІМЕН СОРБЦИЯЛАУ

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Аннотация. Рубидийге сұраныстың артуы және сирек сілтілік металдарды сулы ортадан тиімді бөліп алу қажеттілігі әлсіз қышқыл жағдайда жұмыс істей алатын жаңа сорбциялық материалдарды әзірлеудің өзектілігін айқындайды. Зерттеудің мақсаты — 2-аминоэтилвинил эфирі, яғни моноэтаноламиннің винил эфирі (ВЭМЭА), аллилглицидил эфирі (АГЭ) және полиэтиленимин (ПЭИ) негізіндегі полифункционалды аниониттердің Rb^+ иондарына қатысты сорбциялық сипаттамаларын зерттеу. ВЭМЭА–АГЭ–ПЭИ аниониті алдын ала эпоксидтелген ВЭМЭА-ны АГЭ және ПЭИ-мен поликонденсациялау арқылы синтезделіп, кейін қатайту, фракциялау, жуу және OH^- -формаға ауыстыру сатыларынан өткізілді. Материал ИҚ-спектроскопия әдісімен және негізгі физика-химиялық көрсеткіштері бойынша сипатталды. Рубидий сорбциясы Rb_2SO_4 модельдік ерітінділерін пайдаланып статикалық жағдайда зерттелді. Бастапқы концентрацияның, жанасу уақытының және ерітінді рН-ының әсері бағаланды. Тепе-теңдік деректері Ленгмюр және Фрейндлих модельдері бойынша өңделді, ал

қалдық рубидий концентрациясы атомдық-эмиссиялық спектрометрия әдісімен анықталды. Тәжірибелік максималды сорбциялық сыйымдылық 11,34 мг/г болды, ал тепе-теңдік 1 сағат ішінде орнады. Ленгмюр моделі бойынша $q_{\text{max}} = 8,78$ мг/г, $K_L = 0,313$ л/мг және $R^2 = 0,9993$; Фрейндлих моделі бойынша $K_F = 1,87$, $n = 1,17$ және $R^2 = 0,9981$ алынды. Зерттелген рН 1,87–4,17 аралығында ең жоғары сорбциялық көрсеткіш рН 4,17 кезінде байқалды. ИҚ-спектрлердегі өзгерістер амин және басқа донорлық топтардың рубидий иондарымен әрекеттесуге қатысуы мүмкін екенін көрсетті. Алынған нәтижелер ВЭМЭА–АГЭ–ПЭИ аниониттерін әлсіз қышқыл сулы ортадан рубидийді бөліп алу және концентрлеу үшін қолданудың перспективалы екенін көрсетеді.

Түйін сөздер: рубидий, сорбция, анионит, полиэтиленимин, ион алмасу, сулы ерітінді

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СОРБЦИЯ РУБИДИЯ ИЗ ВОДНЫХ РАСТВОРОВ АНИОНИТАМИ ВЭМЭА–АГЭ–ПЭИ

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Аннотация. Рост потребности в рубидии и необходимость эффективного извлечения редких щелочных металлов из водных сред определяют актуальность разработки новых сорбционных материалов, способных работать в слабокислых условиях. Целью работы являлось исследование сорбционных характеристик полифункциональных анионитов на основе 2-аминоэтилвинилового эфира, или винилового эфира моноэтаноламина (ВЭМЭА), аллилглицидилового эфира (АГЭ) и полиэтиленимина (ПЭИ) по отношению к ионам Rb^+ . Анионит ВЭМЭА–АГЭ–ПЭИ синтезировали поликонденсацией предварительно эпоксицированного ВЭМЭА с АГЭ и ПЭИ с последующим отверждением, фракционированием, промывкой и переводом в OH^- -форму. Материал характеризовали методом ИК-спектроскопии и по основным физико-химическим показателям. Сорбцию рубидия исследовали в статических условиях с использованием модельных растворов Rb_2SO_4 . Изучали влияние исходной концентрации, времени контакта и рН раствора. Равновесные данные обрабатывали с использованием моделей

Ленгмюра и Фрейндлиха, а остаточную концентрацию рубидия определяли методом атомно-эмиссионной спектроскопии. Максимальная экспериментальная сорбционная ёмкость составила 11,34 мг/г, а равновесие достигалось в течение 1 ч. Для модели Ленгмюра получены $q_{\text{max}} = 8,78$ мг/г, $K_L = 0,313$ л/мг и $R^2 = 0,9993$; для модели Фрейндлиха - $K_F = 1,87$, $n = 1,17$ и $R^2 = 0,9981$. В исследованном диапазоне pH 1,87–4,17 максимальные сорбционные показатели наблюдались при pH 4,17. Изменения ИК-спектров указывают на возможное участие аминных и других донорных групп во взаимодействии с ионами рубидия. Полученные результаты показывают перспективность применения анионитов ВЭМЭА–АГЭ–ПЭИ для извлечения и концентрирования рубидия из слабокислых водных сред и разработки новых функциональных ионообменных материалов.

Ключевые слова: рубидий, сорбция, анионит, полиэтиленимин, ионный обмен, водный раствор

Introduction. Rubidium is a dispersed alkali metal of interest for advanced materials, electronics, specialty glass, and other high-technology applications. Because rubidium commonly occurs at relatively low concentrations and together with much more abundant alkali-metal ions, its selective extraction and concentration remain technically challenging. Recent studies and reviews therefore emphasize the development of selective sorbents, ion-imprinted materials, membrane-assisted processes, and hybrid functional materials for rubidium recovery (Pabby et al., 2025; Khan et al., 2026).

Sorption methods occupy an important place among solution purification technologies due to their high efficiency, relative simplicity of equipment design, and suitability for concentrating trace components. For rubidium recovery, sorption-based approaches have been successfully applied to dilute aqueous and brine systems using selective inorganic, polymer-supported, ion-imprinted, and hybrid sorbents (Naidu et al., 2016; Naidu et al., 2017; Zhou et al., 2021; Truong et al., 2023).

A promising direction is the development of functionalized ion-exchange materials containing nitrogen- and oxygen-bearing fragments capable of interacting with metal cations. Such materials can provide heterogeneous binding environments and may combine ion-exchange and coordination contributions. Recent rubidium-specific studies demonstrate that the accessibility and organization of functional sites strongly influence uptake, selectivity, and regeneration behavior (Jiang et al., 2022; Ren et al., 2023; Fei et al., 2024; Cao et al., 2025).

In the present study, the sorption properties of an anion exchanger modified with vinyl ethers of monoethanolamine (VEMEA), allyl glycidyl ether (AGE), and polyethyleneimine (PEI) were investigated with respect to rubidium ions from aqueous solutions in a slightly acidic medium. Particular attention was paid to the study of sorption isotherms, the kinetic characteristics of the process, and the effect of medium acidity on the efficiency of rubidium extraction.

The aim of the present study is to investigate the sorption characteristics of anion exchangers based on VEMEA, AGE, and PEI in the extraction of rubidium ions from aqueous solutions.

Literature Review. Rubidium is a dispersed alkali metal that occurs at relatively low concentrations in natural waters and mineral resources, making its selective recovery technically challenging. Conventional recovery approaches are complicated by the presence of chemically similar and often much more concentrated alkali-metal ions. Consequently, adsorption and ion-exchange methods remain attractive because they combine operational simplicity with the possibility of concentrating Rb^+ from dilute solutions. Polymer-supported hexacyanoferrate sorbents and hydrogel-based composites have demonstrated effective rubidium uptake in saline media, supporting the use of sorption processes for Rb^+ recovery (Naidu et al., 2016; Naidu et al., 2017; Chu et al., 2024).

Recent research has broadened the range of materials considered for rubidium recovery. Ion-imprinted polymers have been developed to create recognition sites with enhanced affinity toward Rb^+ , while magnetic ion-imprinted and surface-imprinted materials have been designed to improve accessibility of active sites and separation convenience (Liu et al., 2019; Zhou et al., 2021; Jiang et al., 2022; Ren et al., 2023). A mordenite/polymer nanofiber composite membrane has also been reported for selective Rb^+ adsorption, illustrating the potential of combining inorganic frameworks with functional polymer phases (Fei et al., 2024).

For brine and saline-water applications, integrated and composite sorption systems are particularly relevant. Polymer-encapsulated potassium copper hexacyanoferrate and metal-organic-framework-containing hexacyanoferrate materials have been investigated for selective rubidium recovery from saline matrices (Naidu et al., 2016; Naidu et al., 2017; Truong et al., 2023). More recently, PAN-KCuFC-PEG and polysulfone/ZIF-8@KCuFC composites have been reported for rubidium enrichment and selective extraction, while AMP@MIL-101(Cr) was studied as a structurally optimized composite for Rb^+ recovery from aqueous solution (Wu et al., 2025; Liu et al., 2025; Cao et al., 2025). These studies indicate that the nature, accessibility, and spatial arrangement of active sites are central factors governing rubidium sorption performance.

Polyethyleneimine is of particular interest as a functional component because its macromolecular structure contains a high density of amino groups capable of participating in protonation, ion exchange, and coordination interactions. Incorporating PEI into a crosslinked ion-exchange matrix together with oxygen-containing fragments can therefore create a heterogeneous set of potential sorption sites. In the VEMEA-AGE-PEI system, amino and hydroxyl/ether-containing fragments are expected to contribute to the interaction with dissolved ions, while the crosslinked polymer structure provides material stability. Previous work established the possibility of synthesizing polyfunctional anion exchangers from VEMEA, AGE, and PEI (Serikbayeva et al., 2025), providing the basis for evaluating their behavior toward rubidium ions.

Despite the diversity of recently proposed Rb^+ adsorbents, the behavior of VEMEA-AGE-PEI anion exchangers in weakly acidic aqueous media has not been sufficiently characterized. In particular, information is required on equilibrium sorption, contact time, pH dependence, and changes in functional groups after sorption. The present work addresses these aspects using model Rb_2SO_4 solutions and combines equilibrium

modeling with FTIR observations. This approach makes it possible to assess both the quantitative sorption characteristics and the probable contribution of functional groups to rubidium uptake.

Materials and Methods. Rubidium sulfate (Rb_2SO_4 , chemically pure grade), deionized water, and a synthesized anion exchanger based on vinyl ethers of monoethanolamine (VEMEA), allyl glycidyl ether (AGE), and polyethylenimine (PEI) were used in this study.

Standard Rb_2SO_4 solutions with concentrations in the range of 0.2-20 mg/L (calculated as Rb^+) were used to prepare model rubidium ion solutions. Rubidium sulfate was selected as a highly soluble and stable rubidium salt. The influence of sulfate ions and ionic strength was not evaluated in this study and may be considered in future research.

The anion exchanger was synthesized via polycondensation of pre-epoxidized VEMEA (epoxy number 25.47%) with allyl glycidyl ether (AGE) and polyethylenimine (PEI) in dimethylformamide solution at a VEMEA:AGE:PEI mass ratio of 1:1:2.5, a reaction temperature of 65-70°C, and a reaction time of 4 h (Serikbayeva et al., 2025). The resulting prepolymer was subsequently cured at 100-110°C for 60 h. After curing, the anion exchanger was crushed, fractionated to obtain particles with a size of 0.5-1.0 mm, washed with distilled water until neutral pH was reached, and converted into the hydroxide form by treatment with a 5wt.% NaOH solution.

To provide a comprehensive characterization of the synthesized material, its key physicochemical properties were determined. The static exchange capacity was found to be 14.31 meq/g, while the moisture content and specific volume were 86.45% and 9.76 cm³ g⁻¹, respectively. IR spectroscopy was used to confirm the structure of the obtained anion exchangers. The absorption spectrum revealed characteristic bands: in the region of 3200-3500 cm⁻¹ corresponding to stretching vibrations of hydroxyl (-OH) and amine (-NH) groups; around 2850-2950 cm⁻¹ assigned to C-N stretching vibrations; as well as intense peaks in the 1000-1200 cm⁻¹ region corresponding to C-O and C-N bond vibrations.

These bands confirm the presence of amine and hydroxyl groups characteristic of VEMEA, AGE and PEI.

Sorption experiments were carried out under static conditions at a temperature of 20±2°C. A 0.02 g portion of the sorbent was placed into conical flasks, 20 mL of Rb_2SO_4 solution of a specified concentration was added. The suspensions were agitated on an orbital shaker for 24 h. Contact time studies were performed at contact times of 0.5, 1, 3, 5, and 24 h under otherwise identical experimental conditions. After sorption, the solution was separated from the sorbent by filtration, and the residual rubidium concentration was determined by atomic emission spectrometry.

Sorption isotherms were obtained in the initial concentration range of 0.2-20 mg/L.

The sorption capacity (q , mg/g) and the extraction efficiency (R , %) were calculated using standard equations:

$$q = (C_0 - C_e) \cdot V / m \quad (1)$$

$$R = (C_0 - C_e) / C_0 \times 100\% \quad (2)$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of rubidium in solution, respectively; V (L) is the solution volume; m (g) is the sorbent mass; q (mg/g) is the sorption capacity; and R (%) is the removal efficiency.

Use of AI tools. During manuscript preparation, ChatGPT (OpenAI, GPT-5.6 Sol) was used solely for language editing, structural organization, and technical formatting. All scientific data, interpretations, calculations, and final wording were reviewed and approved by the authors.

Results

Sorption isotherms

Sorption isotherms of rubidium on the VEMEA-AGE-PEI anion exchanger were constructed at different initial concentrations of the Rb_2SO_4 (0.2-20 mg/L).

The isotherm demonstrates an increase in sorption capacity with increasing Rb^+ concentration, reaching 11.34 mg/g, while the extraction efficiency decreases from 73% to 56.7% due to the saturation of active sites (Figure 1).

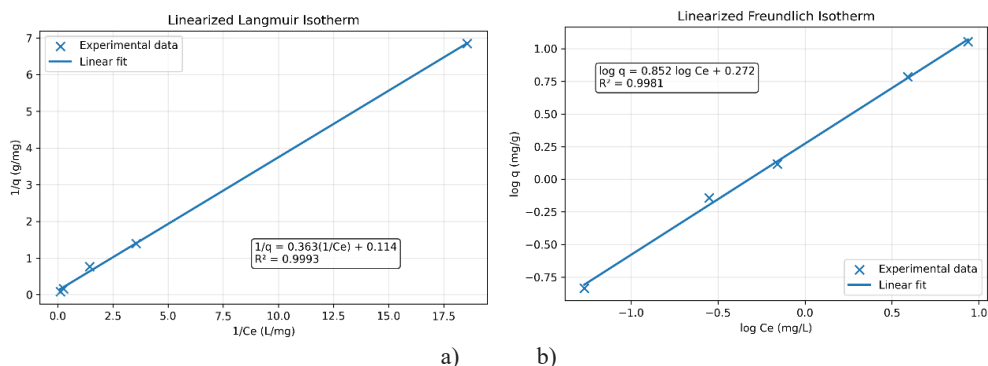


Figure 1 – Linearized Langmuir and Freundlich isotherms for rubidium sorption on the VEMEA-AGE-PEI anion exchanger: (a) Langmuir ($1/q$ vs. $1/C_e$); (b) Freundlich ($\log q$ vs. $\log C_e$).

To describe the experimental data, the Langmuir and Freundlich models were applied. The obtained parameters were as follows:

Langmuir: $q_{\max} = 8.78$ mg/g, $K_L = 0.313$ L/mg;

Freundlich: $K_f = 1.87$, $n = 1.17$.

Effect of contact time

The effect of contact time on sorption showed that equilibrium was reached within 1 hour, at which point the extraction efficiency was 76.05% and the sorption capacity was 0.1499 mg/g.

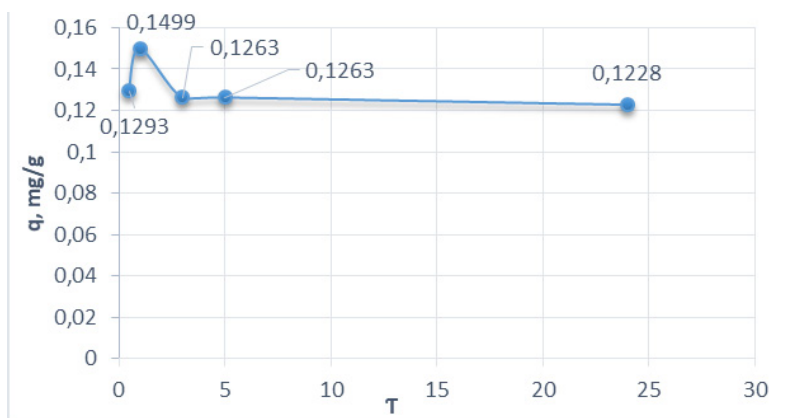


Figure 2 – Effect of contact time on rubidium sorption by the VEMEA-AGE-PEI anion exchanger

4.3. Effect of solution pH

The acidity of the medium has a significant effect on the sorption of rubidium (Figure 3).

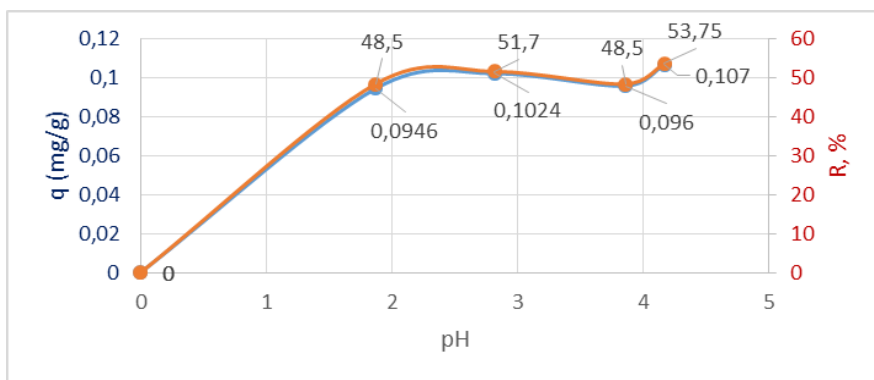


Figure 3 – Effect of pH on rubidium sorption by the VEMEA-AGE-PEI anion exchanger. Experiments were carried out in the pH range of 1.87-4.17. Blue points represent the sorption capacity, q (mg/g), while red points represent the extraction efficiency of Rb^+ (%).

The experiments were carried out in the pH range of 1.87-4.17, which corresponded to the conditions ensuring solution stability and measurement reproducibility. The pH values of the solutions were adjusted by adding hydrochloric acid. The pH was not monitored after the sorption experiments. As shown in Figure 3, an increase in pH led to an increase in both the sorption capacity and the rubidium removal efficiency. The maximum sorption characteristics were observed at pH 4.17 within the investigated pH range. This behavior can be attributed to the reduced competition of H^+ ions for the amino functional groups, which promotes an increase in the sorption capacity and Rb^+ removal efficiency within the studied pH range.

FTIR analysis before and after sorption

To confirm the participation of the sorbent functional groups in the sorption process of rubidium ions, IR spectra of the anion exchanger were recorded before and after sorption (Figure 4).

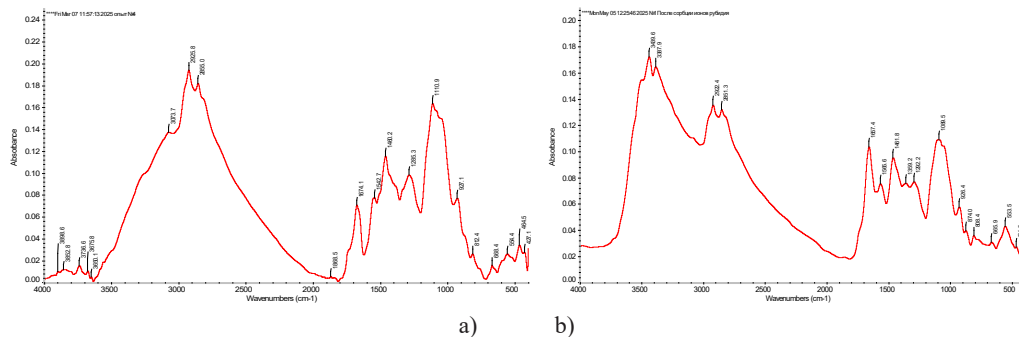


Figure 4 – IR spectra of the VEMEA-AGE-PEI anion exchanger: (a) spectrum before sorption; (b) spectrum after sorption of rubidium ions.

Discussion

Both models describe the experimental data well ($R^2 > 0.98$), which indicates a mixed physicochemical sorption mechanism.

Approximation of the experimental data using the Langmuir and Freundlich models showed good agreement with the experimental results. Linearization according to the Langmuir model ($1/q$ vs. $1/C_e$) yielded the equation $1/q = 0.363 (1/C_e) + 0.114$, corresponding to $q_{\max} = 8.78$ mg/g and $KL = 0.313$ L/mg ($R^2 = 0.9993$). The logarithmic form of the Freundlich model ($\log q$ vs. $\log C_e$) is described by the equation $\log q = 0.852 \log C_e + 0.272$ ($K_f = 1.87$, $n = 1.17$, $R^2 = 0.9981$). The high R^2 values confirm the adequacy of both models, while $n > 1$ indicates favorable and predominantly physicochemical sorption.

It should be noted that the maximum experimental sorption capacity was 11.34 mg/g, whereas $q_{\max} = 8.78$ mg/g is a theoretical parameter derived from the Langmuir model. This difference arises because $q_{\max}$ is calculated from the linearized Langmuir equation and may not fully coincide with the maximum experimentally observed sorption capacity. In addition, this discrepancy may be related to the limited concentration range studied and the heterogeneous nature of the sorption sites, which can lead to deviations from the ideal Langmuir model.

With a further increase in the contact time to 24 h, a slight decrease in the sorption capacity (to 0.1228 mg/g) was observed, which may be related to the interaction of Rb^+ ions with the functional groups of the sorbent (Figure 2). Such behavior is typical for polyamine-containing ion-exchange materials, where the sorption process involves both rapid surface exchange and slower intramatrix redistribution of ions. The lower sorption capacity values observed in the kinetic experiments are attributed to the lower initial Rb^+ concentration (0.2 mg/L) employed in these experiments, whereas the maximum

sorption capacity (11.34 mg/g) was obtained during the sorption isotherm experiments at an initial concentration of 20 mg/L.

Shifts and changes in the intensity of the bands characteristic of N-H and C-N groups may indicate the involvement of PEI amino groups in the interaction with rubidium ions. A decrease in the intensity of the broad band in the region of 3400 cm^{-1} (O-H, N-H) may be associated with the participation of donor groups in the sorption process. The appearance of a new band at 1359 cm^{-1} and an increase in the intensity of the band at 1565 cm^{-1} may indicate the interaction of rubidium ions with the functional groups of the sorbent.

To evaluate the efficiency of the synthesized anion exchanger, the results of this study were considered in the context of published rubidium sorption systems. Ion-imprinted materials can provide high affinity and rapid uptake through specifically organized recognition sites (Liu et al., 2019; Zhou et al., 2021; Jiang et al., 2022; Ren et al., 2023), whereas polymer-supported hexacyanoferrate and hybrid composite sorbents are attractive for Rb^+ recovery from saline media because of their selectivity and suitability for regeneration or process integration (Naidu et al., 2016; Naidu et al., 2017; Chu et al., 2024; Truong et al., 2023; Liu et al., 2025). The capacities reported for these specialized materials should not be compared directly with the present anion exchanger without considering differences in solution composition, pH, initial concentration, sorbent dose, and material structure.

The VEMEA-AGE-PEI anion exchanger investigated here differs from these highly selective inorganic and ion-imprinted sorbents because its functional response is associated with a polyfunctional polymer network containing amine and oxygen-bearing groups. Under the conditions studied, the material showed measurable Rb^+ uptake in a weakly acidic medium and reached equilibrium within 1 h. The FTIR changes observed after sorption support the involvement of functional groups of the polymer matrix, although additional mechanistic studies are required to distinguish the contributions of ion exchange, coordination interactions, and intramatrix redistribution. The obtained results therefore support further development of this material for rubidium concentration from weakly acidic aqueous media.

The equilibrium results show that the sorption behavior cannot be represented solely by an ideal homogeneous-site model. Although the Langmuir linearization produced a high coefficient of determination, the experimentally observed capacity exceeded the calculated Langmuir q_{max} . Together with the similarly high fit of the Freundlich equation, this supports the interpretation that the VEMEA-AGE-PEI matrix contains sorption sites with different local environments and affinities. Therefore, the model parameters should be treated as descriptors of the studied concentration range rather than as direct proof of a single sorption mechanism.

The rapid attainment of equilibrium is an advantageous feature for practical sorption processes. At the same time, the decrease in q after the one-hour maximum indicates that the system continues to redistribute ions after the initial uptake stage. Because the kinetic experiment was conducted at a low initial Rb^+ concentration, the absolute q values are much lower than those obtained in the isotherm experiment. Direct comparison of these

capacities without accounting for the different initial concentrations would therefore be inappropriate.

The pH dependence is consistent with the functional nature of the material. In a more acidic medium, protonation and competition by H^+ can reduce the availability of donor sites for interaction with Rb^+ . As the pH increased within the studied interval, both sorption capacity and removal efficiency increased. Since pH was not measured after equilibrium and the study was limited to pH 1.87–4.17, conclusions should be restricted to this experimental range; additional experiments at broader pH and controlled ionic strength would be useful for a more complete mechanistic assessment.

Conclusion

The sorption of rubidium ions from aqueous solution by a modified anion exchanger based on VEMEA, AGE, and PEI was investigated. The obtained material exhibited pronounced sorption properties in a weakly acidic medium and provided efficient rubidium removal within the pH range of 1.87–4.17. The maximum sorption performance within the studied pH range was observed at pH 4.17.

Sorption isotherms were constructed, and the experimental data were satisfactorily described by the Langmuir and Freundlich models. For the Langmuir model, $q_{max} = 8.78$ mg/g and $KL = 0.313$ L/mg ($R^2 = 0.9993$) were obtained, whereas for the Freundlich model, $K_f = 1.87$ and $n = 1.17$ ($R^2 = 0.9981$) were determined, indicating the complex physicochemical nature of the interactions between rubidium ions and the functional groups of the sorbent. The maximum experimental sorption capacity reached 11.34 mg/g with a removal efficiency of 56.7%.

Kinetic studies showed that sorption equilibrium was achieved within 1 h, indicating favorable sorption kinetics. FTIR analysis suggested the involvement of polyethylenimine amino functional groups in the interaction with rubidium ions.

Comparison with published rubidium sorption studies indicates that sorbent performance depends strongly on material structure and experimental conditions. The present VEMEA–AGE–PEI anion exchanger is therefore considered a promising functional polymer material for further investigation of rubidium extraction from weakly acidic aqueous media.

The obtained results can be used in the development of sorption technologies for the purification and concentration of alkali metals, as well as in the creation of new functional polymer materials of the ion-exchange type.

Conflict of interests: The authors declare that there are no conflicts of interests between the authors to disclose in this article.

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ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

*Managing Editor: A.Shormakova
Editors: D.S. Alenov, T. Apendiev
Computer layout: G.D. Zhadyranova*

Signed for print: September 23, 2026

Format: 70×90 1/16. 24.0 printed sheets. Order No. 3