Uzbekistan Journal of Polymers
journal homepage: https://uzpolymerjournal.com/
ISSN (online): 2181-3256 (print) 2181-3246

NEW FUNCTIONALIZED SORPTION MATERIAL BASED ON INDUSTRIAL ANION EXCHANGER

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ARTICLE INFO

Received: 19 February 2026
Revised: 25 February 2026
Accepted: 19 March 2026

Keywords:
AN-31, chloroacetic acid derivative, sodium hydroxide, hydrochloric acid, lead nitrate, modification, sorption, static exchange capacity.

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ABSTRACT

The origin of the problem is associated with the expansion of application areas of ion-exchange resins used on an industrial scale. The aim of the research is to obtain polyampholytes with new sorption properties through secondary modification of ion-exchange resins.

The methodology involved the use of a heat-resistant round-bottom flask containing AN-31 ion-exchange resin and an aqueous solution of the sodium salt of a chloroacetic acid derivative.

The scientific novelty of the work consists in developing methods for polyampholyte synthesis, studying reaction kinetics and reaction order, and obtaining graphical dependences of static exchange capacity on various parameters.

As a result, the relative ratios of reagents, the dependences of static exchange capacity on temperature, time, and concentration were determined. Infrared spectra were analyzed and the reaction order was calculated. The obtained sample exhibits polyampholytic nature. An increase in the reagent ratio leads to an increase in the static exchange capacity. The synthesis was carried out based on a modification reaction.

DOI: *10.66640/UJP-2026-5-00005*

Introduction

Polyampholytes, one of the important directions of modern polymer chemistry, are high-molecular-weight compounds that simultaneously contain positively and negatively charged functional groups within their structure [1]. This unique feature provides polyampholytes with stimuli-responsive behavior toward changes in environmental parameters such as pH, ionic strength, and temperature. Consequently, polyampholytes show great potential in biomedicine, pharmacy, membrane technologies, water treatment, and the development of smart materials [2].

The synthesis of polyampholytes is of particular significance because it allows targeted control over their physicochemical properties. By regulating monomer composition, the ratio of charged functional groups, and polymer chain architecture during synthesis, materials tailored for specific applications can be obtained. Owing to their behavior closely resembling biological systems, polyampholytes are considered important model materials for studying interactions with proteins and cell membranes [3].

From this perspective, improving synthesis methods and conducting comprehensive investigations of polyampholyte properties are relevant not only for fundamental scientific research but also for applied technologies and pharmaceutical development. The synthesis of

polyampholytes enables the creation of a new generation of highly functional and environmentally adaptive polymer materials [4]. In this regard, the present study proposes a method for synthesizing a novel polyampholyte using an industrial anion-exchange resin.

According to the literature, AN-31 anion-exchange resin is a polymer-based synthetic ion-exchange material capable of selectively adsorbing and exchanging negatively charged ions. It is characterized by high chemical and mechanical stability and is widely applied in industrial, environmental, and laboratory conditions[5].Selective ion exchange: AN-31 efficiently retains negatively charged ions while allowing excess ions to pass through.Chemical resistance: It remains stable in strong acidic and alkaline media.Mechanical stability: The polymer matrix ensures resistance to high pressure and mechanical stress.High efficiency: Owing to its large active surface area, it provides fast and efficient ion-exchange processes [6,7].

The modification of AN-31 with the sodium salt of monochloroacetic acid expands its application range and enables the preparation of specialized reagents as well as optimization of ion-exchange processes. AN-31 is an anion-exchange polymer containing amino functional groups, including $–NH_2$ (primary amine) and –NH– (secondary amine), which exhibit nucleophilic properties. Sodium monochloroacetate ($NaOOC–CH_2–Cl$) contains an electrophilic $–CH_2–Cl$ group and a carboxylate $–COO^-Na^+$ group, making it an effective alkylating (carboxymethylating) reagent [8].

The main reaction proceeds via a nucleophilic substitution mechanism. In the first stage, the $–NH_2$ or –NH– groups of AN-31 attack the carbon atom of the $–CH_2–Cl$ group in monochloroacetic acid:

$$R–NH_2 + Cl–CH_2–COO^-Na^+ \rightarrow R–NH–CH_2–COO^-Na^+ + Cl^-$$

Here, Cl^- acts as the leaving group, resulting in a direct substitution reaction [9]. In the second stage, internal ion pair formation occurs between partially protonated $–NH^+$ groups and negatively charged $–COO^-$ groups. The coexistence of $–NH^+$ and $–CH_2–COO^-$ groups within the same macromolecule is the defining characteristic of a polyampholyte. Under more severe conditions, secondary modification may occur, leading to double carboxymethylation of a single amine group:

$$R–N(CH_2–COO^-)_2 \text{ [10]}$$

This increases the ion-exchange capacity but also enhances steric hindrance.

Partial protonation is present during the process, and the reaction behavior strongly depends on the pH of the medium. Theoretically, in acidic conditions the functional groups exist mainly as $–NH_3^+$/–COOH, whereas in alkaline conditions they are present as –NH/$–COO^-$. Therefore, the resulting polymer exhibits pH-sensitive polyampholytic behavior.

The modification of the AN-31 anion exchange resin with sodium monochloroacetate occurs due to the interaction between the functional groups of the resin and the reactive fragment of monochloroacetic acid[11]. In sodium monochloroacetate, the carboxyl group is blocked by the sodium ion; therefore, it does not actively participate in the reaction process. As a result, the reaction mainly proceeds through the chlorine-containing $–CH_2Cl$ group of monochloroacetic acid. The hydrogen atom of the amino groups present in the structure of the AN-31 anionite interacts with the chlorine atom, which leads to the elimination of hydrogen chloride (HCl). Consequently, the monochloroacetate fragment becomes attached to the polymer matrix of the anionite. Thus, during the modification process, carboxyl functional groups are introduced into the structure of the resin[12]. The presence of these groups leads to the formation of additional active sites on the sorbent surface, which enhances its ability to bind heavy metal ions and improves the sorption properties of the modified material.

Materials and Methods

Initially, the AN-31 anion-exchange resin, which is used on an industrial scale for the removal of anions from wastewater, was washed in an acidic medium (initial pH = 2.08, subsequently adjusted to pH = 4.5). The washed anion-exchange resin was then subjected to a modification process with the sodium salt of a chloroacetic acid derivative in a water bath at controlled temperatures (100–150 °C) for a defined period of time (2–4 h).

During the experiments, the effects of reagent concentration, temperature, and reaction time were systematically investigated to determine optimal conditions. Based on the obtained results, the optimal temperature for the modification process was found to be 120 °C.

Results and Discussion

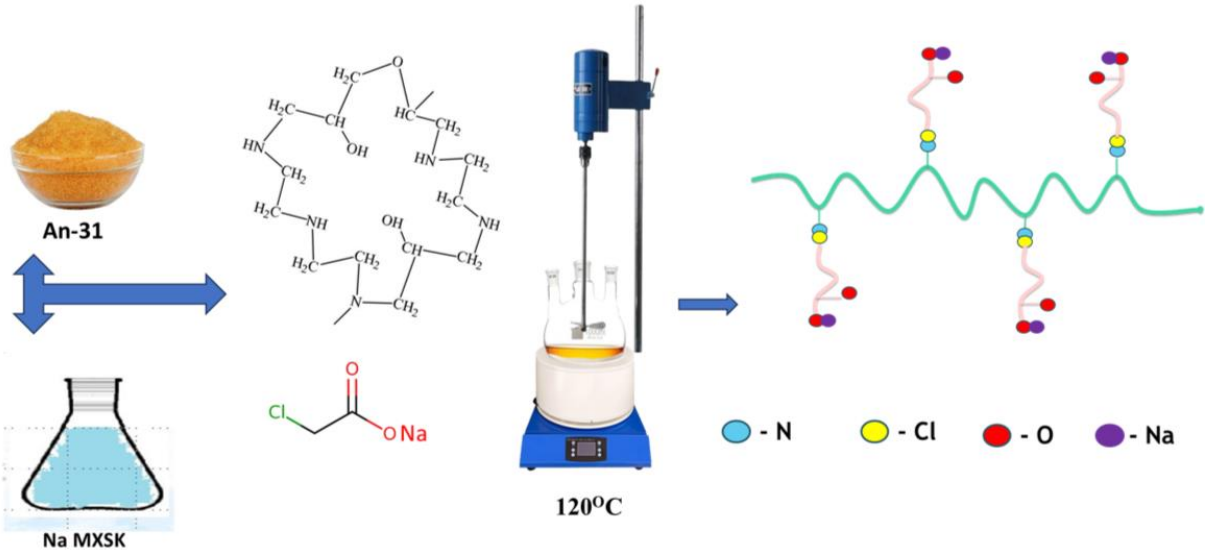

Figure 1. *Schematic representation of the polyampholyte synthesis*

The AN-31 anion-exchange resin is first modified with the sodium salt of monochloroacetic acid in a water bath under controlled temperature and time conditions. Following modification, the resin is activated by sequential treatment with 0.1 M NaOH and 0.1 M HCl solutions, with repeated washing until a near-neutral state is reached. The activated polyampholyte exhibits both cation and anion exchange capacities, which are subsequently determined through titration of filtrates after 24-hour contact with 0.1 M NaOH (for cation exchange) and 0.1 M HCl (for anion exchange). After repeating the washing process until the resins reached a near-neutral state, the polyampholyte was fully activated. Subsequently, the static exchange capacities for both cations and anions were determined.

Considering that the synthesized resin exhibits polyampholytic properties, the following procedures were used:

1. ***Cation Exchange Capacity (CEC):*** 1 g of the neutral polyampholyte was placed in 100 mL of 0.1 M NaOH solution and left for 24 hours. The resin was then filtered, and the filtrate was titrated with 0.1 M HCl to determine the cation exchange capacity.
2. ***Anion Exchange Capacity (AEC):*** Similarly, 1 g of neutral polyampholyte was placed in 100 mL of 0.1 M HCl solution and left for 24 hours. The resin was filtered, and the filtrate was titrated with 0.1 M NaOH to determine the anion exchange capacity.

This procedure allowed accurate measurement of the polyampholyte's dual ion-exchange functionality, confirming its ability to exchange both cations and anions effectively.

During the study, the dependence of the static exchange capacity (SAC) of the polyampholyte on temperature, concentration, and contact time was investigated. The following results were obtained and analyzed, leading to the appropriate conclusions.

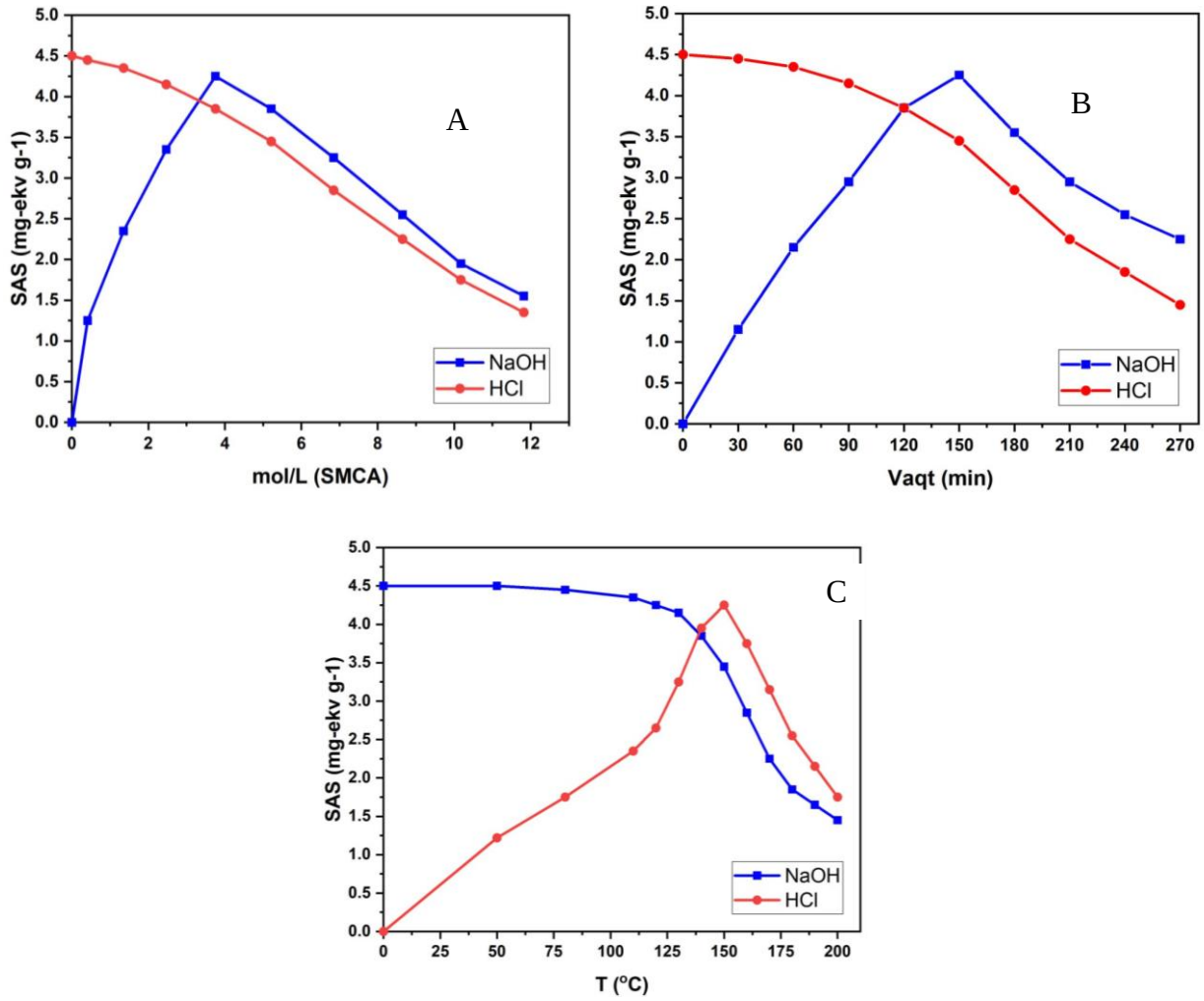

Figure 2. *Dependence of the static exchange capacity (SAC) of the polyampholyte on various parameters: (a) SAC vs. concentration, (b) SAC vs. contact time, (c) SAC vs. temperature.*

From the results, it can be concluded that the static exchange capacity (SAC) exhibited higher values in low-concentration solutions [13]. This behavior can be attributed to improved diffusion and interaction within the system. In dilute solutions, the distances between polymer chains are larger, allowing the modifying reagent molecules to penetrate more easily into the polymer network. This facilitates a uniform and thorough modification process. Additionally, dilute solutions have lower viscosity, which enhances mass transfer and mixing. In contrast, highly concentrated solutions are more viscous, reducing the reaction rate, hindering mixing, and impairing heat transfer. Therefore, in diluted solutions, the modifying reagent is evenly distributed throughout the volume, ensuring uniform modification and improving the quality of the final product.

The observed decrease in SAC with increasing temperature is explained by the loss of chemical functionality of the polymer, i.e., thermal degradation. In this process, polymer chains are broken, leading to a reduction in functional sites. The gradual decrease in SAC with extended modification time is primarily due to the intensification of side-chain reactions [14].

Determining the reaction order for modification reactions is a complex process, as it plays an important role in the modification of ion-exchange resins (e.g., amination, sulfonation,

chlorination, etc.). The reaction kinetics depend on both the interaction of the reagent with the resin and interfacial phenomena. Therefore, when measuring reaction rates, the diffusion step must also be considered. Typically, such reactions are modeled as pseudo-first-order or pseudo-second-order because the concentration of functional groups on the resin surface is considered constant.

Based on the experimental data, the dependence of the conversion degree on reagent concentration can be expressed as:

$$V = K \cdot [\mathrm{SMCA}]^{1.6} [15]$$

The reaction order (n > 1) is consistent with literature reports for heterogeneous reactions under similar conditions.

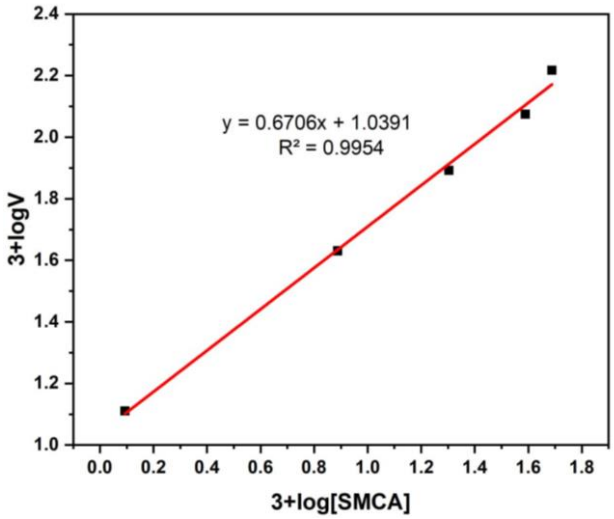

Figure 2*. Logarithmic dependence of AN-31 and SMCA concentrations on SMCA concentration (b) at T = 403 K and t = 4 h*

In this equation, Krepresents the calculated reaction rate constant, which was determined to be 1.55 s·L/mol. The logarithmic dependence of the modification reaction rate on temperature was analyzed, and the tangent of the slope, $\tan\alpha = 1.55$, was used to calculate the activation energy (E) of the modification reaction according to the following formula:

$$E = -R \cdot \tan\alpha$$

where $R$is the universal gas constant. Based on this calculation, the activation energy was found to be 12.88 kJ/mol. In our study, the activation energy of the modification reaction in the presence of SMCA was also determined to be 12.88 kJ/mol [16].

From these results, it can be concluded that during the initial stage of the modification of AN-31 anion-exchange resin with SMCA, the amino groups in the polymer act as neighboring functional groups that accelerate the reaction. The experimentally determined activation energy value is characteristic of heterogeneous processes.

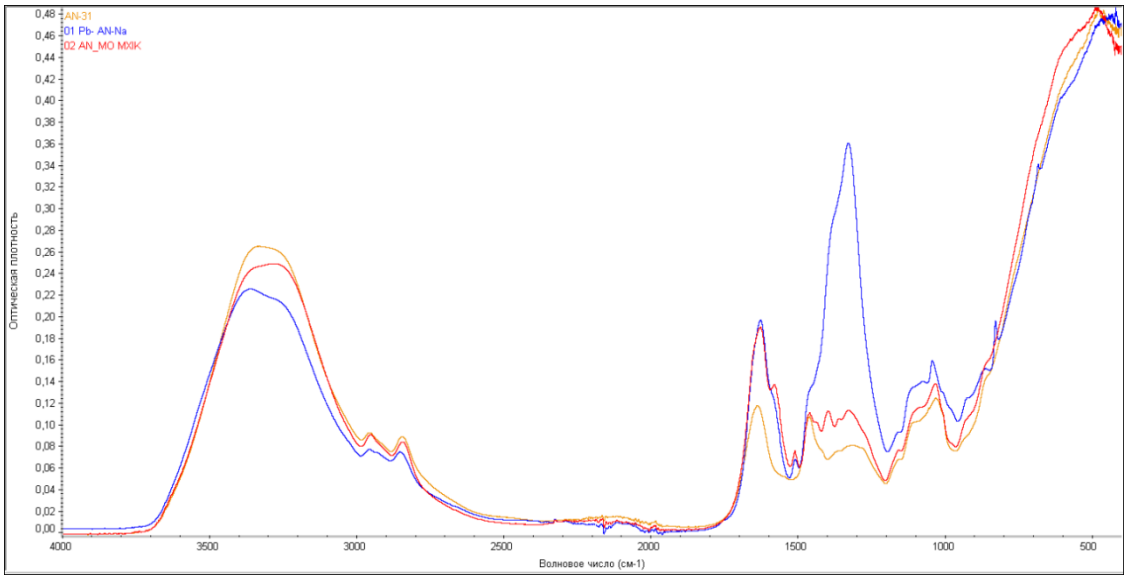

***Figure 3**. Infrared (IR) spectra:(a) AN-31 anion-exchange resin, (b) AN-31 modified with SMCA polyampholyte*

The infrared (IR) spectral analysis revealed that in the range of 3600–3200 cm^{-1}, a broad and intense absorption band (~3400 cm^{-1}) is observed, corresponding to –OH (from –COOH) and –NH/–NH_2 groups (from amino groups of AN-31). The broadness of this band indicates the presence of hydrogen bonding, characteristic of polymeric materials.

Medium-intensity peaks in the 3000–2800 cm^{-1} region are attributed to aliphatic C–H (–CH_2–, –CH_3) stretching vibrations, confirming the polymer chain structure. Strong peaks observed in the 1750–1600 cm^{-1} region (1600–1650 cm^{-1}) correspond to C=O asymmetric stretching vibrations of carboxylate (–COO^-) or amide C=O (if amidation occurred during modification), indicating successful incorporation of carboxyl groups from sodium monochloroacetate.

Multiple peaks in the 1550–1400 cm^{-1} region correspond to symmetric –COO^- vibrations (~1400 cm^{-1}) and N–H deformation vibrations, confirming the formation of a polyampholyte structure. The complex multiplet region from 1300–1000 cm^{-1} is asso ciated with C–N, C–O, and C–O–Na vibrations, indicating the presence of sodium salt form (–COO^-Na^+). The 900–600 cm^{-1} region corresponds to skeletal vibrations of the polymer backbone and substituents.

From these results, it can be concluded that:

- The amino groups of the AN-31 resin were retained,
- Successful modification with sodium monochloroacetate was achieved,
- Both –NH_2^+ and –COO^- groups are present in the system,
- The polyampholyte was successfully formed.

Comparison of the IR spectra shows that in unmodified AN-31, only amino functional groups are present and no carboxyl groups are observed. After modification, new C=O and –COO^- peaks appear, and the 3400 cm^{-1} region broadens (–NH + –OH), indicating chemical changes and confirming successful modification.

The reaction kinetics showed that the modification reaction follows a higher-order process, with tg $\alpha = 1.55$, ln $k = 0.44$ ($k \approx 1.55$ s·L/mol), indicating a high reaction rate. The negative values of ΔH and ΔG confirm that the synthesis is thermodynamically favorable and spontaneous. The activation energy was calculated as 12.88 kJ/mol, which is relatively low, indicating that the reaction proceeds easily and rapidly.

The presented figure - 4 illustrates the sorption kinetics of Pb(II) ions onto the newly synthesized ion-exchange sorption material obtained from industrial anionite AN-31. The adsorption capacity (Qe, mg·g^{-1}) is shown as a function of contact time (t, min) at different initial Pb(II) concentrations (0.00625 M, 0.0125 M, 0.025 M, and 0.05 M).

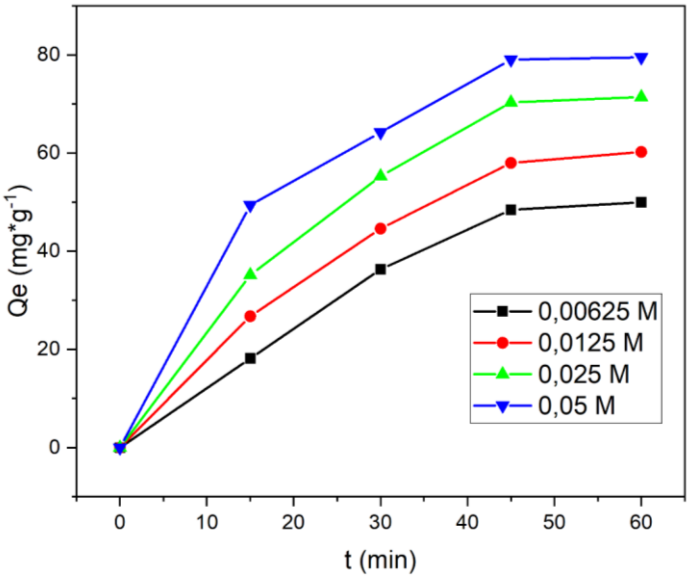

Figure 4. *Kinetic Analysis of Pb(II) Ion Sorption on the New Ion-Exchange Material Based on Industrial Anionite AN-31*

1. Effect of Contact Time

The curves demonstrate a rapid increase in sorption capacity during the initial stage (0–15 minutes). This behavior indicates that a large number of active sites are initially available on the sorbent surface, allowing fast binding of Pb(II) ions.

After the first 15–30 minutes, the sorption rate gradually decreases, and equilibrium is approached around 45–60 minutes. The slowing of the process suggests progressive occupation of active sites and possible diffusion limitations within the internal structure of the sorbent particles.

2. Effect of Initial Concentration

The adsorption capacity significantly increases with increasing initial Pb(II) concentration:

- At 0.00625 M, Qe reaches approximately 50 $mg \cdot g^{-1}$
- At 0.0125 M, Qe reaches approximately 60 $mg \cdot g^{-1}$
- At 0.025 M, Qe reaches approximately 70 $mg \cdot g^{-1}$
- At 0.05 M, Qe reaches approximately 80 $mg \cdot g^{-1}$

This trend indicates that higher metal ion concentration enhances the driving force of mass transfer between the solution and the sorbent surface, resulting in greater sorption capacity.

3. Kinetic Behavior and Mechanism

The overall kinetic profile suggests that the sorption process likely follows a pseudo-second-order kinetic model, which is typical for chemisorption mechanisms involving valence forces, electron sharing, or ion exchange. The rapid initial stage corresponds to surface adsorption, while the slower later stage may be controlled by intraparticle diffusion.

The high sorption capacity and relatively short equilibrium time (about 45–60 minutes) demonstrate that the modified AN-31-based material exhibits strong affinity toward Pb(II) ions.

4. Practical Significance

The results confirm that the newly developed ion-exchange sorption material based on industrial anionite AN-31 is highly effective for the removal of Pb(II) ions from aqueous solutions. Its high adsorption capacity, fast kinetics, and stability make it a promising candidate for wastewater treatment and heavy metal removal applications.

Conclusion

During this study, a polyampholyte with both cationic and anionic exchange properties was successfully synthesized using industrial AN-31 anion-exchange resin and the sodium salt of

monochloroacetic acid. IR analysis confirmed that unmodified AN-31 contains only amino functional groups, whereas the modified polyampholyte shows new C=O and $–COO^-$ peaks and broadening in the 3400 cm^{-1} region (–NH + –OH), confirming chemical modification. The reaction order and kinetics indicate a high-order, rapid reaction. Thermodynamic parameters (ΔH, ΔG) are negative, and the activation energy is 12.88 kJ/mol, demonstrating that the reaction is energetically favorable, spontaneous, and proceeds efficiently.

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