CREATING THEORETICAL AND PRACTICAL FOUNDATIONS FOR OBTAINING AN ANION EXCHANGER BASED ON PVC AND PVAm

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Abstract: The modification of polyvinyl chloride (PVC) with polyvinylamine (PVAm) via nucleophilic substitution was systematically optimized to obtain an efficient anion-exchange resin. The most effective structural transformation was achieved at a PVC:PVAm molar ratio of 1:1.25, at which the substitution of chlorine atoms by amino groups was maximized. Under these conditions, the degree of modification reached approximately 83.5%, indicating substantial incorporation of functional amine groups into the polymer backbone. Furthermore, the modified resin exhibited a high static exchange capacity (SEC) of 2.97 meq g^{-1}, confirming its excellent ion-exchange performance. These results demonstrate that the synthesized material is a promising candidate for applications in water purification and ion-separation processes requiring high anion-exchange efficiency. The nucleophilic substitution pathway ensures effective functionalization while maintaining chemical stability and practical applicability.

Keywords: *PVC modification, PVAm, anion exchange resin, SEC, modification degree.*

1. Introduction

Anion exchangers are ion-exchange materials widely used in chemistry, environmental protection, pharmaceuticals, and many other fields. They have the ability to effectively capture and separate anions in solutions and are especially important in water purification, separation of metal ions, and extraction of biologically active substances. The ion-exchange capacity of anion exchangers depends on their chemical structure and the active groups in their composition, and these aspects determine their selectivity and efficiency [1].

Anion exchangers are mainly produced based on synthetic polymers and are divided into weakly or strongly basic types according to their structure. Strongly basic anion exchangers, for example, are developed based on quaternary ammonium groups, while weakly basic anion exchangers are obtained from amine and its derivatives [2]. Weakly basic anion exchangers are sensitive to pH, and their ion exchange properties change depending on pH conditions. This feature makes them very useful in special applications, such as isolating nucleic acids from biological fluids or removing pollutants from the environment [3].

Currently, several principal methods are employed for the synthesis of anion exchangers. Among these, the most commonly used approaches include:

1. **Polycondensation method** — based on the formation of branched polymers with anion-exchange properties through the polycondensation of phenol–formaldehyde or other polymeric systems. This method yields anion exchangers characterized by high mechanical strength and structural stability [4–5].
2. **Radical polymerization method** — involves the synthesis of a polymer from suitable monomers followed by its functionalization with modifiers containing specific amino groups.

Polymers based on acrylic and styrenic systems are widely used in this approach due to their versatility and ease of modification [6–7].

3. **Modification method** — consists of introducing ion-exchange functional groups into pre-formed polymers through chemical modification with specialized reagents. This method is particularly effective for the synthesis of strongly basic anion exchangers based on polyvinyl chloride (PVC) and polyvinylamine (PVAm) [8–9].

In this study, a modification approach aimed at synthesizing a strongly basic anion exchanger based on polyvinyl chloride (PVC) and polyvinylamine (PVAm) was investigated. During the modification process, chlorine atoms in the PVC polymer chain are substituted by amino groups from PVAm, leading to the formation of a new material with pronounced ion-exchange properties. This approach is both simple and effective, enabling the rational utilization of polymer resources in the production of anion exchangers [10].

The present article highlights the significance of anion-exchange materials and describes the principal stages involved in the preparation of a PVC/PVAm-based anion exchanger, including the synthesis procedure and material balance calculations. In addition, the physicochemical properties of the synthesized material are examined, and its ion-exchange performance is systematically evaluated. The findings of this study contribute to the development of efficient anion-exchange materials with potential applications in water purification, pharmaceutical, and chemical industries [11–12].

Due to the expanding production and application areas of anion exchangers, improving their production technologies and searching for new effective methods is one of the urgent tasks. Currently, anion exchangers are used in many fields. In particular, their ion-exchange properties are utilized in the purification of water and industrial wastewater, adsorption of heavy metal ions, pharmaceuticals and biomedicine, as well as in the petrochemical and food industries [13].

Anion exchangers play a crucial role in water purification systems. Specifically, they are used to remove nitrate, sulfate, chloride, and other harmful anions from water. Strong and weak base anion exchangers serve to purify water from minerals and improve its quality through ion exchange reactions [14]. Today, the importance of anion exchangers in combating environmental problems is increasing, and they are being used as effective adsorbents for neutralizing harmful substances in industrial waste.

Anion-exchange resins (anion exchangers) play a significant role in the pharmaceutical industry, where they are used to enhance the biological activity of drugs through the purification, separation, and ion-exchange of medicinal substances [15]. For example, anion exchangers are essential tools for the separation of nucleic acids and for obtaining biologically active molecules in high-purity form. In addition, ion-exchange resins are employed in the manufacture of pharmaceuticals that regulate blood-clotting processes [16].

In the chemical industry, anion exchangers are widely utilized as catalysts or as agents for improving reaction selectivity. They are particularly important in polymer production, the separation and recovery of non-ferrous metal ions, and the fabrication of ion-exchange membranes. In the petrochemical sector, anion exchangers are used for the separation of by-products and for controlling the composition of the reaction medium [17].

Various methods exist for the synthesis of ion-exchange resins, each possessing specific advantages and limitations. As discussed above, polycondensation and radical polymerization are the most commonly employed techniques for producing anion exchangers. In addition, the modification method plays a crucial role in the development of advanced anion-exchange materials, particularly when tailored functional properties are required.

2. Experimental part

The synthesis of an anion exchange resin based on polyvinyl chloride (PVC) and polyvinyl alcohol (PVAm) proceeds through the following chemical reaction, which reflects the formation of a cross-linked polymer matrix capable of anion exchange functionality:

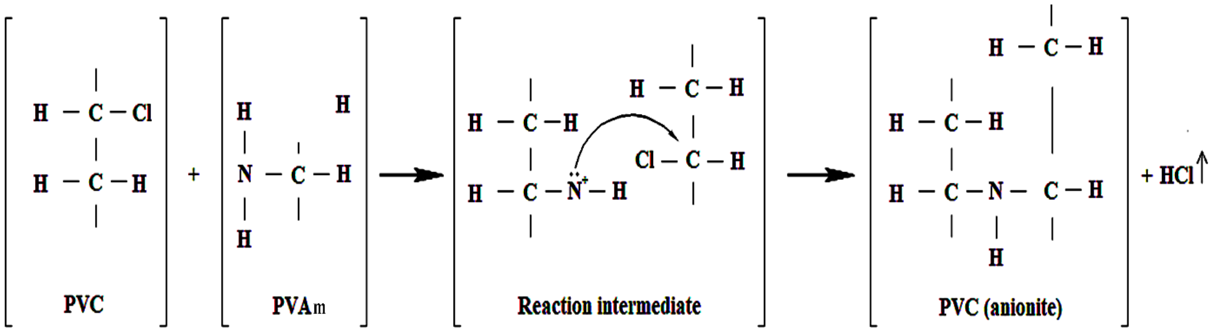


Fig. 1. Reaction scheme for the formation of the anion exchange resin from PVC and PVAm

A strong basic anion exchange resin was synthesized using PVC and PVAm as base materials. The following reagents were used in the synthesis process.

2.1. Materials

1. PVC – granulated form, purity >99%, purchased from ASL-Kimyo (Uzbekistan).
2. PVAm – used as a source of amino groups, molecular weight approximately 103 g/mol per amino group, supplied by ASL-Kimyo.
3. Ethanol (C_2H_5OH) – used as a solvent, analytical grade, 99.5% purity.
4. Calcined soda (Na_2CO_3) – applied as a reaction initiator.
5. Buffer solutions – used to maintain pH stability during synthesis.
6. Ethyl acetate – used for washing to remove unreacted PVC at the end of the process, purity 98.7%, obtained from ASL-Kimyo.

All chemicals were used as received without additional purification. The modification of PVC with PVAm was carried out under controlled temperature and reaction conditions. The synthesis was based on a nucleophilic substitution mechanism, where the chlorine atoms in the PVC backbone were replaced by the amino groups from PVAm. The process consisted of the following stages below.

2.2. Experimental Methodology

1. *Preparation of PVC solution.* Granulated PVC was dissolved in ethanol and stirred continuously using a magnetic stirrer (Intllab MS-500) at a temperature of 50–70 °C to obtain a homogeneous solution.
2. *Addition of PVAm.* PVAm was gradually added to the PVC solution under constant stirring.
3. *Substitution reaction.* The reaction mixture was transferred to a Ross HSM-40 Vacuum Double Helical Mixer Reactor [18], where it was heated to 80–100 °C and maintained at that temperature for 5–6 hours under continuous stirring. This setup ensured efficient substitution of chlorine atoms in PVC by amino groups from PVAm under uniform thermal and mixing conditions.
4. *Precipitation and washing.* After completion of the reaction, the mixture was cooled, and the modified polymer was precipitated using ethyl acetate. The resulting product was washed with distilled water to remove residual solvent and unreacted PVAm.
5. *Drying.* The final anion exchange resin was dried in an SNOL 67/350 drying oven at 50–60 °C until constant weight was achieved.

2.3. Methodology for Determining Modification Degree. The degree of modification was determined from the amount of hydrogen chloride (HCl) released during the reaction between polyvinyl chloride (PVC) and polyvinylamine (PVAm). As the modification proceeds, chlorine atoms in the PVC macromolecular chains are substituted by amino groups from PVAm, accompanied by the elimination of HCl.

To quantify the released HCl, the gaseous reaction by-product was absorbed in a known volume of a standard sodium hydroxide (NaOH) solution. The excess NaOH was subsequently back-titrated with a standard hydrochloric acid (HCl) solution using phenolphthalein as an indicator. The amount of HCl evolved during the reaction was calculated from the titration results.

The degree of modification (MD) was calculated using the following equation:

$$\boldsymbol{Modification\ degree} = \frac{Mass\ of\ HCl\ released\ (g)}{Theoritical\ total\ Cl\ mass\ in\ starting\ PVC\ (g)} \times 100\% \quad (1)$$

2.4. Physicochemical characterization techniques. The chemical structure and functional groups of the modified anion exchange resin were characterized using Fourier Transform Infrared Spectroscopy (FTIR). The analysis was conducted with a Dw-FTIR530A (China Laboratory Spectrophotometer FTIR Spectrometer) under standard conditions. The FTIR spectra were recorded in the range of 4000–400 cm^{-1}, allowing the identification of characteristic functional groups associated with the polymer matrix and any modifications introduced during synthesis. The obtained spectra provided clear insights into the presence of hydroxyl, carbonyl, and other functional groups, confirming the chemical modification of the anion exchange resin [19].

The surface morphology of the anion exchange resin synthesized based on PVC and PVAm was analyzed using Scanning Electron Microscopy (SEM) with a JEOL JSM-IT500 instrument, and the elemental composition was determined by Energy Dispersive Spectroscopy (EDS). The measurements were performed under high vacuum conditions at an acceleration voltage of 20.0 kV, with a working distance of 11.7 mm and a magnification of ×95. The live time was 30 seconds, real time 43.89 seconds, count rate 70228 CPS, and dead time 31.00%. EDS analysis provided both qualitative and quantitative data on the elemental distribution in the sample [20-22].

All graphical analyses and data visualizations were performed using OriginPro 2021 (OriginLab Corporation, Northampton, MA, USA) and ChemDraw 21 to process the experimental results and generate corresponding plots.

3. Result and discussion

During the research, a surface-based anion exchanger was synthesized by modifying polyvinyl chloride PVC and PVAm. Throughout the reaction process, various parameters were optimized, including temperature, reaction duration, and raw material ratios. As a result of the modification, the chlorine atoms in PVC were replaced with amino groups. The results are presented in Table 1.

Table 1. Results of the modification process at various ratios of PVC and PVA

PVC (g)	PVAm (g)	Molar ratio (PVC: PVAm)	Modified PVC (g)
100	164.8	1:1	229.12
100	181.28	1:1.1	238.90
100	197.76	1:1.2	251.01
100	206	1:1.25	258.57
100	214.24	1:1.3	266.58
100	230.72	1:1.4	282.95
100	247.2	1:1.5	299.38

According to Table 1, the analysis shows that as the mass of PVAm increases, the molar ratio of PVC to PVAm rises from 1:1 to 1:1.5, leading to an increase in the mass of the modified PVC from 229.12 g to 299.38 g. The higher PVAm content promotes the chlorine–amine substitution process, thereby increasing the degree of modification. Significant changes are observed at ratios of 1:1.3 and 1:1.4, which may indicate the optimal modification range. Since the PVC mass remains constant, the mass of modified PVC primarily depends on the PVAm mass and the degree of chlorine exchange, increasing with the addition of a larger mass of PVAm.

After conducting theoretical calculations, the degree of PVC modification was determined.

$$\boldsymbol{Modification\ degree} = \frac{47.43\ (g)}{56.8\ (g)} \times 100\% = 83.5\% \tag{2}$$

Subsequently, a graph was constructed to illustrate the relationship between the mass of the resulting anionite, the molar ratios of PVC to PVAm, and the degree of modification. The corresponding results are depicted in Fig. 2.

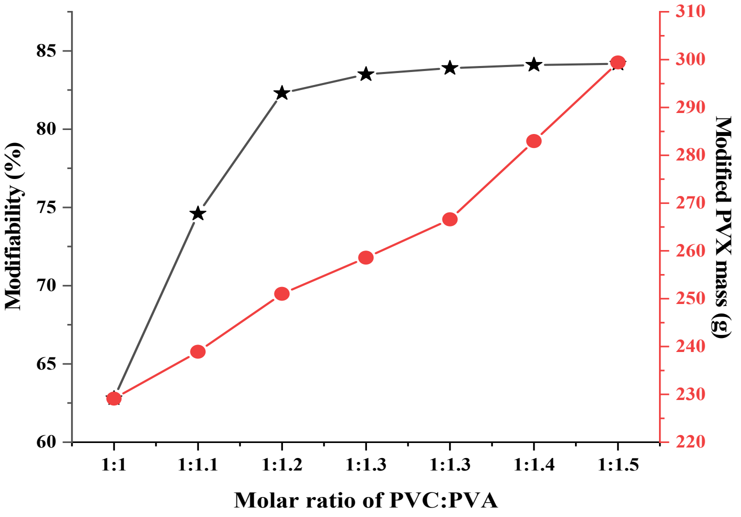


Fig. 2. Dependence of the modified PVC mass and degree of modification on the PVX:PVAm molar ratio

According to Figure 2, as the PVC:PVAm molar ratio increases, the degree of modification rapidly rises and then stabilizes after a certain point, while the mass of the modified PVC continues to increase steadily.

The black star line represents the degree of modification, and the red dotted line represents the mass of the modified PVC. The degree of modification increases rapidly from 1:1 to 1:1.2, indicating that PVAm effectively replaces chlorine atoms in PVC. After 1:1.3, the degree of modification remains almost unchanged, suggesting that the maximum number of amino groups has been incorporated. The mass of modified PVC continues to increase up to 1:1.5, indicating that the increase in PVAm amount contributes to the formation of the modified PVC structure. As shown in the graph, the ratios between 1:1.2 and 1:1.3 are the most effective, providing the optimal degree of modification.

After establishing the most efficient PVC:PVAm ratio for structural modification, the static exchange capacity (SEC) of the synthesized anion exchanger was subsequently determined.

The graph above reflects this correlation and helps identify the ideal modification ratio for achieving high ion-exchange performance.

Fig. 3 clearly demonstrates that increasing the PVC:PVAm ratio from 1:1 to 1:1.3 leads to a significant rise in the degree of modification. The peak is observed between 1:1.3 and 1:1.4, indicating the maximum incorporation of amino groups into the PVC structure. Beyond a PVC:PVAm molar ratio of 1:1.4, a noticeable decrease in the degree of modification is observed, indicating that an excess of PVAm may hinder the efficiency of the modification process. Consequently, the optimal modification range lies between 1:1.25 and 1:1.3. Among these conditions, a PVC:PVAm ratio of 1:1.25 was identified as the most favorable for achieving efficient modification.

Following the determination of the optimal modification conditions, infrared (IR) spectroscopic analysis of the anion exchanger synthesized at this ratio was performed. The corresponding IR spectra are presented in Fig. 4.

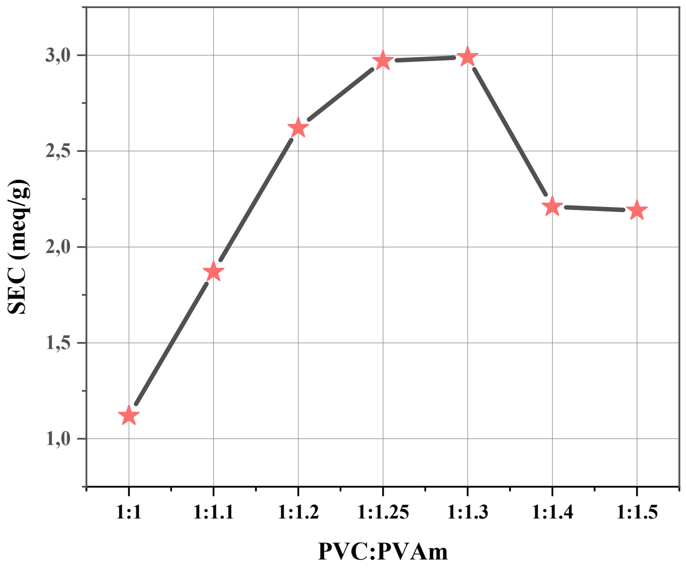


Fig. 3. Effect of PVC: PVAm Ratio on Static Exchange Capacity (SEC)

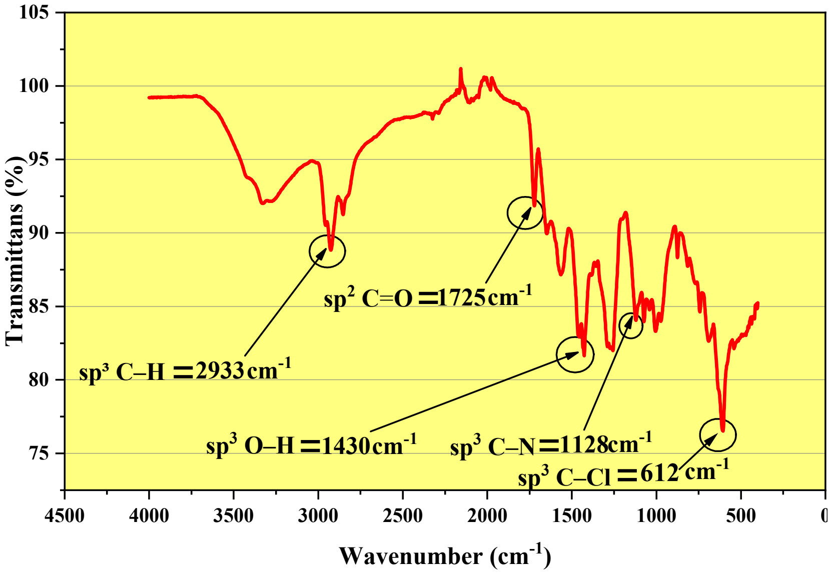


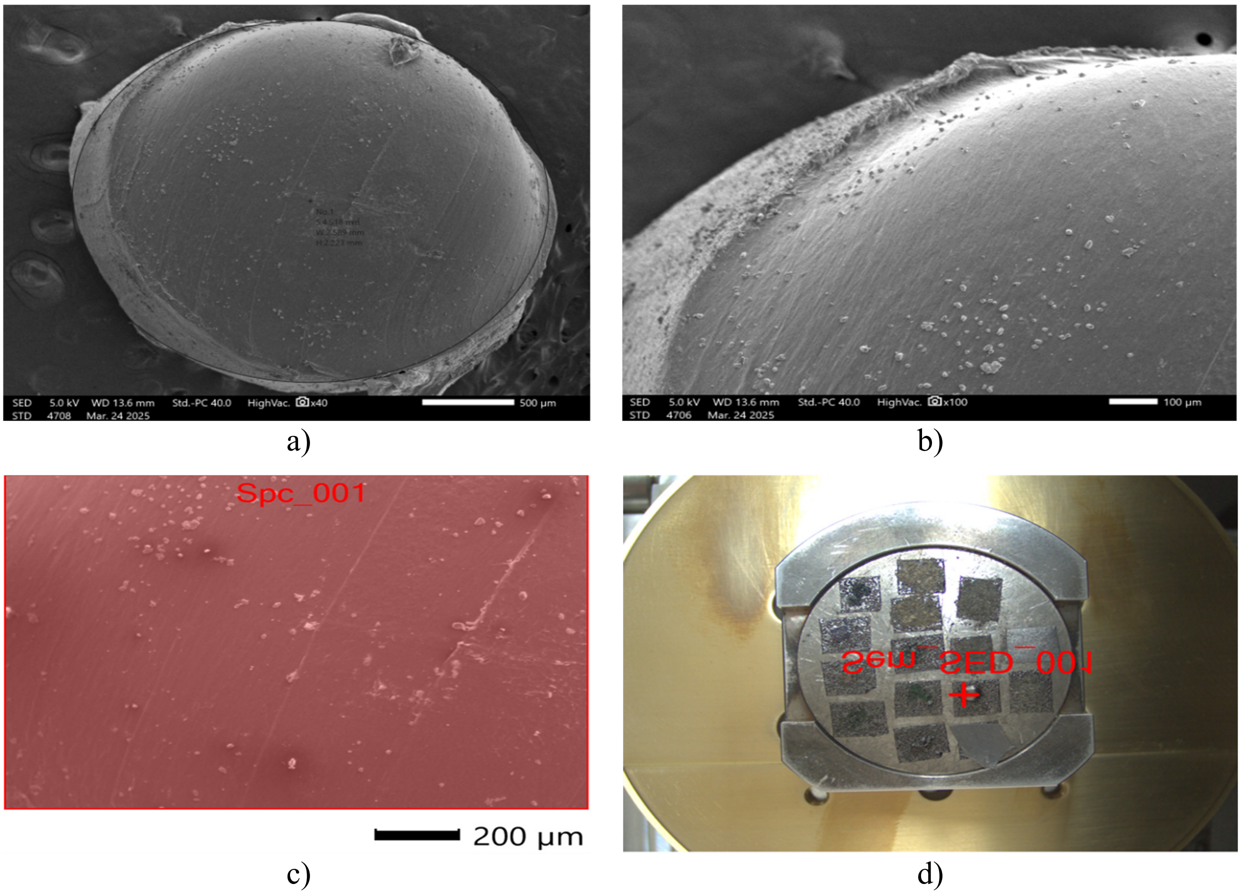
Fig. 4. FTIR Analysis of a Modified PVC Sample

According to Figure 4, the FTIR spectrum of the synthesized anion exchange resin based on PVA and PVC reveals several significant absorption peaks, indicating the presence of key functional groups introduced or retained during the modification process:

- The absorption band at 2933 cm^{-1} corresponds to the stretching vibrations of sp^3 hybridized C–H bonds, confirming the presence of saturated aliphatic chains derived from the polymer backbone.
- A distinct peak at 1725 cm^{-1} is attributed to the C=O stretching vibrations, which suggests either partial oxidation of PVAm or the formation of new carbonyl-containing linkages due to crosslinking reactions or post-functionalization with aldehydes.
- The peak observed at 1430 cm^{-1} corresponds to the bending vibrations of hydroxyl (O–H) groups, indicating that some hydroxyl functionalities from the PVAm remain intact, contributing to the material's hydrophilic character.
- The appearance of a band at 1128 cm^{-1} is indicative of C–N stretching, confirming the successful introduction of amine groups into the polymer matrix through nucleophilic substitution of chlorine atoms in PVC. This functionalization imparts anion exchange properties to the material.

- Lastly, the peak at 612 cm⁻¹ corresponds to C–Cl stretching vibrations, revealing that a portion of the original PVC structure remains unmodified, and not all chlorine atoms were substituted during the synthesis.

To improve the accuracy of the results and to better understand the morphology of the anion exchange resin particles, SEM and EDS analyses were conducted on the modified PVC sample. In order to ensure data reliability, the analyses were carried out under optimized conditions, and the obtained results are presented in Fig. 5.



a) b)

c) d)

Fig. 5. SEM (a) and EDS (b) characterization of PVC modified with PVA as anion exchange resin

According to Fig. 5:

a) The SEM image at 500 µm magnification presents the overall morphology of a single synthesized resin particle. The particle exhibits a near-spherical shape with a relatively smooth surface, indicating homogeneous polymer formation. According to the dimensional analysis, the projected area of the particle is 4.518 mm², with an approximate width of 2.589 mm and height of 2.221 mm. The absence of surface fractures or deformation suggests strong mechanical stability and structural integrity.

(b) At 100 µm magnification, the edge of the resin particle is shown in closer detail. No delamination or surface cracks are observed, implying that the PVC and PVAm components are well integrated. The compact and continuous structure further confirms the quality of the synthesis process.

(c) This image, taken at 200 µm magnification and marked as "Spc_001", illustrates the surface region where EDS mapping was performed. The distribution of bright spots across the surface suggests the presence of functional groups or elemental zones such as Cl, O, and Na, which are characteristic of active anion-exchange regions.

(d) The final image displays the sample holder (stub) containing multiple synthesized resin particles prepared for SEM analysis. The central area labeled "Sem_SED_001" indicates the scanning location. This setup allows for efficient comparison of surface morphology across different samples under consistent conditions.

Following the morphological analysis using SEM at different magnifications, elemental characterization of the synthesized PVC–PVAm-based anion exchange resin was conducted using Energy Dispersive X-ray Spectroscopy (EDS) attached to the SEM instrument. This analysis helps identify the elemental composition of the sample surface and confirm the presence of functional components responsible for ion exchange.

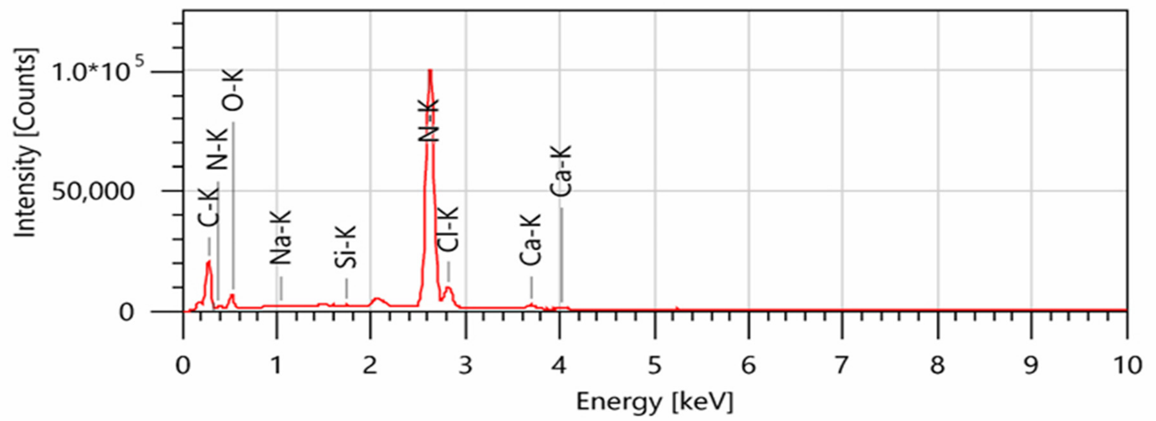


Fig. 6. EDS spectrum of the synthesized anion exchange resin

EDS spectrum of the PVC–PVAm-based anion exchange resin surface. The spectrum shows characteristic peaks corresponding to the elements C, N, O, Cl, Na, Si, and Ca, indicating their presence on the surface of the resin. The prominent peaks of C-K, N-K, O-K, and Cl-K confirm the incorporation of functional groups related to polyvinyl chloride and polyvinyl alcohol structure, as well as the successful introduction of anion-exchange active sites. Trace peaks of Na and Ca may originate from residual reagents or environmental contamination.

Following the qualitative EDS spectrum, a quantitative elemental analysis was also performed using the same SEM-EDS system. This analysis provides mass and atomic percentages of the elements present on the surface of the synthesized anion exchange resin. The results of the elemental composition are summarized in Table 2.

Table 2. EDS-based quantitative analysis of surface elements

Element	**Line**	**Mass % ± SD**	**Atom % ± SD**
C	K	55.07 ± 0.15	67.68 ± 0.18
N	K	21.19 ± 0.04	8.82 ± 0.02
O	K	11.16 ± 0.10	10.29 ± 0.09
Na	K	0.13 ± 0.01	0.08 ± 0.00
Cl	K	12.45 ± 0.18	13.12 ± 0.19
Total	-	100.00	100.00

According to Table 2, the EDS quantitative analysis confirms that carbon (C) is the dominant element on the resin surface, comprising 55.07% by mass and 67.68% by atom, which is consistent with the presence of a polymer matrix based on PVC and PVAm. A significant amount of nitrogen (21.19% mass) indicates successful incorporation of amine or quaternary ammonium functional groups, essential for anion exchange activity. Oxygen and chlorine are also notably present, supporting the structural integration of both polymer backbones and ion-exchange functionalities. Minor traces of sodium suggest either residual reagents or ionic contamination. Overall, the elemental distribution confirms the formation of a functionalized anion exchange resin with expected surface characteristics.

4. Conclusion

1. *Optimal molar ratio:* The optimal PVC:PVAm molar ratio was identified as 1:1.25, providing the most efficient substitution of chlorine atoms with amino groups. This composition ensured balanced reactivity and structural stability in the modified polymer.
2. *Static Exchange Capacity (SEC):* At the PVC:PVAm molar ratio of 1:1.25, the anion exchanger exhibited a static exchange capacity of 2.97 meq/g, confirming the high ion-exchange efficiency of the modified polymer.
3. *Degree of modification:* Under the optimal PVC:PVAm molar ratio of 1:1.25, the degree of modification reached approximately 83.5%, indicating efficient substitution of chlorine atoms and near-saturation of reactive sites within the polymer structure.

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