

Obtaining and Physical-Chemical Properties of Polycomplexone

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Abstract In this study, a novel polyampholytic polymer complex (SMAF) was successfully synthesized by chemically modifying polyacrylonitrile (PAN) fiber with hexamethylenediamine (HMDA), followed by phosphorylation using phosphite acid (H_3PO_3) and formaldehyde (CH_2O). The reaction conditions were optimized based on static exchange capacity (SEC), reaching a maximum value of 4.3 meq/g at 5–7 hours with 60% phosphite acid. Physicochemical characterization was conducted using FT-IR spectroscopy and potentiometric titration. FT-IR spectra confirmed the incorporation of amine and aminomethylenephosphonate groups ($-\text{NH}-\text{CH}_2-\text{PO}_3\text{H}_2$), showing characteristic bands at $2800\text{--}2850\text{ cm}^{-1}$ and $968\text{--}1170\text{ cm}^{-1}$, alongside a reduced nitrile ($-\text{C}\equiv\text{N}$) band intensity at 2242 cm^{-1} due to nucleophilic modification. Potentiometric titration curves exhibited differential peaks at $[\text{H}^+] = 1.7\text{ meq/g}$ and $[\text{OH}^-] = 2.7\text{ meq/g}$, confirming the amphoteric nature and presence of functional groups with dual basicities and acidic phosphonic groups. The resulting SMAF polyampholyte demonstrates a crosslinked, insoluble matrix, proving highly effective for industrial wastewater treatment and heavy metal ion recovery.

Keywords Polyacrylonitrile, Hexamethylenediamine, Phosphite acid, Polycomplex, Static exchange capacity

1. Introduction

Today, ion-exchange materials are widely used in various sectors of the economy, and the demand for them is constantly growing. Ion-exchange polymer materials play a special role in the separation and concentration of colored, rare, heavy, and precious metals, as well as in the preparation and purification of industrial water [1]. In particular, ion-exchange sorbents have been successfully used to solve many environmental problems [2].

In this regard, the synthesis of ion-exchange materials and the study of their sorption properties remain a pressing issue. As is known from the literature, polymer materials that combine complex properties are mainly obtained by chemically modifying polymers bearing various functional groups. In this process, the initial structure of the polymer material is preserved [3].

Polyampholytes containing nitrogen and phosphorus exhibit both ion exchange and chelation processes simultaneously. Such polymer materials have high sorption properties, characterized by high sorption capacity and selectivity for a number of heavy and colored metals, which is also due to the polydentate nature of the polymer chelating

agent, both due to the chelating effect of complex formation involving amino and phosphonic groups [4,5].

Ion exchangers are widely used for solving a range of practical problems, including:

- water treatment processes, such as desalination, softening, and complete deionization of water for technological and industrial applications;
- separation, concentration, and recovery of metal ions and other valuable components in the hydrometallurgy of non-ferrous and precious metals;
- removal of chemically active ionic and polar impurities from industrial process streams, including the purification of certain gases and liquid media;
- modification of the ion-exchange properties of soils and controlled delivery of essential micronutrients and fertilizers to improve plant growth and nutrient availability.

Thus, ion-exchange materials have found broad application in water purification, hydrometallurgy, industrial separation processes, and agriculture due to their high selectivity, exchange capacity, and ability to reversibly bind ionic species [6].

With the expansion and development of industrial enterprises, the demand for anion-exchange and chelating sorbents increases. The synthesis of these sorbents is carried out by modifying various chemical reagents to alter the functional groups of the sorbents used in industrial enterprises

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[7,8]. Therefore, the process of obtaining ion-exchange, complex-forming materials from granular and local polyvinyl raw materials, and the study of their physicochemical properties, is one of the pressing tasks in physical chemistry and the chemistry of macromolecular compounds.

The processes for obtaining ion-exchange sorbents by chemically modifying polyacrylonitrile (nitron) fiber with various amine-containing and hydroxylamine-containing reagents have been thoroughly studied. In the studies, the kinetics of modification reactions of nitron fiber with dimethylhydrazine, hydroxylamine, hexamethylenediamine, and ethylenediamine, the reaction medium conditions, and their sorption properties were investigated in detail [9,10]. In particular, the scientific basis has been established for modifying the nature of modifiers and introducing solvents such as dichloroethane into the reaction medium, thereby attaching various functional groups to the polymer chain and synthesizing anion-exchange materials with high capacity.

2. Method

To obtain a strong-base ion-exchange sorbent, PAN fibers were modified with hexamethylenediamine (HMDA) in a reaction, and the SMA-1 sorbent was synthesized [11]. In the next step, the SMA-1 anionite was treated with phosphite acid, and the SMAF polyampholytic sorbent was synthesized.

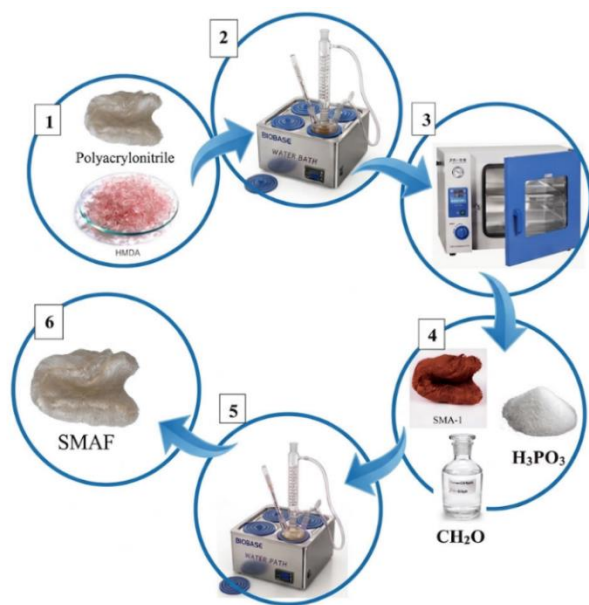


Figure 1. Schematic representation of the step-by-step synthesis of PAN-based SMAF polyampholytic sorbent

As is known from the literature, phosphite acid (by virtue of its structure) is a nucleophile due to the electron pair on the phosphorus atom. In the first stage, the polymer formed undergoes a chemical modification via secondary amine groups, resulting in the formation of $-PO_3H_2$ groups.

Identifying the new functional groups in the resulting polymer requires special conditions and presents a number of

challenges; therefore, the static exchange capacity (SEC) was determined to characterize the cyan group exchange level of the ion-exchange materials. The SEC value of the synthesized sorbents was determined using 0.1 N HCl and NaOH solutions as the degree of substitution during the chemical modification of the polymers.

To determine the optimal temperature for the chemical modification of SMA-1 fiber with phosphite acid, the kinetics of the modification process were studied at various temperatures.

The maximum SEC value was observed when the reaction was carried out for 5–7 hours, and it was determined that SEC increased with increasing phosphite acid concentration. The maximum SEC value (4.3 meq/g) was recorded when the reaction time was 7 hours and the H_3PO_3 concentration was 60%.

The synthesized polyampholyte PAN is insoluble in solvents, organic solvents, and strong acids and bases, which indicates that it has transitioned into a crosslinked state as a result of polymer modification.

3. Results and Discussion

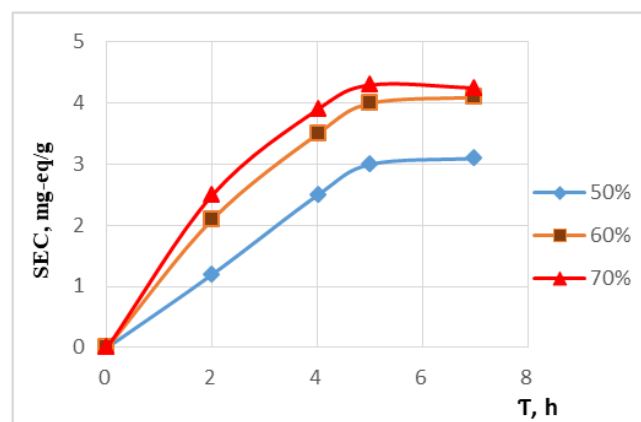


Figure 2. Dependence of the SEC of the polyampholyte on the reaction time at various concentrations of H_3PO_3

As shown in Figure 2, the kinetic study of the modification process demonstrates the influence of reaction time and phosphite acid concentration on the SEC. The SEC value increases rapidly within the first 4–5 hours of reaction and reaches a plateau after 5–7 hours. Increasing the phosphite acid concentration from 50% to 70% leads to a higher degree of functionalization, yielding a maximum exchange capacity of 4.3 meq/g. This behavior confirms the complete saturation of reactive centers along the polymer chain under optimal conditions.

To characterize the chemical structure of the synthesized polymer, its IR spectrum and samples were examined by potentiometric titration to assess the ionic equilibrium between a polyampholytic and an aqueous medium. An IR spectrum was obtained to characterize the chemical structure of the synthesized polymer.

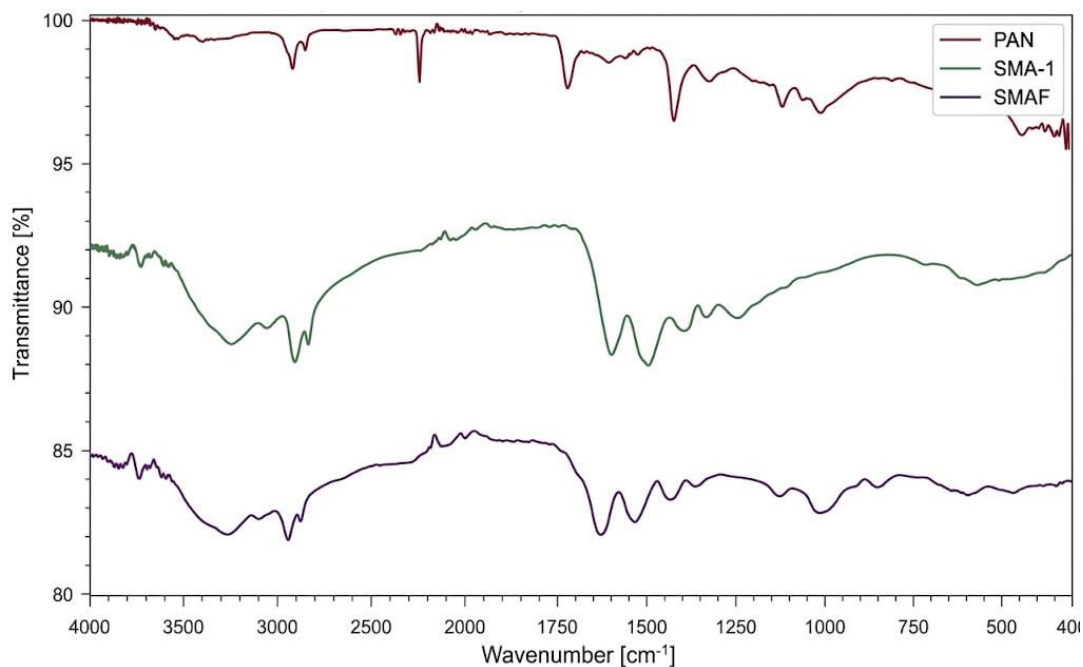


Figure 3. IR spectra of PAN, SMA-1, and SMAF samples

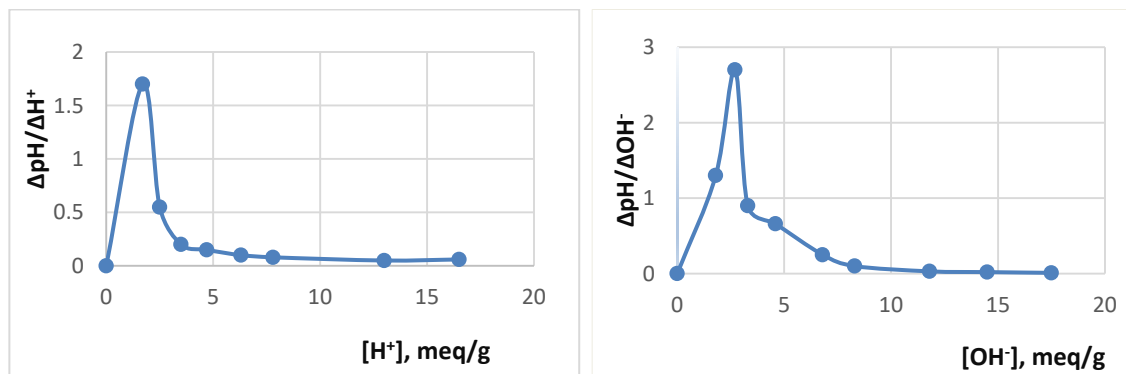


Figure 4. Differential curve of the potentiometric titration of the SMAF-1 polyampholyte with HCl (a) and NaOH (b) solutions

Unlike the spectrum of initial PAN, the intensity of the characteristic absorption band at 2242 cm^{-1} , corresponding to the stretching vibrations of the nitrile ($\text{-C}\equiv\text{N}$) group, decreases significantly in SMA-1 and SMAF [11]. This reduction is attributed to the nucleophilic addition of HMDA to the nitrile groups during modification, leading to the formation of imino (-C=NH) and amine (-NH-) bonds [12,13]. The residual weak absorption at 2242 cm^{-1} indicates that a fraction of the nitrile groups within the polymer backbone remained unreacted due to steric hindrance [14]. Furthermore, new bands appearing at 1565 cm^{-1} ($>\text{NH}$ bending) and 1658 cm^{-1} (-NH_2 bending and $>\text{C=N-}$ stretching) confirm successful amine functionalization [15].

In the FT-IR spectrum of the SMAF polyampholyte, new intense absorption bands observed at 968 , 1099 , and 1170 cm^{-1} are assigned to the characteristic vibrations of phosphonic acid groups (-P(O)(OH)_2) [16,17]. Additionally, the absorption in the $2800\text{--}2850\text{ cm}^{-1}$ region corresponds to the symmetric and asymmetric stretching vibrations of methylene ($\text{-CH}_2\text{-}$) groups linked within the aminomethylenephosphonate

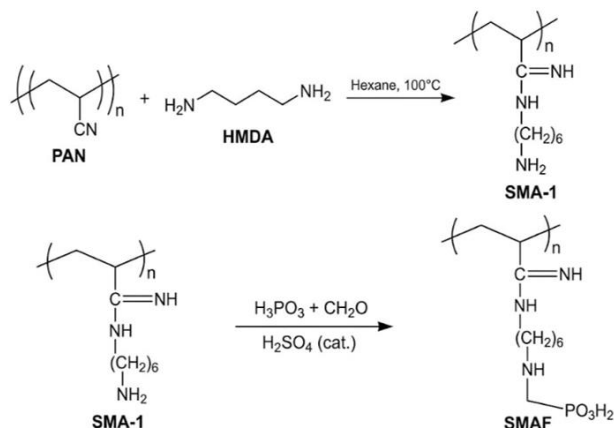
fragments ($\text{-NH-CH}_2\text{-PO}_3\text{H}_2$) [18,19]. The presence of adjacent electron-withdrawing phosphonate groups and nitrogen atoms alters the local electron density, causing these characteristic C-H stretching bands to appear clearly in this region [19,20].

The potentiometric titration curves of the SMAF-1 polyampholyte clearly demonstrate its polyamphoteric nature. The differential anion-exchange titration curve (Figure 4a) exhibits a sharp peak at $[\text{H}^+] = 1.7\text{ meq/g}$. This data indicates the presence of functional groups with two distinct basicities in the synthesized anionite. Specifically, the stronger basicity is attributed to the primary and secondary aliphatic amine groups ($\text{-CH}_2\text{-NH-}$ and -NH_2) originating from the HMDA modifier, whereas the weaker basicity corresponds to the imino/amidin (-C=NH) groups formed during the chemical modification of PAN nitrile bonds. The differing protonation abilities (pK_a values) of these two nitrogen-containing groups account for the observed basicity characteristics.

Conversely, the cation-exchange titration curve (Figure 4b) displays a maximum peak at $[\text{OH}^-] = 2.7\text{ meq/g}$, which confirms the incorporation of acidic phosphonic acid groups

(-P(O)(OH)₂) attached to the macromolecular backbone. The simultaneous coexistence of these distinct basic amine/imino groups and acidic phosphonic acid groups validates the successful synthesis of a crosslinked polyampholytic sorbent with dual functionality.

Based on the obtained results, the modification of PAN with HMDA and phosphite acid can be explained as proceeding according to the following scheme:



Scheme 1

4. Conclusions

As a result of the conducted research, a new type of polycomplex with ampholytic properties based on PAN was synthesized, and the optimal conditions for the reaction process were determined. The research results indicate that reaction medium parameters, including reagent ratios, temperature, and reaction time, directly affect the sorbent's physicochemical properties. As a result of optimizing these factors, the polyampholyte's static exchange capacity increased significantly. The IR spectrum of the obtained polycomplex was recorded and analyzed, and potentiometric titration was carried out to characterize the ionogenic groups. According to the research results, the new polyampholyte obtained can be used as a promising sorbent for purifying industrial wastewater from harmful ions, recovering valuable metal ions from technological solutions, and recycling secondary resources.

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DISCLOSURE

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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