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Enhanced removal of iodine from wastewater in the presence of two-step sulfo and amine functionalized polyvinylchloride

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Enhanced removal of iodine from wastewater in the presence of two-step sulfo and amine functionalized polyvinylchloride

Abstract

The release of nuclear energy and medical wastewater containing the radioactive isotopes iodine (^{129}I and ^{131}I) into the environment is causing various environmental problems. In this study, a sulfo- and aminated polyvinylchloride (PVC-(SO_3H)-NH-PAM) sorption material was synthesised to effectively remove iodine from wastewater. Sulfonation and amination reactions of polyvinyl chloride were carried out under heterogeneous conditions. It was determined that the order of the amination reaction for the sulfocation exchange resin made from polyvinyl chloride is 1.1 and that the reaction activation energy is 70 kJ/mol. Synthesised functional PVC-(SO_3H)-NH-PAM sorption material was characterised using FTIR, SEM-EDX, TGA, DSC, and BET and BJH surface analysis to identify its structure, morphology, and physico-chemical properties. In addition, functional PVC-(SO_3H)-NH-PAM material was used to remove iodine from aqueous media. A pseudo first, second order model to describe sorption kinetics as well as Langmuir and the Freundlich isotherm models to explain adsorption mechanisms, were used. The Langmuir isotherm and the pseudo-second order kinetic model led to the most consistent results in describing the removal of iodine from solution. In the case of iodine, the maximum adsorption capacity was 705 mg g^{-1}. The correlation coefficients R^2 values are 0.9987 for I_3^- ions, and the concentration change shows that the adsorption process obeys the Langmuir monomolecular adsorption theory (R_L is favourable). In addition, the adsorption kinetics followed a pseudo-second-order model ($R^2 > 0.999$). The development of functional sorption material offers a sustainable and environmentally friendly method for the effective removal of toxic iodine from medical wastewater.

Keywords: Ion exchanger, Modification, Polyampholyte, Sorption, Wastewater treatment.

Introduction

Toxic radioactive iodine isotopes are highly concentrated in wastewater from the medical (Zhou et all. 2023), disinfection (Zhang et all. 2018), and nuclear power plant (Li et all. 2020) industries. The release of radioactive iodine-containing wastewater from these industries into the environment causes

several environmental problems (Nakayama et all. 2015). Although nuclear power plants are not in large numbers worldwide, toxic radioactive iodine-containing preparations are widely used in medicine and disinfection worldwide (Zhang et all. 2017). The half-life of radioactive iodine isotope ^{129}I $t_{1/2} = 1.57 \times 10^7$ years, while the radioactive isotope ^{131}I, which is used in medical diagnostics and radioactive isotope therapy, has a half-life of $t_{1/2}$ = 8.02 days and is considered relatively more dangerous due to its high radioactivity (Li et all. 2022). The accumulation of such toxic iodine isotopes in water resources leads to some dangerous thyroid cancer, leukaemia, and metabolic disorders (Mao et all. 2016). Therefore, it is important to ensure the safe and reliable disposal of radioactive iodine isotopes in the aquatic environment. The main removal methods are physical (Du et all. 2022) and chemical (Cui et all. 2024) adsorption in the presence of sorbents, which are considered more effective than other methods. The chemical sorption method is currently the most common method in the world, mainly using sorbents based on inorganic and organic polymer matrices (Dai et all. 2024).

There are a number of technological methods for the purification of radioactive toxic ions from wastewater. These include ion exchange (Asmussen et all. 2024; Theiss eta all. 2014), adsorption (Chen etall. 2019), membrane separation (Ambashta et all. 2012), chemical precipitation (Liu et all. 2016), photocatalytic degradation (Lefevre et all. 1999), and other methods. The ion exchange method is the most widely used method for the purification of radioactive iodine compared to other types of methods. Functional sorbents, i.e., sorbents doped with metal oxides, hydroxides, and metals (Ag, Cu, Bi, Zr), have been used to remove radioactive iodine from wastewater with high efficiency (Liu et all. 2015). Metal-organic frameworks (MOFs) also have the property of highly efficient sorption of radioactive iodine ions (Long et all. 2020). The technology for synthesising such metal-containing sorbents is difficult, expensive, and unstable, so they are not widely used, despite their high sorption properties. In this situation, ion exchange materials synthesised based on organic polymers are relatively inexpensive, stable, and have a high sorption capacity (Zhang et all. 2026). The use of ion-exchange materials obtained by modifying synthetic and natural polymers is recommended for the removal of radioactive iodine from wastewater (Li et all. 2019). The synthesis of polymer-based ion-exchange materials is technologically easy and inexpensive, and their ability to be effectively reused multiple times in wastewater treatment is advantageous.

Since synthetic and natural polymers are widely used in our lives, they can be used as the main polymer matrix for the synthesis of ion exchange materials (Kayan et all. 2021; Allan et all. 2015; Matei et all. 2022; Rustamov et all. 2014; Makvandi et all. 2021; Himoyat et all. 2020). By modifying such polymers in various ways, ion exchange materials with high sorption properties, stability, and

multiple reuse properties can be synthesised (Zhang et all. 2021; Sato et all. 2023; Shatalov et all. 2007). In this study (Li et all. 2022), a functional sorbent for the purification of wastewater from radioactive iodine was synthesised based on the natural polymer chitosan. A chitosan-based sorbent demonstrated the ability to remove 90 per cent of radioactive iodine from solution. The sorbent's iodine adsorption capacity was 0.8087 mmol g^{-1}, and after five repeated uses, its adsorption efficiency dropped to just 91%. Similarly, in another study (Obid et all. 2024), the authors synthesised a green adsorbent by modifying the croslinked chitosan with hydrophobic montmorillonite. The synthesised adsorbent adsorbed 90 per cent of the ^{127}I ions in the solution within 40 minutes.

Additionally, ion exchange materials based on synthetic polymers can be used to treat wastewater contaminated with radioactive iodine. In this particular study, the authors (Zhang et all. 2024) synthesised a highly amine-functionalized, thermally stable ion-exchange material with a large surface area by amidoxymating polyacrylonitrile. The synthesised PAN-AO ion exchange material (1534.4 mg/g) adsorbed 20 times more iodine than PAN. In this study, authors (Chen et all. 2025) prepared nitrogen-rich groups and iodine, amino functionalized mesoporous SBA-15 (NH_2@FS) materials were prepared by a simple impregnation method. The synthesised functional soption NH_2@FS material was efficiently used to remove I_2 and CH_3I gas. In addition, in the following research works, various sorbents based on aerogels (Wang et all. 2025) and palygorskite (Ping et all. 2025) were synthesised and used to purify wastewater from radioactive iodine. Several ion exchange materials have been synthesised based on polyvinyl chloride, which is produced in large quantities in industry (Bekchanov et all. 2025; Doi et all. 2020; Khoiruddin et all. 2020). The same polyvinylchloride-based ion exchange materials can be used to purify wastewater from radioactive iodine.

From the data described above, it is clear that the sorption of radioactive iodine from wastewater onto ion exchange materials synthesised on the basis of polyvinylchloride (PVC) has not been studied. Therefore, in this study, we synthesised for the first time a functional polyampholyte that effectively removes radioactive iodine from medical wastewater through a two-step sulfonation and amination of polyvinyl chloride. It was found that the mechanism of the amination process of the polymer material occurred according to first-order reactions. This confirmed that the modification efficiency depends on the modifier concentration in the solution. Based on the results of SEM, BET, and BJH analysis, it was determined that the synthesised functional sorption material has a mesoporous structure. FTIR results also confirmed that the synthesised functional sorption material contained secondary and tertiary amine groups and sulfo groups. TGA and DSC results showed that the thermal stability of the synthesised functional sorption material increased as a result of the

crosslinking of PVC macromolecules during the modification of polyvinyl chloride. Adsorption studies were conducted in artificial solutions to evaluate the adsorption capacity of the functionalized sorption material obtained since the study for triiodide ions (I_3^-). The highest adsorption capacity of triiodide ions (I_3^-) at a temperature of 30 ^{0}C in solutions of various concentrations was 705 mg g^{-1}. In addition, the functional PVC-(SO_3H)-NH-PAM sorption material demonstrated its ability to effectively remove radioactive toxic iodine from wastewater from medical clinics for a long time.

Materials and Methods

Materials

Reagents, which were used in the synthesis of polyampholyte, based on PVC plastic and sorption of iodines into polyampholyte: plastic PVC $[-CH_2-CHCI-]_n$ brand I40-13A, manufacturer "NAVOIAZOT" JSC (Uzbekistan). The other chemicals obtained from Sigma-Aldrich: sulfur powder (S), polyethylenepolyamine (PEPA) $[-CH_2-CH_2-NH-]_n$, where n = 3-6 (PEPA), liquid density 1.015 g mL^{-1}, iodine solution, nitric acid (HNO_3), sodium hydroxide (NaOH), hydrochloric acid (HCl). All chemicals fulfilled analytical grade requirements and were made afresh using deionised water. Initially, a material containing disulfide and hydrosulfide groups was synthesised by modifying PVC with powdered sulfur (2:1 mass ratio). The hydrosulfide groups in the polymer macromolecule are oxidised to sulfo groups in the presence of nitric acid. To obtain a polyampholyte containing amine and sulfo groups, 10 g of the synthesised sulfation exchanger was placed in a 250 ml round-bottomed flask, then 150 ml of a 70-80% polyethylenepolyamine solution was poured in, and the reaction was carried out in a thermostat for 3-4 hours. For this, a FAITHFUL (China) thermostat was used.

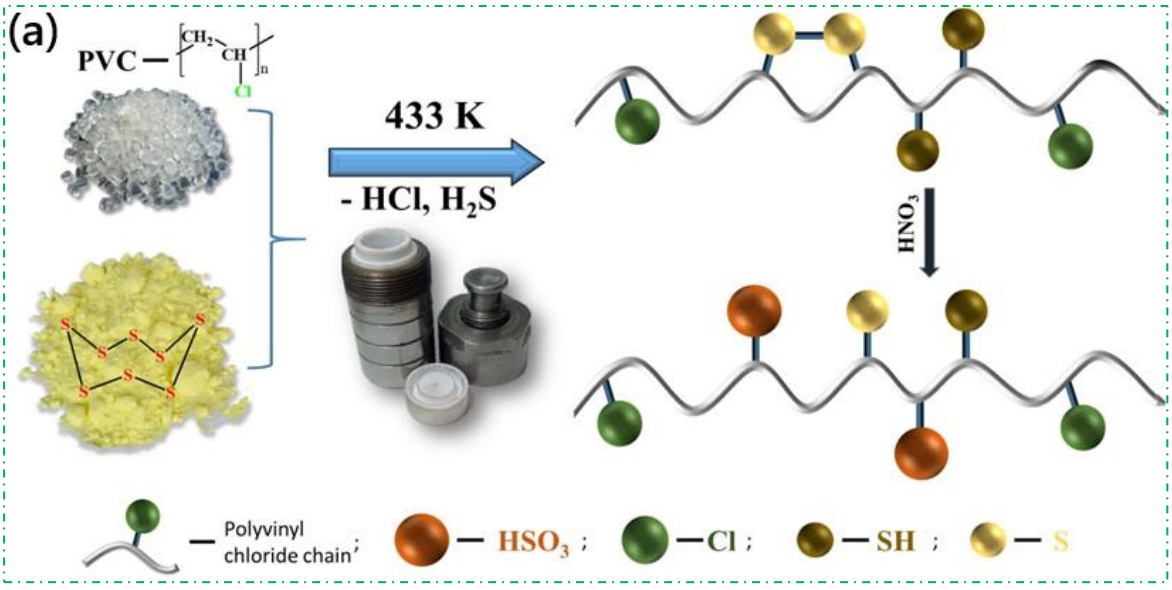
Characterisation

The initial and synthesised materials were identified using the following analytical methods. Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray (EDX) analysis was performed using an EVO MA-10 microscope (Carl Zeiss, Oberkochen, Germany) with an Oxford Instruments EDX detector (Abingdon, UK). Fourier Transform Infrared (FT-IR) spectroscopy was performed on a Bruker INVENIO-X spectrometer (Bruker Optik GmbH, Ettlingen, Germany) from 400–8000 cm^{-1} at 4 cm^{-1} resolution. Raman spectroscopy was carried out using a Bruker BRAVO spectrometer (Bruker Optik GmbH, Ettlingen, Germany) with a 785 nm diode laser (50 mW), recording spectra from 300 cm^{-1} to 3200 cm^{-1} at 2 cm^{-1} resolutions on powdered samples in glass vials. Nitrogen adsorption-desorption isotherms were measured at 77 K using an Autosorb iQ instrument (Quantachrome Instruments, Boynton Beach, FL, USA) to determine Brunauer-Emmett-

Teller (BET) surface areas and Barrett-Joyner-Halenda (BJH) pore size distributions. Samples were degassed at 120°C for 6 hours under a 10^{-5} mbar vacuum. The thermal stability of the functional materials was evaluated using a Linseis STA PT 1600 TGA/DSC synchronous thermal analyser (Linseis Messgeräte GmbH, Selb, Germany). Samples (10 ± 0.1 mg) in Al_2O_3 crucibles (70 µL) were heated from 25°C to 800°C at 10°C/min under nitrogen (30 mL/min, 99.99% purity), calibrated with $CaCO_3$ and indium standards.

Synthesis of sorption materials

Polyvinyl chloride was chosen as the polymer matrix for synthesising a functional sorbent material bearing sulfo and amino groups. Initially, polyvinyl chloride was modified by liquefying sulfur powder (433 K) for 6 hours to synthesise a material containing sulfide and hydrosulfide groups. Subsequently, by treating the synthesised material with nitric acid, the hydro sulfide groups were oxidised to sulfon groups, and a cation-exchange material (PVC-SO_3H) was synthesised (See Figure 1 (a)). 10 g of PVC-based PVC-SO_3H was poured into a 250 ml flask, and then 150 ml of 70-80% polyethylenepolyamine was added and heated in a water bath. The reaction was carried out at 423-433 K for 5-6 hours. The resulting product, PVC-(SO_3H)-NH-PAM, was washed in distilled water until neutral and dried in air. It was determined that the SEC (static exchange capacity) value of the polyampholyte containing amino and sulfo groups, PVC-(SO_3H)-NH-PAM, for NaOH was 3.5 mg-eq $g^{-1,}$ and the SEC value in HCl was 4.5 mg-eq g^{-1}, with the titration method. The reaction scheme for obtaining PVC-SO_3H (Figure 1 (a)) and PVC-(SO_3H)-NH-PAM (Figure 1 (b)) sorption materials by two-step modification of polyvinyl chloride is presented below.



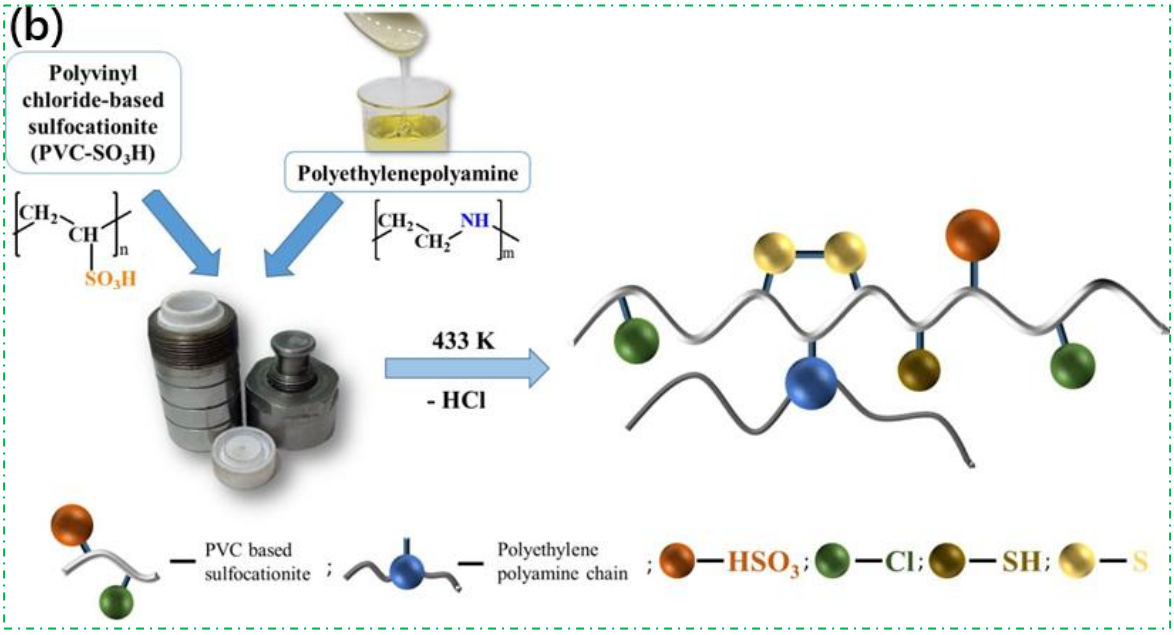


Figure 1. Synthesis of PVC-based (a) sulfocation exchanger-(PVC-SO_3H), (b) functional (PVC-(SO_3H)-NH-PAM) sorption material

In this figure, we can see that the PVC-based ionic bonding material contains amino (>NH) and sulfo groups (-SO_3H). This polyampholyte has the property of forming complexes with various iodine ions by ionic bonding.

Adsorption of iodine from solutions

To investigate the adsorption of triiodide ions (I_3^-) onto the synthesised functional PVC-(SO_3)-NH-PAM sorption material, I_3^- ions are adsorbed from an artificial solution under various conditions. To prepare the I_3^--containing solution, 3.175 g of crystalline iodine was weighed on an analytical balance and dissolved in 250 mL of water with saturated KI solutions to obtain a 0.1 mol·L^{-1} solution. Solutions with a concentration of 0.01 mol/L were prepared, and the sorption duration of I_3^- ions from the prepared artificial solutions was studied at 1, 2, 4, 6, 8, and 10 hours, at temperatures of 293, 303, and 313 K. To do this, a dry functional PVC-(SO_3)-NH-PAM sorption material was weighed from 0.5 g on an analytical balance and placed in conical flasks with a volume of 250 and 100 ml of I_3^- ions solution was poured (static exchange capacity of 4.5 mg-eq g^{-1} for HCl and 3.5 mg-eq g^{-1} for NaOH). The sorption of I_3^- ions onto the functional PVC-(SO_3)-NH-PAM sorption material was carried out in a Thermo Shaker Incubator (IKA KS 3000i control), thereby ensuring a precise temperature and stirring speed for the sorption process. Changes in the concentration of I_3^- ions in solutions before and after sorption were recorded using a spectrophotometer (Shimadzu UV-Vis 1900i, for I_3^- at a wavelength of 290-320 nm).

The amount of iodine ions absorbed in the ion exchanger is calculated by the following Equation.

$$q_e = \frac{(C_0 - C_e)}{m} \times V \qquad (1)$$

where q_e is the amount of metal ion absorbed on the ion exchange resin in mg· g^{-1}, C_0 and C_e are the initial and equilibrium concentrations, respectively, of the metal ions in mg · L^{-1}, V is the volume of the solution in L, and m is the mass of dry sorbent in g.

Adsorption kinetics

To investigate the triiodide ions (I_3^-) adsorption kinetics from an aqueous solution on a functional adsorption material containing sulfon and amino groups, pseudo-first-order and pseudo-second-order kinetic models were used. The pseudo-first-order kinetic model is expressed by the following Lagergren Equation (Huang et all. 2021):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (2)$$

In this equation: q_t and q_e are the amounts of iodine sorbed by the sorbent at a given time and in equilibrium (mg·g^{-1}). k_1 is the rate constant (min^{-1}) of the first-order sorption process, and the slope of the intercept on the linear plot of log (q_e - q_t) versus time t is k_1/2.303. The pseudo-second-order kinetic model is expressed by the following Equation (Ho et all. 1999).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + (\frac{1}{q_e})t \qquad (3)$$

The initial sorption level (t=0) is found as follows:

$$h = k_2 q_e^{\,2} \qquad (4)$$

In the given equations, k_2 is the rate constant, qe is the amount of iodine ions absorbed by a certain mass of sorbent (mg·g-1), and t is time (minutes).

Adsorption isotherm models

In general, the Langmuir model assumes that the adsorbed molecules are attached to the adsorbent surface as a monolayer. As well as Freundlich, isotherm equation is used to describe the adsorption on heterogeneous surface, and the Freundlich. In this regard, Langmuir and the Freundlich isotherm models were used to investigate the mechanism of iodine adsorption onto the functional sorption material. To find the Langmuir constant (K_L), the Langmuir Equation is linearised as shown below (Bekchanov et all. 2023; Bulgariu et all. 2023).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} \cdot C_e \qquad (5)$$

The values of q_{max} and K_L are determined from the graph of C_e/q_e versus C_e.

From isotherm graphics, the Langmuir constants were calculated for the sorption processes of triiodide ions (I_3^-) from solutions onto PVC-based polyampholyte at temperatures from 293 K to 313 K. The Langmuir constants were determined from the linear plot of Ce/qe versus Ce. The slope of the line (tgα) corresponds to 1/qmax, while the intercept corresponds to:

$$\frac{1}{q_{\max} K_L} \qquad (6)$$

Using these relationships, the maximum sorption capacity (qmax) and Langmuir constant (K_L) were calculated.

$$tg\alpha = \frac{1}{q_{\max}} \qquad \text{or} \qquad ctg\alpha = q_{\max} \qquad (7)$$

The Freundlich isotherm equation can also be used to study sorption processes in various (non-ideal) solutions. The linear Equation of this model can be expressed as follows:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \qquad (8)$$

In this equation: q_e - is the amount of iodine ions adsorbed on a given mass of sorbent ($mg \cdot g^{-1}$), K_F is the Freundlich constant, C_e is the equilibrium concentration of the solution ($mg \cdot L^{-1}$), and 1/n is the sorption intensity. The Freundlich constants K_F and n (n ≈ 1-10) are found by the angle of the slope of the intersection of the linear graph of lgq_e with lgC_e.

Thermodynamic analysis

In this study, adsorption was investigated at 293K, 303K, and 313K. Adsorption can be expressed by using the equilibrium constant:

$$K_L = \frac{q_e}{C_e} \qquad (9)$$

to account for the change in the free energy of the process:

$$\Delta G^0 = -RT \ln K_L \qquad (10)$$

In the linear plot of $\ln K_L$ versus 1/T, ΔH° and ΔS° values were estimated using the angular value of the intersection slope (Gubbuk et all. 2011).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (11)$$

Results and Discussion

Efficiency and kinetics of the amination reaction

The first sign of the formation of ion-exchange materials is the appearance of ion-exchange properties in polymers. To check the presence of ionogenic groups, the SEC values of the polyampholyte obtained as a result of modification were determined in HCl (0.1 N solution) and NaOH (0.1 N solution). The PEPA modification of the PVC-based sulfonation exchanger was initially studied in PEPA solutions with different concentrations. Based on the results obtained, it can be seen in Figure 2(a) that increasing the concentration of PEPA solution in the amination reaction leads to an increase in the SEC value of the polyampholyte.

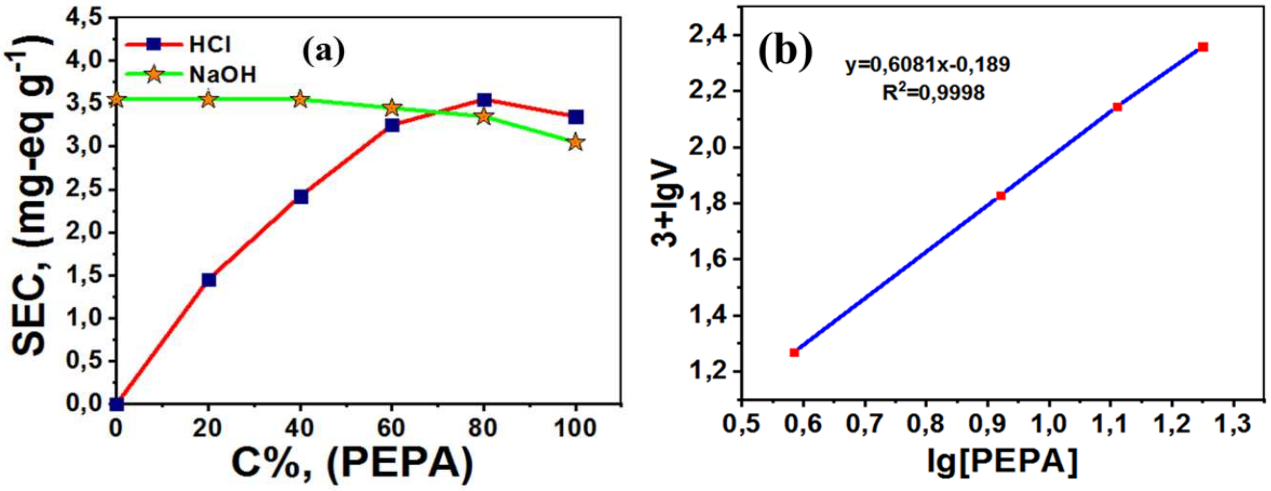


Figure 2. Dependence of the SEC value of the PVC-(SO_3H)-NH-PAM on the PEPA concentration (a) and the logarithmic dependence of the concentration level of the PEPA modification reaction on the PEPA concentration (b) (T=423 K; t=5 h).

Figure 2(a) shows that when the reaction is carried out at a concentration higher than 80%, the SEC value of the polyampholyte obtained as a result of the amination reaction decreases. This is because at high concentrations, PEPA molecules react more with the ion exchange surface, forming a network-like structure of macromolecules, making it difficult for PEPA molecules to diffuse to the inner surface of the granule. In somewhat diluted solutions, PEPA molecules may have penetrated to the inner surface of the polymer due to the facilitated movement. Using the graph in Figure 2(b), the reaction order was found based on the slope of this curve, which is equal to 1.1. Thus, the dependence of the degree of conversion of the reaction on the concentration is as follows:

$$V=K\cdot[PEPA]^{1.1} \qquad (12)$$

The obtained value (n>1) is consistent with the literature data on the classical conduct of the reaction under heterogeneous conditions. Where K is the reaction rate constant calculated according to this equation and is found to be equal to $3.15\cdot10^{-3}$ sec·l/mol. Based on the slope of the modification reaction rate and the inverse temperature dependence graph (tgα=8413), the activation energy of the

modification reaction was calculated using the following formula: E=-R•tgα (where R is the universal gas constant). The value of E was found to be 69.945 kJ/mol. In the works carried out so far, the activation energy of the modification of polyvinyl chloride directly in the presence of PEPA was equal to 138.5 kJ/mol, and in our study, the activation energy of the modification of sulfonated polyvinyl chloride in the presence of PEPA was equal to 70 kJ/mol. From the above results, it can be concluded that the modification of sulfonated polyvinyl chloride with PEPA initially involves sulfo groups in the polymer as adjacent functional groups that accelerate the reaction. The activation energy value of the reaction calculated in the experiment is typical for such heterogeneous processes.

FTIR spectroscopy analysis of functional polymer materials

FTIR spectrum analysis was carried out to identify the functional polymer material based on PVC. The FTIR spectra of the samples are analysed in Figure 3 below. It can be seen from the data in Figure 3(a) that in the FTIR spectra of the resulting polymers, absorption lines were observed in the 1300-1200 cm^{-1} regions; these absorptions are characteristic of the valence vibrations of the >C=C< bonds (Campanale et all. 2023). The appearance of these lines is associated with the dehydrochlorination of vinyl groups. The line in the 1100 cm^{-1} region in Figure 3(b) is characteristic of the valence vibration of the thio group (C=S) (Tham et all. 2019). For all the studied samples, absorption lines in the 1480 cm^{-1} region were observed in Figure 3(b), which are characteristic of skeletal C-C, deformation C-H, and deformation CH_2 vibrations. In the FTIR spectra of the samples, intense absorption lines were detected at wavelengths of 650 cm^{-1}, which, in turn, are characteristic of C-Cl valence vibrations (Villegas et all. 2024). The infrared spectroscopic comparative analysis data in Figure 3(c) and (d) show that the cationite and polyampholyte contain monovalent $-SO_3H$ sulfo groups in the regions of 1723 cm^{-1} (Na et all. 2025). Also, the absorption in the region of 3288 cm^{-1} in Figure 3(d) characterises the deformation vibrations of the >N-H bond (Montoya-Rodríguez 2025). The presence of broad absorption bands in the region of 1281 cm^{-1}, which characterise secondary and primary amine salts, indicates the presence of amino and sulfo groups in the form of internal salts in polycomplexons (Akram 2024; Al-Amin et all. 2025].

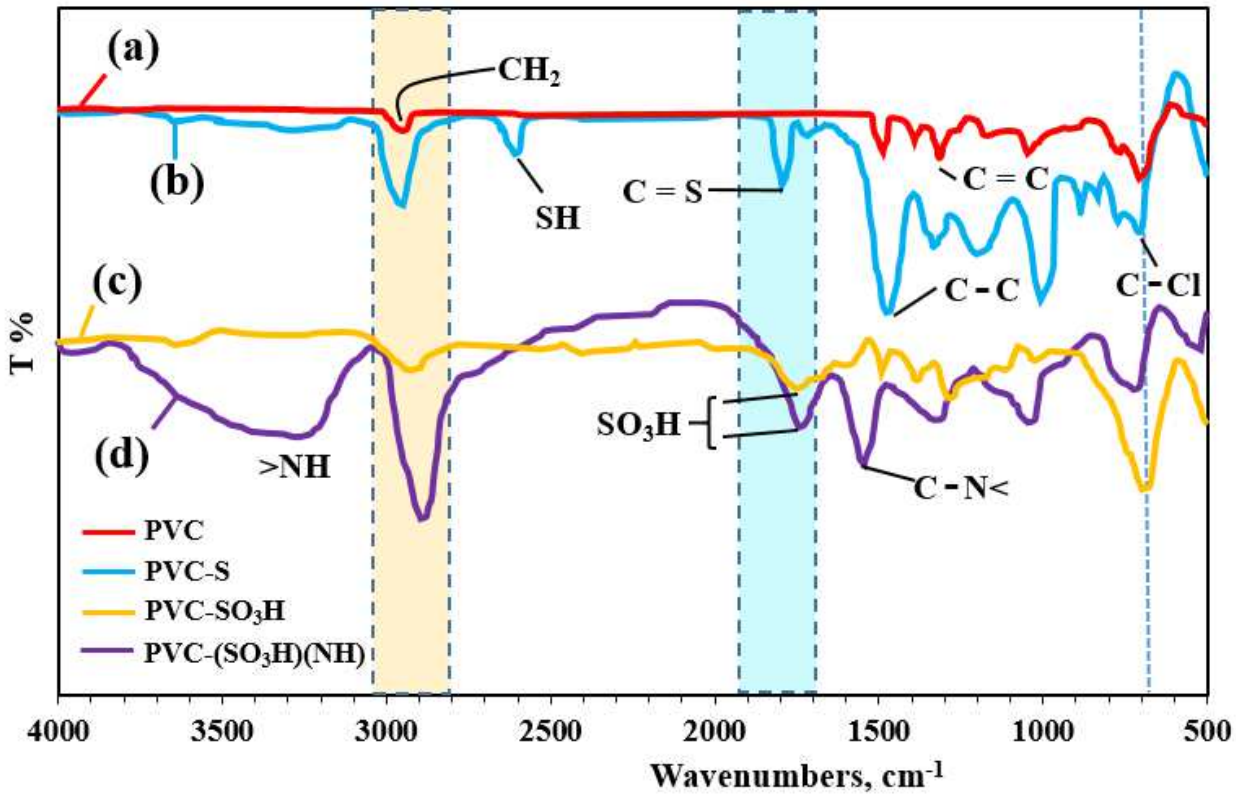


Figure 3. FTIR spectra of (a) polyvinyl chloride (PVC), (b) sulfurised polyvinyl chloride (PVC-S), (c) polyvinyl chloride-based sulfocation exchanger (PVC-SO_3H), (d) functional (PVC-(SO_3H)-NH-PAM) sorption material.

Thus, based on the results of FTIR spectroscopy, elemental analysis, and potentiometric titration, a sulfocation exchanger obtained based on PVC was chemically modified with polyethylenepolyamine to obtain a polyampholyte.

Scanning electron microscopic analysis of functional polymer materials

The surface structure and porosity of sorption materials are parameters that affect their sorption properties. SEM analysis is commonly used to study the structural morphology of sorbents. In this study, the surface morphology of the functional materials synthesised at each stage was studied using SEM. The results of the comparison of microphotographs of the polymer materials before and after modifications are presented in Figure 4. As can be seen from the SEM micrographs presented in Figure 4(a), the surface of the plastic PVC has a flat structure, and the sample with sulfur added after the extraction process is slightly more porous than the PVC. Figure 4(b) after the sulfur in the sample was converted to sulfo groups in the presence of oxidants; a polymer with a porous structure was formed in Figure 4(c). In the next step, the surface of the aminated polymer, as can be seen from Figure 4(d), formed folds of the same structure on the obtained samples. This indicates that the

sorbent formed based on PVC has a large surface area. The presence of such a morphological structure is the basis for its high sorption properties towards various iodine ions.

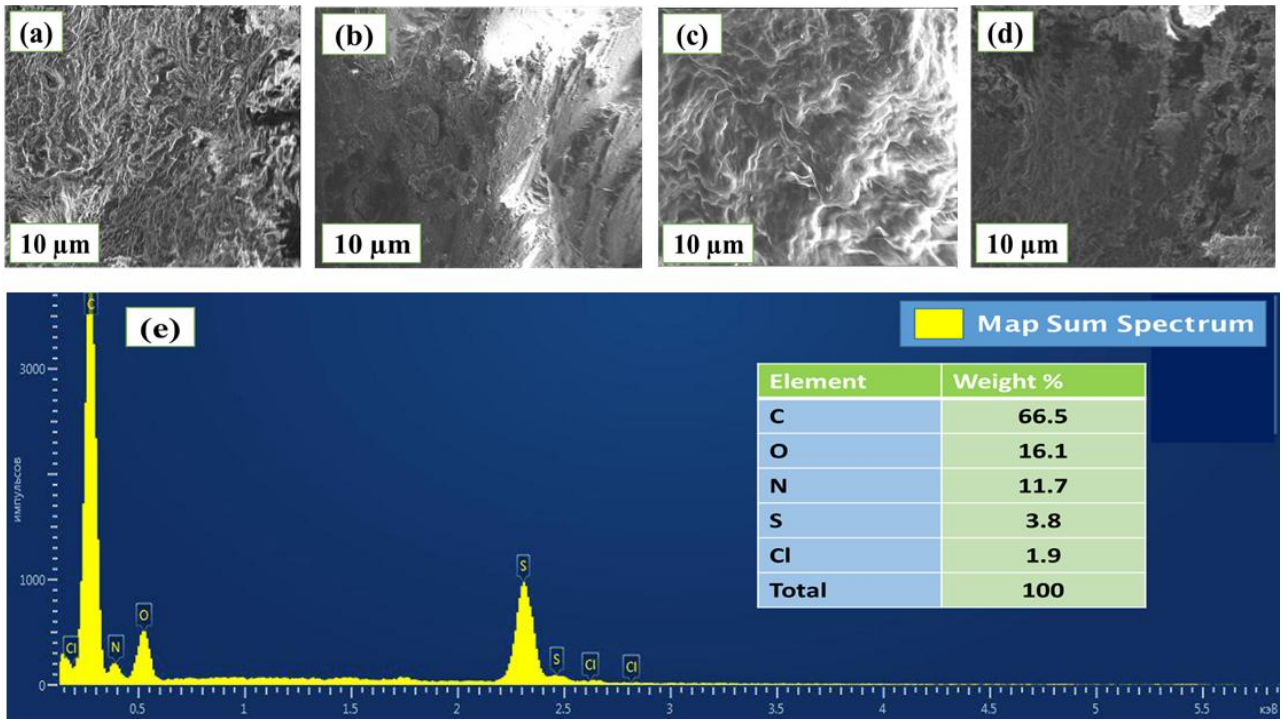


Figure 4. SEM micrographs (a) polyvinyl chloride (PVC), (b) sulfurised polyvinyl chloride (PVC-S, (c) polyvinyl chloride-based sulfocationite (PVC-SO_3H), (d) Polyampholyte (PVC-(SO_3H)-NH-PAM), and (e) X-ray (EDS) elemental analysis.

In addition, in Figure 4(e), the energy dispersive X-ray (EDS) elemental microanalysis of the estimated elements in the polycomplex composition showed that the mass fractions of sulfur and nitrogen were 3.8% and 11.7%, respectively. This can be seen from the relatively low sulfur content in the results obtained with the elemental analysis on the EuroEA Elemental Analyser above. This is due to the fact that the amination reaction was the last stage, and there were more amino groups than sulfo groups on the surface of the granules. Energy-dispersive X-ray (EDS) microanalysis shows the quantitative fraction of elements on the surface of the particle.

Thermal analysis of functional materials

The temperature stability of polymers is determined in the temperature range at which thermal and thermooxidative destruction begins, and then molecular compounds are separated. Thermogravimetric (TG) analysis based on mass loss under the influence of temperature is widely used. The TG and differential thermogravimetric analysis (DTG) curves of the starting product, PVC and its modified products are presented in Figure 5.

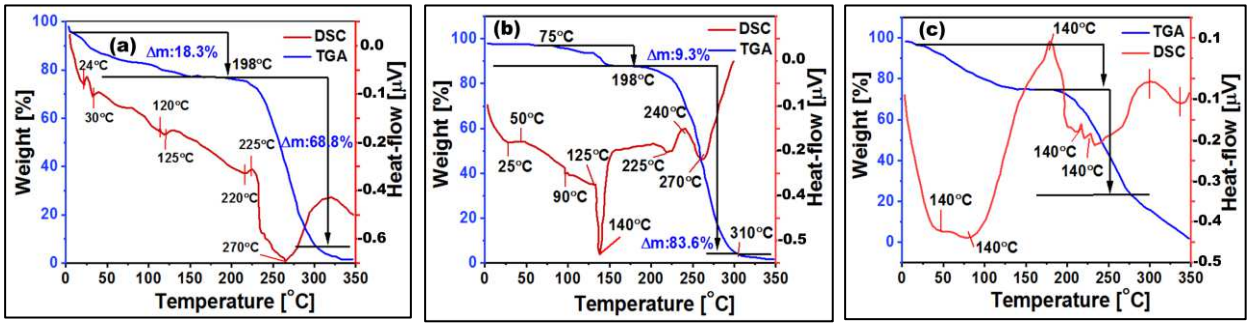


Figure 5. TGA and DSC thermograms of (a) polyvinyl chloride (PVC); (b) polyvinyl chloride-based sulfocation exchanger (PVC-SO_3H); (c) Polyampholyte (PVC-(SO_3H)-NH-PAM).

The results of the thermogravimetric (TG) analysis show that the starting material (Figure 5(a) undergoes thermal decomposition when heated to 245.5°C. In the case of the PVC-based sulfonate, thermal decomposition occurs when heated to temperatures above 254°C, leading to a loss of up to 32% of the sample mass from the initial mass and the absorption of energy (endothermic peak) of -130 J g^{-1}. Figure 5(b) shows the thermogravimetric diagram of the sulfonate. The data indicate that the sample has an amorphous structure, and in the temperature range of 230-370°C, mass loss occurs in two stages; the first is in the range of 130-160°C, during which the liquefaction of the ordered systems in the sample occurs with a mass loss of -6.07%. In the DSC curves, an endothermic peak with an energy absorption of -28.13 J g^{-1} is observed - T_{max} = 154.8°C. For other polyampholytes used in industry, an endothermic peak with an energy absorption of 80-140°C is observed. Also, the thermogravimetric analysis data of the polyampholyte presented in Figure 5(c) show that a destruction phenomenon is observed when heated to a temperature of 224°C. This indicates a slightly lower resistance to thermal destruction compared to the sulfocationite. This may be due to the presence of amino groups in the obtained polyampholyte. Since with increasing temperature, the probability of ammonia gas release from polymers containing amino groups increases. We can see that the thermal destruction of the industrially used polyampholyte (APFC-45(4-VP+CF-5)) was observed at 240°C. Thermal analysis data indicate that the polyampholyte has an amorphous structure (no clear liquefaction peak is observed). Mass loss occurs in two stages, the first in the range of 50-140°C with Δm=-13.97% (this may be due to the loss of adsorbed moisture). The second stage of mass loss occurs in the range of 224-360°C, which is associated with the decomposition of the sample with a residual mass of 41% at 363°C. Using the above data, we can conclude that a polyampholyte based on PVC containing amino and sulfo groups can be used on an industrial scale.

Surface area and pore size distribution

The surface area and porosity of pristine cation exchanger based on polyvinyl chloride (PVC-SO_3H) and polyampholyte obtained with modifying polyethylenepolyamine to a polyampholyte (PVC-

(SO$_3$H)-NH-PAM) were analysed using the Brunauer-Emmett-Teller (BET) method, with nitrogen adsorption-desorption isotherms recorded at 77 K on a Micromeritics Gemini VII 2390 and Quantachrome ASiQwin instruments. Samples were degassed at 100°C for 24 hours under vacuum before measurement. The isotherms for all samples (See Figures 6 (a and b)) exhibited a Type IV(a) pattern with H3/H4 hysteresis loops in the relative pressure (P/P_0) range of 0.3 - 0.9, confirming their mesoporous nature. The BET surface area of PVC-SO$_3$H was the highest at 7.70 $m^2 \cdot g^{-1}$, while sulfonation reduced it to 5.50 $m^2 \cdot g^{-1}$ in PVC-(SO$_3$H)-NH-PAM.

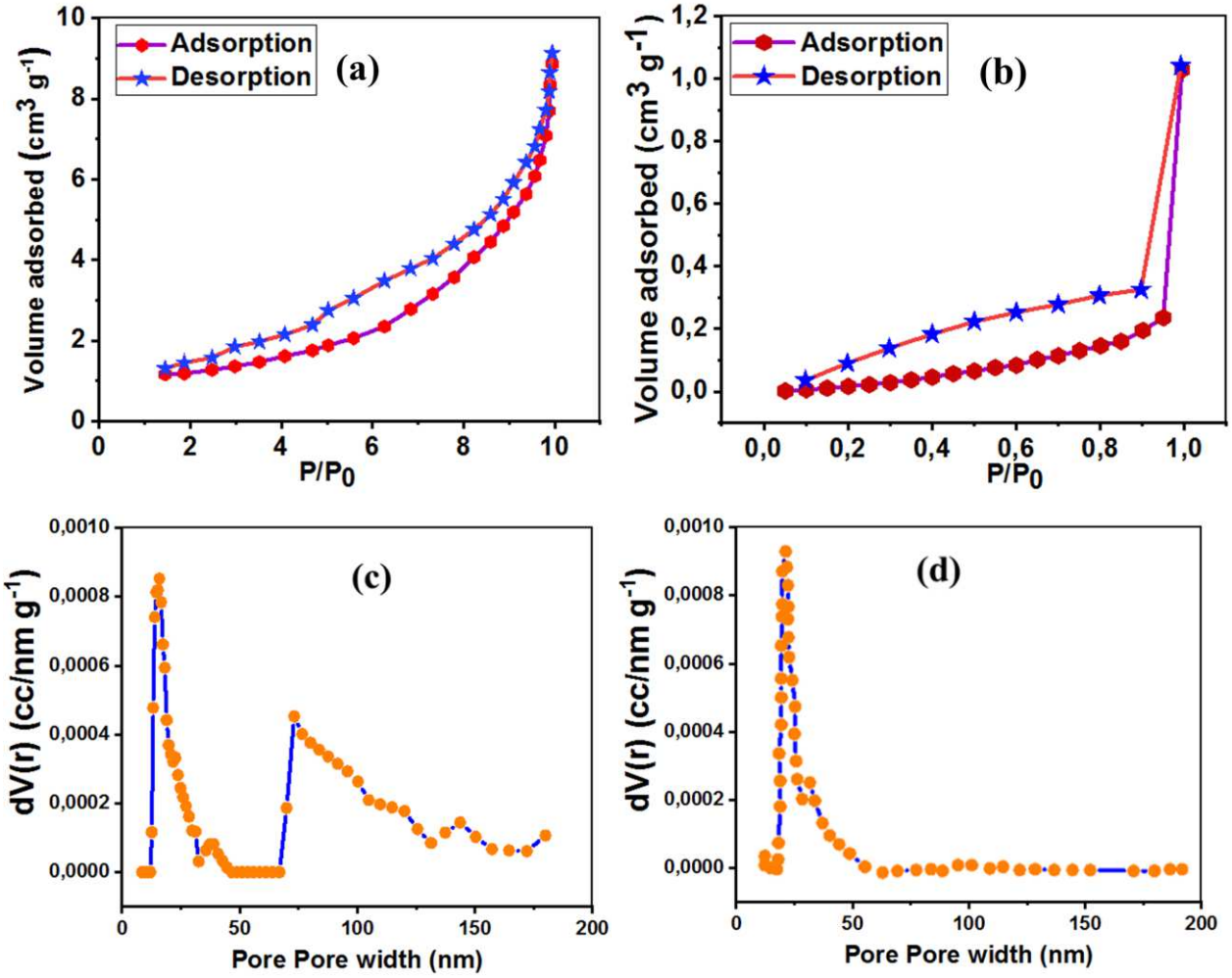


Figure 6. N$_2$ adsorption-desorption curve on polyvinyl chloride-based sulfocationite (PVC-SO$_3$H) (a) and polyampholyte (PVC-(SO$_3$H)-NH-PAM) (b), BJH pore size distribution (PVC-SO$_3$H) (c) and polyampholyte (PVC-(SO$_3$H)-NH-PAM) (d).

Pore size distributions, determined using the Barrett-Joyner-Halenda (BJH) method (See Figure 6 (c and d)), revealed that PVC-SO$_3$H had the largest adsorption pore diameter at 13.43 nm. For functional ion exchange materials, the desorption pore diameter increased from 14.58 nm (PVC-(SO$_3$H)-NH-PAM). The total pore volume was highest for PVC-SO$_3$H (0.0188 $cm^3 \cdot g^{-1}$), followed by

PVC-(SO_3H)-NH-PAM. DFT analysis for (PVC-SO_3H) and (PVC-(SO_3H)-NH-PAM) showed a predominance of mesopores and macropores, with significant pore volume contributions from pores larger than 35.14 nm. The increase in surface area and pore volume in PVC-(SO_3H)-NH-PAM compared to PVC-SO_3H highlights the enhancement of textural properties in PVC-based sulfocationite (PVC-SO_3H), while the opposite trend in polyampholyte (PVC-SO_3H to PVC-(SO_3H)-NH-PAM) suggests pore restructuring. These modifications, along with the mesoporous structure confirmed by the Type IV(a) isotherms, indicate that PVC-based sulfocationite (PVC-SO_3H) may offer improved adsorption capacity for applications such as pollutant removal, whereas polyampholyte PVC-SO_3H to PVC-(SO_3H)-NH-PAM may be suited for processes involving larger molecules due to their increased pore diameter.

Adsorption study

Polyampholytes containing sulphate and amino groups are highly sorptive due to their bifunctional properties. Therefore, the sorption of the examined iodine ions occurs due to the electrostatic and coordination bonding of iodine ions with these functional groups. In addition, the presence of an amino group in the polyampholyte promotes the binding of iodine ions via coordination. In the experiment, solutions of triiodide ions (I_3^-) with concentrations of 0.05, 0.025, 0.0125, and 0.01 $mol \cdot L^{-1}$ were prepared on functional PVC-(SO_3H)-NH-PAM sorption material. As well as the duration of triiodide ions (I_3^-) sorption from the prepared artificial solutions was studied for 1, 2, 4, 6, 8 and 10 hours at temperatures of 293, 303, and 313 K. For this, 0.5 g of dry sorbent with a static exchange capacity of 4.5 $mg\text{-}eq \cdot g^{-1}$ for HCl and 3.5 $mg\text{-}eq \cdot g^{-1}$ for NaOH was weighed on an analytical balance, placed in conical flasks with a volume of 250 ml, and 110 ml of solutions were poured. The concentration change of iodine ions in solutions before and after sorption was determined using a spectrophotometer (Shimadzu, Japan) (wavelength 290-320 nm for I_3^-).

The degree of ion sorption depends on the degree of ionisation of the functional groups of the polyampholyte, which in turn depends on the pH of the iodine ion solutions. Therefore, studies on the sorption of the examined iodine ions are conducted in specific pH media (Khushvaktov et all. 2025; Belousov et all. 2025; Choung et all. 2014).

Adsorption study in different conditions

The active groups of ion-exchange materials (amino, sulfo, and other functional centres) directly affect their ion sorption capacity. This process largely depends on the pH of the medium, as the degree of ionisation of the active sites on the ionite surface and the different forms of ions determine the efficiency of sorption. For instance, amino groups become protonated under acidic conditions,

acquiring a positive charge, which facilitates the effective uptake of negatively charged iodine species (I^-, I_3^-, and IO_3^-) (Wu et all. 2021). In contrast, sulfo groups remain negatively charged over a wide pH range, thereby ensuring electrostatic balance and selectivity on the ionite surface. In this study, the dependence of iodine ion uptake on pH by the functional polyampholyte is presented in Figure 7.

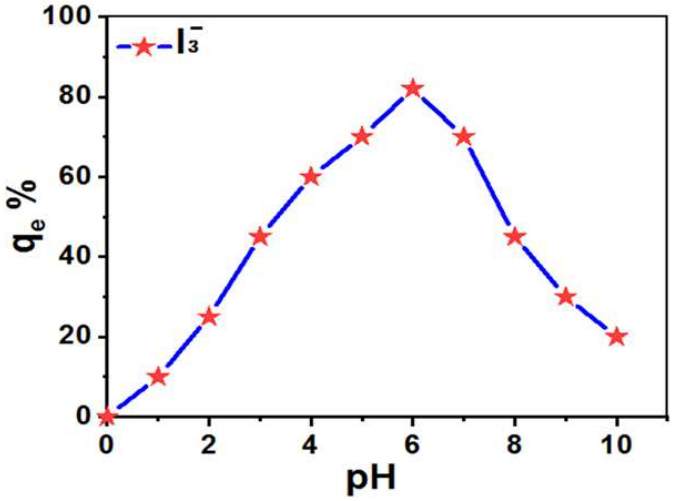


Figure 7. pH-dependent adsorption behaviour of triiodide ions (I_3^-) on functional PVC-(SO_3H)-NH-PAM sorption material (T = 313K).

The presented graph illustrates the dependence of the sorption efficiency of I_3^- ions (q_e, %) on the pH of the medium. As can be seen, at low pH values (0-2), the sorption is negligible, indicating that the functional groups on the ion-exchange material surface are not effectively interacting with the iodide species under strongly acidic conditions. With increasing pH, particularly in the range of pH 4–6, the sorption efficiency rises sharply and reaches its maximum (above 80%) at around pH 6–7. This behaviour can be attributed to the simultaneous presence of protonated amino groups, which provide positively charged sites, and sulfo groups, which remain negatively charged over a wide pH range. Such a combination creates favourable electrostatic interactions and equilibrium conditions on the surface of the ion-exchange material, resulting in selective and efficient uptake of triiodide ions (I_3^-). Beyond pH **7**, the sorption efficiency decreases significantly. In alkaline conditions, amino groups lose their protonation ability, thereby reducing the number of positively charged sites available for binding iodide ions. As a result, the ion-exchange material exhibits weaker sorption performance. Functional ion-exchange materials containing amino and sulfo groups demonstrate maximum selectivity and sorption efficiency toward iodide ions in the near-neutral range (pH 6–7), where electrostatic interactions are most favourable.

Sorption materials are widely used in oil fields for the sorption of triiodide ions (I_3^-) from associated waters. In addition, sorbents containing triiodide ions (I_3^-) are used in portable systems for

the disinfection of drinking water from microorganisms. Therefore, the possibility of sorption of triiodide ions (I_3^-) using a synthesised polyvinyl chloride-based functional PVC-(SO_3H)-NH-PAM sorption material was studied. As is known, molecular iodine is insoluble in water; therefore, it is dissolved in an aqueous solution of potassium iodide. The dissolution of iodine is carried out according to the following reaction scheme:

$$I_2 + KI = KI_3$$

As a result, iodine in potassium iodide solution is in the anionic state (Zhang et all. 2016). To study the time dependence of the absorption of triiodide ions (I_3^-) from artificial solutions into the functional PVC-(SO_3H)-NH-PAM sorption material, solutions of iodine crystals with different concentrations were prepared in the presence of potassium iodide, and the absorption rate at different times was determined. The results are presented in Figure 8(a).

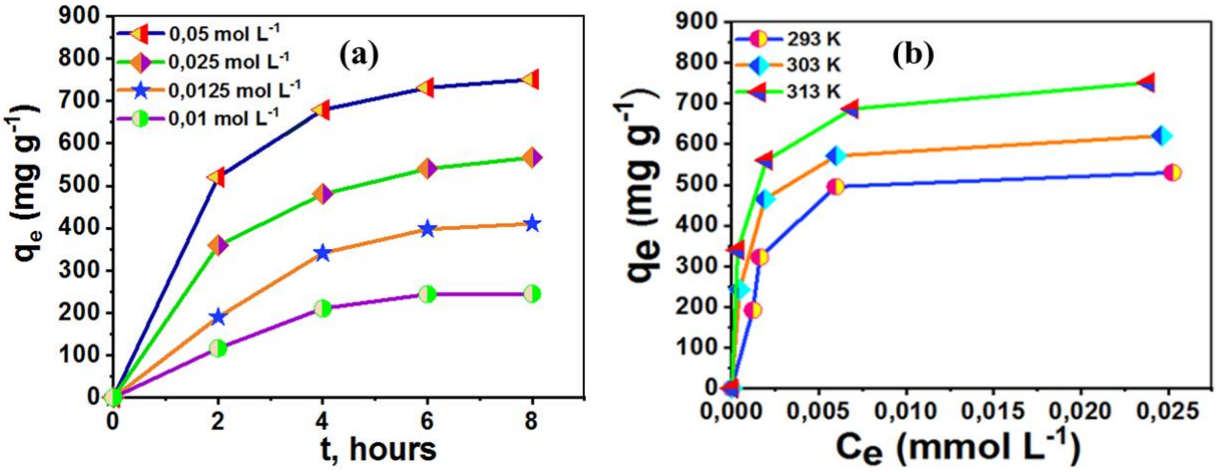


Figure 8. Sorption kinetics (a) and isotherm (b) of triiodide ions (I_3^-) on functional PVC-(SO_3H)-NH-PAM sorption material (T=293K, 303K and 313K, t=8 h).

From the above Figure 8(a), it can be seen that the amount of triiodide ions (I_3^-) absorbed by the functional PVC-(SO_3H)-NH-PAM sorption material increases with time. The sorption of iodine ions occurs based on the effect of ionic bonds between iodine anions and groups on the surface of the ionite. This indicates that the process proceeds by chemical sorption. The equilibrium states of sorption of I_3^- ions in solutions of the polyampholyte obtained as a result of amination of the PVC-based sulfocation exchanger in the presence of polyethylenepolyamine were studied. The amount of I_3^- ions that the resulting functional PVC-(SO_3H)-NH-PAM sorption material can adsorb was determined at different temperatures (293K, 303K and 313K).

Based on the results obtained, an isotherm of the sorption process was constructed. Figure 8(b) shows a graph of the dependence of the amount of iodine ions on the solution equilibrium concentration of the functional PVC-(SO_3H)-NH-PAM sorption material at different temperatures. It can be seen that the amount of iodine ions absorbed by the polyampholyte increases with increasing temperature. This is because the ion exchange process improves due to the acceleration of the movement of ions between the polyampholyte and negative iodine ions.

Adsorption isotherms

Adsorption isotherms are the most important tool for analysing equilibrium processes. The most widely used and convenient for representing equilibrium processes in liquid and solid systems are the Langmuir and the Freundlich models.

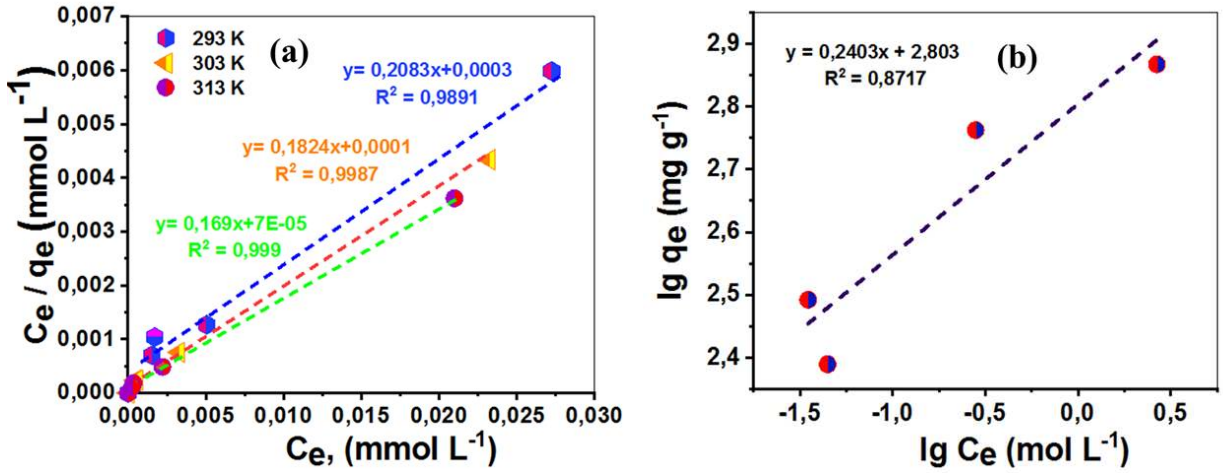


Figure 9. Langmuir (a) and Freundlich (b) isotherms for triiodide ions (I_3^-) sorption

Using Figure 9(b) above, Freundlich constants were calculated for the sorption processes of triiodide ions (I_3^-) from solutions onto a functional PVC-(SO_3H)-NH-PAM sorption material at temperatures of 298 K, 303 K and 313 K. The calculated results are presented in Table 1.

Table 1. Langmuir and Freundlich constant values for the sorption of triiodide ions (I_3^-) onto a functional PVC-(SO_3H)-NH-PAM sorption material

Ion	Langmuir constant				Freundlich constant		
	q_{max}, (mmol g^{-1})	K_L ($mmol^{-1}$)	R_L	R^2	n	K_F ($mmol\ g^{-1}$)($L\ mmol^{-1}$)$^{1/n}$)	R^2
I_3^- (Iodine)	6.23	2241	0.931	0.9987	3.86	7336	0.838

Table 1 presents all the calculated results of the sorption isotherm according to the Langmuir and the Freundlich equations. According to the Freundlich parameter values, I_3^- ions are equal to n = 3.86, which indicates a high degree of sorption of I_3^- ions to the functional PVC-(SO_3H) NH-PAM sorption material. The correlation coefficients R^2 values for I_3^- ions are equal to 0.9987, and the concentration

change shows that the adsorption process obeys the Langmuir monomolecular adsorption theory (R_L-favorable).

Adsorption kinetics

It is known that kinetic models are used to determine the mechanism of the sorption process (chemical reaction rate, diffusion control, and mass transfer). In recent years, various kinetic models have been used, including pseudo-first-order, pseudo-second-order, and several other methods. For this purpose, a polyampholyte containing amino and sulfo groups, obtained from plastic PVC, with a granule size of not less than 0.315-1.875 mm, is used. The following kinetic models were used in this study: The pseudo-first-order kinetic model is represented by the following Lagergren equation, and calculations were made based on Equation 1.

In this equation, q_t and q_e are the amounts of iodine sorbed by the sorbent at a given time and in equilibrium ($mg \cdot g^{-1}$). k_1 is the rate constant (min^{-1}) of the first-order sorption process, and the slope of the intercept on the linear graph of log (q_e - q_t) versus t is $k_1/2.303$. The kinetics of the sorption process of iodine ions onto the functional PVC-(SO_3H)-NH-PAM sorption material, calculated in the experiment, is evaluated by finding the pseudo-first-order kinetic parameters from the graph of log (q_e - q_t) versus t in Figure 10(a). In addition, the kinetics of the sorption process of iodine ions onto the PVC-based polyampholyte is evaluated by finding the pseudo-second-order kinetic parameters. In addition, the pseudo-second-order kinetic model is expressed by the following equation and calculations were made based on formula 2 above. The initial sorption rate (t=0) is found as follows, and calculations were made based on formula 3 above. In the given equations, k_2 is the rate constant, q_e is the amount of iodine ions absorbed by a certain mass of sorbent ($mg \cdot g^{-1}$), and t is the time (minutes).

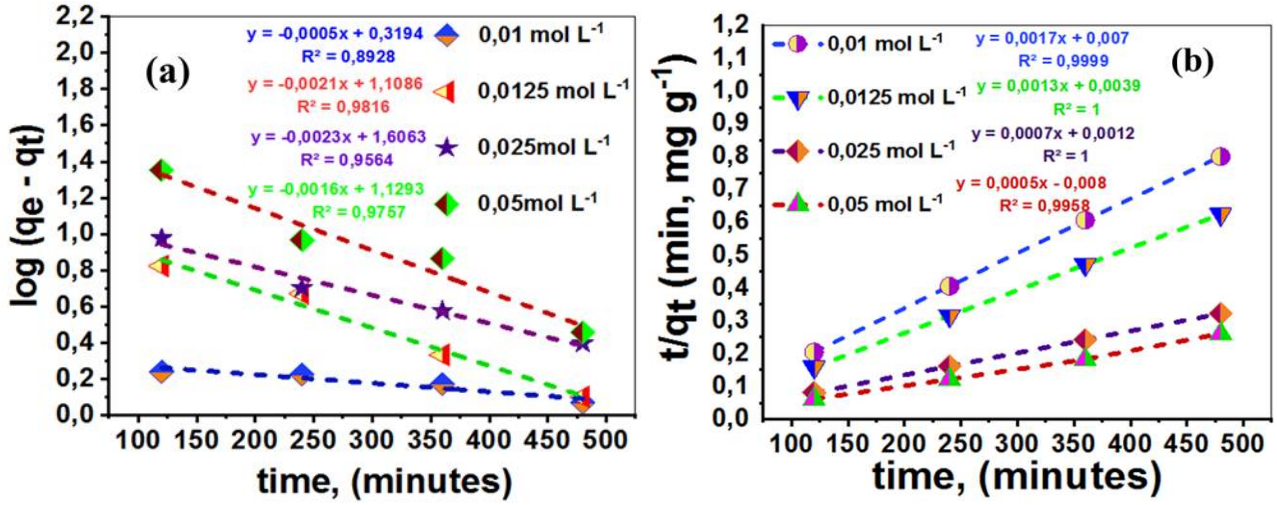


Figure 10. Pseudo-first-order (a) and pseudo-second-order (b) kinetic models of sorption triiodide ions (I_3^-) on functional PVC-(SO_3H)-NH-PAM sorption material

The kinetics of iodine ion sorption onto functional PVC-(SO_3H)-NH-PAM sorption material is estimated by finding pseudo-second-order kinetic parameters from the graph of t/q_e and t versus time plotted in Figure 10(b). The rate constants (k_1 and k_2) and correlation coefficients (R^2) obtained using Figures 10(a) and (b) are given in Table 2. The data presented below show that the kinetics of the sorption process of iodine ions onto PVC-based polyampholyte are closer to the data of the second-order model than to the first-order model. The results of the first-order model parameters show that the initial adsorption of iodine ions onto the polyampholyte proceeded rapidly, and then the sorption rate slowed down. This can be explained by the accumulation of triiodide ions (I_3^-) on the surface of the adsorbent and the establishment of an equilibrium between ions. In the graph of the second-order sorption process (Figures 10(a) and (b)), the correlation coefficient is close to unity compared to the first-order adsorption correlation coefficient (R^2), and the values of the kinetic parameters in the table indicate that the adsorption of iodine ions onto functional PVC-(SO_3H)-NH-PAM sorption materialobeys the second-order adsorption kinetics.

Table 2. Kinetic parameters for triiodide ions (I_3^-) adsorbing onto functional PVC-(SO_3H)-NH-PAM sorption material

sorbent	Ion	Initial conc., mole l^{-1}	Pseudo-first order			Pseudo-second order		
			Equilibrium adsorption quantity q_e(mg·g^{-1})	k_1 ($g\ mg^{-1}\ min^{-1}$)	R^2	Equilibrium adsorption quantity q_e(mg·g^{-1})	k_2 ($g\ mg^{-1}\ min^{-1}$)	R^2
1	2	3	4	5	6	7	8	9
Polyampholyte	I_3^-	0,010	243,5	0,00253	0,893	275,2	0,0007866	**0,998**
		0,0125	297,6	0,00241	0,981	350,5	0,0005378	**0,999**
		0,025	540,5	0,00233	0,975	625,6	0,0003939	**0,999**
		0,050	731.5	0,00233	0,956	851,5	0,0003571	**0,999**
		Average	**k_1 and k_2**	**0,00222**			**0,0000736**	

This indicates that the sorption process is influenced not only by the nature of the ions but also by the amino and sulfo groups in the ionite. In these kinetic studies, the sorption of triiodide ions (I_3^-) in artificial solutions on a new functional PVC-(SO_3H)-NH-PAM sorption material based on the plastic PVC containing amino and sulfo groups was studied at different initial concentrations and temperatures. The values of the kinetic parameters of this process show that the absorption of triiodide ions (I_3^-) by the polyampholyte proceeds according to the laws of second-order adsorption kinetics.

This indicates that the sorption of iodine ions on the polyampholyte obtained on the basis of PVC is influenced not only by triiodide ions (I_3^-) but also by amino and sulfo groups in the sorbent.

Adsorption thermodynamics

From the above data, we can see that the sorption of triiodide ions (I_3^-) from solutions to the polyampholyte increases with increasing temperature from 293 K to 313 K. As the sorption proceeds from the initial state to the equilibrium state, the free energy of the system changes as a result of ion exchange processes on the sorbent surface and in the solution.

The values, $\Delta H, \Delta S$ the sorption process at different temperatures is calculated from the following equation.

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (16)$$

Here, the values of ΔH and ΔS are equal to the angle of the line at the intersection points of the LnK_L and 1/T dependence graphs (See Figure 11).

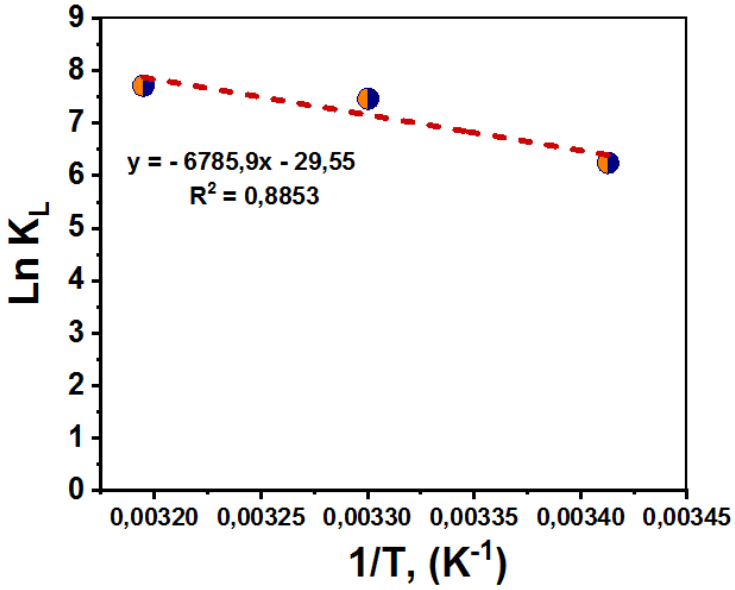


Figure 11. The dependence of lnK on 1/T

The changes in thermodynamic parameters during the sorption processes of triiodide ions (I_3^-) from solutions onto PVC-based polyampholytes at temperatures ranging from 293 K to 313 K are presented in Table 3. It can be seen from Table 1 that the value of q_{max} calculated based on the Langmuir equilibrium constant increased at temperatures of 293, 303, and 313 K.

Table 3. Thermodynamic characteristics for sorption of iodine ions on functional PVC-(SO_3H) -NH-PAM sorption material

Iodine ion in solution	T, K	q_{max}, mg g^{-1}	K, L mol^{-1}	-ΔG,	ΔH,	ΔS,

				kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} •K^{-1}
I_3^- (Iodine)	293	578,15	515,5	15,2	56,418	245,7
	303	707,74	1747	18,8		
	313	731,35	2241	20,0		

The ΔH given in the same table is positive, indicating that the adsorption process is endothermic. In addition, the increase in the entropy of the system indicates that an ionisation reaction occurred between the $>N^+$ ions on the surface of the sorbent and the triiodide ions (I_3^-) in the solution. The decrease in the free energy indicates that the sorption of triiodide ions (I_3^-) to the polyampholyte occurred spontaneously.

Based on the conducted studies and the obtained results, the polyampholyte obtained by amination of the sulfocationite synthesised for the first time based on polyvinyl chloride in the presence of polyethylenepolyamine can be recommended for the removal of triiodide ions (I_3^-) in the treatment of technological waters.

Reusability of functional sorption material

Reusability is considered one of the main properties of sorbents. In this study, the functional PVC-(SO_3)-NH-PAM sorption material, synthesised on a PVC base, was investigated for its ability to repeatedly adsorb triiodide ions (I_3^-) from an artificial solution. For this purpose, firstly, to study the dynamic exchange capacity and desorption, functional PVC-(SO_3)-NH-PAM sorption material was placed in a column. Solutions containing I_3^- ions of various concentrations were passed through the column with the sorbent until the concentration of the solution leaving the column equalled the initial concentration. Solutions containing the studied iodine ions were passed through the column at a rate of 1, 2, and 3 ml·min^{-1} in a countercurrent manner. The change in the concentration of iodine ions in the solutions before and after sorption was determined using a UV-Vis spectrophotometer. Figure 12 below shows the dependence of the concentration of iodine ions in the solution leaving the column on the volume of the solution passing through the sorbent.

Figure 12 shows the breakthrough curves describing the dependence of the dynamic sorption capacity of iodine ions on the flow rate of the solution through the column packed with the functional sorption material PVC-(SO_3H)-NH-PAM. It can be observed that with an increase in the flow rate from 1 to 3 mL min^{-1}, the breakthrough point shifts to lower solution volumes. This behaviour can be explained by the reduction of contact time between iodine ions and the active functional groups of the sorbent surface at higher flow rates. At lower flow rates, the interaction time between the sorbate and sorbent increases, resulting in more efficient adsorption and a higher dynamic sorption capacity. These results demonstrate that the mass transfer process plays an important role in the

adsorption mechanism. The stability of the breakthrough curves also indicates that the functional groups of the polymer matrix remain active during operation, which is important for the regeneration and repeated use of the sorption material.

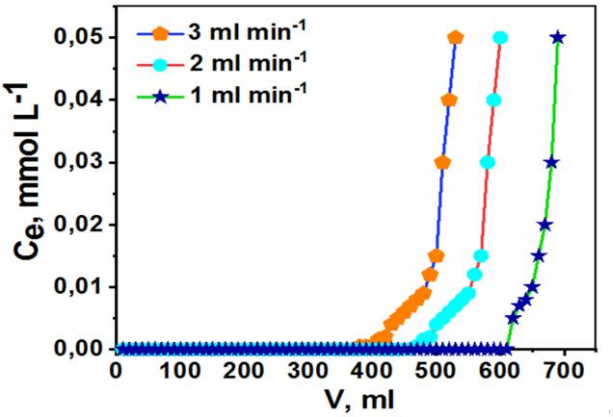


Figure 12. Breakthrough curves showing the dependence of the dynamic sorption capacity of iodine ions on the solution flow rate through the column packed with PVC-(SO_3H)-NH-PAM functional sorption material (C_M = 0.05 mol L^{-1}).

Reusability and stability of sorption materials are crucial aspects for practical application in industry. Therefore, to test the reusability and stability of the functional PVC-(SO_3H)-NH-PAM sorption material synthesised based on PVC, 10 cycles of sorption and desorption of iodine ions from the solution were performed. The reusability efficiency of the functional PVC-(SO_3H)-NH-PAM sorption material is shown in Figure 13. To regenerate iodine ions absorbed into the functional PVC-(SO_3H)-NH-PAM sorption material, a 0.1 mol·L-1 solution of NaOH is used. A 0.1 mol·L-1 HCl solution was used to activate the sorbent after regeneration.

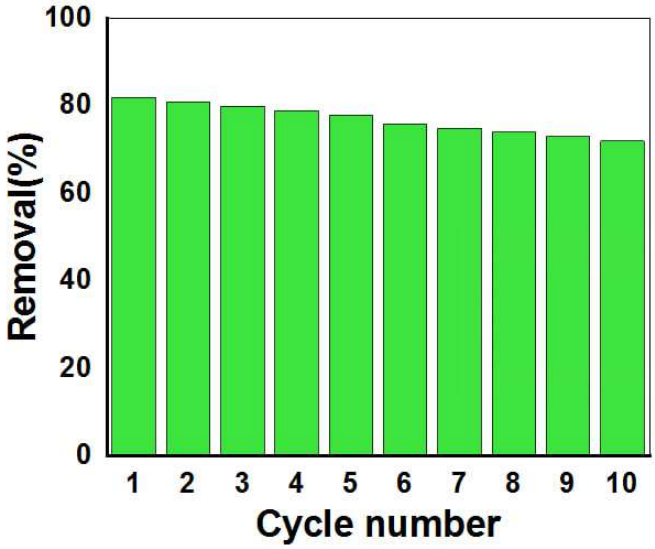


Figure 13. Sorption cycles of iodine ions by functional PVC-(SO_3H)-NH-PAM sorption material

From the data in Figure 13 above, it can be seen that the sorption efficiency of the sorption material remained almost unchanged during the 10-fold repeated sorption-desorption of iodine ions onto the functional PVC-(SO_3H)-NH-PAM sorption material. From these data, it can be concluded that the functional PVC-(SO_3H)-NH-PAM sorption material can be used for the effective purification of toxic iodine from wastewater from the Medical clinics.

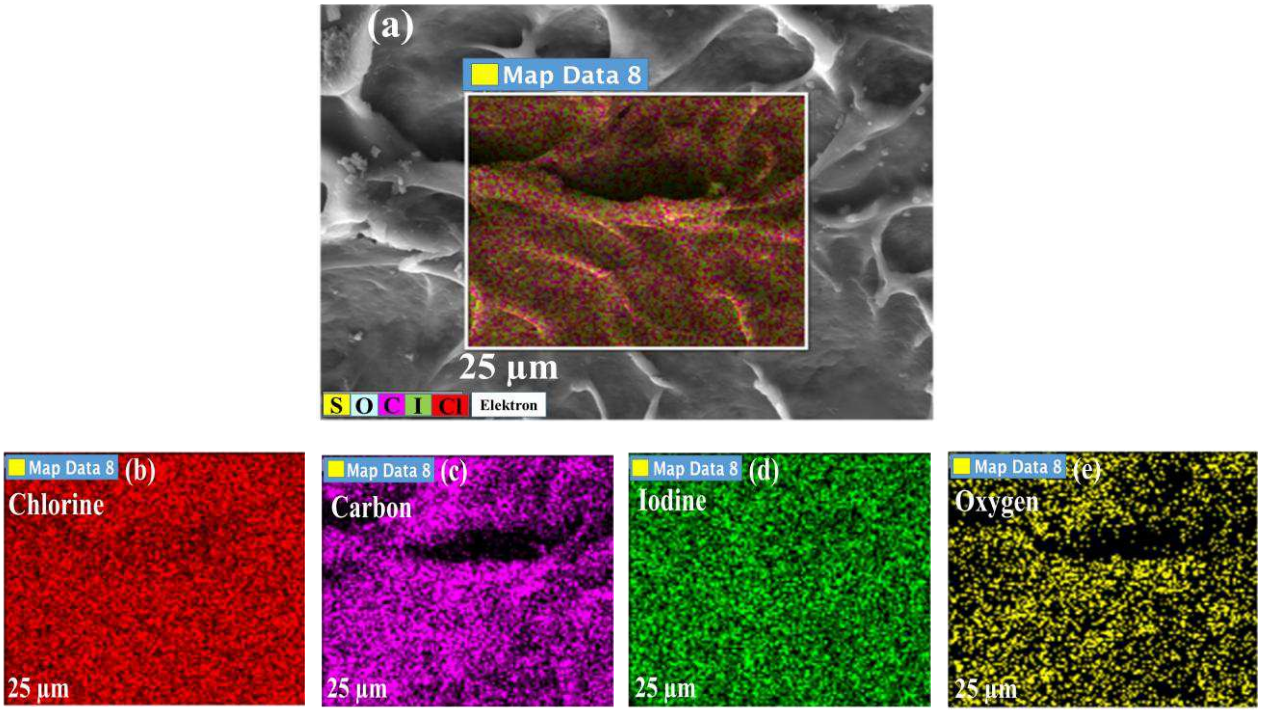
Purifying wastewater from triiodide ions (I_3^-) is a very important task. Since wastewater from the wastewater treatment Medical clinics contains radioactive iodine isotope. Sorption materials are mainly used to purify wastewater from toxic iodine. Table 4 presents data on the efficiency of various sorbents in removing toxic iodine from solutions.

Table 4. Comparative table of the sorption properties of iodine ions on the functional (PVC-(SO_3H)-NH-PAM) sorption material, with other sorption materials

№	Ion-exchange materials	Target iodine ion	Optimal pH range	Note/Selectivity mechanism	q_{max} maximum sorption (mg/g)	Reusability	Reference
1.	Anion exchange resin (Amberlite IRA-400)	I^-	3 – 7	Retains I^- ions well in near-neutral conditions	96,1 – 98,2	3 or 4	(Zhang et all. 2016)
2.	Cation exchange resin (Dowex 50WX8)	IO_3^-	1 – 3	Strong adsorption of IO_3^- in highly acidic environments	200 – 450	3 or 4	(Kumar et all. 2018)
3.	Sol-gel-based SiO_2-TiO_2 composite	I^- - IO_3^-	5 – 9	Effective under neutral to mildly basic conditions	350 – 450	4 – 5	(Santschi et all. 2017)
4.	Modified chitosan (with amino groups)	I^-	4 – 6	Protonated amino groups bind with I^- ions efficiently	450 – 520	4 – 5	(Anitha et all. 2015)
5.	Zeolite (Na^+-form)	I^-	6 – 8	Shows good selectivity in slightly basic/saline media	420 – 550	4 – 5	(He et all. 2014)
6.	Functional polymer (photoactive)	IO_3^-	2 – 5	Enhanced selectivity under weakly acidic and light-activated conditions	525 – 720	4 – 5	(Malamis et all. 2013)
7.	Activated carbon / biochar	I^-	5 – 7	Works well at neutral pH; limited ion-exchange but strong adsorption	550 – 580	5 – 6	(Lin et all. 2013)
8.	Functional ion exchanger material (PVC-(SO_3H)-NH-PAM)	I_3^-	5.5 – 6.5	Protonated amino groups bind with I_3^- ions efficiently	550 – 750	6 – 7	**Present work**

From the above information, we can see that a high amount of iodine ions was adsorbed onto the sorbents in acidic and neutral solution pH environments. The selectivity of various ion-exchange materials toward toxic iodine is strongly influenced by pH, which is determined by factors such as the surface chemistry of the material, the ionic state, structural characteristics, and charge balance. Each material exhibits high efficiency under specific pH conditions, making the identification of appropriate sorbents and operational environments essential for practical applications. By controlling the pH, the process of selective adsorption can be effectively regulated. Moreover, a functional ion-exchange material containing both amino and sulfonic acid groups, such as PVC-(SO_3H) NH-PAM, demonstrates high selectivity toward triiodide ions (I_3^-) within a moderate pH range (5.5–6.5). This is primarily attributed to the protonation of amino groups and the resulting electrostatic interactions. In addition, the presence of sulfonic acid groups in the structure of the functional ion exchanger facilitates the distribution of ionic charges across the ion-exchange matrix and enhances the selective interaction with anionic species.

In studies, it is seen that the SEM method is widely used to determine the morphological and surface structure of many adsorbent materials. Because the morphological structure of the adsorbents has a wide impact on their physicochemical properties. In this case, the corrected microphotographs of iodine ions adsorbed on a PVC-based functionalized polymer material are shown in Figure 14.



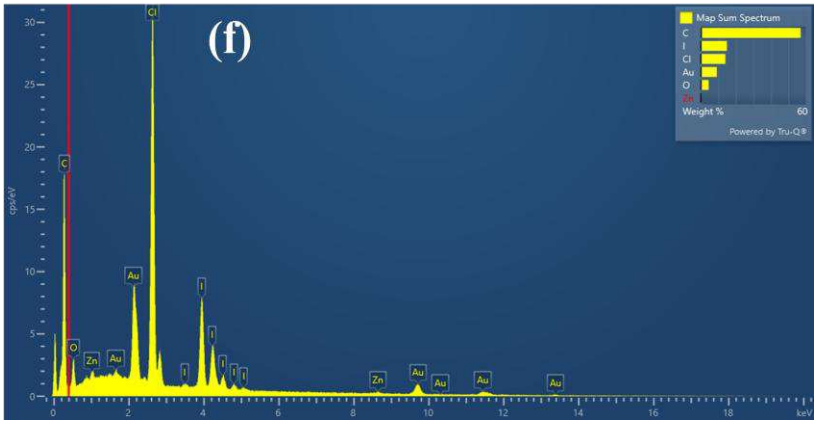


Figure 14. SEM micrographs and X-ray (EDS) elemental analysis (f), (a) adsorption of iodine ions into general polyampholyte (PVC-(SO_3H)-NH-PAM); (b) chlorine; (c) carbon; (d) iodine; (e) oxygen.

As can be seen from the SEM micrographs presented here, Figure 14(a) shows samples of functionalized polyampholyte with iodine ions adsorbed. Figure 14(b) also shows the presence of chlorine atoms, Figure 14 (c) carbon atoms, Figure 14(d) iodine atoms, and Figure 14(e) oxygen atoms. According to the figure, Figure 14(f) shows that the energy dispersive X-ray (EDS) quantitative element microanalysis of polycomplex iodine ions after sorption found that the estimated mass fraction of the element iodine in the composition was more than 10%. It can be seen that this is almost equal to the relative chlorine element fraction in the results obtained by element analysis on the EuroEA Elemental Analyser apparatus above. Energy-dispersive X-ray (EDS) microanalysis shows the quantitative fraction of elements on the surface of the particle.

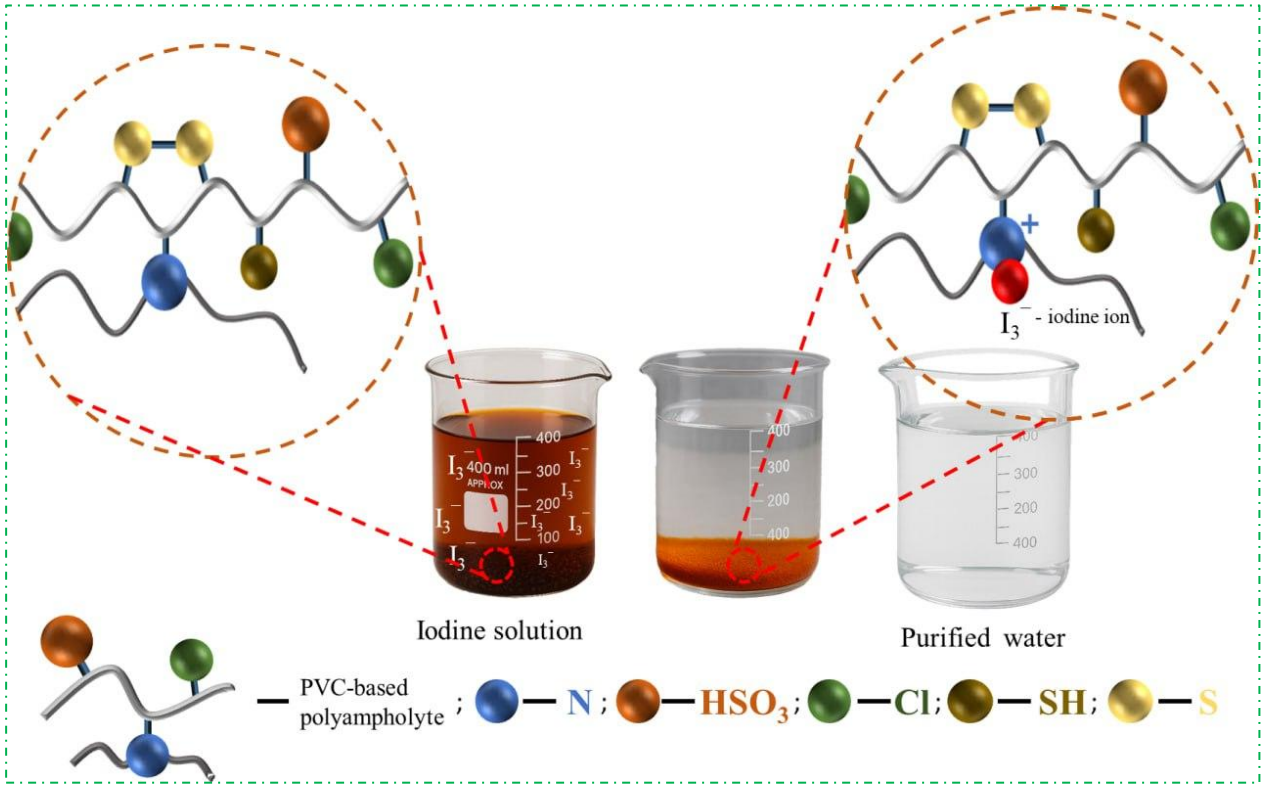


Figure 15. Mechanism of triiodide ions (I_3^-) removal on functional PVC-(SO_3H)-NH-PAM sorption material

The proposed mechanism of iodine ion adsorption onto the functional PVC-(SO_3H)-NH-PAM sorption material based on kinetics, isotherms, thermodynamics, as well as SEM microphotography and element maps data is presented in Figure 15 above. The proposed sorption mechanism suggests that the tertiary and secondary amine groups in the PVC macromolecule sorb iodine ions in solution through ion exchange. The functional sorbent can be regenerated by desorbing iodine ions absorbed into the functional sorbent using a NaOH solution. Thus, the functional PVC-(SO_3H)-NH-PAM sorption material can be effectively reused in the purification of wastewater from toxic iodine ions.

Purification of wastewater

Finally, the functional PVC-(SO_3H)-NH-PAM material was tested under real conditions by removing iodine from the wastewater of the Medical clinic of Uzbekistan, of the concentration of iodine in the wastewater was 162 $mg \cdot L^{-1}$. In the table 5 shows the concentration of iodine in the wastewater of the Medical clinic after sorption of each cycle. For this purpose, 0.5 g of synthesised functional PVC-(SO_3H)-NH-PAM material was taken. To start the process of sorption of iodine, functional PVC-(SO_3H)-NH-PAM material was added to wastewater and sorption was carried out at 25°C and under static conditions.

Table 5. Efficient purification of the functional PVC-(SO_3H)-NH-PAM material in the

wastewater of the Medical clinic from the radioactive iodine

Sorption/desorption cycles	1	2	3	4	5	6	7	8	9	10
Iodine concentration in the wastewater after sorption (mg L^{-1})	29.0	31.3	32.6	34.4	35.8	37.0	38.1	39.0	41.2	42.0

The treatment of wastewater from the iodine with the functional PVC-(SO_3H)-NH-PAM material was reused ten times, as a result of which the efficiency of the sorption material in removing the iodine decreased to 90 %. From the obtained practical results, it can be concluded that the functional PVC-(SO_3H)-NH-PAM material can be recommended for the long-term effective treatment of wastewater from the Medical clinics from toxic iodine. According to World Health Organisation standards, the permissible concentration of iodine ions in wastewater is set at 40-50 $mg \cdot L^{-1}$. It follows that the synthesised functional PVC-(SO3H)-NH-PAM material can be reused more than 10 times for the effective purification of wastewater from triiodide ions.

Conclusions

A new functional sorption material was synthesised from polyvinylchloride by two-step modification with sulphur and polyethilenpolyamine, and has been found to efficiently remove highly toxic triiodide ions. It was found that the amination process of the PVC-based sulfo cation exchanger proceeded as a first-order reaction, and the amination reaction yield depended on the amount of modifier. The activation energy value of the amination reaction was found to be typical of surface modification reactions. Physicochemical analysis methods have proven that the obtained functional sorption material, a mesoporous material with a large surface area, as well as its binding to the PVC chain to form sulfo- and amine groups, have the necessary properties. Sorption of the obtained functional sorption material, in artificial solutions containing iodine ions at different initial concentrations and temperatures, showed that the subordination to the theory of Langmuir adsorption and the values of kinetic parameters show the absorption of iodine ions into functional PVC-(SO_3H)-NH-PAM sorption material. The study of the thermodynamics of the sorption process showed that changes in the values of the thermodynamic parameters of the sorption process - free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) - indicate that I_3^- ions are adsorbed through an ion exchange reaction. The above data will show that obtaining functional PVC-(SO_3H)-NH-PAM sorption material can be used multiple times as an effective ion exchange for the purification of wastewater from iodine ions. On the other hand, the synthesised functional sorption material has the property of efficiently sorbing iodine ions compared to analogous adsorbents. Based on the practical results, the functional PVC-

(SO_3H)-NH-PAM sorption material can be recommended for long-term effective purification of toxic iodine from wastewater from medical clinics.

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