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Electrochemical formation of polyacrylamide-sulfur composite coatings on titanium surfaces

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ABSTRACT

In this study, titanium was chosen as the substrate material to form composite coatings that replace traditional metal sheets. Colloidal nanoparticles, which are heterogeneous in nature, exhibit variations in size, shape, and composition that significantly affect their catalytic behavior.

These variations are crucial for understanding the interactions between individual particles, as they can alter the efficiency and performance of the coating. The role of electrolysis in controlling the deposition and stability of nanoparticles on titanium surfaces is also examined.

Sulfur wastes can be recycled into functionally active products by using polyacrylamide, a flocculating agent derived from indigenous polymers. This approach aims to expand the potential applications and improve the performance of these materials under practical conditions. Therefore, research in this area is of great importance, focusing on innovative methods for converting sulfur wastes into valuable bioactive compounds.

This research focuses on the formation of a composite material based on polyacrylamide and sulfur on the surface of a titanium plate through electrolysis. The study employed scanning electron microscopy (SEM) to analyze the resulting composite material. The findings revealed that the amide groups (-CONH$_2$) in polyacrylamide interact effectively with sulfur, enhancing the adhesion and stability of the deposited sulfur layer. Additionally, polyacrylamide plays a critical role in stabilizing the microstructure of sulfur, facilitating the integration and uniform formation of the composite coating. This innovative approach demonstrates the potential for creating robust composite materials with promising applications.

1. Introduction

In contemporary scientific research, the exploration of colloidal nanoparticles has gained significant attention due to their potential to advance materials and technologies across various fields. Among the diverse physicochemical methods available, electrolysis stands out as a versatile and effective technique. This method is particularly valuable for the electrochemical recovery of ionogenic polymers (macroions) from solutions onto electrode surfaces of different shapes and geometries. By leveraging electrolysis, it is possible to deposit functional coatings that exhibit tailored properties, such as enhanced corrosion resistance, mechanical strength, or chemical stability. These coatings are crucial for improving the performance of materials in demanding environments, including biomedical, aerospace, and industrial applications (Table 1).

The electrochemical application of polyacrylamide-sulfur (PAM-S) composite coatings on titanium surfaces has several innovative aspects that contribute to its scientific novelty. For example, polyacrylamide (PAM) provides flexibility, hydrophilicity, and excellent adhesion, while sulfur enhances chemical stability, antimicrobial properties, and corrosion resistance. The combination of the polymer matrix with sulfur creates a synergistic effect.

The electrochemical synthesis method of the electrochemical formation of the PAM-S composite coating is itself novel because it allows for simultaneous polymerization and sulfur addition under controlled conditions. Tuning of the surface properties by adjusting the deposition parameters (e.g., current density, voltage). Compared to conventional methods, electrochemical deposition provides strong adhesion to the titanium substrate and reduces defects. Titanium is widely used in biomedical implants, aerospace, and marine applications.

Improving its surface properties with a PAM-S composite coating provides: Improved corrosion resistance, especially in aggressive environments. Enhanced chemical stability, protecting titanium from oxidizing and acidic environments.

The composite coating has multiple functional advantages, including: Corrosion protection: Sulfur acts as a barrier against corrosive

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Table 1
Molecular mass characteristics of polyacrylamide samples:

Sample	[η],dl/g	$K \times 10^{-3}$, dl/g	α	$M \times 10^{6}$	$\langle h \rangle$,*nm*	*R*,*nm*
PAA	10.5	6.31	0.80	3.361	372	152
aPAA (16)%	14.8	6.15	0.82	3.675	511	208
aPAA (30)%	17.5	6.45	0.83	3.754	590	240

agents, while PAM provides a hydrophilic shield that limits water penetration.

The electrochemical process is environmentally friendly compared to traditional chemical deposition methods, which often require toxic solvents or generate hazardous waste. The use of water-soluble polyacrylamide and sulfur is consistent with sustainable practices and reduces the environmental footprint.

The electrochemical method allows for the creation of customized coatings through modification. This research combines polymer science and electrochemistry, providing insight into how polymers and inorganic materials can be electrochemically deposited together.

This helps to understand the mechanisms of composite formation and their effects on surface properties, paving the way for further innovations in functional coatings. In conclusion, the scientific novelty of electrochemical polyacrylamide-sulfur composite coatings lies in their hybrid functionality, advanced deposition method, and potential to improve the performance of titanium in demanding environments.

This innovative approach opens up new possibilities for durable, corrosion-resistant, and multifunctional coatings in industrial and biomedical applications.

A critical application of this approach involves the use of macroions as regenerative materials for medical implants. In such cases, the biocompatibility, bioactivity, and safety of the resulting coatings are of great importance. These properties ensure that the coatings are suitable for integration with biological systems, making them safe and effective for medical use. Researchers working in this field have developed various innovative strategies to enhance these properties, some of which are outlined below.

This study emphasizes the role of electrolysis in the development of advanced biomaterials, showcasing its potential for producing coatings with tailored properties for medical and other high-value applications (Wang et al., 2022). In this study, titanium was chosen instead of a metal plate.

In this study, titanium was chosen as the substrate material for the formation of composite coatings, replacing traditional metal plates. Colloidal nanoparticles, which are inherently heterogeneous, exhibit variations in size, shape, and composition that significantly influence their catalytic behavior. These variations are crucial to understanding how individual particles interact within a catalytic system, as they can alter the effectiveness and efficiency of the coating. The study explores how these particle-to-particle differences impact the overall performance of the coatings, particularly in catalytic processes. The role of electrolysis in controlling the deposition and stability of nanoparticles on titanium surfaces is also examined, with a focus on optimizing the catalytic properties of the final composite material. The findings aim to enhance our understanding of colloidal nanoparticle behavior in practical applications, such as catalysis and material engineering (Song et al., 2024) behavior will be critical to realizing more stable, selective, and efficient catalyst systems, but it remains difficult to generate this understanding using conventional characterization techniques.

A number of targeted scientific studies and it has been shown It is possible in principle to use the electrolysis method to create a micro-sized coating on the dental surface of titanium due to the presence of an implant based on chitosan biopolymer due to the presence of an amine (NH_2^{+}) group in the elementary units, its action is activated under the influence of an electric field as a polyelectrolyte during electrolysis (Khramenkova et al., 2023). Structural polymer composite (Yuan et al., 2021; Khakkulov et al., 2024) materials (PCMs) are used in various industries: aircraft, rocket, shipbuilding, automotive and electrical industry, construction, sports industry, chemical and special engineering, medicine, etc. Key studies in this field mainly use various kinds of modifications of large micromechanical models, created at one time for the description of polymer composites properties in general (Venkatram et al., 2016).

According to the scientific data presented in the scientific articles of Scott D. Hopkins and others he presence of sufficient active groups for polyacrylamide to behave well under the influence of an electric field as a macroion, ie. polyacrylamide, n-PAM, formed by n acrylamide monomers [$-CH_2CH(CONH_2)-$] (Das et al., 2024). The polymer backbone contains two carbon atoms, one of which is connected to an amide group (Mardonovich et al., 2021) $(NH_2) - C{=}O$. All the resulting polymers are syndiotactic, with amide groups alternating on both sides of the chain.

Zheng, H. et al. The synthesis of anionic polyacrylamide and some of its properties are presented in scientific articles (Zheng et al., 2013). Yongzhi Liu et al reported results on the photocatalytic synthesis of cationic polyacrylamide and evaluation of its surface flocculation and dewatering (Liu et al., 2018).

Homogeneous polymerization includes polymerization processes in solvents in which both the monomer and the polymer are soluble. The number of such solvents for polyacrylamide (PAA) (Vshivkov et al., 2019) is small: water, formamide, acetic and formic acids, dimethyl sulfoxide (DMSO) (Casti et al., 2022), as well as some water-organic mixtures. In addition, PAA has limited solubility in dimethylformamide (DMF) (Eom and Kim, 2014), ethylene glycol, and glycerol. Polymethacrylamide (PMAA) is much less soluble than PAA. N,N-dimethyl- and N,N-diethylacrylamide polymers are soluble in water and insoluble in hydrocarbons (Eckert and Abetz, 2020). Poly-N,N-diethylacrylamide is soluble in acetone. Polymers with longer alkyl substituents on the nitrogen atom are less soluble in water but more soluble in organic solvents (Lewoczko et al., 2021). Poly-N-methyl- and poly-N-n-butylmethacrylamide are readily soluble in DMF, polymer N-(2-ethylhexyl)-methacrylamide-toluene (Park et al., 2017). Acrylic and methacrylic polymers dissolve in concentrated solutions of hydrochloric acid (Li et al., 2024).

High molecular weight polyacrylamides are also highly effective and are widely used as flocculants, thickeners, structure and film formers. In medicine, as tampons, pampers, napkins, superabsorbents for wound dressings, as a film-forming agent for controlling the prolonged effect of pharmaceutical drugs, as hydrogels (Liang et al., 2021) for ophthalmological contact lenses (Franco and De Marco, 2021). In agriculture, they are used as supersorbents for soil reshaping, forming a crust film for seeds, fertilizers, insecticides, herbicides and fungicides (Duke et al., 2023).

Crystalline (density 2,07 kg/dm^3) (Kholodovych et al., 2007) which is referred to as α-modification of sulfur, pale yellow rhomboid (Zheng et al., 2021)(cell parameters: a = 1.04646, b = 1.28660, c = 2.4486 nm) is stable at temperatures up to 98.38 °C under normal conditions. When the temperature exceeds 95.38 °C, β −modification monoclinic sulfur (Lau et al., 2017)(cell parameters: a = 1.090, b = 1.096, c = 1.102 nm) crystal (density 1.96 kg/dm^3) becomes stable (Xiao et al., 2024).

Hill, C. R., et al. (Hill et al., 2023), scientific findings cited in the scientific article indicate that dietary requirements for sulfur are mainly sulfur-containing amino acids to meet the demand for the synthesis of proteins, enzymes, coenzymes, vitamins, and hormones. (SAA) is calculated based on the requirements for cysteine and methionine. SAA is abundant in animal sources and relatively low in plant sources. While glucosinolates are predominantly found in Brassica vegetables (e.g., broccoli, cabbage, and kale), Allium vegetables (e.g., garlic, onions, and leeks) contain a different class of sulfur-containing compounds, primarily cysteine sulfoxides. Both types of sulfur compounds contribute significantly to the health benefits and defense mechanisms of these plants, but they are distinct in their structure and effects (Miękus et al., 2020). Therefore, sodium produced and obtained on the basis of our scientific research does not cause any harm to plants and nature.

Dordevic D and others in their scientific article also gave conclusions about which compounds sulfur has a positive effect on, that is, sulfur (S) (Dordevic et al., 2023) is an important element and necessary for all living organisms. It is a part of bioorganic compounds, for example, proteins (in the form of combined amino acids, for example, cysteine and methionine), antibiotics and antimicrobial compounds (for example,sulfonamides, allicin). F. Kh. Urakaev et al (Urakaev and Boldyrev, 2000). mentioned the mechanochemical synthesis of colloidal sulfur particles.

In fact, sulfur occurs in nature together with a number of elements (Meyer, 1976) (Fig. 1a) and makes up 0.05 % of the earth's crust. Currently, natural sulfur deposits exist in Italy, the USA, Japan, Mexico, and Central Asia (Ruckmick et al., 1979), and sulfur is extracted from them by melting, and it is recommended for use in the form of granules (Fig. 1 b) or powder (Fig. 1 c).

Today, about half of the sulfur raw materials produced in the world is sulfuric acid (Torrent-Sucarrat et al., 2012) (H_2SO_4), 25 % is obtained from sulfites, 10–15 % is from agricultural crops (mainly copper sulfate for vines and cotton $CuSO_4\ SH_2O$) is used in the fight against harmful insects, 10 % is used in vulcanization in the rubber industry. Also, sulfur paints and pigments, explosives (Buyondo et al., 2022) (gunpowder), synthetic fibers, luminaphors, matches, oil, medicines are produced.

2. Research Methodology

Electrochemical formation of polyacrylamide-sulfur composite coatings on titanium surfaces is proposed as a novel approach to improve surface properties. This method provides a controllable and scalable solution to improve the durability and performance of titanium in a variety of applications.

The electrolysis method is a key process for the formation of polyacrylamide-sulfur (PAM-S) composite coatings. It involves applying an electrical current to drive the simultaneous polymerization of polyacrylamide and deposition of sulfur onto the titanium surface.

Electrolysis method. Electrolysis is a chemical process in which an electric current passes through an electrolyte – either in a heated dilute state or as a solution in water – causing oxidation–reduction (redox) reactions at the electrodes. This leads to the decomposition of the electrolyte and the release or deposition of substances at the electrodes (Yang et al., 2021). It is known that any electrolyte solution consists of cations and anions. Cations and anions move irregularly in solution. If positive and negative electrodes (anode and cathode) (Luo et al., 2022) are placed in such a solution, the movement of ions in the solution will follow a certain pattern: anions will move towards the anode, cations will move towards the cathode. Cations go to the cathode and take electrons from it, and anions, on the contrary, give excess electrons to the anode; reduction occurs at the cathode and oxidation occurs at the anode.

In the reactions taking place at the cathode, the energy of hydration of the cation with water molecules should be taken into account, for example, sodium reacts more actively with water than calcium, even though it is located lower than calcium in the electrochemical series.

The English scientist M. Faraday (Khakkulov et al., 2021) first established (in 1836) that there is a quantitative connection between electric current and chemical processes that occur under the influence of electric energy. M. Faraday introduced the concepts of electrode, anode, cathode, anion, electrolyte, electrolysis to science (Scott, 2019). These terms have been used until now. During his experiments, Faraday connected several galvanic elements in series and formed a battery: he used this battery as a source of electric current during electrolysis. As a result of his investigations, he discovered the following laws of electrolysis:

Faraday's 1st law In the process of electrolysis, the mass of the substance released at the electrode is directly proportional to the amount of electric current passing through the solution.

If we denote the mass of the substance deposited on the electrode by t, the amount of electricity by $\boldsymbol{Q}$, the current by $\boldsymbol{I}$, and the time by $\boldsymbol{t}$, Faraday's 1st law is written as follows:

$$m = kQ = kIt \tag{1}$$

Faraday's 2nd law of Electrolysis states that when the same quantity of electric charge is passed through multiple electrolytic cells connected in series, the masses of the substances deposited or released at the electrodes are directly proportional to their respective chemical equivalents. This principle is foundational in electrochemistry and helps to predict the outcome of electrolysis in a series of electrolyzers.

Chitosan biopolymer (Milusheva and Rashidova, 2022) is now widely used in the production of multi-layered carbon nanotubes (Mallakpour et al., 2021). This method was developed by scientists from the Hong Kong Polytechnic University and the Shanghai Institute of Materia Medica, and is based on the noncovalent modification of chitosan on the surface of carbon nanotubes (Ali Mohammadi et al., 2015).

Analysis of the literature shows that phosphate, calcium, copper, gold, nickel ions, as well as biopolymers such as chitosan, fibroin etc, macroions can be such substances. The main issue here is to determine the parameters of electrolysis for the production of coatings based on given substances. During electrolysis, the range of direct current supplied to plastic (0.1–10 mA), temperature range (30–70 °C), concentrations of selected biologically active substance solutions and mixtures (0.1–10 %), electrolysis time (1–20 h) are displayed. The main attention is paid to the physical characteristics of the surface of the plates and their smoothness and roughness. Fig. 2 shows a schematic view of the electrolysis of solution ions on the surface of the plates.

Currently, the use of tricalcium phosphate ($Ca_3(PO_4)_2$) ions, which contain divalent calcium (Ca^{2+}) and pentavalent phosphorus (P^{5+}), as a binder is a topic of increasing interest in electrochemical and biomedical applications due to their unique properties.

Previous studies have investigated the behavior of silk fibroin and tricalcium phosphate salt in combination with an electric field. This is because fibroin contains amine ($-NH_2$) and carboxyl ($-COOH$) functional groups that are important for electrochemical interactions.

During electrolysis, fibroin undergoes electrochemical regeneration, where its functional groups are activated and adsorbed onto the metal

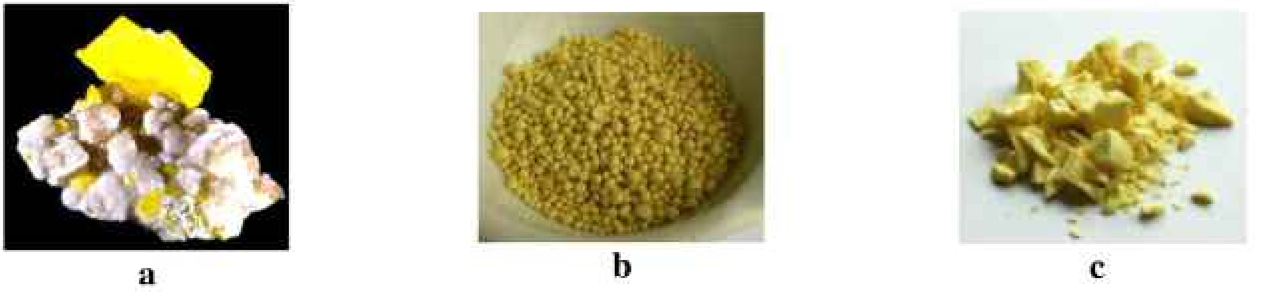

Fig. 1. Natural composition of sulfur with calcium carbonate ($CaCO_3$), aragonite (a), pure S granule (b) and powder (c).

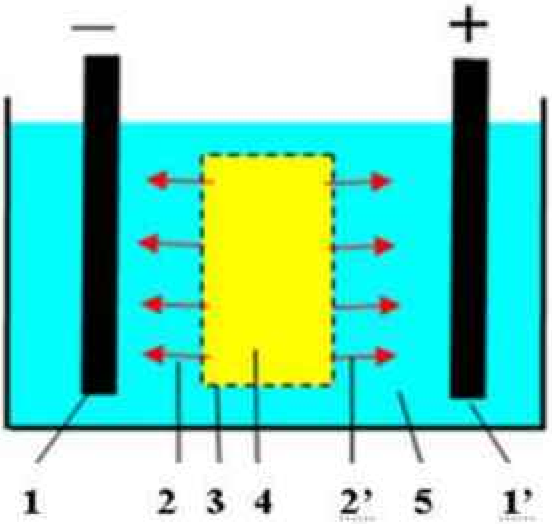

Fig. 2. The principle diagram of using the electrolysis method for solutions with salt ions: 1, 1′-carbon electrodes on the surface of which ions are regenerated and oxidized; 2, 2′ – ions moving towards the electrodes; 3 – membranes for solution; 4 – polymer solution; 5 – dialysate.

surface. This regeneration process creates a reactive interface that interacts with tricalcium phosphate ions (Tuwalska et al., 2022).

The described electrolytic method requires precise control over various parameters, variations in which can lead to inconsistent coating quality on titanium plates.

The electrolytic method used to coat titanium plates is very sensitive to various parameters, and maintaining precise control over these parameters is essential to ensure consistent and high-quality coatings. Variations in factors such as current density, voltage, temperature, electrolyte composition can significantly affect the coating process, leading to inconsistent results. There are some key parameters that must be controlled to ensure a uniform and high-quality coating on titanium plates. The amount of current applied to the electrolytic process directly affects the deposition rate and uniformity of the coating. Too high or too low a current density can result in poor adhesion, rough surface textures, or uneven coating thickness.

In addition, the applied voltage can affect the electrochemical reactions that occur on the electrode surface. Voltage variations can lead to inconsistent deposition, altered microstructure, and uneven coating quality. Maintaining a stable voltage is essential to ensure smooth and consistent coating formation. The chemical composition of the electrolyte plays a significant role in the nature of the coating. Variations in the concentration of metal salts, pH, and other additives can lead to differences in coating structure, adhesion, and uniformity. Maintaining the correct electrolyte concentration is critical for consistent deposition. The temperature of the electrolyte affects the rate of chemical reactions, ion mobility, and the overall efficiency of the coating process. High temperatures can cause excessive oxidation or degradation of the electrolyte, while low temperatures can slow the deposition rate or cause poor coating adhesion. Electrode surface preparation is also an important parameter, as can the surface condition of titanium plates prior to electrolysis. Insufficient cleaning of the plate surface can result in poor adhesion or uneven coating thickness.

Time is also important in the electrolysis process. The duration of the electrolysis process also plays a role in determining the thickness and uniformity of the coating. Too short a time can lead to insufficient coating, while too long a time can lead to excessive deposition and lead to defects.

To solve these problems, it is very important to implement strict control measures, including monitoring and regulating each of these parameters during the process. Automation and real-time sensors also help maintain stable conditions and ensure the production of high-quality coatings.

In this research work, in order to minimize the occurrence of the above problems in the electrolysis method, the electrolysis time was set to $t = 5$–18 h, the current $I = 10$–30 mA, the temperature was maintained at $T = 50$ degrees Celsius using a thermostat, and the surface of the titanium plate was cleaned by physical and chemical methods.

3. Analysis and results

Since it is important to conduct research with pure sulfur particles in the research work, in order to remove residual elemental masses from the composition of mechanically crushed powders, they were first treated with water, sulfur:water (1:10 ratio), then with acetone, sulfur: acetone (1:5 ratio) is washed and cleaned. When the absolute masses of sulfur powder before and after washing are compared, it was found that its mass decreases to 4 g. This result shows that the mass composition of the powder is 99 % sulfur.

In order for the powder particles to be in the micro- and nano-sized range, they were additionally crushed by mechanical action on the surface of a sieve with holes (holes) of $1 \div 10$ μm.

It was observed that these micro-sized sulfur particles have stronger odor dispersing properties than previous sulfur waste. This situation can be explained by two aspects:

- firstly, elemental sulfur in the environment and air, oxygen, which has been purified from additional substances, has the ability to emit more odors for moisture;
- –secondly, the grinding of sulfur allows the relative surface of its micro-sized particles to increase and the energy to be more exposed to oxygen, substances in the air, and moisture, to pass to the gas phase of regeneration and evaporation.

The insolubility of sulfur in water environment, its micro-particles helped to prepare the suspension.

When applying a thin layer of sulfur suspension on a glass surface with very low viscosity, it was observed that water molecules evaporate easily, and sulfur particles return to the dust state and scatter under the influence of relatively weak external influences (wind, blowing).

This is the case when sulfur microparticles are used in practice, for example, when they are recommended as insecticides, it is necessary to enrich them with additives that keep them on the surface.

Thus, by extracting sulfur from the composition of natural gas processing waste, grinding to the level of microparticles, washing and drying in an environment of water and acetone, and additional grinding, particles with a size of less than 5 μm and 100 nm and preparation of water suspensions based on them possibility is determined. The main feature of such particles is that as their size decreases, they emit a stronger sulfur smell.

The insolubility of sulfur in an aqueous environment is based on its chemical properties, and this property makes it possible to prepare stable suspensions based on sulfur micro- and nanoparticles. Sulfur does not react with water and is insoluble in water because it is a nonpolar element. Water, on the other hand, consists of polar molecules, with which sulfur does not interact. Van der Waals forces are dominant between sulfur molecules, which separates them from hydrophilic environments.

Molecular mass characteristics of polyacrylamide. Polyacrylamide (PAM) is a high-molecular-weight polymer with important applications in a variety of fields such as water treatment, biomedical devices, and as a flocculant in suspensions. The molecular mass (or molecular weight) of polyacrylamide plays a critical role in determining its physical and chemical properties, such as solubility, viscosity, and ability to form gels.

To obtain anionic modified polyacrylamide (PAA-S) in a sulfur suspension, some monomer units were partially hydrolyzed in sodium hydroxide (NaOH) medium, carboxylate groups were introduced to increase the ionogenicity of the microparticles. Specifically, 2.5 mL of 5 M NaOH aqueous solution was added to 50 mL of 1 g/dL polyacrylamide solution. Alkaline hydrolysis was carried out at 50 °C for 1 h and 2 h, resulting in two separate samples.

The hydrolysis products were then analyzed by potentiometric titration using 0.1 M HCl and 0.5 M NaOH titrants, with distilled water as the reference. The degrees of hydrolysis (DH) were determined to be 18 % and 30 %, respectively. As a result, two anionic polyacrylamide samples were prepared: aPAA (18 %) and aPAA (30 %).

Further studies were conducted on the basis of comparative analysis of the following three samples:

PAA – Nonionic polyacrylamide (PAA-HD)
aPAA (18 %) – Anionic polyacrylamide (HD = 18 %)
aPAA (30 %) – Anionic polyacrylamide (HD = 30 %)

A Ubbelohde viscometer was used to determine the molecular weights of these samples. The capillary flow time of the solvent water was $t_0 = 80$ s. Sample solutions with C = 0.1 g/dL were prepared. Distilled water was used as the solvent for nonionic PAA, while a binary solvent consisting of 0.2 % NaCl + water was used for the ionic aPAA (18 %) and aPAA (30 %) samples to mitigate the effects of any concentration anomalies.

The viscosity measurements were performed at a constant temperature of 25 °C. The solutions were gradually diluted by adding the solvent in discrete steps, reducing the concentration from *0.1 g/dl* to *0.02 g/dL*. The flow times (t_i) of these diluted solutions were recorded using a viscometer. The relative ($\eta_{relative} = t_i/t_0$), specific ($\eta_{specific} = (\eta_{relative} - 1)$ and quoted ($\eta_{specific}/C$) viscosities were determined depending on the concentration (C) and graphs of (η_{sol}/C) dependence on C were constructed according to the Haggins formula $\eta_{specific}/C = [\eta] + k[\eta]C$ and are presented in Fig. 3.

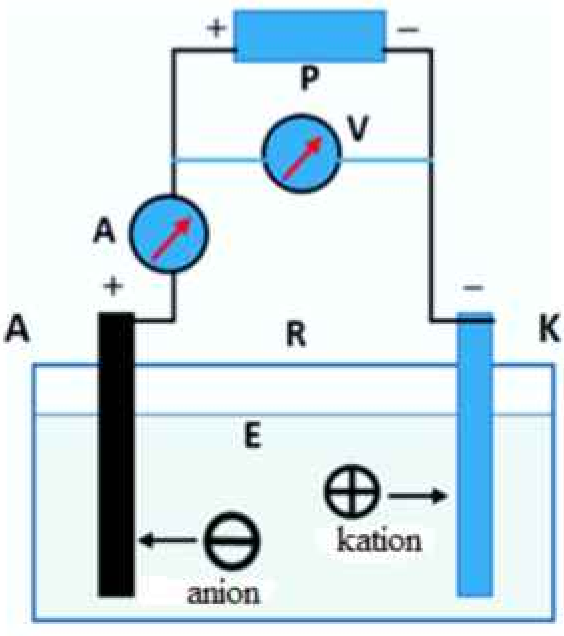

Fig. 3. Graphs of the relationship between reduced viscosity ($\eta_{specific}/C$) and concentration (C): 1 (Yellow markers): Represents PAA (unhydrolyzed polyacrylamide). 2 (Gray markers): Represents aPAA (18% hydrolyzed polyacrylamide). 3 (Red markers): Represents aPAA (30% hydrolyzed polyacrylamide). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

1. PAA (Sample 1): The plot has a relatively gentle slope. The low slope suggests minimal interaction between polymer chains and solvent due to the absence of charged groups.
2. aPAA (18 %) (Sample 2): The slope is slightly steeper compared to Sample 1.
   This indicates moderate electrostatic interactions, consistent with a partial degree of hydrolysis (18 %).
3. aPAA (30 %) (Sample 3): The steepest slope among all three samples. This suggests a significant increase in hydrodynamic volume and stronger electrostatic interactions due to the higher degree of hydrolysis (30 %).

The trend confirms that as the degree of hydrolysis increases, the reduced specific viscosity.

$\eta_{specific}/C$ increases due to stronger polymer–solvent interactions and greater chain expansion in solution. This aligns with the expected behavior for anionic polyacrylamides with higher carboxylate content.

If the graph is extrapolated to $C \to 0$, the condition $k[\eta]^2C = 0$ and $\eta_{specific}/\ C = [\eta]$ is satisfied in the Haggins formula. Based on this, the characteristic viscosities [η] of the samples are determined from the graphs and based on them, the molecular masses of the samples (*M*), distance between the ends of the macromolecular chains $< h>$, and the radii of the elementary units (*R*) were calculated (1-table). The coefficients *K* and **α** of the Mark-Kuhn-Havnik equation corresponding to the degree of hydrolysis were found, and the molecular masses of the samples $M = ([\eta]/K)^{1/\alpha}$ were calculated. Taking the swelling coefficient of the samples as $\alpha = 1$ and the hydrodynamic Flory parameter as $F = 2$, $84*10^{21}$ *dl/g*, the distance between the chain ends, which represents the conformational state of macromolecules, was calculated according to the Flory formula $[\eta] = \left(< h^2 > \right)^{3/2} F\alpha^3/M$ and determined from the average values of the effective radii of macromolecular clusters.

The comparative analysis of the results in the table demonstrates that the partial alkaline hydrolysis of the samples, reaching hydrolysis degrees (HD) of 18 % and 30 %, led to an increase in the carboxylate group content in the monomeric units. As a result, the molecular masses increased by factors of 1.09 and 1.12, respectively. Additionally, the average distances between the ends of the macromolecular chains increased by a factor of 1.37 for the HD 18 % sample and by 1.57 for the HD 30 % sample. Similar differences were observed in the radii of the elementary units.

These changes indicate the formation of active ionogenic groups in the hydrolyzed polyacrylamide samples, leading to a more extended conformation of molecular chains in solutions. This extended state enhances the polyelectrolyte and flocculation properties, creating favorable conditions for more effective performance, particularly in electrolysis processes. This improved functionality makes the hydrolyzed samples more efficient in their applications, especially in processes that require ion-exchange or flocculation capabilities.

UV Spectroscopic features of sulfur micro- and nanoparticles. The results of the analysis using ***Specord D20*** ultraviolet spectroscopy revealed important information in the analysis of the composition of sulfur micro- and nanoparticles. Fig. 4.

The presence of sulfur and its properties are confirmed by the appearance of spectral peaks characteristic of sulfur at a wavelength of ***λ ≈ 210 nm*** in the study.

The wavelength of λ ≈ 210 nm is characteristic of sulfur, and the appearance of this peak indicates the presence of sulfur atoms or small molecular aggregates. At this wavelength, ultraviolet radiation excites transitions characteristic of the electronic states of sulfur, which are clearly visible in the spectroscope.

The peaks obtained by Specord D20 spectroscopy confirm the stability of sulfur particles in the dispersion and their composition. The spectral peaks of sulfur at *λ≈210* nm allow the detection of sulfur among a large number of other components, which provides high sensitivity.

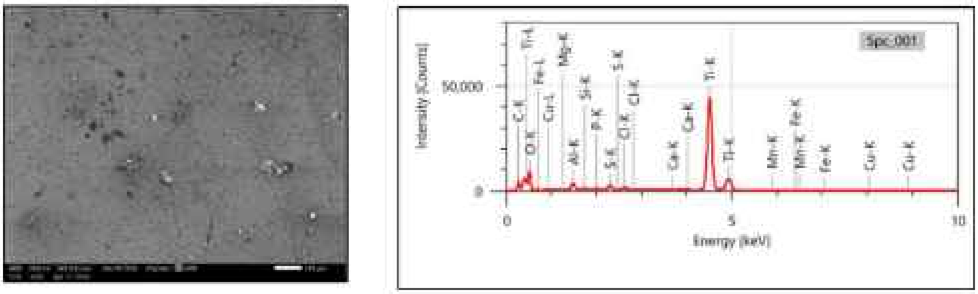

Fig. 4. Ultraviolet spectroscopy spectrum of sulfur micro- and nanoparticles.

The spectral properties of micro- and nanoparticles ultraviolet spectroscopy help to understand how they interact with other materials.

It is used to qualitatively and quantitatively evaluate sulfur coatings on substrates such as titanium plates.

Obtaining information about the chemical composition and stability of nanoparticles using ultraviolet spectroscopy, and the prominent peaks of sulfur in the ultraviolet spectroscopy spectrum allow for a deeper understanding of its electronic and optical properties.

The physical and chemical state of materials is very important in the production of composite materials, as they directly affect the performance and functionality of the material. Sulfur-polyacrylamide suspensions were used in the study, which ensures their dual role of actively contributing to the formation of composite coatings through the electrochemical regeneration of macroions in the electrolyte and on the surface of the titanium plate under an electric field.

From a physical point of view, sulfur micro- and nanoparticles in suspension have high reactivity in the electrolyte due to their high surface area, and the hydrophilic polymer chain of polyacrylamide keeps the sulfur particles stable in the dispersion state. Chemically, the –$CONH_2$ groups in the polyacrylamide chain bind to the sulfur particles, helping them stabilize in an electric field. The degree of ionization of macroions in the suspension helps electrochemical processes.

In this research work, the principle drawing of the electrolysis device and a simple laboratory device for its implementation are presented in Fig. 5. The device consists of a current source (P), a voltmeter (V), an ammeter (A), and an electrolytic cell (R). When the electrolyte is placed inside the cell, the ions or macroions in them appear in the form of anions and cations depending on their negative and positive charges and move towards the anode (a) and cathode (b) under the influence of electric current.

The results of the study show that the electrolysis of colloidal sulfur solution in hydrochloric acid (HCl) and water, combined with polyacrylamide and saline medium under an electric field, leads to the formation of a coating on the metal surface. The main experimental conditions and analysis results are as follows. Electrolysis conditions: the current supplied from the source is $I = 10 - 30$ mA, the electrolysis duration: $t = 5 - 15$ h, the electrolyte composition is HCl and colloidal sulfur in water, and polyacrylamide macroion is provided to increase stability and facilitate the formation of the coating, and a saline medium is provided to ensure ionic conductivity. To understand the mechanism of coating formation on the surface of the plate, that is, sulfur deposition, sulfur colloid undergoes electrochemical regeneration under an electric field and sulfur atoms are restored to the metal surface, and polyacrylamide chains help stabilize the coating and improve adhesion to the substrate.

Nanoparticles of different sizes or shapes can have significantly

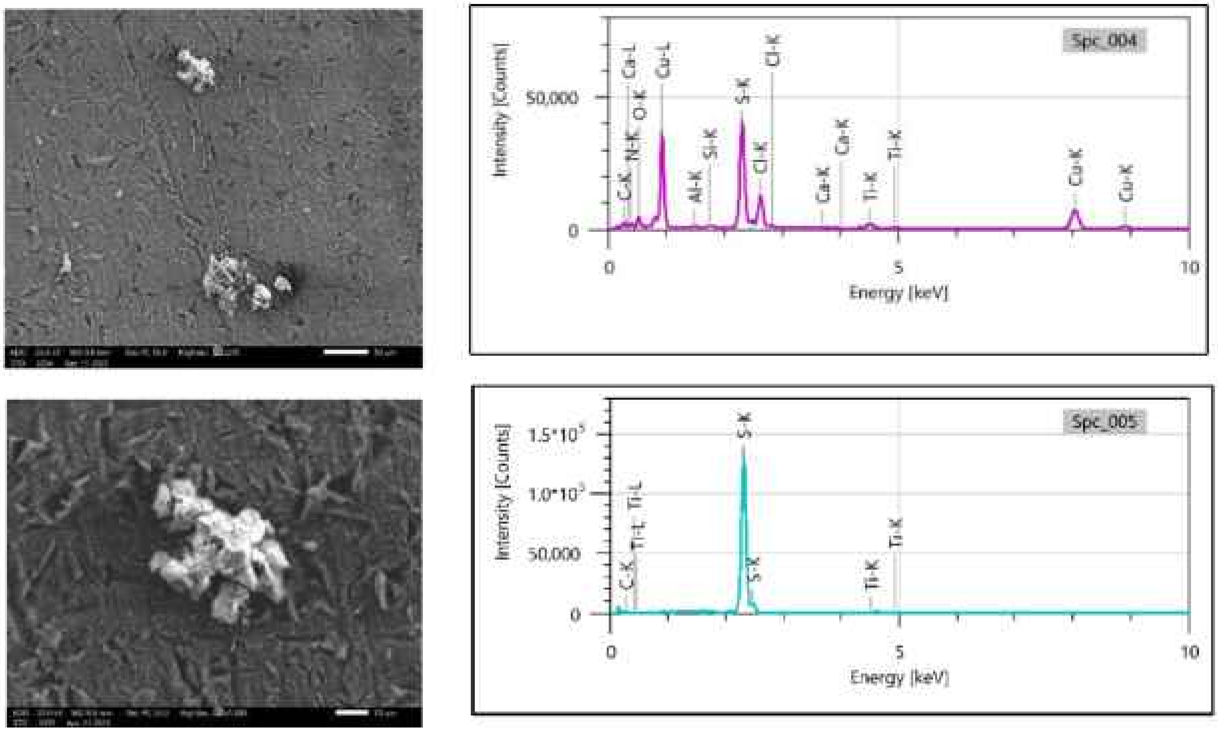

Fig. 5. Schematic drawing of the electrolysis system.

different physical and chemical properties, such as surface area, reactivity, optical behavior, and stability. This makes it difficult to predict how the entire colloidal system will behave based on the properties of individual nanoparticles. Due to the variability of the particles, the overall performance of the colloidal system (e.g., in catalysis, drug delivery, or sensing applications) may not be consistent. Some particles may perform better than others, leading to less predictable results.

Heterogeneous colloidal nanoparticles may experience different aggregation or degradation rates depending on their size and surface properties. Smaller nanoparticles may be more prone to aggregation, which affects the stability of the colloidal suspension.

Composite coatings obtained by electrolysis method Modern Scanning Electron Microscope (SEM)-(EDS) Energy Dispersive Spectroscopy: Jeol JSM-IT200LA (Japan) was used for high-resolution imaging of the metal surface and analyzed.

Spectral analysis was performed to determine the elemental composition of the coating by energy dispersive spectroscopy (EDS). Surface morphology SEM imaging revealed a uniform coating with clear microstructural features indicating successful deposition.

EDS analysis of the elemental composition confirmed the presence of sulfur (S) and other elements (e.g., carbon (C) and nitrogen (N) are evidence supporting the formation of a composite material from polyacrylamide.

The peaks in the spectra are aligned with sulfur and polymer components, confirming their successful integration into the coating.

The SEM images and spectral analyses presented in the study provide detailed insights into the atomic and molecular transformations of polyacrylamide and sulfur on the surface of the titanium plate during the electrolysis process. These findings enhance the understanding of the interaction mechanisms and enable a deeper analysis of the substances formed during the coating process.

In terms of the interaction between polyacrylamide and sulfur, SEM analyses reveal the distribution of sulfur microparticles and polyacrylamide chains on the titanium plate. The –CONH$_2$ groups in polyacrylamide interact with sulfur, facilitating the adhesion and stability of the deposited sulfur layer.

During the electrolysis process, sulfur is reduced to the atomic level and deposited on the titanium surface. Polyacrylamide enhances integration by stabilizing the microstructure of sulfur, facilitating the formation of a composite coating.

As for the molecular composition, EDS spectra confirm the presence of sulfur, carbon, and nitrogen, which correspond to the polyacrylamide-sulfur complex. Changes in the distribution of elements reflect the electrochemical reactions and bonding processes that occur during the coating formation process Fig. 6.

Spectral analysis results Spectrum 004: Sulfur (S) content: 17.08 %, Carbon (C) content: 36.17 %, Nitrogen (N) content: 16.34 %, Spectrum 005: Sulfur (S) content: 46.53 %, Carbon (C)) content: 53.37 %.

These results indicate that polyacrylamide and sulfur are combined in the form of atomic fragments on the surface of the titanium plate during the electrolysis process. In particular, the change in the **S** and **C** ratios is a confirmation of the molecular degradation of polyacrylamide and the formation of compounds with sulfur.

The molecular formula of polyacrylamide is $(C_3H_5NO)_n$. During electrolysis, the partial cleavage of the ***C-N*** and ***C=O*** bonds under the influence of high-energy ions and an electric field indicates the decomposition of polyacrylamide into macroionic fragments.

During electrolysis, sulfur is reduced to an atomic state (in the form of S^{0} or $S^{\ 2}$). These atoms combine with polyacrylamide fragments to form new structures.

The surface of the titanium plate acts as a substrate for chemical reactions during electrolysis. The carbon and nitrogen atoms of polyacrylamide and the sulfur fragments are attached to the titanium surface through chemical bonds.

The presence of ***N*** atoms in the 004 spectrum indicates that the primary structure ***(C-N)*** of polyacrylamide is preserved. The absence of nitrogen atoms and an increase in the sulfur content in the 005 spectrum indicates that polyacrylamide is further decomposed and ***S-C*** bonds are

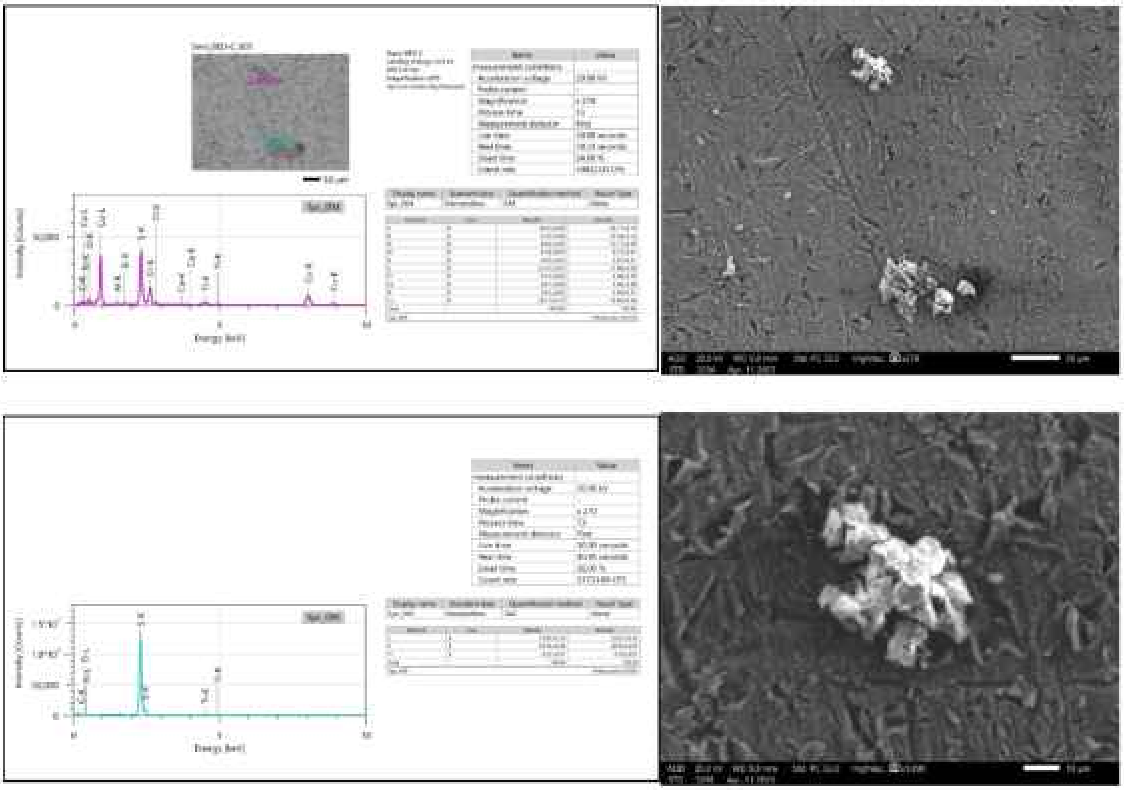

Fig. 6. Surface morphology (SEM Analysis) and Spectral Features (EDS Analysis) of the coating.

formed. The high content of carbon, nitrogen and sulfur in the chemical compounds on the surface of titanium confirms the formation of a new composite coating, and the coating can impart various properties (corrosion resistance, pesticide resistance) to the surface of the titanium plate.

The studies carried out in an electrolysis unit highlight the unique interplay between macroions and ions during combined electrochemical reduction processes. These findings demonstrate that such interactions are highly dependent on specific chemical and physical parameters, offering valuable insights into the underlying mechanisms of electrochemical systems.

4. Conclusion

In conclusion, successful modification of polyacrylamide by hydrolysis in sodium hydroxide and subsequent introduction of a carboxylate group significantly increases its ionogenicity and helps to form a stable sulfur suspension. The molecular weight properties of the polymer are slightly affected, but remain sufficient to form functional PAA-S composites with potential for various applications.

The results of the analysis performed by Specord D20 ultraviolet spectroscopy allow for the effective determination of the composition and properties of sulfur micro- and nanoparticles. Spectral peaks obtained at a wavelength of $\lambda \approx 210$ nm reliably confirm the presence of sulfur and are of great importance in studying its physicochemical state. This method can be used as a basic scientific tool in the study of micro- and nanoparticles and in their application areas.

During the electrolysis process, polyacrylamide macroions and sulfur atoms are attached to the surface of the titanium plate, forming a new composite material. The spectra 004 and 005 show different stages of polyacrylamide degradation and chemical changes on the titanium surface. A high concentration of sulfur (spectrum 005) may be of great importance in enhancing the pesticidal or antifungal properties of the titanium coating.

The combined regeneration of macroions and ions during electrolysis can be used as a basic technological approach to create new materials. The coatings formed on the titanium plate will have different functional properties depending on the structure of the macroions and the properties of the ions, and a number of technological innovations can be introduced as a result of further study and optimization of this mechanism.

The use of sulfur-polyacrylamide suspensions as macroions in electrochemical regeneration processes has opened up new opportunities in the production of composite coatings. The coating formed on the surface of titanium plates has high mechanical and chemical properties, indicating its great potential for application in agricultural, industrial and environmental sectors.

CRediT authorship contribution statement

Khakkulov Jakhongir: Writing – original draft, Methodology, Formal analysis, Data curation. **Temirov Zokirjon:** Visualization, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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