ELECTROCHEMICAL COATING OF POLYACRYLAMIDE MACROION AND SULFUR COLLOIDAL PARTICLES ON THE ELECTRODE SURFACE

Khakkulov J. M., Temirov Z. Sh.

National University of Uzbekistan named after Mirzo Ulugbek, Tashkent, 100174, Republic of Uzbekistan

Abstract

There are huge amounts of sulfur waste in natural gas production enterprises in the world, and it is urgent to prepare bioactive preparations for specific purposes using polyacrylamide with flocculating properties from local polymers to obtain various functionally active products by processing them and increasing the possibilities and efficiency of their practical application. Special attention is paid to scientific research as a task.

In this study, the structural and phase changes of polyacrylamide $(C_3H_5NO)_n$ samples and suspensions based on sulfur (S) micro and nano particles in different regimes of longitudinal and shear flow, as well as the physical characteristics of the formed composites were determined and polyacrylamide $(C_3H_5NO)_n$ was widely used in the electrolysis device. and the scientifically based principles and parameters of the formation of coatings from sulfur (S) suspension were determined and the images and spectra of the samples were analyzed using a modern electron microscope *Jeol JSM-IT200LA (Japan) SEM-EDS.*

According to the obtained results, the percentage of elements *(S, 23.35-69.78%), (C, 18.53%), (N, 9.76%), (O, 8.68%)* appeared on the surface of the titanium plate. It indicates that polyacrylamide $(C_3H_5NO)_n$ and sulfur (S) macroins are restored on the surface of the plate. Therefore, based on the results of this scientific research, it is scientifically based on the possibility of forming a composite coating on the metal surface based on colloidal nanoparticles of sulfur (S) and high molecular compounds.

Keywords: macroion, nanoparticle, polyacrylamide, sulfur, electrolysis, titanium plate

1. Introduction

Today, within the framework of world science, scientific experiments are being carried out on the basis of colloidal nanoparticles in various physicochemical methods, one of these methods is the electrolysis method, that is, the extraction of ionogenic polymers (macroions) from solutions on the surface of electrodes of various shapes by electrochemical recovery. In this case, when using macroions as a regenerative electrode for medical implants, it is very important that the formed coatings have biocompatible, bioactive and harmless properties [1]. In this study, titanium was chosen instead of a metal plate

Colloidal nanoparticles are inherently heterogeneous, exhibiting variations in size, shape, or composition that will impact their catalytic behavior. Understanding these particle-to-particle variations in catalytic 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[2].

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[3,13]. Structural polymer composite materials (PCMs) are used in various industries: aircraft, rocket, shipbuilding, automotive and electrical industry, construction, sports industry, chemical and special engineering, medicine, etc [4]. 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 [5,12].

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 [-$CH_2CH(CONH_2)$-] [6]. The polymer backbone contains two carbon atoms, one of which is connected to an amide group *(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[10]. Yongzhi Liu et al reported results on the photocatalytic synthesis of cationic polyacrylamide and evaluation of its surface flocculation and dewatering [11].

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) is small: water, formamide, acetic and formic acids, dimethyl sulfoxide (DMSO), as well as some water-organic mixtures. In addition, PAA has limited solubility in dimethylformamide (DMF), 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. 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. Poly-N-methyl- and poly-N-n-butylmethacrylamide are readily soluble in DMF, polymer N-(2-ethylhexyl)-methacrylamide-toluene. Acrylic and methacrylic polymers dissolve in concentrated solutions of hydrochloric acid.

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 for ophthalmological contact lenses. In agriculture, they are used as supersorbents for soil reshaping, forming a crust film for seeds, fertilizers, insecticides, herbicides and fungicides.

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

Hill, C. R., et al., 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. However, some plants, particularly allium vegetables, contain many protective sulfur compounds such as glucosinolates and cysteine sulfoxides [7]. 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) 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, penicillins, sulfonamides, allicin) [8]. F. Kh. Urakaev et al. mentioned the mechanochemical synthesis of colloidal sulfur particles [9].

In fact, sulfur occurs in nature together with a number of elements (Fig. 1a) and makes up 0.05% of the earth's crust [12]. Currently, natural sulfur deposits exist in Italy, the USA, Japan, Mexico, and Central Asia, 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).

a **b** **c**

Figure1. Natural composition of sulfur with calcium carbonate ($CaCO_3$), aragonite (a), pure S granule (b) and powder (c).

Today, about half of the sulfur raw materials produced in the world is sulfuric acid (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 (gunpowder), synthetic fibers, luminaphors, matches, oil, medicines are produced.

2. Research Methodology

Electrolysis method. The oxidation-reduction "recovery" process that occurs when an electric current passes through a heated liquefied electrolyte or its solution in water is called electrolysis. 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) [14] 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 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 [14,15]. 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[14, 16].

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

$$m=kQ=kIt \qquad (1)$$

Faraday's 2nd law. If the electrolyte solution in several electrolyzers connected in series increases, when passing the same amount of electric current, the mass amounts of substances released at the electrodes will be proportional to the chemical equivalents of those substances[16].

Chitosan biopolymer [17] is now widely used in the production of multi-layered carbon nanotubes. 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.

Analysis of the literature shows that phosphate, calcium, copper, gold, nickel ions, as well as biopolymers such as chitosan, fibroin, etc [18,19]. - 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 ^{o}C), concentrations of selected biologically active substance solutions and mixtures (0.1-10%), electrolysis time (1 - 20 hours) are displayed. The main attention is paid to the physical characteristics of the surface of the plates and their smoothness and roughness. Figure 2 shows a schematic view of the electrolysis of solution ions on the surface of the plates.

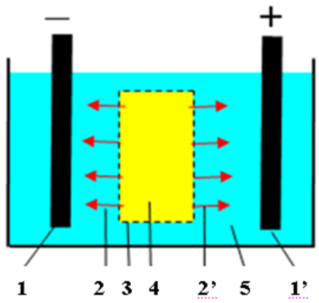

Figure 2. The principle diagram of using the electrolysis method for solutions with salt ions: 1, 1'- carbon electrodes on the surface of which ions are regenerated and oxidized; 2, 2' - ions moving towards the electrodes; 3 – membranes for solution; 4 – polymer solution; 5 - dialysate.

Currently, the use of tricalcium phosphate ($Ca_3(PO_4)_2$) ions, that is, divalent Ca and pentavalent P, is of interest as such a binder. In the previous research works, scientific results were obtained that the amine and carboxyl groups of fibroin and its molecule are electrochemically regenerated on the metal surface and interact with tricalcium phosphate during electrolysis with the participation of natural silk fibroin and tricalcium phosphate.

3. Results and Discussion

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 grams. 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÷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.

One of the important aspects in the production of composite materials is their physical and chemical state. In the study, the mentioned sulfur and polyacrylamide suspensions were prepared, and it was determined that their effect as macroions in the electric field (electrolyte) and the formation of a composite coating on the surface of the titanium plate through electrochemical regeneration.

In this research work, the principle drawing of the electrolysis device and a simple laboratory device for its implementation are presented in Figure 3. 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.

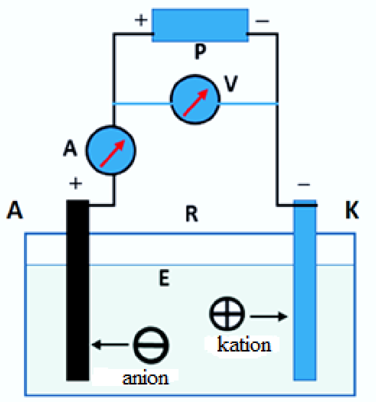

Figure 3. Schematic drawing of the electrolysis system

As a result of the conducted research, it was observed that the electrolysis process of the colloidal solution of sulfur in *HCl* acid and water together with polyacrylamide and a saline environment under the influence of an electric field produces a coating on the metal surface when the current strength is in the range *I=10-30 mA* and the electrolysis time is *t=5-10* hours, and it was obtained the results show that it is possible to analyze the images taken with a modern scanning electron microscope *Jeol JSM-IT200LA (Japan) SEM-EDS* and the spectral results of the coating on the surface.

Anions give their charge to the anode and become neutral, turn into particles, settle on the surface of the electrode and recover. When electricity is supplied from the source, electrons, ions, and macroions move from the anode to the cathode, deposit on the surface, and recover electrochemically. As a result, the mass covers the surface of the electrode, and this process is also called material transfer.

Modern methods were used to determine the structure and physicochemical properties of the electrochemically restored composite coating on the surface of the electrode as a result of electrolysis.

First, spectral analysis and SEM images of the titanium plate selected as a sample were obtained. From these obtained results, it can be seen that *Ti (53.2 %), O (33.3 %), C (7.7 %) Al (1.6 %) S (1.1 %)* and other metal compounds are also present and in some parts The appearance of spectra of sulfur indicates that it can be concluded that it was recovered during electrolysis (Fig. 4).

The obtained SEM images and spectra show that during electrolysis, the percentage of sulfur recovery on the titanium plate surface (S) is higher, that is, in the 004 spectrum (S, 23.35%), and in the 005 spectrum (S, 69.78%) and (C, 18.53%) , (N, 9.76%), (O, 8.68%) spectra of these elements indicate the presence of polyacrylamide ((C_3H_5NO)n –structural formula of polyacrylamide) macroins in the atomic state on the surface of the plate. Fig. 5.

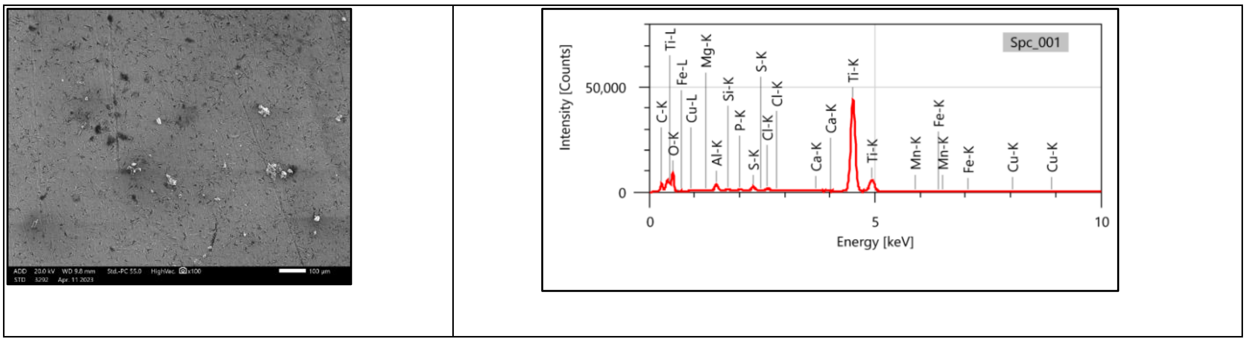

Figure 4. SEM image and (001) spectrum analysis of the composite coating formed on the titanium plate surface.

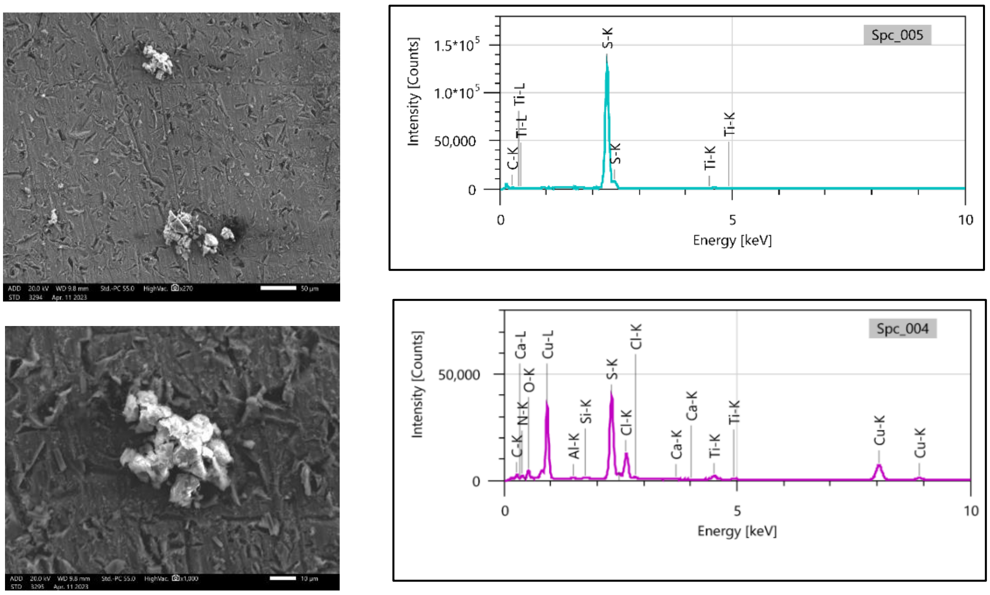

Figure 5. SEM image spectrum analysis of sulfur (S) and polyacrylamide ($(C_3H_5NO)_n$) formed on titanium plate surface.

Thus, the research conducted in the electrolysis setup showed the possibilities of the electrochemical recovery of macroions and ions together. Based on the obtained results, it is possible to make a scientific conclusion that by forming the above composite coating on the metal surface, metals can meet corrosion and act as a protective layer against various effects.

4. Conclusion

Sulfur powders were crushed and microparticles were obtained, mixed with polyacrylamide samples in different proportions, suspensions of different concentrations were prepared.

The scientifically based principles and parameters of the formation of coatings from polyacrylamide and sulfur suspension using the electrolysis device were determined, and the structural characteristics of the obtained coating materials were determined using the capabilities of the SEM electron microscope. These results are undoubtedly of great scientific and practical importance in the creation of micro- and nano-coated polymer materials.

Scientifically based principles and parameters of coating formation from polyacrylamide (C_3H_5NO)n and sulfur (S) suspension using electrolysis device were determined and modern electron microscope (SEM) images and spectra were obtained. According to the obtained results, the presence of spectra (S, 23.35-69.78%), (C, 18.53%), (N, 9.76%), (O, 8.68%) on the surface of the titanium plate (C_3H_5NO) It indicates the recovery of n and (S) macroins on the surface of the plate and provides a scientific basis for obtaining composite materials through the electrochemical recovery of colloidal particles on the metal surface.

According to the obtained scientific results, it can be noted that composite layered metals based on sulfur and polyacrylamide can be effective in combating various pests in agricultural warehouses.

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