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Valorization of citrus fruit processing waste in order to obtain a natural plant sorbent for the removal of heavy metals

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ABSTRACT

The efficiency of technology is determined by the amount of waste. The purpose of this work - valorization of citrus fruit processing waste in order to obtain a natural plant sorbent for the removal of heavy metals; is the processing of waste - citrus peels, after squeezing the juices from them, to obtain effective sorbents for the removal of heavy metals. At the same time, ecological problems are solved - the ecological situation in the country is improved (utilization of waste and heavy metals) and the economic one - the company receives a high profit without any significant additional costs for the production of the sorbent. In addition to its practical significance, the project has scientific significance: for the first time, a technological scheme has been developed for the production of pectin and Na+-pectate sorbents in liquid and solid form from citrus processing waste: lemon, tangerine, orange and pomelo; For the first time, pectin isolates were concentrated using the baromembrane method of membrane technology - ultrafiltration, and this reduced the consumption of pectin precipitant by 12 times; was identified for the first time by high-performance liquid chromatography composition of pectin and sorbent obtained on its basis. The laws of sorption of divalent metal ions by pectin polysaccharides: their complexing ability with heavy metals from 0.02 M $CuSO_4 \cdot 5H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $Pb(CH_3COO)_2 \cdot 3H_2O$ methods were studied by potentiometry and conductometry. To determine the kinetics of heavy metal sorption by the obtained liquid sorbent, the resulting mixture was left for 1, 2, 4, 6, 8, 12 and 24 hours. The structure of the sorbent is confirmed by IR spectra It was established that ion exchange plays an important role in the process of complex formation. Also found: similarity of sorption isotherms of copper and lead ions, influence of metal nature on sorption capacity of corresponding pectin polysaccharides; sorption activity of pectin polysaccharides in relation to lead ions higher than that of copper; The possibility of applying the linear equation of Langmuir in the wide range of concentrations of the external solution, for the estimation of the maximum capacity of the sorbent.

Keywords: waste, pectin, closed cycle, heavy metal, electrical conductivity, sorbent.

INTRODUCTION

Environmental pollution has a great impact on the human body, despite the fact that it is able to adapt to changing environmental conditions. It is possible to maintain health only by improving the ecological state, proper nutrition, and increasing human immunity to toxic environments and diseases. Food is a carrier of important biologically active substances that increase the body's immunity to undesirable effects. In modern conditions, it is impossible to provide the human body with the optimal amount of biologically important substances using ordinary food products. To solve this problem, it is necessary to create and use specialized products with valuable food additives of protective action. Pectin can be considered such a food additive, but pectin is imported into our country and therefore has a high cost and the cost is not always affordable for the general population.

Another important issue that has arisen is the pollution of the environment by heavy metals, including radionuclides. About 30 metals and metalloids are potentially toxic to humans [Chiarelli, & Roccheri, 2014]. Some metals that are essential to one organism are toxic to another. Metals pollute ecosystems. This pollution is less visible and direct than other types of pollution [Khansari et al., 2015]. The presence of some heavy metals in ecosystems has a negative impact on them because they do not decompose and have a long half-life. They can bioaccumulate in living tissues and cause toxic symptoms [Jakimska et al., 2011].

Heavy metals are practically insoluble in water, have a tendency to adsorb on solid particles, their effect when they enter living organisms and the environment and manifest themselves not immediately in some cases only after 6 years. [White, 2015]. The duration of action of heavy metals on the body has a significant effect on their bioaccumulation. Sometimes, although the duration of action is small, the amount of metal deposited by the organism can be significant [Jadhav et al., 2010]. The most important property of pectin substances is the ability to form complexes based on the interaction of pectin molecules with metal ions. This property led to the inclusion of pectin in the diet of people who are in an environment contaminated with radionuclides and in contact with heavy metals. The factor stopping the introduction of pectin is the high price of imported pectin. The scientific and practical interest of the research consisted in obtaining a soluble and insoluble sorbent based on pectin polysaccharides from plant residues, studying the ability to complex with heavy metal ions, and establishing the regularities of this process [Fidalgo et al., 2016].

In recent years, a large number of studies have been aimed at studying the processes of complexation involving various ligands, in particular, at studying complexes of biopolymers with various metals. The formation of complexes is aimed at obtaining new effective biologically active substances based on metals, which will have a wide range of important physicochemical properties.

In the complexes of many organic compounds, the interaction of electron-donating groups with cations of heavy metals occurs, resulting in covalent bonds with sulfohydryl groups of proteins and complexes based on amino, phosphate, carboxyl and hydroxyl groups. At this time, the toxic effect of heavy metals decreases, as they react with almost all substances involved in metabolism (porphyrins, phospholipids, coenzymes, nucleotides and enzymes).

It has been established that heavy metals, when interacting with groups of active centers of enzymes, which are part of microorganisms, replace various ions in enzymes and thus cause suppression of the natural activity of enzymes [Bagaeva, 2013]. In work Kurchenko et al. [2016] data on biosorption of radioactive elements - thorium and uranium on the cell walls of fungi (*Rhizopus arhrizus*) – sporogiophores. The authors argue that complex formation and physical adsorption take place in this process.

According to Novinyuk [2017], metal sorption should be carried out by bacteria used as strong biosorbents, since highly rough surfaces have been found in bacterial cell membranes, which have a positive effect on the sorption process. In Dinu [2015] and Nikiforova [2019] was shown that pure strains of some types of microbes have high abilities for selective absorption of metals from various metal-containing solutions. In Nikiforova [2014] and Gusev [2015] the sorption properties of chitin and its processed products are discussed. It was shown that chitosan has a wide range of biological activity, since it has high positive charges and its sorption is carried out by mechanisms typical for the sorption of lipids, pesticides, proteins and dye molecules, as well as similar to the sorption of metal ions (Cu^{+2}, Ni^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}, Pb^{+2}, Cr^{+3}, VO_2^{2+}, UO_2^{2+}) and chelation of radionuclides [Mykots, 2010; Hamidi, 2022].

Sorption capacity of isolated from the mass of chitin-glucan and chitosan-glucan polymers in relation to Pb^{2+} ions is lower (81.29 mg/g.), than that of the deacetylated biocomplex (152.67 mg/g). According to the authors, this is due to the presence of highly active primary amino groups in the deacetylated biocomplex. After establishing the sorption of Pb^{2+} ions on chitin-glucan and chitosan-glucan complexes, the mechanisms and regularities [Khattab, 2022] of the adsorption interaction of biopolymer complexes with adsorption centers and adsorbates are established. It is established that stable chelate complexes are formed. Complexation of metal ions with humic compounds of the soil is discussed in. Conditional stability constants of some metal-humic complexes of substances were determined experimentally. Experiments were conducted on ions of Al^{3+}, Sr^{2+}, Mg^{2+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+}. Based on the obtained data and calculated stability constants of the complexes, the authors compiled the following chain of “metal activity”: $Fe^{3+} > Cu^{2+} > Al^{3+} > Co > Ni^{2+} >> Cd^{2+} > Zn^{2+} > Cr^{3+} > Mg^{2+} >> Sr^{2+} > Ca^{2+} > Mn^{2+}$

In works [Abboud et al., 2019] the sorption of metal ions by cellulose-containing materials is discussed, the structure, amount, nature and presence of functional groups of the obtained complex are studied, the properties and structure of biopolymers are determined, as well as their sorption centers and sorption characteristics.

Currently, a large number of different methods of extracting heavy metals from aqueous solutions using biopolymers have been developed. These methods are based on the use of modified chemical, biochemical, physical-chemical and physical methods, which are recommended for water purification (for use in water supply, medicine, pharmaceutical and food industry) and various food solutions (wine, juices, etc.) from heavy metals. Polysaccharide complexes, which are remnants of sorption of indispensable micro- and macroelements, are used in the production of biologically active additives (nets). Sorbents after the sorption process can be used in concrete production [Bejanidze et al., 2019].

The studied ability of pectins to form complexes with metals [Conteratto et al., 2021; Durán-Aranguren et al., 2022; Gómez-Mejía et al., 2019] depending on the pH of the medium. Optimum values of environmental pH are determined - pH=4-10, at which the ability to form pectin and metal complexes will be maximal.

In Fidalgo et al. [2016] the importance of nickel and zinc ions in the performance of various vital functions in the human body is shown. The creation of new biologically active compounds based on pectin polymers and specified metals will allow to expand the assortment of new soluble complexes obtained on their basis.

Pectin substances are acidic polysaccharides, in which the state of carboxyl groups limits their properties – the ability to interact with cations, amines and other organic and inorganic substances. The most characteristic property of pectin is its ability to form complexes with s, p and d metal ions. Both free carboxyl groups of pectin molecules (Fig. 1) and their products, in particular salts of alkali metals, which react with metals to form complexes with cations of divalent metals, take part in complex formation. The complexes formed are insoluble in water and stand out from solutions in the form of gels [Guo et al., 2014].

The most studied complex formation of pectin with metals: Ca^{2+} and Mg^{2+}. Among d-metals the most studied complex formation of pectin with Cu^{+2} cations [Karasaeva et al., 2013]. It was established that the ligand node in the Cu^{+2} complexes has a pseudo-octahedral configuration, while in the equatorial plane the Cu^{+2} cation is coordinated by four oxygen atoms.

In recent decades, the processes of complex formation of various compounds, including biopolymers with metals, have attracted the attention of scientists not only in terms of obtaining new theoretical knowledge about the properties and synthesis of metal complexes, but also in connection with the search for the creation of new effective drugs among metal complexes. It has been established that complex formation increases the therapeutic activity of ligands, reduces their toxicity, gives specific therapeutic action and immunological activity. Currently, the solubility of metal complexes in water is important, as it increases the bioavailability of medicinal products and creates the possibility of their wide practical use [Durán-Aranguren et al., 2022].

The complex-forming ability does not depend on the mass of the pectin molecule, it is determined by the coefficient of selectivity of the

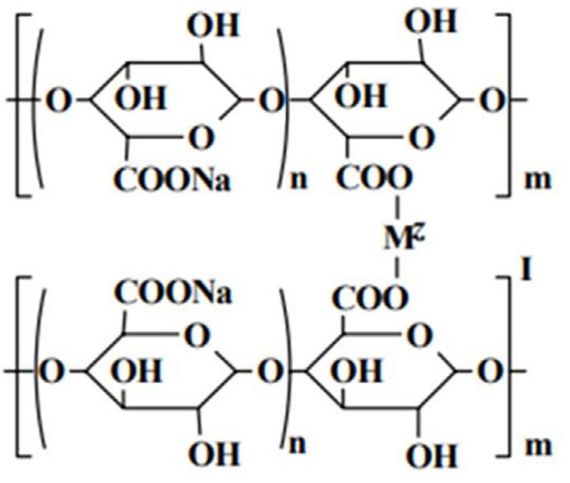


Figure 1. Mechanism of formation of polymetallocomplexes

cation exchange, which is a characteristic of the saturation of pectin substances with divalent cations. It is known that complex-forming properties of pectin substances depend on the content of carboxyl groups, that is, on the degree of esterification of the main chain of pectins - polycarboxyl polymer chain - esterification of carboxyl groups with methanol. The degree of esterification determines the linear charge density of the macromolecule and, accordingly, the strength and character of the cationic connection.

Highly esterified carboxyl groups or carboxyl anions are located at a distance from each other. As the degree of esterification decreases, the charge of the macromolecule increases and, accordingly, the strength of the connection between pectins and cations increases. Fully de-esterified pectin with pectin acid forms the most stable complexes. If the degree of esterification is 40%, then a change in the conformation of macromolecules begins, which leads to the aggregation of pectin macromolecules and the formation of a stable intramolecular chelate bond [Tovar et al., 2019; Gómez-Mejía et al., 2019].

The complex-forming ability of pectin depends on the pH of the medium. Maximal complex formation for each type of pectin is individual and depends on the pectin-containing raw material. All pectin substances show a high complexing ability in the interval pH from 4 to 12 and the maximum value at pH = 5 and pH = 9. Their solubility is an important factor in the development of methods for obtaining target metal complexes of d-metals. Known metal complexes of pectins are insoluble in water [Guo et al., 2017]. The economic development of the country is determined by the growth of national incomes, which cannot be realized without the gradual development and technical retooling of the processing industries, the creation and implementation of ecologically clean and efficient complex technologies.

In a linear economy, most natural resources are converted into waste. In the circular economy, the chain “raw materials - production - use - utilization” closes in a continuous production cycle, where waste is used as secondary production resources, the production process becomes safe and does not cause environmental pollution. Circular economy is not only and not so much recycling of waste, but also the opportunities, including economic ones, which lie before recycling and contribute to the maximum use of raw materials [Davitadze, 2023]. Actual problems include rational use of primary raw materials and complex processing and safe utilization of secondary raw materials. To solve this problem, it is necessary to increase and strengthen the production base of the processing industry of the agro-industrial complex, improve the use of raw materials, and develop new progressive, energy-saving technologies for the complex processing of valuable secondary raw materials based on the latest technological achievements. A partial solution to this problem is possible by increasing the production of high-quality food fiber-pectin substances and expanding the assortment.

One of the most important directions for increasing the production volumes of pectin-containing food products is to expand the base of pectin-containing raw materials with non-traditional sources, to develop new methods of processing pectin and pectin products from traditional and non-traditional production raw materials. The efficiency of modern production will increase with the creation of low-waste and efficient technologies, with the wide inclusion of secondary raw materials in the agricultural circulation. The production of pectin and pectin products from secondary raw materials (beetroot, grape and citrus juice, etc.) meets these requirements the most. The use of secondary raw materials is only 10-15% of the total amount [Davitadze et al., 2023]

In ecologically clean areas, the minimum preventive norm of pectin consumption is 2 g, 30–40 g per day. With annual consumption, it is ≥ 70.000 tons per 100 million people. The pectin content in food products is actually several times lower than the norm. The demand for pectin significantly exceeds the purchase volume.

In Adjara, ~80.000 tons are produced annually using traditional technology. Processing of citrus fruits does not produce a perfect use of waste (6000–8000 tons), they are thrown away, rot, thereby polluting the soil, water and air, i.e. unprocessed waste worsens the ecological condition of the environment due to microbial degradation and release of greenhouse gases.

In addition to plant residues, it produces environmental pollution with toxicants, in particular heavy metal cations, which have a negative effect on the human body, causing pathological changes. Currently, it is accepted in world practice to separate heavy metal cations by chemical and physical methods, with expensive synthetic pectin. Therefore, today, more than ever, the role of food additives with a protective, dietary and curative preventive effect is increasing for all categories of the population, and especially for children, which leads to the need to expand the production of pectin as a natural food fiber – detoxifier.

Pectin is one of the most common polysaccharides, which is contained in sufficient quantities as a secondary resource of plant raw materials. Currently, a paradoxical situation has been created: pectin has not become cheap and available, it is not produced in Georgia and is imported: 1 kg. The cost of pectin is $25–35, medical pectin - $60–120 (depending on purity) [Davitadze et al., 2023].

The need to increase the range of functional foods and the volume of production has led to a significant expansion of the food hydrocolloids market (currently it is estimated at $3 billion). Pectin production is only 10.91% of the total volume of hydrocolloids. In recent years, the demand for pectins has been growing by 3.0–3.5% per year. In addition, pectin - a soluble dietary fiber, is included in the composition of nutriseptics of a healthy diet. The multifaceted range of therapeutic action determines the use of pharmaceutical and biopectin in the production of medicinal preparations.

The commercial market for pectin and pectin-derived hydrocolloids is expanding and is predicted to become huge. Pectin is widely used in food and non-food production, therefore it is very important and relevant for the project participants to continue researching the structure and properties of pectin polysaccharides, to directly participate in the introduction of pectin and sorbents production technology and, accordingly, in the creation of domestic production of pectin. This will reduce and finally stop the purchase of pectin in Europe, reduce the cost of pectin-based products, and pectin production will develop in a new promising direction.

Pectin has multifunctional applications, including in the food, healthcare and pharmaceutical sectors, as well as in packaging systems. Pectin can be widely used as a texturizer, stabilizer and emulsifier in various foods: in the food industry, as an additive in jams, jellies and low-calorie foods, the demand for which is increasing every year. Pectin can be used as a food film and coating, a substitute for paper and foam.

Pectin is an important component of pharmaceutical products with emulsifying and stabilizing properties and is widely used in pharmaceutical production for the preparation of drugs that reduce blood cholesterol, treat gastrointestinal disorders, pectin is effective in wound healing and has a synergistic effect on drugs in cancer therapy. Commercial sources of pectin are very limited, except for its presence in plants. Therefore, there is an urgent need to find other sources or to modify the existing sources in order to obtain pectin with the desired qualitative characteristics, i.e. preventive properties.

It is a very promising direction – mixing pectin not only according to raw materials, but also by adding additives to it, which practically expands the existing and creates new possibilities for using pectin.

- Ecological:
  - environmental cleanliness will be maintained by using waste and removing heavy metals. Nature survives pollution;
- Economical:
  - a new modern, reagent-free, ecologically clean, efficient and promising method of obtaining pectin - food fiber and vegetable sorbent will be started and introduced in Georgia efficient membrane technology;
  - the profitability of production will increase by processing waste and receiving expensive pectin (2.4 kg of pectin is released from the waste obtained by processing 1 ton of citrus fruits, which amounts to at least $1285 and $15420000 per 12000 tons);
  - adoption of mixed sorbents for citrus fruits, as well as other fruits, vegetables and fruit-vegetables will be introduced, that is, production along with processing of fruits will simultaneously process waste and receive effective mixed sorbents practically free of charge;
  - the technology of production of pectin as food fiber will be introduced from plant, fruit and vegetable waste, the need to import expensive pectin from Europe will be removed.
- Social – in pharmacy:
  - with additional processing of sorbents, medical pectin can be obtained, which the population will use as an enterosorbent for releasing toxic elements - heavy metals and radionuclides.;
  - pectin consumption will reduce the growth and development of synovial cells;
  - production of hard capsules will be introduced;
  - pectin of exceptional purity will be used in the production of medicinal and dietary food;
  - pectin contains galacturonic acid, its introduction will make effective healing ointments for wounds and sores.

The purpose of this work is to enrich citrus processing waste in order to obtain, without reagents, using modern environmentally friendly membrane technologies, a water-soluble and insoluble natural plant sorbent effective for removing heavy metals, studying its composition, properties, ability to form complexes with heavy metals and establishing the patterns of this process.

MATERIALS AND METHODS

Objects of study

The research was carried out on whole and morphologically divided (skin: albedo and flavedo, partitions) citrus fruits: tangerine "Unshiu", orange: "Washington-Naveli" Georgian and Turkish, lemon Georgian and "Meer", Chinese pomelo. Pectin isolates were obtained and then pectin extraction was performed from the isolates. After squeezing the juice from citrus residues: lemon, tangerine, orange and pomelo, in particular from their skin (albedo, flavedo), pulp and juice sacs, depending on the time of collection and conditions of fruit cultivation, pectin is isolated, pre-concentrated on an ultrafiltration device UPL-0.6.

Research methods

To isolate pectin from citrus fruits, juice was squeezed, the squeezes were washed well with running water, crushed, and then pectin was extracted with a mixture of water and acid HCl (fruit: mixture ratio was 1:5, mixture pH 1.6–1.8) (Tables 1–4). The concentration of isolates was carried out by tangential filtration in dynamic mode on a UPL-06 unit (Fig. 2), an AR-2.0 ultrafiltration separating apparatus was used as a membrane, which was located vertically in the unit and was a ready-made module with a filtration area of 2 m^2, obtained on the basis of polyamide and phenylone - C 2-B hollow fibers VPU-15PA with a pore size of 500 A°, working pressure of filtration 1.8 atm. Ultrafiltration was carried out in circulation mode to the maximum possible concentration of the extract. Ultrafiltration achieves a high degree of purification and concentration of the extract, since hollow fibers are almost completely removed from the isolate, i.e. concentrate pectin substances. The purified pectin isolate and, accordingly, the pectin isolated from it will be of high quality. From the concentrated isolate,

Table 1. Composition of the isolated sorbent

No.	Substance	Delay time
1	Pectin	6.170
2	Galacturonic acid	8.110
3	Polygalacturonis acid	10.997

Table 2. Spectrogram analysis of the Ni complex of orange pectin

Wave number, cm^{-1}	Relevant groups
1014.32	CH Flat deformation oscillations, primary alcohol
1403.17	- N=N-. OH groups
1594.24	Aromatic cores. primary and secondary amines
2356.33	O=C=O R$_2$NH$_2$
3263.12	Intra and intermolecular H bonds in polymers. amide groups. bonded OH associated NH$_2$ groups and NH

Table 3. Spectrogram analysis of the Ni complex of pomelo pectin

Wave number, cm $^{-1}$	Relevant groups
1010.81	CH$_2$- methylene group – cyclopropane
1141.70	Tertiary alcohols C(CH$_2$)$_2$. RSO$_2$R
1221.63	Carbonyl group CO
1732.37	Saturated aliphatic aldehydes. involved in the formation of H bonds. ά-halo acids. dicarbon ά -amino acids
2025.33	Diazone compounds
2362.09	R$_2$NH$_2^+$; R$_3$NH$^+$
3324.08	Intra and intermolecular H bonds in polymers. amide groups. connected OH associated NH$_2$ groups and NH. NH$_2$ group. primary amides -CO- NH$_2$ (associated NH$_2$ group). secondary amides CONHR. imines C=NH

Table 4. Spectrogram analysis of the Ni complex of tangerine pectin

Wave number, cm^{-1}	Relevant groups
952.88	Aromatic nucleus, oxides of aliphatic amines
1013.59	Primary alcohols
1093.68	CH plane deformation vibrations, secondary alcohols, aliphatic COC, aliphatic amines, C=S
1139.84	Tertiary alcohols, ethers with large rings
1403.91	Deformation oscillations of CH bonds in alkenes, ROH, phenols, OH groups, azo compounds –N=N-
1595.07	- NH^+, NH3+ deformation, valence oscillations of the aromatic ring
2104.02	RC Ξ C, NH_3^+ deformational oscillations, primary NH2 secondary N2NH, NH+
3270.98	CH bonds, intramolecular and intermolecular H bonds, secondary amides CONHR associated NH_2 groups, imines C=NH and NH associated groups, carboxylic acids

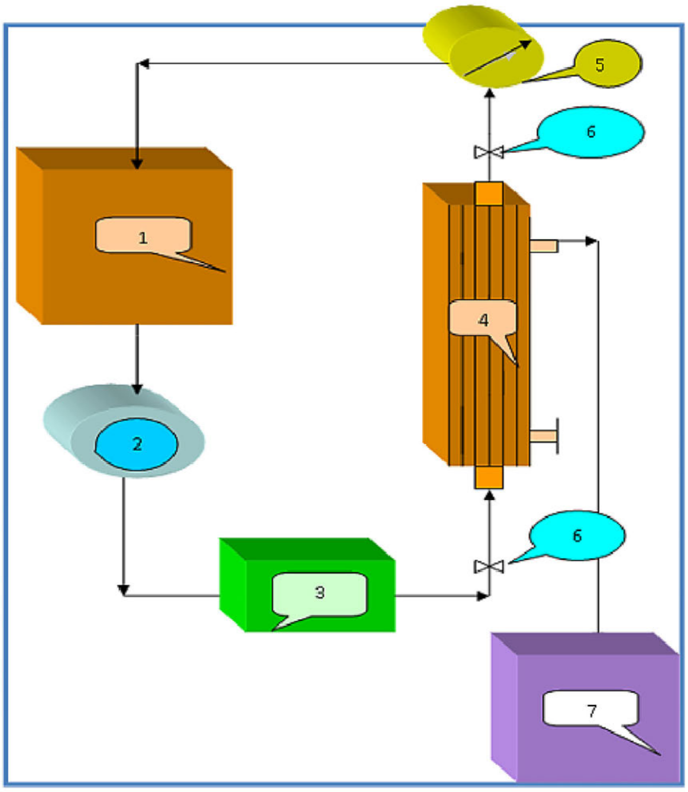


Figure 2. Scheme of the ultrafiltration process: 1 – tank of the initial pectin isolate and concentrate collection: 2 – pump; 3–mechanical filter; 4 – membrane module; 5 – manometer; 6 – valve for pressure regulation; 7 – container for collecting permeate

pectin was extracted with 95% ethyl alcohol; with the addition of dry NaOH sodium pectate sorbent was obtained. Soluble pectin was precipitated from the concentrated extract with ethyl alcohol, i.e. converted to an insoluble form. The resulting precipitate was thoroughly washed with alcohol and then dried at T = 55 °C. The sorbents: pectin and Na^+-pectate were obtained in liquid and solid state according to the technological scheme developed by us (Fig. 3). Identification of the obtained pectin and sorbent identified by high-performance liquid chromatography (LC-20AD Prominance-Shimadzu chromatograph). Pectin was used as a standard substance (Fig. 4). Chromatograms are shown in Figure 5.

Orange: albedo + HCl

Obtained: practically all samples contain pectin and galacturonic acid and do not contain polygalacturonic acid, that is, this testifies to the complete extraction of pectin (Fig. 6). The structure of the sorbent was confirmed by IR spectra (spectrometer – TENSOR II (BRUKER). Using the tables, the structural composition of the samples was determined The assessment of the metal sorption process was carried out by measuring the electrical conductivity of the metal solution under study before and after sorption, and was determined by the difference in values. The specific conductivity of the solution before and after sorption by the sorbent was determined. The

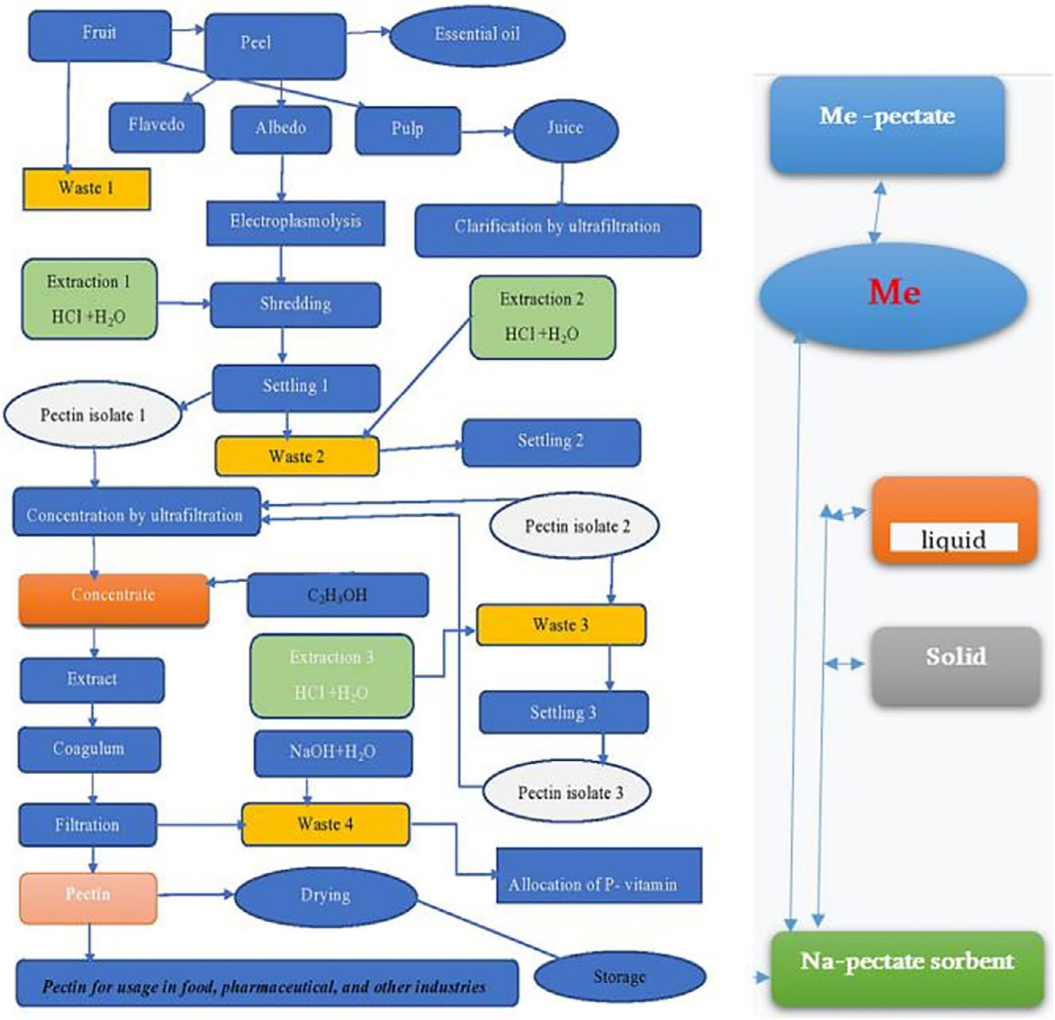


Figure 3. Technological scheme for the production of pectin and pectin sorbent

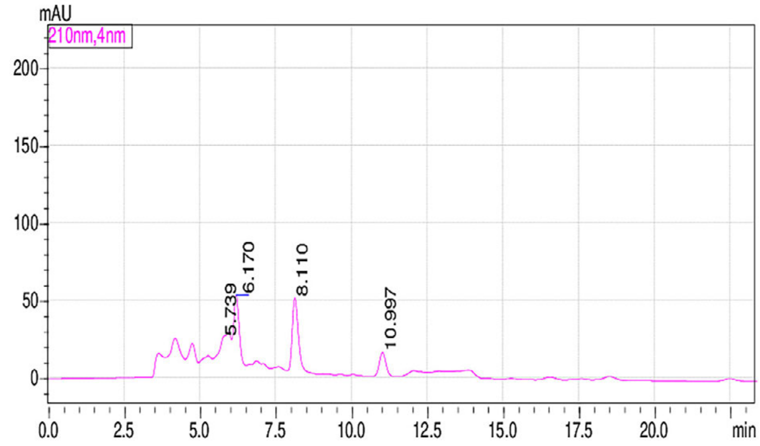
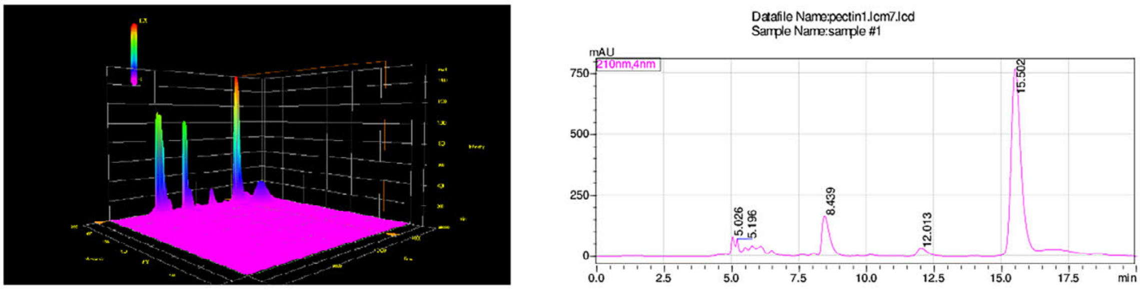
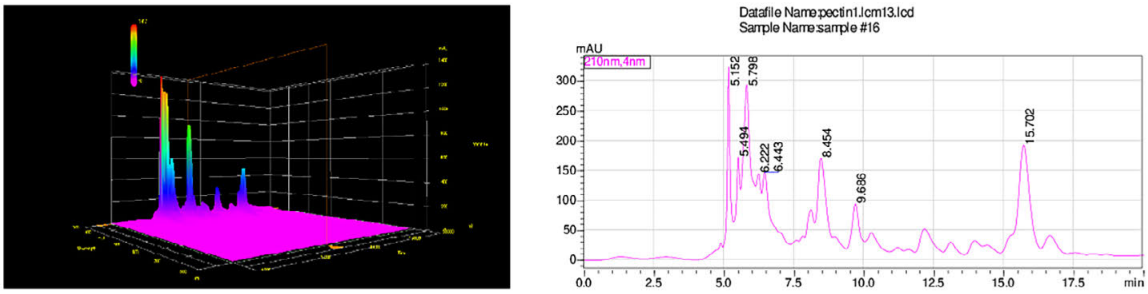


Figure 4. Pectin standard sample 0.02 g/ml

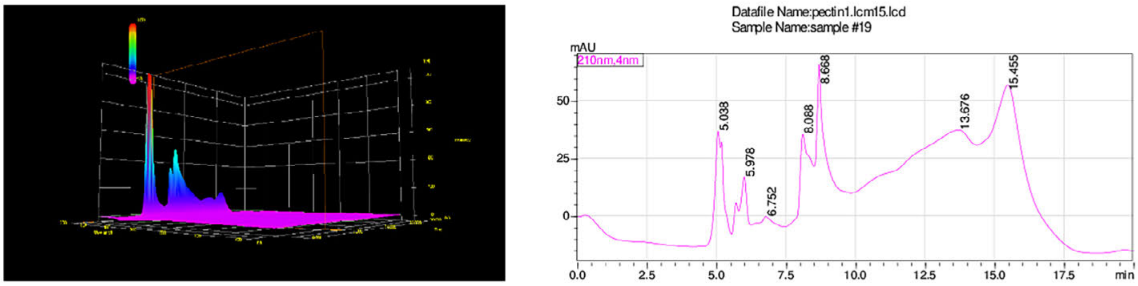
Orange: albedo +HCl



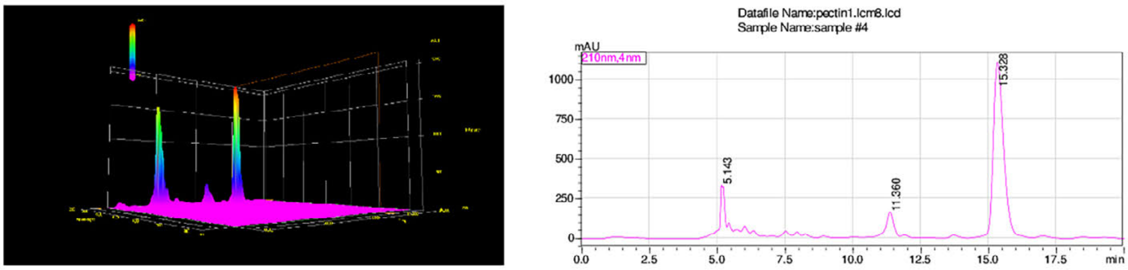
Orange (Türkiye): peel (albedo + flavedo)+HCl



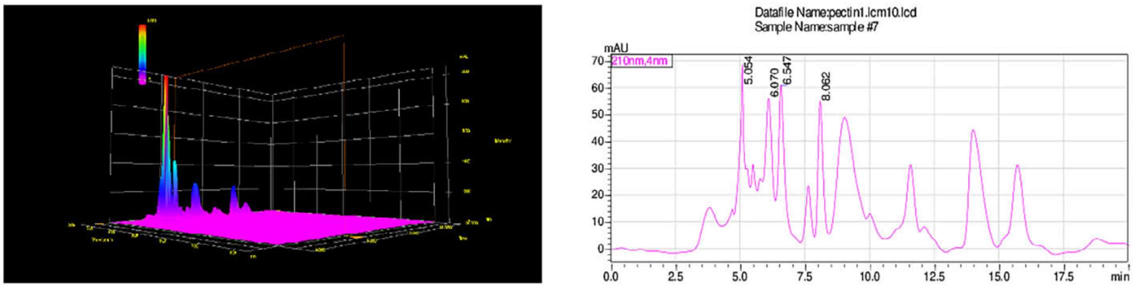
Orange : albedo +HCl + C_2H_5OH



Lemon Meer: albedo +HCl

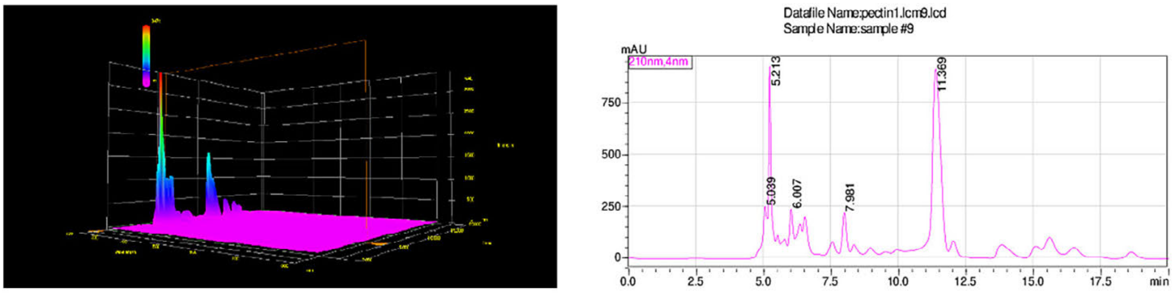


Lemon Georgian: albedo +HCl

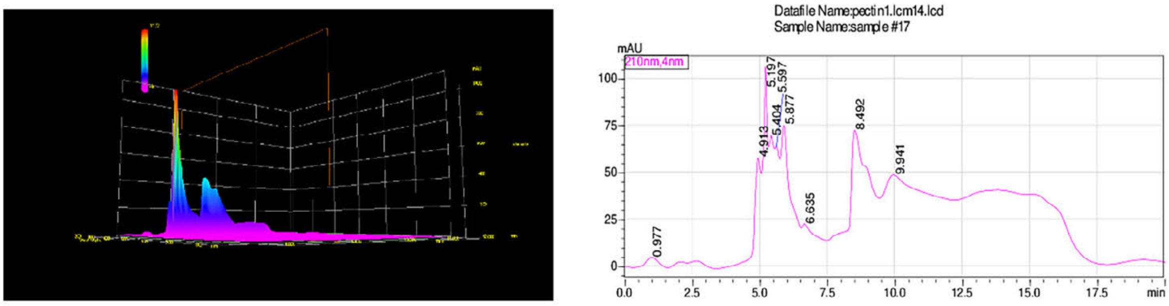


Lemon (georgia): partitions+HCl

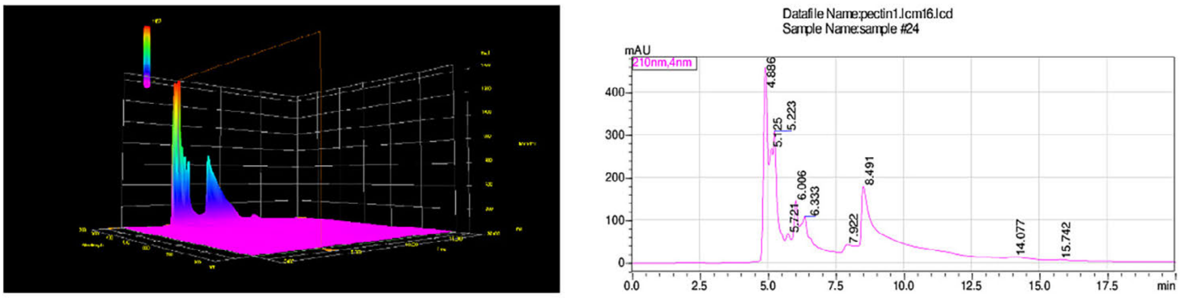
Figure 5. Chromatograms of pectins



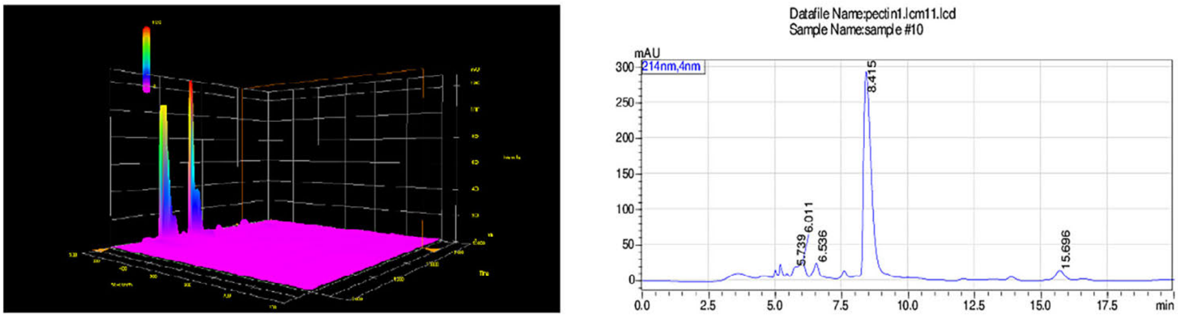
Lemon „Meer“: albedo +HCl + C_2H_5OH



Lemon (georgia): partitions +HCl + C_2H_5OH



Tangerine : albedo + HCl



Pomelo: albedo + HCl

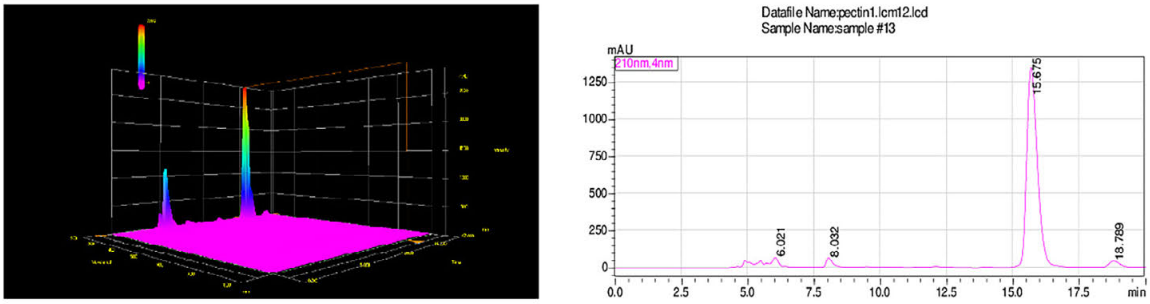


Figure 5. Cont. Chromatograms of pectins

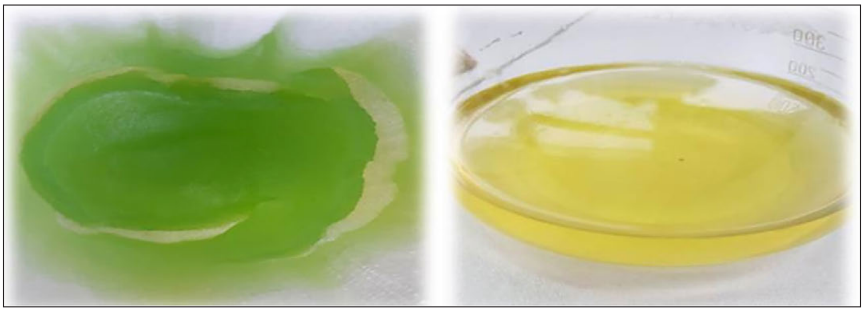


Figure 6. Na+ pectate sorbents

electrical conductivity of the solutions was measured on a LASANY conductometer. To determine the kinetics of heavy metal sorption by the obtained liquid sorbent, metal solutions (0.02 M $CuSO_4 \cdot 5H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, Pb $(CH_3COO)_2 \cdot 3H_2O$) were added in a 1:1 ratio, the resulting mixture was left for 1, 2, 4, 6, 8, 12 and 24 hours.

RESULTS

It is known that the value of electrical conductivity depends on the nature of the solution, concentration (saturation) and temperature. It increases with increasing temperature, which is due to an increase in the speed of movement due to a decrease in ion solvation and a decrease in the viscosity of the solution. Figure 7 shows the electrical conductivity of solutions of heavy metals before the sorption process. It was found that the highest conductivity of a nickel solution and the lowest conductivity of a lead solution. As the concentration of solutions decreases, the electrical conductivity of the solution classically decreases. The results of studying the kinetics of metal sorption are presented in Fig. 8–11, in the form of changes in the electrical conductivity of solutions over time.

It is established that the electrical conductivity of filtrates obtained as a result of sorption from a solution of cobalt chloride does not change practically during sorption. It increases slightly after 1, 12 and 24 hours of sorption. The maximum value is obtained from the sorbent obtained from the waste of orange fruits (fig.8a,b). Maximal sorption of lead, copper and nickel is reached on the pomelo-sorbent after 6, 8 an12 hours, respectively (Fig. 8b, Fig. 9a,b). Figure 10 shows the sorption of metals by citrus fruits depending on the type of sorbent.

Ni^{+2} ion sorption (on pomelo, lemon and tangerine sorbents practically does not take place, it

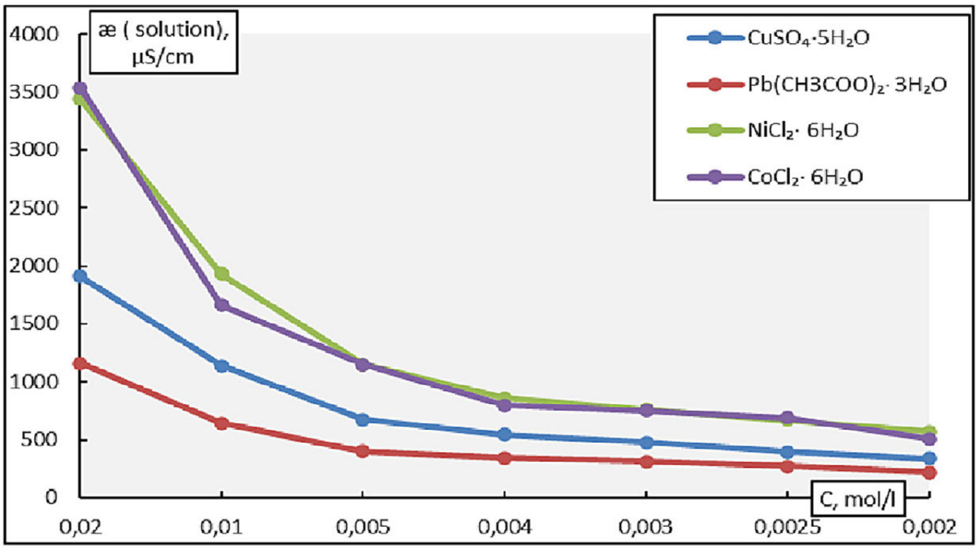


Figure 7. Electrical conductivity of initial metal solutions

only takes place slightly on orange sorbent and amounts to 0.003 g/100 g of sorbent (2 and 24 hours). Sorption of nickel ions was carried out from nickel chloride solution. The maximum sorption of nickel ions was observed on the sorbent obtained from orange fruit, the time of sorption was 12 hours. According to the cobalt ion, the sorbent obtained from pomelo waste shows the highest sorption capacity, followed by lemon, orange and tangerine. Maximum sorption of cobalt ion is reached during the first hour of the process. According to the kinetics of sorption, that is, according to the increase in the amount of absorbed copper (%), citrus fruits will be located in the following order:

- 1 hour: lemon (88.4) – pomelo (90.2) – tangerine (91.1) – orange (91.7);
- 2 hours: lemon (90.8) – tangerine (92.5) - pomelo (93.1) – orange (93.5);
- 4 hours: orange (92.7) – lemon (93) = Tangerine (93) – pomelo (93.1);
- 6 hours: orange (91.4) – tangerine (90.8) – pomelo (92.1) – lemon (93);
- 8 hours: lemon (90.8) – tangerine (91.4) – pomelo (91.9) – orange (93);
- 12 hours: orange (89.6) – lemon (91.6) – tangerine (91.9) = pomelo (91.9);
- 24 hours: orange (90.1) – pomelo (92.3) – tangerine (91.4) – lemon (91.5).

Comparing the data on the sorption of copper on the sorbents of lemon, orange, tangerine and pomelo, it was established that during the first hour the sorption of copper on the Na-pectate sorbent obtained from orange is 91.7%, during the second hour this trend is maintained and the sorption reaches The maximum value is 93.5% (Fig. 12). On the sorbent obtained from other citrus fruits, maximum absorption - 93% is reached in 4 hours. It has been established that sorption on the liquid sorbent occurs unevenly and does not reach 100%, which is probably due to steric difficulties arising

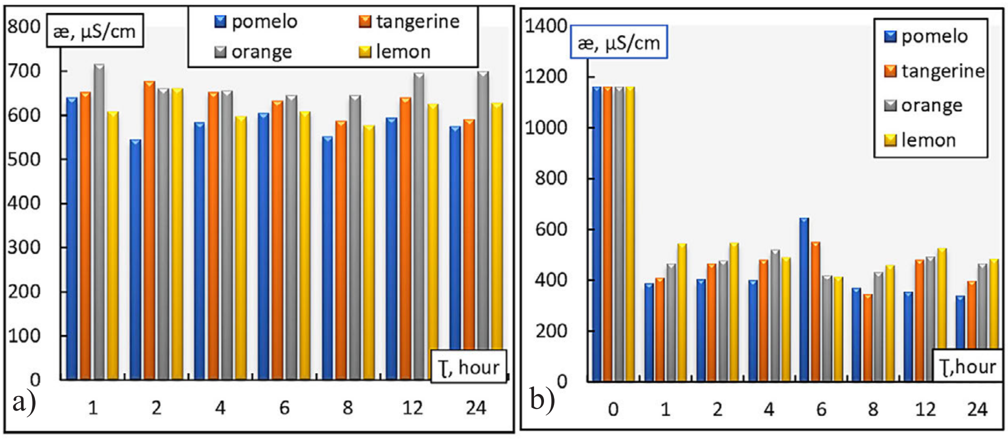


Figure 8. Electrical conductivity of the filtrate obtained as a result of sorption from a 0.02 M solution: (a) $CoCl_2 \cdot 6H_2O$ (æ (original solution) = 3540 μS/cm; (b) $Pb(CH_3COO)_2 \cdot 3H_2O$ (æ (original solution) = 1162 μS/cm)

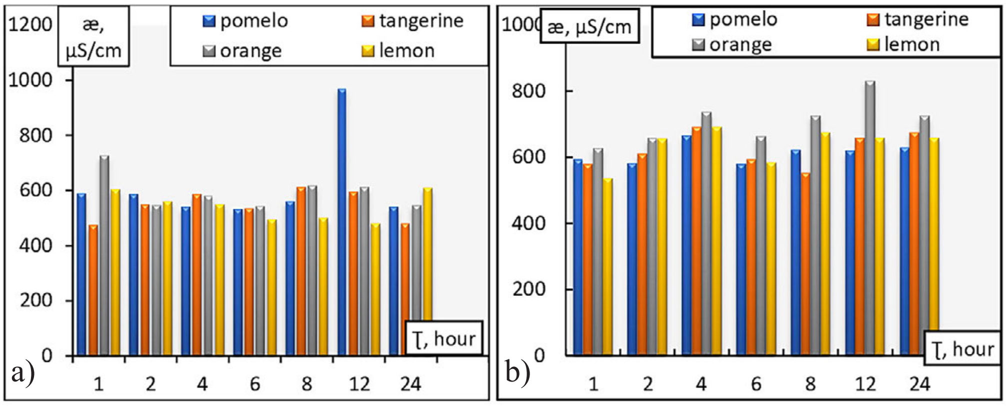


Figure 9. Electrical conductivity of the filtrate obtained as a result of sorption from a 0.02 M solution (a) $CuSO_4 \cdot 5H_2O$ (æ (original solution) = 1897 μS/cm); (b) $NiCl_2 \cdot 6H_2O$ (æ (original solution) = 3440 μS/cm)

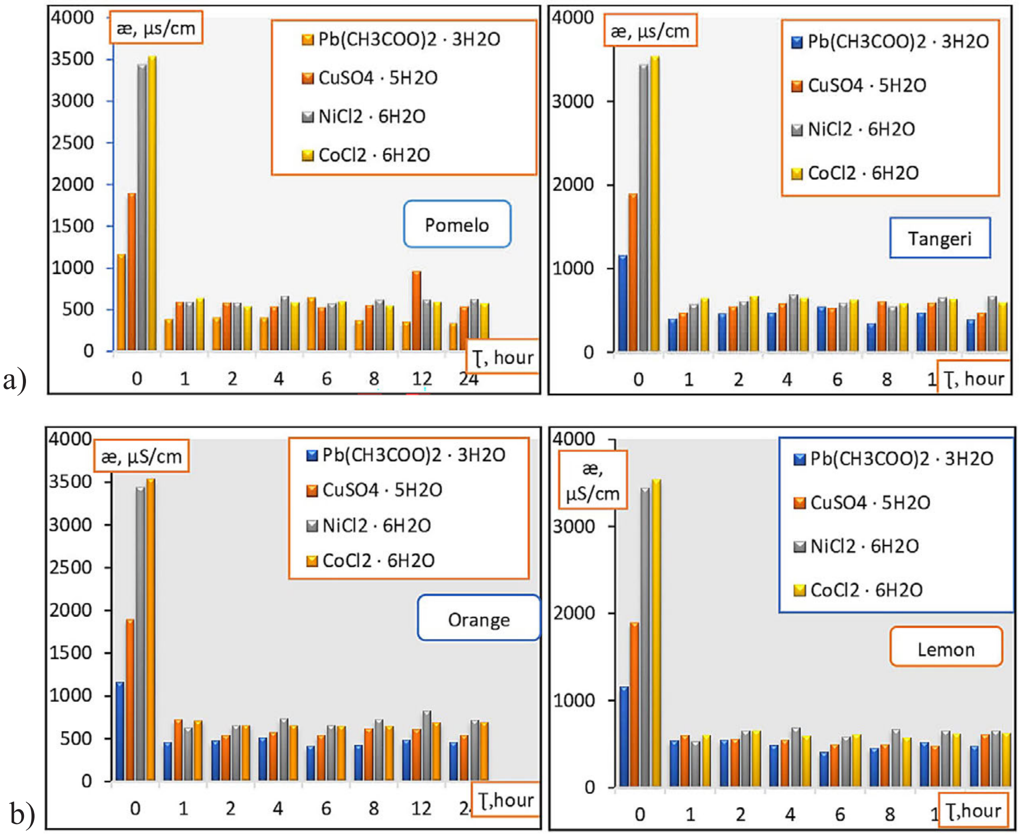


Figure 10. (a) Dependence of the electrical conductivity of the filtrate obtained as a result of sorption on the type of solution (sorbent -pomelo and tangerine); (b) dependence of the electrical conductivity of the filtrate obtained as a result of sorption on the type of solution (sorbent orange and lemon)

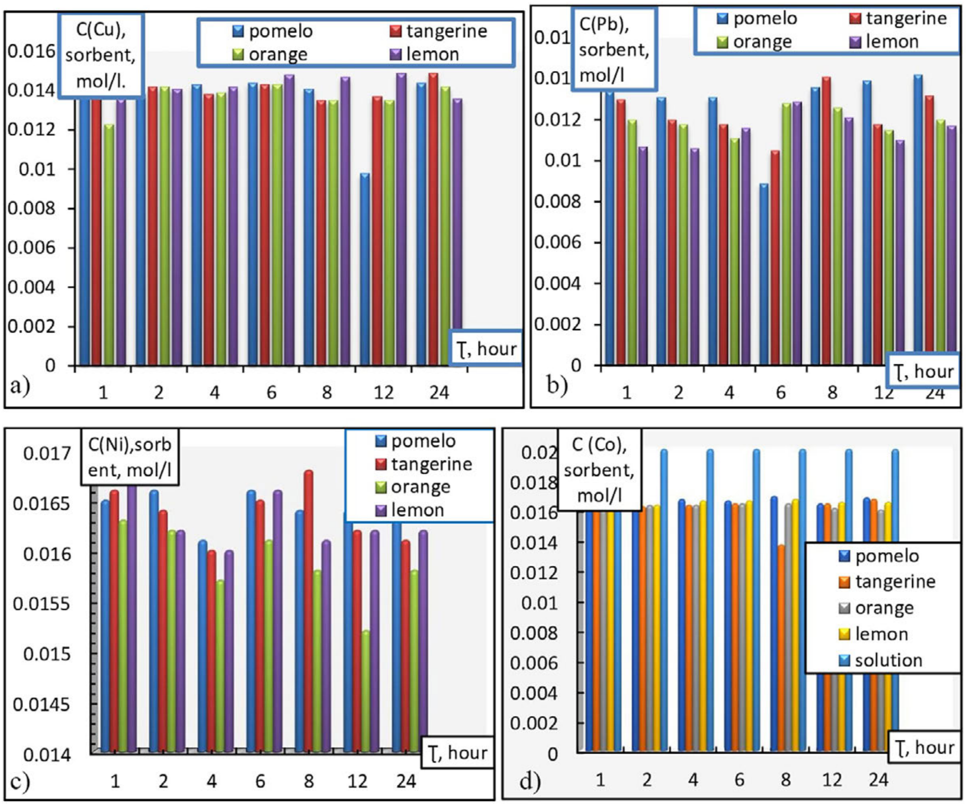


Figure 11. Kinetics sorption by Na$^+$-pectate sorbent, (a) Cu^{+2}, (b) Pb^{+2}, (c) Ni^{2+}, (d) Co^{2+}

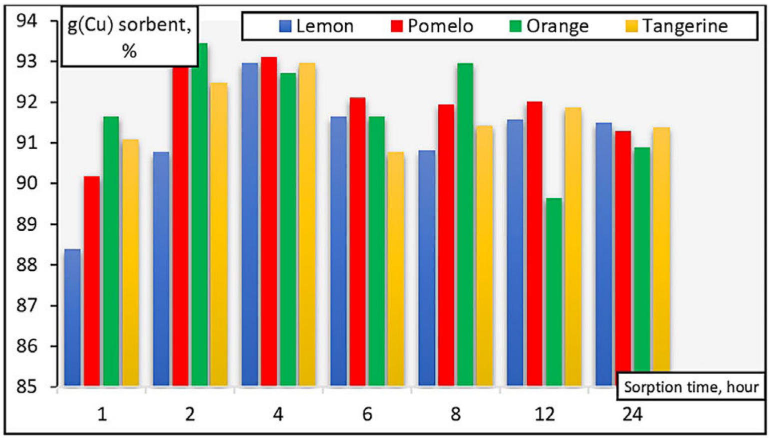


Figure 12. Kinetics of Co^{2+} ion sorption by Na^{+} -pectate sorbent, %

during sorption on a branched polymer of large mass due to the fact that it contains long spirally twisted chains. It is typical lyophilic colloid with gel structure. The kinetics of sorption of heavy metals Co^{+2}, Ni^{+2}, Cu^{+2} and Pb^{+2} ions by pectin sorbents, the dependence of maximum sorption on the type of sorbent is established (Fig. 13). The results of the maximum sorption of metals were obtained:

- Co^{2} -> Ni^{2} -> Pb^{2} -> Cu^{2}
- Fruits will be placed in the following order according to the maximum sorption:
- Co^{2}: tangerine (83.1) – pomelo (81.4) – lemon (70.3) – orange (69.9)
- Ni^{2}: orange (50.9) – lemon (18.6) – tangerine (6.8) – poelo (5.9)
- Pb^{2}: lemon (31.7) – pomelo (19.3) – orange (18.1) – tangerine (7.6)
- Cu^{2}: orange (9.34) – pomelo (9.31) – tangerine (9.29) = lemon (9.29).

It has been established that copper is most actively sorbed on the pomelo sorbent, the electrical

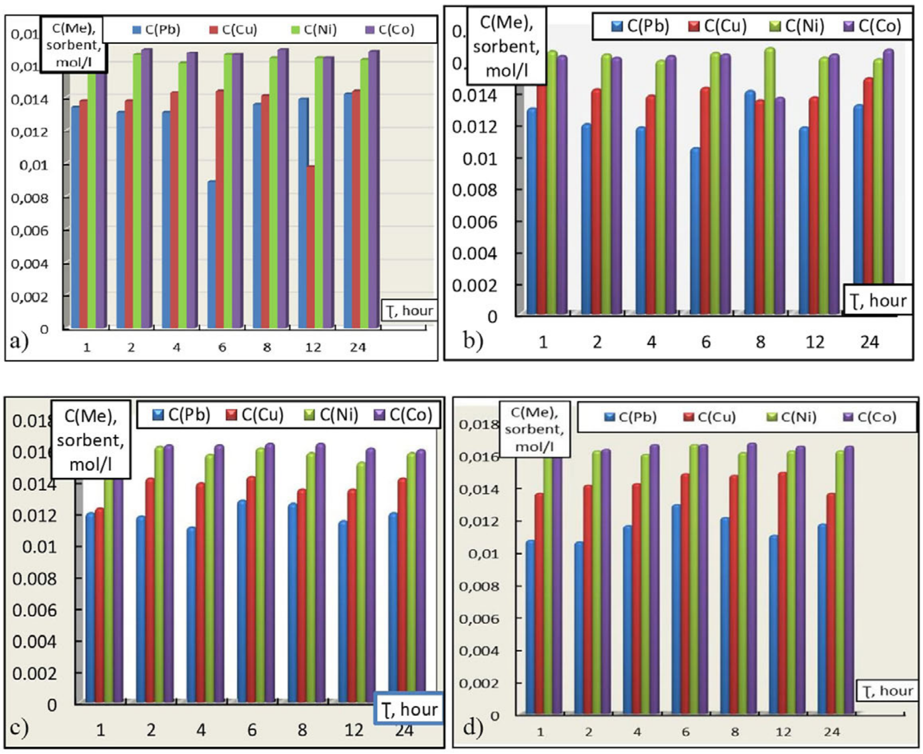


Figure 13. Dependence of the kinetics of sorption of heavy metals on the sorbent - Na+-pectate on the type of citrus fruit from whose processing waste the sorbents were obtained; (a) pomelo, (b) tangerine, (c) orange, (d) lemon

conductivity of the initial solution decreases by 7 times, on the mandarin sorbent – cobalt, on the orange and lemon sorbents – nickel ions.

CONCLUSIONS

Pectin polysaccharides were obtained from citrus fruit waste: mandarin, orange, lemon and pomelo by static acid extraction and based on them a technological scheme for obtaining a 100% salt content, fully deesterifiable, broad spectrum pectate Na^+ sorbent was developed. The obtained plant sorbent has high ion exchange and complex formation ability; polymetal complexes were obtained with biogenic d-metals-microelements (Co^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}). Kinetics of sorption of heavy metals Co^{+2}, Ni^{+2}, Cu^{+2} and Pb^{+2} ions by pectin sorbents, dependence of maximum sorption on type of sorbent: type of sorbent, i.e. selectivity of pectin sorbents to individual metals, is established.Optimal process conditions were established, the limit concentration of metals – 0.02 M. A technology for obtaining polymetal complexes of pectin polysaccharides with cations of biogenic metals was developed. The sorbent and metal complexes were obtained in water-soluble and insoluble forms. Technological schemes for ultrafiltration, pectin and sodium pectate sorbent were developed. Concentration of pectin isolates by ultrafiltration has been used for the first time. This reduced the amount of extractant by 10–12 times.Potentiometric and conductometric titrations were performed. It was established that the nature of the metals affects the sorption capacity of the corresponding pectin polysaccharides: the activity towards lead ions is higher than towards copper. It was established that, independently of the nature of the pectin polysaccharide, the sorption of lead and copper ions is significantly influenced by the galacturonic acid residue, as indicated by the relationship between the maximum capacities of lead and copper and also by the relationship between the bound and free concentrations of galacturonic acid in the initial polymer. The regularities of sorption of divalent metal ions by pectin polysaccharides have been studied. The important role of ion exchange in the complex formation process has been established. Pectin polysaccharides can be used as an effective enterosorbent – dietary fiber – to remove heavy metals from the body.

The developed technology is environmentally friendly and allows solving two problems: economic – processing waste and receiving expensive pectin – the profitability of production will increase and ecological – the ecological purity of the environment will be maintained.

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