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CAVITATION TECHNOLOGY FOR INTENSIFICATION OF PLANT RAW MATERIALS EXTRACTION

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Abstract. Traditional technologies and equipment for extraction do not meet the needs of industrial production in the constant increase in the volume of finished products due to the low efficiency of extraction of target components, their high energy consumption and duration. This makes it relevant to search for modern, more effective technologies and equipment, the use of which will significantly increase overall production productivity, reduce overall specific energy consumption, improve the quality of the finished products and safety of processes for the environment. The paper analyzes and generalizes methods for intensifying extraction processes from plant materials. The most effective ways to intensify hydrodynamic processes include methods based on cavitation phenomena. Transformation and redistribution of energy, which occur during the formation and collapse of vapor bubbles due to the creation of a high difference in pressure, temperature, and potential, contribute to a significant increase in the efficiency of dynamic effects on complex heterogeneous systems during extraction. Cavitation technologies ensure ecological purity and safety of the process, make it possible to accelerate mass transfer processes, activate the extractant, obtain a high yield of biologically active substances (BAS) and maintain their properties. Acoustic and hydrodynamic cavitation are most commonly used. Modern research is conducted in search of new solutions to optimize technologies, as well as improvement of cavitation equipment. Examples of hydrodynamic cavitation devices of static and dynamic types are cylindrical and disk rotor-pulsation devices, valve-type high-pressure homogenizers, pulsating dispersers, centrifugal pumps and Venturi tubes. They are used to intensify the processes at the stages of preparation of plant raw materials, activation of the extractant, as well as the extraction itself. Static-type cavitation devices based on the Venturi tube have a number of advantages in terms of design, technological and economic solution.

Key words: extraction intensification, mass transfer processes, cavitation, supercritical liquid extraction method, acoustic cavitation, hydrodynamic cavitation, Venturi tube, methods of electropulse treatment.

Introduction. Formulation of the problem

The production of natural products and preparations in an economical and environmentally friendly way is of great importance for many industries. These products include herbal extracts. The demand for plant extracts, characterized by a high content of aromatic, flavoring and BAS of natural origin and a wide range of biological activity, is constantly increasing. They are widely used in the pharmaceutical, cosmetic and food industries for the production of standalone products and preparations or as semi-raw materials for subsequent use in the production of concentrates, beverages, tinctures, powders, creams, desserts, etc. Predominantly dried plant material is used to extract BAS. Thus, extraction is one of the most common classical mass-transfer processes of the transition of multicomponent compounds from one phase to another, mainly in the “solid–liquid” system. Each type of plant material has its own characteristics which affect the technological conditions of the extraction process and the choice of equipment. The completeness of the extraction of biologically active substances and their complexes is determined by the physical and chemical properties of the raw material and depends on many factors, such as the choice of the extraction method, the determination of the rational type and parameters of physical, chemical or combined exposure at the stages of preparing raw materials and obtaining an extract, extraction solvent, requirements for the finished product and others [1-5].

Analysis of recent research and publications

The constant increase in the production of products and preparations using extracts of various types necessitates the improvement of existing and the development of new high-quality extraction methods and equipment for their implementation. This determines the relevance of the search for modern, more intensive methods of processing plant materials to obtain extracts. The efficiency of extraction of a solid with a liquid depends on its solubility and the rate of transition from one phase to another.

Solubility can be improved by selecting a suitable solvent, accelerating the rate of transition of a substance from a solid phase to a solution by increasing the contact area of the solid phase particles by grinding the raw material or by constantly supplying fresh solvent at the phase boundary. In cases where excessive grinding is undesirable, the intensification of the impact can occur due to the creation of high velocity gradients in the surface layers and an increase in the interfacial transfer coefficients. In general, the intensification of such processes is associated with the solution of the problem of creating controlled hydrodynamic flow conditions in multiphase heterogeneous systems and the necessary intensity of stresses in the particles of the dispersed phase distributed in volume and time. To a large extent, the combination of different types of influences allows to intensify chemical-technological processes and obtain new improved results. The main criterion for the efficiency of the process, which determines the practical usefulness of applying the intensification method, is the overall increase in the productivity of the technological line with a high degree of impact of individual devices on the processed medium while reducing specific energy consumption [2,6-8]. When carrying out the intensification of extraction, special attention should be paid to studies to determine the effect on the disperse system of the hydrodynamic conditions of the process in order to increase the mass transfer rate and overall productivity, reduce the duration of limiting stages (modernization or replacement of the most energy-intensive technological processes and equipment), reduce energy costs, use continuous processes, etc. [1,2,7,9,10].

The purpose of the paper is the analysis and generalization of methods of intensification of extraction processes from plant raw materials by cavitation.

Objectives of the research:

1. Analysis of advantages and disadvantages of traditional methods and equipment for extraction
2. Determination of intensification methods of heat-mass exchange and hydrodynamic processes to increase the impact on complex heterogeneous systems during the extraction of BAS from plant raw materials.
3. Analysis and generalization of methods, devices, and equipment for intensification extraction processes using cavitation phenomena and effects.

Results of the research and their discussion

Each of the known extraction methods has its own advantages and disadvantages. One of the main problems of classical static and dynamic methods of extracting plant materials is the low efficiency of extraction of target components, which determines the practical expediency of using intensification methods.

Traditional methods of extraction of BAS from plant or animal raw materials include most of the methods known since ancient times. Examples of such technologies are maceration, percolation, hydrodistillation, etc.

Maceration (from Latin «macerare» is to soak) is the oldest method of extraction. When obtaining an extract by maceration, raw materials with a certain degree of grinding are loaded into a macerator, poured with a calculated amount of extractant and infused for the required amount of time. After that, the resulting extract is drained and settled. The advantages of the method are the availability and simplicity of technology and equipment, but extraction occurs mainly as a result of molecular diffusion, therefore, the disadvantages include the high duration and incomplete extraction of the BAS complex. Previously, this method was widely used to obtain herbal tinctures. Currently, its use is gradually declining and for the most part it is used for comparison with other methods. In order to intensify the extraction, the process is carried out with constant stirring in mechanical mixers, rotating tanks or with constant circulation of the extractant [3,11-13].

Remaceration differs from maceration in that the extractant is divided into several parts and the prepared plant material is sequentially extracted. After the first infusion, the resulting extract is drained and poured with the next portion of the extractant. Bismaceration is more commonly used, that is, the extractant is divided into two parts.The advantages of the method are some acceleration of the extraction process and an increase in the yield of BAS due to an increase in the difference in concentrations in the raw material and the extractant [3,11,13].

The percolation method (from Latin «percolare» is to discolor) is carried out in special percolator, which is a cylinder with a double bottom and a drain valve located at the bottom. The essence of the method lies in the fact that a continuous flow of the extractant is directed through a layer of raw materials. As a result of maintaining the mobility of the extractant and the occurrence of turbulent pulsations in the volume of the percolator during extraction, convective diffusion of high speed predominates, so the percolation method is more efficient and faster [3,13,14].

Repercolation differs from the percolation in that the raw material is divided into several equal or unequal parts (usually three parts) and each subsequent portion is extracted with an extract obtained from the previous one. For this, a battery of percolators (3–5 pieces) is used. The method allows to save the maximum possible difference in the concentration of extractive substances between the raw material and the extractant.

Some intensification is achieved by using the ***circulation extraction method***, based on multiple extraction of the material with a pure extractant. As an extractant, volatile organic solvents having a low boiling point, such as ether, chloroform, methylene chloride, or mixtures thereof, are used. Circulating extraction is carried out in Soxhlet extractor. The advantages of this method are the use of a small amount of extractant, the creation of a high concentration difference at the phase boundary, a reduction in the extraction time and a high yield of BAS. Among the shortcomings, it should be noted the high heat consumption for the distillation of the extractant and the long-term temperature effect on plant raw materials [15-18].

An important condition for the intensification of technological processes is the use of flow type equipment. Recirculation of a heterogeneous mixture from the passive zone to the active zone is associated with the movement of large volumes of material in the apparatus, which leads to significant waste of energy. When using flow-type devices, a prevention of repeated recycling of the extracted part of the material is achieved and, as a result, a reduction in the level of energy consumption.

The principle of ***countercurrent extraction methods*** is that the raw material and the extractant move towards each other. This ensures constant contact of the plant material with the pure extractant, which increases the difference between the concentrations of the substance in the raw material and the extract. Extractors are designed using transport means such as vertical and horizontal auger conveyors, belts, buckets, screws, etc.

The advantages of these methods are an increase in the efficiency of mass transfer processes due to the continuity of the flow, maintaining a high difference in concentrations in the raw material and the extractant, the possibility of automating labor-intensive processes and increasing the yield of biologically active substances in the extract. Nevertheless, they are characterized by high energy consumption. In general, such methods can be recognized as the most effective among those listed, but at the same time, a relatively low productivity of mass transfer processes is observed when extracting raw materials with high strength of plant cell walls [3,17].

Thus, a review of existing traditional methods and equipment for extraction showed that many methods are energy-intensive, multi-stage, time consuming and therefore low in energy efficiency. Some of the traditional methods have reached the technological natural limit in their development.

The methods of intensification of mass transfer processes of extraction by creating controlled hydrodynamic conditions include methods of *vortex extraction or turboextraction*.

The methods of vortex extraction or turbo extraction are based on the use of intensive vortex mixing and simultaneous grinding of plant materials and extractant using high-speed mixers. The intensification of mass transfer processes in the turbulent flow of the extractant is explained by a sharp decrease in the thickness of the diffusion layer at the distribution boundary between the solid and liquid phases. In addition, turbulence and pulsation of velocities, as well as intense mechanical impacts of solid particles of raw materials on the blades and outer walls of the mixer lead to multiple deformation of the particles, which contributes to the accelerated transition of water-soluble substances through the membrane walls and the penetration of new portion of the extractant into the plant cell. Thus, the extraction time is significantly reduced. The disadvantage of the method is the increase in the temperature of the dispersion of vegetable raw materials in the working volume of the mixer due to intense mechanical action and high specific energy consumption. In this case, it is possible to change the properties of BAS, evaporation of a part of the extractant and contamination of the extract with finely dispersed insoluble substances [1,3,19].

Analyzing these extraction methods from the point of view of supplying external energy to the system (mechanical mixing, mechanical vibration, jet methods), it can be concluded that all of them have common general patterns that reduce their efficiency, namely, they realize effective specific power only in a small area energy input V_{loc} (on the rotor disk, at the edge of the agitator blade, in the jet entry zone). An increase in the working volume of the apparatus leads to an increase in the duration of the dispersion processing due to the multiple recirculation of the liquid from the passive zone to the active zone and to large unproductive energy losses. When a certain level of intensification is reached, a further increase in power will not lead to a further acceleration of the process, but to an increase in unproductive energy costs. Therefore, the level of specific power W must necessarily exceed effective power W_{ef}, but without a significant excess of energy consumption $W \le W_{ef}$ [7,20,21].

The high efficiency of extraction through the use of impulse methods of exposure has been proven. Considering that with a decrease in the duration of the process, the energy consumption also decreases, the methods of pulsed energy input make it possible to choose the methods of influence in a fundamentally new way. To accelerate hydrodynamic processes, it is desirable to divide the entire working area into a large number of active zones and create in each of them the optimal level of specific power $W_{act} \leq W_{ef}$. Provided that energy is introduced discretely into each of the active zones, the processing time will be minimal, that is, pulsed. Hydrodynamic processes can proceed only under the action of a driving force, which for hydromechanical processes is determined by the pressure difference. The high rate of pressure change ensures the release of effective specific power $W_{ef}=dP/d\tau$, which provides the necessary level of intensification and contributes to the most efficient use of the input energy. Thus, the input of energy in the form of powerful but short-term pulses makes it possible to reduce non-production energy costs, significantly intensify hydromechanical processes, and rationally approach the choice of methods of influence [20-22].

One of the most effective ways to intensify heat and mass transfer, hydrodynamic, chemical and biochemical processes while achieving high energy efficiency in technologies associated with the processing of liquid dispersed media is the use of cavitation phenomena and effects [23]. Their effectiveness is determined by the multifactorial nature and local energy impact on dispersed particles at the microlevel. Cavitation is a phenomenon that occurs as a result of liquid breaks and the formation of bubbles filled with vapor or gas when a vacuum is created in a limited area. Cavitation can occur in liquids at rest or in motion and is observed both in the bulk of the liquid and at its boundaries. As a result of a sharp change in pressure below a certain critical value Pcav. (cavitation threshold) at certain points of the system, a liquid breaks up with the formation of a cavitation cluster and the process of the emergence, growth and collapse of steam, gas or steam-gas bubbles occurs. A further decrease in pressure to a certain critical value leads to the fact that the cavitation zone begins to spread beyond the points of its occurrence, the bubbles acquire the property of unlimited growth. With a sharp increase in pressure due to the creation of a large pressure difference between the liquid and vapor phases, the size of the bubbles rapidly increases and, as a result of the exhaustion of kinetic energy, they collapse. A large number of dynamically developing bubbles have the properties of microtransformers that convert the potential energy accumulated in the system into the kinetic energy of the liquid, discretely distributed in space and time. In the presence of solid or liquid dispersed phases in a liquid, bubbles contribute to a uniform distribution of energy in the volume and its most rational use. When a bubble collapses directly near solid particles, the kinetic energy of the radial motion of the liquid is converted into the mechanical energy of a liquid cumulative microjet with a high impact intensity, accompanied by the occurrence of abnormally high local pressures, temperatures, velocities and accelerations. The imbalance of a two-phase vapor-liquid system by creating a difference in pressures, temperatures and potentials that control the intensity of mass, momentum and energy transfer through the interface initiates hydrodynamic, heat and mass transfer, adsorption and other processes to stabilize the system. Such transformation of energy contributes to a significant increase in the efficiency of dynamic action on complex heterogeneous systems [7,9,23-25].

In general, cavitation can be formed by various methods: by hydrodynamic pressure reduction in the flow to critical values (hydrodynamic cavitation), ultrasonic radiation (acoustic), spark discharge, pulsed transmission of high voltage current (electrohydraulic shock). All types of cavitation are used to produce extracts, but acoustic and hydrodynamic cavitation are most effective in obtaining the desired chemical and physical changes in a liquid medium. The intensity of cavitation occurrence is determined by such factors as the power density of the input energy, the power consumption of the emitter, the flow velocity (for hydrodynamic cavitation), the amplitude of pressure pulses, the intensity or energy density of acoustic waves, the amplitude of the displacement of velocity or acceleration, as well as the properties of the disperse system itself [23-25].

Cavitation technologies ensure environmental cleanliness and safety of the process, allow accelerating mass transfer processes, activating the extractant, obtaining a high yield of BAS and preserving their properties. At the same time, by changing the technological parameters of the process, it is possible to influence the quality indicators of the obtained finished extract. Modern scientific research is carried out both in search of new solutions for optimizing the cavitation technology itself, and in improving devices that use this technology [26-30].

Technologies using ***supercritical fluid extraction (SFE), high pressure liquid extraction (PLE) and pressurized hot water extraction (PHWE)*** are characterized by a high degree of extraction intensification. These are extraction processes using a critical fluid as a solvent. Diffusion coefficients of supercritical fluids are typically one to two orders of magnitude higher than those of fluids, providing exceptional mass transfer properties. Near-zero surface tension, as well as low viscosity, similar to gases, allows supercritical fluids to easily penetrate the microporous matrix material to produce the desired compounds. The synergistic combination of density, viscosity, surface tension, diffusion coefficient and dependence on pressure and temperature allows supercritical fluids to have exceptional extraction properties. The high intensity of the action of supercritical fluids can be explained from the point of view of the cavitation theory, and the explosive growth and subsequent compression of gas bubbles due to the presence of temperature and pressure in the supercritical zone can be considered vapor-gas cavitation. The vapor inside the bubble and the liquid adjacent to its surface go far into the supercritical region, where the substance is neither a liquid nor a vapor for a short time, but is in a new state, which in physics of fluids is interpreted as the fourth state of aggregation [31].

This direction of intensification is aimed at increasing the efficiency of extractants, reducing their quantity and toxicity. Supercritical water and supercritical carbon dioxide have received the greatest interest and distribution in connection with certain properties.

SFE method is based on the fact that a liquid (or gas) becomes supercritical when the temperature and pressure rise above its critical point and cause cavitation [32].

The critical temperature is the maximum temperature at which a gas can turn into a liquid when the pressure is increased and the critical pressure is the maximum pressure at which a liquid can turn into a gas when the temperature is increased. Along the liquid-gas curve, both phases coexist. In this state, the properties of vapor and liquid converge, supercritical fluids exhibit common functions with vapor and some with liquid. In particular, a supercritical fluid has a density approaching that of the liquid phase and diffusion and viscosity coefficients approaching the vapor phase. Supercritical fluids mix with each other indefinitely, so when the critical point of the mixture is reached, the system will always be single-phase. Their physical properties can be made more liquid or more gaseous by changing temperature and pressure. This unique behavior makes a supercritical fluid an effective solvent for various applications [33].

The properties of critical liquids are a positive factor, allowing better penetration into the solid plant structure and more efficient dissolution of the necessary substances than with conventional organic solvents. The main transport mechanism during mass transfer is convection in the supercritical phase of the solvent.

When using liquefied gases as an extractant, such as butane, propane, nitrogen, ammonia, carbon dioxide, freons, argon and others with a boiling point below room temperature, the processes of oxidation, decomposition, loss of valuable substances or changes in their properties during evaporation are excluded (these extractants volatilize at room temperature). Liquefied gases, having high wetting and penetrating power, as well as low viscosity, are able to easily and quickly get inside the plant cell of raw materials and extract up to 88–98% of active substances, which is much more than using traditional extraction methods: maceration, percolation, etc. The resulting extracts are distinguished by a high content of fat-soluble and a lower content of water-soluble substances. Extraction can be carried out both periodically and continuously. The supercritical fluid is removed easily when the pressure is reduced.

The most widely used supercritical gases (liquids) are carbon dioxide due to its low toxicity, low critical temperature (31°C) and pressure (72 bar). The viscosity of liquid carbon dioxide is 14 times less than the viscosity of water and 65 times less than the viscosity of ethyl alcohol, which explains its high extraction ability. In addition, liquefied carbon dioxide is easily and quickly distilled off from the extract at room temperature, which is especially important in the production of extracts from raw materials containing thermolabile substances and essential oils. Extraction can be carried out either intermittently or continuously in high pressure equipment.

Extraction of vegetable raw materials with liquefied carbon dioxide is carried out at room temperature (not more than 28°C) and a pressure of 66–71 bar. The boiling point of liquefied carbon dioxide, depending on the pressure, ranges from –55.6 to +31°C. This allows the gas to be quickly removed from the extract and keep the extracted substances in the extract unchanged.

This method is mainly used for the most complete extraction of lipophilic biologically active substances from plant materials, supercritical separation of essential oils, oleoresins, fatty oils, carotenoids, lycopene, sterols and other BAS. Extraction is fast, selective and does not require further purification. Another big advantage is the possibility of direct integration with analytical chromatographic methods such as gas chromatography (GC) and supercritical fluid chromatography (SFC) [34-36].

The technology is environmentally friendly and makes it possible not only to design environmentally friendly solvent-free processes, but also to process thermolabile biological materials and other valuable products at low temperatures [17,37].

Despite the significant advantages of this method, its implementation requires significant investment costs, as well as the solution of complex technological and technical issues for the implementation of mass transfer processes, and the equipment is highly complex. The method has found rather wide application in the USA, Germany and France [17,38-40].

The principle of ***pressurized fluid extraction (PLE)*** exploits the property that a fluid in a supercritical fluid state has the unique ability to dissolve almost all organic matter, as well as extremely large volumes of various gases and some solids that are practically insoluble in condensed water. In the fluid state, the electrical conductivity of water and the degree of ionization of its molecules increase by 5–8 orders of magnitude. Similar effects are observed when exposed to high pressures, even if the water temperature is below the critical temperature.

Its effectiveness is attributed to the improvement in the solubility of the active compounds of the plant material by raising the temperature of the solvent above the boiling point under pressure. ***Pressurized Hot Water Extraction*** (PHWE) is based on the same principles as PLE, but using water as the extraction solvent [31,41].

Ultrasonic extraction occurs under the influence of intense ultrasonic radiation (oscillation frequency from 1,0x10^5 to 1,0x10^9 Hz) of the cavitation generator. In the ultrasonic range, piezoelectric and magnetostrictive cavitation generators are most common. The ultrasound generator is attached to the maceration tank filled with extractant and raw materials. Ultrasonic waves form vibrations with rapid changes in high and low pressure cycles, which leads to the appearance of acoustic (ultrasonic) cavitation, turbulent and vortex flows. This type of influence promotes intensive mixing and turbulence, rapid dissolution of substances in plant cells and convective diffusion gradually replaces molecular one, which leads to intensification of mass transfer. Because of ultrasonic action, solid and liquid particles vibrate and accelerate, the extractant intensively penetrates into plant cells, solid particles swell and grind, the phase contact area increases, the maximum difference in concentrations is created and substances from plant cells quickly diffuse from the solid phase into the extract. An increase in the intensity of ultrasonic radiation leads to an acceleration of mass transfer processes. In addition, the output of active substances is affected by the duration of ultrasonic irradiation, temperature, the ratio of raw materials and extractant (hydraulic module).

The main advantages of using ultrasound are the efficiency and reduction of the duration of the extraction, as well as the minimum consumption of the solvent. At the same time, the detrimental effect of ultrasound energy (> 20 kHz) is possible due to the formation of free radicals, enhancement of redox processes, partial destruction of organic compounds, which leads to undesirable changes in drug molecules [3,12,28,42,43].

Another interesting stimulation technique is the use of ***ultrasonic supercritical fluid extraction (HP-UAE)***. This is a relatively new method, but its implementation has shown significant promise. The method is to use sonication and supercritical extraction (UASFE) or sonication and pressurized liquid extraction (UAPLE) simultaneously in the same reactor. The combination of high-pressure extraction methods with ultrasonic cavitation depends on the influence of the main operating parameters (for example, pressure, temperature, particle size, ultrasonic power, time, etc.), which must be carefully studied when using a high-pressure ultrasonic system. The method has advantages and disadvantages characteristic of both processes. It can significantly improve the conditions for mass transfer and extraction of phytocomponents from many natural products, minimize the use of toxic organic solvents, reduce the duration and lower the extraction temperature, but it is difficult to organize the process and requires large investment costs [44-47].

A new effective method based on bubble cavitation for extracting BAS from plant materials is ***Negative Pressure Cavitation Extraction (NPCE***). Negative pressure is generated by connecting a vacuum pump to the extraction system. Under the action of negative pressure in the "liquid-solid phase" system, small gas bubbles develop and rise, which leads to the formation of an unstable "gas-liquid-solid phase" system. When the bubbles enter the slurry zone, the size of the bubbles changes rapidly along with the change in external pressure. Bubbles grow and collapse in certain areas of the negative pressure flow. The explosive growth of gas bubbles mixes and turbulizes the mixture, which accelerates the interfacial mass transfer. This method is effective in the processing of heat-labile raw materials [48].

Using this method, highly efficient extraction can be achieved by combining cavitation and intense turbulence created by continuous gas flow in a " liquid-solid system". This phenomenon leads to better mixing of substrate and solvent and better mass transfer. There are several important advantages to using the NPCE method as opposed to traditional extraction methods. These advantages include environmental friendliness, fast duration of processes, mild operating conditions (relatively low process temperatures), scalability, energy and financial efficiency and [49-52].

The use of methods that use the action of an electric current is promising. In this case, the phenomena of a ***spark discharge and the effect of electrohydraulic shock*** develop. These methods generate localized cavitation and are used to treat limited volumes of liquids. In the case of a spark discharge and an electrohydraulic shock, a break in the integrity of the flow in a liquid with subsequent propagation of a shock wave is observed in the area between the electrodes. As a result of electrical breakdown in the liquid, high-pulse pressures develop in the flow volume surrounding the discharge channel. In this case, cavitation acts as an auxiliary factor in the processing of the medium. Under the action of an electric current, the electrical potentials of the substances of plant materials change, the movement of ions accelerates, the coefficient of internal diffusion and the acceleration of the passage of molecules through cell membranes increase. During extraction, this makes it possible to accelerate the extraction rate of substances related to electrolytes [53].

Extraction using electroplasmolysis and electrodialysis. The effect of electroplasmolysis on a plant cell consists in a profound effect of destruction on the plant cell membrane. As a result of processing raw materials with low and high frequency current, coagulation of the protein-lipid substances of the membrane occurs.

Extraction is carried out in electroplasmizers, which are devices, the body of which is made of a dielectric material and electrodes of various designs located inside. These devices are most often used for fresh raw materials of plant and animal origin. The duration of the processing of raw materials by electric current is in milliseconds. Under the action of electric current and mechanical extraction, the yield of target substances into the extract increases by 20–25%.

In electrodialysis, the driving force is the difference in the concentrations of substances inside the cell and the intercellular space, the movement of BAS ions in the cells and capillaries of cellular structures is accelerated. As a result, the internal diffusion coefficient increases [54].

Extraction using electropulse methods. With the electric pulse extraction method, the intensification of mass transfer is achieved using a high-voltage discharge, which is formed as a result of the accumulation of electrical energy and its release in short periods of time. Electric discharges accelerate intracellular diffusion due to the occurrence of convective diffusion and partial destruction of cell membranes. The method is implemented in pulsed electroplasmizers. Movable or fixed electrodes are placed inside the extractor with the processed raw materials, which supply a pulsed current of high or ultrahigh frequency. A high-voltage pulsed discharge causes ultra-high hydraulic pressures of the order of 108–1010 atm and powerful cavitation processes. This method allows to create powerful hydraulic shocks in the "raw material-extractant" system with a given frequency from several Hz to several tens of kHz. The duration of each beat is a few microseconds. Due to the spark discharge, plasma bubbles are formed, which grow and collapse, forming microjets that break cell membranes. This releases a large amount of energy. The occurrence of shock waves contributes to intensive mixing and reduction of the diffusion layer, penetration of the extractant into the cell, which accelerates intracellular diffusion. As a result, the extraction time is significantly reduced [55,56].

This method is promising, but the disadvantages include the possibility of destruction of molecules, the creation of a high level of noise due to hydraulic shocks, and the high cost of the product [3,57].

The use of electric pulse discharges significantly improves the extraction rates, ensures the safety of biologically active components and ensures their extraction up to 90% of the original content. In the extractor, the processes of destruction of raw materials, processing it with pulsed currents, high turbulence of the liquid phase, disinfection of the environment and others are simultaneously carried out.

One of the new promising technologies for the production of phytopreparations is ***electropulse plasma-dynamic extraction of plant substances (EIPDE)***. The method was developed on the basis of the Yutkin effect. Its essence lies in the fact that in order to intensify the extraction process, the influence of different force fields on the mixture of raw materials and extractant is used. A mixture of vegetable raw materials and an extractant (solvent) is placed in the extractor, which is pierced by an electric discharge of great strength, that is, there is a short-term, but pulsed (pulse interval 0.5 s) effect on the mixture of high-voltage currents. Under the action of forces caused by a high-voltage discharge, instantaneous waves arise in the mixture of the extractant and plant materials in milliseconds, which create a high impulse pressure, the entire mixture is intensively mixed in the extractor, the diffusion boundary layer is thinned or completely disappears and the convective diffusion sharply increases. Sharp shock waves contribute to the rapid penetration of the extractant through the cytoplasmic membranes into the cell, which greatly accelerates intracellular diffusion. At the moment of breakdown of the spark discharge, plasma cavities appear in the liquid. These cavity bubbles constantly pulsate: having reached the maximum possible volume, they collapse. Shock collapse further increases the speed of movement of the extractant around the crushed particles of raw materials. This process sharply increases the speed of extraction, so that the coefficient of convective diffusion increases sharply. At the same time, a large amount of energy is released in the reactor vessel and an explosion occurs, which destroys the outer and inner cell membranes of the plant material. The process of extraction is sharply accelerated.

The prospects and efficiency of the method lie in the complex effect of a number of factors on the raw material, which make it possible to intensify the extraction process [56-58].

Positive results of the plant material extraction were obtained using ***electromagnetic pulse radiation***. In general, the principle is that the swollen plant material and the appropriate extractant (or their mixture) are placed in a container, which is heated by a microwave oven under pressure. Usually, the extraction lasts from 5 to 20 minutes, then the mixture is cooled and filtered. The electromagnetic energy of microwaves during absorption by the material is transformed into thermal energy. The oscillation frequency of 2450 MHz (2.45 GHz) with a power of 600–700 W is most often used [38,59].

The intensification of the process using this method occurs by increasing the pressure inside the capillaries of plant raw materials, with their subsequent destruction and maximum delivery of the target component into the extractant. This is a simple, environmentally friendly, and economical method of extracting biologically active compounds from plant materials. Unlike other extraction methods, in microwave ovens, the entire mass of swollen raw material is heated simultaneously. The advantage of microwave heating during extraction is the breaking of weak intermolecular hydrogen bonds, which contributes to the dipole rotation of molecules [39,60,61].

Sample components absorb microwave energy according to their dielectric constants [37]. In the case the plant material is immersed in the extractant, the heat of microwave radiation directly reaches the solid phase of the plant material without being absorbed by the solvent. As a result, the residual moisture in the plant material is instantly heated and depends on the microwave properties of the solvent. Heating provokes the evaporation of moisture and creates high steam pressure, which breaks the cell walls of the substrate and releases the contents into the extract. As a result, the processing time is significantly reduced and the extraction efficiency is increased [61].

The method is effective and allows organize soft extraction process, increases extractive substances output by approximately 2 times, and significantly reduces the duration of the process, compared to classical methods. However, for the most part, it is at the stage of developing pilot equipment, so it has not yet been widely used in industry. Developments in this direction are carried out in the USA, Canada and France.

An effective technique for intensifying the extraction process is the use of complex influences. These include extraction methods using rotary-pulsation apparatus (RPA), which belong to hydrodynamic emitters. The high efficiency and expediency of using RPA is due to the fact that during processing, a liquid heterogeneous medium is subjected to pulsed multifactorial influence: mechanical influence of structural elements, shear stress in the gaps between working bodies, the occurrence of acoustic and hydrodynamic cavitation, etc. and accompanying phenomena and effects. This makes it possible to significantly intensify various chemical and technological processes. These devices combine the principles of operation of colloid mills, dismemberers, pumps, mixers, and extractors [26]. The technology for the production of extracts using RPA involves the grinding of plant raw materials in a solvent environment with simultaneous extraction and subsequent separation of the solid (meal) and liquid phases in a centrifuge. At the same time, the extraction process proceeds 2–3 times faster than with traditional methods, the output of active substances increases to 40%, and the specific consumption of electricity decreases by 2–3 times. However, the use of RPA also has its limitations due to the possibility of using mainly water as an extractant and the need for a rational choice of system dispersion [62-64].

The RPA refers to devices in which the principle of discrete-pulse energy input (DPEI) is implemented. During DPEI mechanisms implementation, physical prerequisites are created that ensure discrete and local distribution of energy in space and impulse influence in time. The use of DPEI allows us to practically realize all the advantages of temporal and spatial discretization of the energy introduced into the device in order to maximally reduce unproductive energy consumption. This approach assumes that the dissipation of energy introduced into the device and its useful implementation is carried out mainly near the dispersed particle or directly on its surface, and the factors contributing to energy loss outside these local zones must be removed. The most complete implementation of the DPEI principle can be achieved if the concentration of discrete zones with pulsed energy input has the same order of magnitude as the concentration of particles of the dispersed phase, so that equally favorable conditions are uniformly created near each particle [7,9,23].

DPEI devices with the same productivity and corresponding efficiency of material processing, differ from traditional devices of the same purpose with higher efficiency, small dimensions, low metal consumption, simplicity of construction and duration of continuous work.

Another example of the successful implementation of the DPEI method for obtaining extracts is a pneumatic-pulsation apparatus for valerian root extraction developed at the Institute of Engineering Thermophysics (IET) of the National Academy of Sciences of Ukraine. The effective hydrodynamic effect created on this apparatus (pulse extractor) allows not only to extract of the necessary bioactive components but also to grind off the original plant raw materials, which are insoluble fractions, to the required degree of dispersion. In the future, this allows us to supply the obtained multicomponent liquid system (suspension) to the atomizer in the drying apparatus of the spray type.

The extraction apparatus, which implements the method of discrete-pulse energy input, works as follows: a vacuum is created by a vacuum pump in the upper part of the membrane valve, due to the flexible membrane that separates the membrane valve, a vacuum is also created in the pulsator, and a mixture of raw materials with a solvent (water) from the reactor heated by heaters, being drawn into the pulsator, boils. The source of compressed air in the upper part of the membrane valve creates increased pressure, which is transmitted through the flexible membrane to the pulsator. At the same time, the boiling of the mixture is extinguished and a column of the mixture is pushed out of the pulsator into the reactor, creating intense jet streams. In the apparatus, pressure changes from 0.02–0.05 to 0.20 MPa with a frequency of 0.67–1 s^{-1}. Pressure is created by compressed air. During experiments, the liquid system may heat up. To prevent the liquid from cooling as it rises and is pushed out of the pulsator, heaters attached to the pulsator are used. Air inlet and outlet from the upper part of the membrane valve are carried out by electromagnetic valves with a frequency set by the control device. Thus, in this apparatus, conditions are created for active hydrodynamic influence, which causes active mass transfer and active mixing in the reactor. The time of the process is reduced by 10–20 times, depending on the physical and chemical properties of the plant material and the solvent. In most cases, the limit concentrations of extractive substances increase by 3–4 times. A small percentage of the insoluble fraction (fiber) in the complex composition of the dry extract performs its therapeutic and preventive function. This technology makes it possible to simplify the technological scheme and obtain a high yield of the final product in the dry form [31].

The dynamic of real processes in devices and apparatus that implement the DPEI principle is determined by the simultaneous influence of many factors. At the same time, the intensity of the influence of a particular effect can be strengthened or weakened by other factors. Conventionally, the hard and soft mechanisms of DPEI are distinguished. Soft mechanisms use intensive mixing of multicomponent media to accelerate interphase heat and mass exchange processes. To stimulate and intensify technological processes related to the destruction of solid or liquid dispersions, colloidal particles, micellar structures, and cells of microorganisms, it is advisable to use the hard mechanisms of DPEI. The most effective mechanism of directed influence on the course of nano- and micro-processes in complex heterogeneous systems is the phenomenon of cavitation. It is during the initiation of cavitation mechanisms that the possibility of creating high-amplitude energy pulses with a duration of several seconds and concentrating the energy of such pulses in discrete local zones of nanometer sizes is realized [6,7,9].

According to many scientists, it is the cavitation phenomena that largely determine the high efficiency of the DPEI mechanisms.

In RPA and pulsating dispersers, the condition for initiating cavitation mechanisms is fulfilled due to the periodic overlapping of the channels of static and dynamic elements, which leads to periodic braking and acceleration of the flow, and, as a result, to periodic decrease and increase in pressure. In apparatuses of these types, the liquid flow is unsteady and the process of formation, growth and subsequent collapse of bubbles is regularly repeated in each cycle of channel closure [9,20,21].

Hydrodynamic cavitation occurs in sections of the flow with local narrowing and subsequent expansion of the channel (closing and regulating bodies, pipe elbows, etc.) with or without the use of moving parts. Cavitation phenomena occur when the pressure locally decreases to values much lower than the saturated vapor pressure of a liquid at a given temperature, and then rapidly increases to values that exceed the saturated vapor pressure. As a result of a sudden change in hydrodynamic conditions, steam-gas bubbles appear and begin their evolution. Hydrodynamic cavitation principally does not differ from acoustic cavitation. In hydroturbines, pumps, and various shut-off devices, where the above pressure drop conditions are realized, cavitation inevitably occurs, and a pulsating cavitation cluster appears. The periodicity of bubble collapse, the amplitude of pressure and temperature pulses, and the intensity of the spherical shock wave emitted by the cluster depend on the flow rate and channel geometry in the cavitation zone. In the processes of acoustic or hydrodynamic cavitation, the pressure in the liquid can fall to negative values due to tensile stresses. Under these conditions, the liquid is in a very unstable, metastable state [7].

In some cases, the occurrence of cavitation is possible even without flow expansion, for example, in constant-pressure pipes during high-speed flow of liquid heated to a temperature close to the temperature of saturated vapors, as well as hydraulic shocks [29,65-69].

Liquid processing in hydrodynamic cavitation devices is carried out by pulsed multifactorial effects: vortex formation, microscale pressure pulsations, intense cavitation, shock waves and nonlinear hydroacoustic effects. The spatial and temporal concentration of energy makes it possible to obtain a large power of impulse energy impact, to release the internal energy of matter, to initiate numerous quanta, catalytic, chain, avalanche-like and other energy-rich processes. The gas bubble that is formed as a result of cavitation is both an object of influence and input energy transformer. With intensive expansion, compression or pulsation of bubbles under the influence of external pressure, which periodically changes, mixing processes are activated both at the micro level for an individual particle of the solid phase, and at the macro level, for the entire working volume, due to the turbulence of the interfacial surface. The combined effect of these factors increases the overall mass transfer coefficient in the system [23,70-71].

The hydrodynamic method of cavitation generation makes it possible to shift to a promising flow processing scheme during extraction. This is a significant advantage over other types of cavitation, which are implemented, for the most part, in batch equipment of periodic action.

In the manufacturing technology of extractions from vegetable raw materials, hydrodynamic cavitation devices are used for significant intensification of processes at the stages of preparation of vegetable raw materials, the extractant, as well as the extraction itself. At the stage of preparation of raw materials in cavitation devices, the following occurs: grinding of plant raw materials to increase the dispersion of solid particles, ensuring the development of the contact surface of phases, as well as active cavitation effect on plant cell membranes to reduce stiffness and increase the permeability of the extractant. At the stage of preparation of the extractant, as a result of the occurrence of hydrodynamic cavitation and the evolution and collapse of cavitation bubbles, ionized molecules and free radicals are formed, which leads to the activation of the extractant, changes in its physicochemical and electrochemical properties. These properties change the conditions of the extraction process, and also affect the final quality of the extract. The use of hydrodynamic cavitation devices at the stage of direct extraction allows it to be combined with the previous stages of preparation of raw materials, swelling and activation of the extractant.

The design and principles of operation of a specific device significantly affect the intensity of cavitation effects. The most common devices are static and dynamic, which are divided into centrifugal, nozzle, slit, jet, and many others. Examples of devices by type of cavitation generators are cylindrical and disc rotor-pulsation devices, high-pressure valve homogenizers, pulsation dispersants, centrifugal pumps, Venturi nozzles. Trends in the development of cavitation device designs are characterized by the desire to obtain the maximum cavitation effect and achieve the required properties of the obtained extract, as well as economic efficiency due to the reduction of energy consumption for processing.

To date, a significant number of modifications of flow static or dynamic cavitation mixers have been described. Dynamic type devices [23,28] are hydrodynamic apparatuses where the flow energy is transmitted by special nozzles which rotated. The designs of these apparatuses provide multiple reconstructions of the velocity field and changes in the direction of movement of the flow of liquid and mixed components due to dynamic elements (impellers, blades) of various configurations, which contribute to the formation of caverns on the surface of the working bodies or behind them. Such apparatuses perform the functions of both a pump and a cavitator at the same time.

Static cavitation devices have a number of advantages from the point of view of a constructive, technological and economic solution. Static cavitation devices are equipped with stationary cavitators (nozzles, discs) that prevent the movement of the flow. Cavitation zones in these devices are not formed on the surface of the working bodies of the cavitation generator but behind them. Static-type devices (passive activators) use the energy received from the pump when acting on the dispersion system. Devices of this type have small dimensions with high productivity. The economic efficiency of using static cavitation devices is due to the low metal consumption of the equipment, the simplicity and reliability of the design, and low costs for repair and maintenance [23]. The common element in the designs of various static flow cavitation mixers is the cavitator (or a set of cavitators) installed in the flow chamber of the device. Their number, design, degree of mobility, and some other parameters differ and are determined by the solution of specific technological problems: reducing energy intensity, regulating the intensity of the cavitation field, increasing the degree of cavitation influence, etc. Very often in the production of extracts, flow hydrodynamic cavitation generators based on a Venturi tube, partitions or discs with one or more channels are used [23,26,28,31].

Cavitation devices based on a Venturi tube are a serially connected inlet pipe, a confusor, a flow chamber, a diffuser and an outlet pipe. The hydrodynamic conditions for the occurrence of cavitation in certain sections of the Venturi tube are presented as follows: in the section of the channel with a reduced cross-sectional area (confuser and nozzle neck), the velocity of the stationary flow increases and, in accordance with Bernoulli's law, the pressure in the liquid drops to values lower than the saturated vapor pressure. As a result, the formation and intensive growth of cavitation bubbles take place in this area, that is, the stage of cavitation boiling of the liquid is realized. In the next section of the channel, where the cross-sectional area of the channel increases (diffuser), the flow slows down and the pressure of the liquid increases sharply to values higher than the pressure of the saturated vapor. This leads to the compression and collapse of cavitation bubbles collection [23,26,31,67].

The intensification of static cavitation devices relates mainly to the improvement of the nozzle design. When the liquid passes through the venturi nozzle, the potential energy of the compressed liquid is transformed into kinetic energy at the nozzle throat and the further transformation of kinetic energy into potential energy at the exit of the nozzle. During the movement of the liquid flow at higher speeds, with constant pressure at the nozzle inlet, the flow rate and pressure within the cavitation zone change rapidly during the initial development of cavitation, and then remain practically constant and do not depend on the number of hydraulic losses. Eddies, separation flow, and cavitation occurs in the liquid flow when the liquid passes through the narrowing and then the expansion of the channel. The listed effects impact on the liquid particles and contribute to their intense grinding, disruption of the boundary layers on the particles, and an increase of the mass transfer coefficient, crushing and homogenization [23,31].

Therefore, intensive extraction methods have the following advantages: achieving a high BAS yield and accelerating extraction.

Conclusion

Plant extracts with a high content of aromatic, flavoring, and biologically active substances of natural origin and a wide range of biological activity are in high demand in various industries in the production of a wide range of products and preparations.

A review of existing traditional methods and equipment for extraction showed their high-energy intensity, process duration, multi-stage and low energy efficiency. It determines the urgency of the search for modern, more intensive methods of processing plant raw materials to obtain extracts.

The use of cavitation phenomena and its effects is considered to be one of the most effective methods of intensification of heat-mass exchange, hydrodynamic, chemical, and biochemical processes while achieving high energy efficiency in technologies related to the processing of liquid dispersed media.

For the extracts production, technologies, and equipment are used with various conditions for the occurrence of cavitation: by hydrodynamic pressure reduction in the flow to critical values (hydrodynamic cavitation), ultrasonic radiation (acoustic cavitation), spark discharge, pulsed high-voltage current transmission (electro-hydraulic shock).

Acoustic and hydrodynamic cavitations are the most effective in carrying out mass exchange processes and are widely used in various technologies for extracts production.

The high efficiency of hydrodynamic cavitation devices during processing dispersed systems of the "liquid-solid" type is due to the pulsed multifactorial effect: intense cavitation, vortex formation, micro-scale pressure pulsations, shock waves and nonlinear hydroacoustic effects. The combination of these factors allows us to obtain the high intensity of micro- and nano-level effects on the particles of plant material and increases the overall mass transfer coefficient in the system.

Examples of hydrodynamic cavitation devices are cylindrical and disc rotor-pulsation apparatus, high-pressure valve type homogenizers, pulsation dispersers, centrifugal pumps, which are used for significant intensification of processes at the stages of preparation of plant raw materials, preparation of the extractant, as well as the extraction itself.

Very often in extracts production, flow hydrodynamic cavitation generators based on Venturi tube are used.

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КАВІТАЦІЙНІ МЕТОДИ ДЛЯ ІНТЕНСИФІКАЦІЇ ЕКСТРАГУВАННЯ РОСЛИННОЇ СИРОВИНИ

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Анотація. Традиційні технології і обладнання для екстрагування не задовольняють потреби промислових виробництв у постійному збільшенні об'ємів готової продукції через низьку ефективність вилучення цільових компонентів, їх високу енергоємність і тривалість. Це робить актуальним пошук сучасних, більш інтенсивних технологій та обладнання, використання яких дозволить суттєво збільшити загальну продуктивність виробництва, знизити загальні питомі енерговитрати, покращити якість готового продуктів і безпечність процесів для навколишнього середовища. В статті проведений аналіз і дано узагальнення методів інтенсифікації процесів екстрагування із рослинної сировини. До найбільш дієвих способів інтенсифікації гідродинамічних процесів відносяться кавітаційні явища. Трансформація і перерозподіл енергії, які відбуваються при утворенні і схлопуванні парогазових бульбашок внаслідок створення високої різниці тисків, температур і потенціалів, сприяють значному підвищенню ефективності динамічного впливу на складні гетерогенні системи при екстрагуванні. Кавітаційні технології забезпечують екологічну чистоту та безпечність процесу, дають можливість пришвидшити масообмінні процеси, провести активацію екстрагента, отримати високий вихід біологічно активних речовин (БАР) та збереження їх властивостей. Найчастіше використовуються акустична та гідродинамічна кавітація. Сучасні наукові дослідження проводяться у пошуках нових рішень для оптимізації технологій, а також вдосконаленні кавітаційного обладнання. Прикладами гідродинамічних кавітаційних апаратів статичного і динамічного типу є: циліндричні та дискові роторно-пульсаційні апарати, клапанні гомогенізатори високого тиску, пульсаційні диспергатори, відцентрові насоси та трубки Вентурі. Їх використовують для інтенсифікації процесів на етапах підготовки рослинної сировини, активації екстрагенту, а також проведення самого екстрагування. Кавітаційні апарати статичного типу на основі трубки Вентурі мають низку переваг з погляду конструктивного, технологічного та економічного рішення.

Ключові слова: інтенсифікація екстрагування,масообмінні процеси, кавітація, метод надкритичної рідинної екстракції,акустична кавітація, гідродинамічна кавітація, трубка Вентурі, електроімпульсні методи.