SCIENTIFIC
ARTICLE

SORPTION METHODS AND MATERIALS

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Table of Contents

SORPTION METHODS AND MATERIALS

Sorption methods in water treatment are the processes of removing impurities from water in a layer of granular sorption material running on the surface or in the pores of its granules. Sorptive loads used in water treatment can be divided into groups:

- Ion-exchange materials - designed to remove charged particles from the solution;
- Porous adsorbents (activated carbon) - designed to remove molecular impurities;
- Catalytic sorbents - intended for the removal of specific impurities using the sorption-catalytic properties of loading granules;
- Sorption materials of complex action - used for simultaneous removal of various types of pollution.

2.1. ION EXCHANGE AND ITS USE IN WATER PREPARATION

Ionites are solid substances, which capable to absorb positively or negatively charged ions from an electrolyte solution in exchange for an equivalent amount of other ions of the same sign contained in the ionite. According to the sign of the charge of the mobile group, ionites are divided into **cationites** and **anionites.** There are also amphoteric ionites or **ampholytes**, capable of simultaneous cation and anion exchange. From the general series, ionites capable of complex formation with ions absorbed from the solution can be distinguished, so-called **complexites**.

2.1.1. BASICS OF THE METHOD

Ion exchange resins are small granules that consist of a branched **polymer matrix** and **functional groups.** The charge of a fixed part of functional groups is compensated by ions capable of exchange - **counterions.** The form of the ionite is determined by the type of counterions: for example, if metal cations (for example, sodium) act as the counterions of the cationites, then the initial form of the ionite is salt. If the ionite contains H^+ as a counterion, then it is said to be in the hydrogen form **(Fig. 2.1)**.

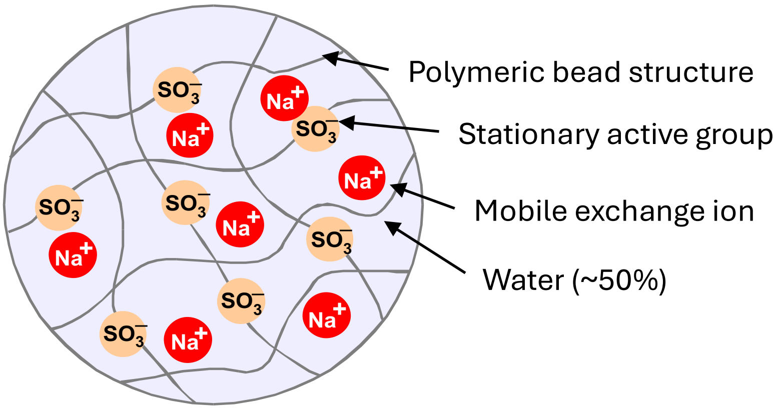

Fig. 2.1. The structure of the ion exchange resin

A similar situation occurs with anions, if the mobile group is OH^-, then it is a hydroxyl form, if the mobile group is salt anions (for example, Cl^-), then it is a salt form.

In an aqueous environment, counterions can pass into the liquid phase if the ions from the aqueous environment compensate for the charge of the framework, ensuring electroneutrality.

Reactions of ion exchange processes are reversible, that is, spent ionites can be regenerated and repeatedly used in technological processes.

Polymer matrices of ion-exchange resins are classified depending on the types of polymers that act as a linear frame and a cross-linking agent. The most used crosslinking agent is divinylbenzene (DVB). During the polymerization of styrene with divinylbenzene, a polymer is formed, a separate link of which is shown in **Figure 2.2a**. Resins with such a matrix are called styrenedivinylbenzene, or SDVB for short.

In ion-exchange resins with an SDVB matrix, each molecule of divinylbenzene, as a bridge, connects two adjacent linear polystyrene chains. SDVB resins have gained the widest distribution due to the high stability, strength and elasticity of the SDVB matrix. Another example of a polymer matrix is — acryldivinylbenzene, or ADVB for short **(Fig. 2.2b)**. There are also phenol formaldehyde, vinyl pyridine, polyalkylamine and polyacrylamine resins, but in practice they are much less common than SDVB and ADVB.

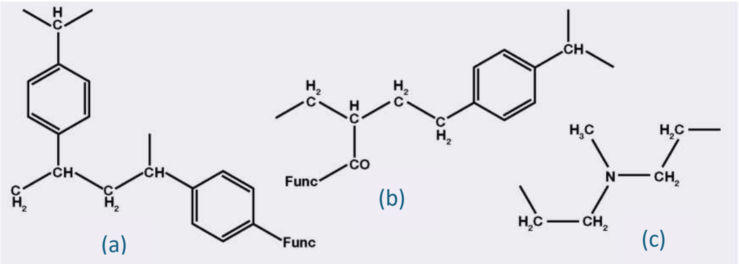

Fig. 2.2. The structure of styrenedivinylbenzene (a), acryldivinylbenzene (b) and polyethylene polyamine (c) matrices of ion exchange resins

2.1.2. METHODS OF SYNTHESIS OF IONITES

Polymer matrices can be synthesized by two mechanisms:

1. Polymerization — a reaction involving the joining of molecules without the release of low-molecular-weight products, such as water. According to this mechanism, SDVB and ADVB resins are obtained.

2. Polycondensation — a reaction between molecules with the release of low molecular weight reaction products. According to this mechanism, for example, **phenol formaldehyde** and **polyethylene polyamine** resins **(PEPA)** are obtained **— Fig. 2.3.**

Ion-exchange resins of the polymerization type are granules of a regular spherical shape **(Fig. 2.3a, 2.3b)**, and resins of the polycondensation type are irregularly shaped particles obtained as a result of mechanical crushing of large polymer agglomerates **(Fig. 2.3c).**

Fig. 2.3. Ion-exchange resins of polymerization (a, b) and polycondensation (c) types; polydisperse (a, c) and monodisperse (b) granulometric composition

Another classification of ion exchange resins is based on the porous type of the polymer matrix, according to which **gel** and **macroporous** resins are distinguished. Gel ones are obtained as a result of simple polymerization or polycondensation, and macroporous ones are obtained with the use of inert pore-forming substances in the synthesis process. Gel matrices are heterogeneous and in the dry state do not contain pores in an obvious form. Their polymer chains form a mesh structure, and the internal volume of the grains becomes available for ion diffusion only in a swollen state**.**

The average size of the cells of such a grid depends on the amount of crosslinking agent — **the degree of crosslinking**. According to a rough estimate, the average cell size of the gel matrix is from 5 to 20 A **(Fig. 2.4a)**.

Steric effects together with the heterogeneity of the gel matrix complicate the sorption of large organic ions by such resins. Desorption of large ions from the gel matrix also causes difficulties. In natural water purification processes, these effects lead to the so-called "poisoning" of ion exchange resins by organic substances of natural origin.

The matrix of macroporous resins is characterized by a clear porous structure that exists in the dry state**.** Macroporous matrices are aggregates of globules of the gel phase and a continuous network of voids — pores and channels. The sizes of some pores of such matrices can be from 20 to 2000 A, but the size of most of the pores is 150-250 A **(Fig. 2.4b**).

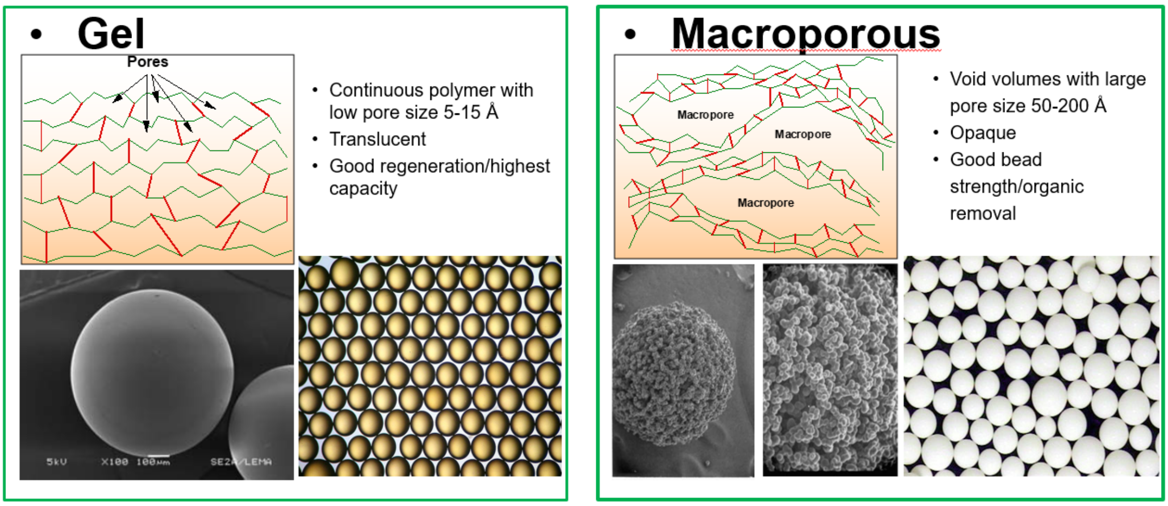

Fig. 2.4. The grain structure of gel (a) and macroporous (b) ion exchange resins

The presence of macropores gives ion-exchange resins the ability to sorb large organic ions. In addition, such resins are characterized by increased mechanical stability of the grains and better kinetic characteristics.

2.1.3. FUNCTIONAL CHARACTERISTICS OF IONITES

Charge-carrying groups — fixed ions — are attached to the matrix of the ion exchange resin. The following are most often used as fixed ions in cationites: $-SO_3^-$, $-COO^-$, $-PO_3^{2-}$, and in anionites: NH_3^+, $=NH_2^+$, $=N^+$. Thus, ion exchange resins are polyelectrolytes with a branched three-dimensional structure.

The type of fixed ions plays an important role in ion exchange. For example, sulfogroups $-SO_3^-$ are completely dissociated and therefore carry out exchange in a wide pH range, while – $-COO^-$ in neutral and acidic solutions are mostly in an undissociated state. Depending on the value of the dissociation constant of functional groups, cations are divided into **strongly acidic** and **weakly acidic**, and anions are divided into **strongly basic** and **weakly basic (Fig. 2.5).**

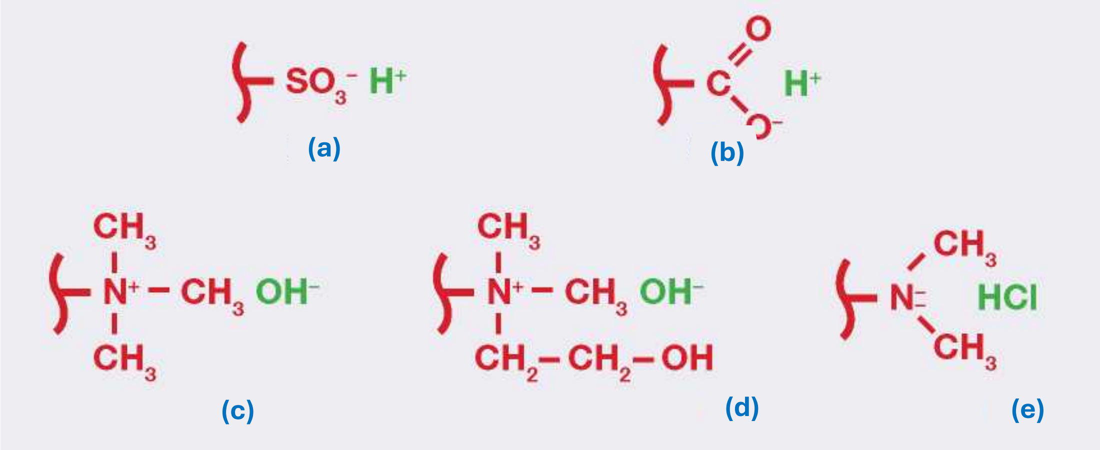

Fig. 2.5. Functional groups of ion exchange resins: strongly acidic (a); weakly acidic (b); strongly basic, type I (c) and type II (d); weakly basic (e)

2.1.4. MECHANISM OF ION EXCHANGE

The most widespread is the use of ionites in water softening and demineralization processes. However, due to the selective effect of ion exchange materials, their use is quite effective for removing heavy metal ions (mercury, cadmium, arsenic, lead, etc.), ions of organic substances (humic substances, antibiotics, etc.), nitrate ions, etc.

The process of softening water can be described by reactions 2.1-2.3:

Removal of the total hardness of water with strongly acidic cationite:

$$2R\text{-}Na + CaCl_2 \leftrightarrow R_2Ca + 2NaCl \qquad (2.1)$$

$$2R\text{-}Na + MgCl_2 \leftrightarrow R_2Mg + 2NaCl \qquad (2.2)$$

To carry out the regeneration process, a solution of NaCl in a concentration of 8-10% is used.

Removal of temporary hardness with weakly acidic cationite:

$$2\ R\text{-}H + Ca(HCO_3)_2 \rightarrow R_2\text{-}Ca + 2CO_2 + H_2O \qquad (2.3)$$

The process of water demineralization can be described by the reactions of H-cationization (2.4) and OH-anionization (2.5):

$$R\text{-}H + NaCl \leftrightarrow R\text{-}Na + HCl \qquad (2.4)$$

$$R\text{◪◪◪-}OH + HCl \leftrightarrow R\text{-}Cl + H_2O \qquad (2.5)$$

Regeneration of the cationite is carried out, using solutions of HCl or H_2SO_4 acids, and regeneration of the anionite - with a NaOH solution.

The process of removing heavy metal compounds from water can be described using the example of removing mercury compounds by reactions 2.6 and 2.7:

$$R\text{-}'Cl + HgCl_2 \rightarrow R\text{-}HgCl_3 \qquad (2.6)$$

$$R\text{-}'Cl + NaHgCl_3 \rightarrow R\text{-}HgCl_3 + NaCl \qquad (2.7)$$

Mercury removal occurs through the interaction of mercury compounds with special complexing highly basic anion exchangers (complexites). The process is not reversible, anion exchanger regeneration is possible only with the use of expensive complexing agents, which makes it impractical.

2.1.5. REGENERATION OF EXHAUSTED IONITES

At the end of the work cycle, when the resin has already been used up and pollutants begin to enter the purified water, it is necessary to carry out ionite regeneration **(Fig. 2.6)**.

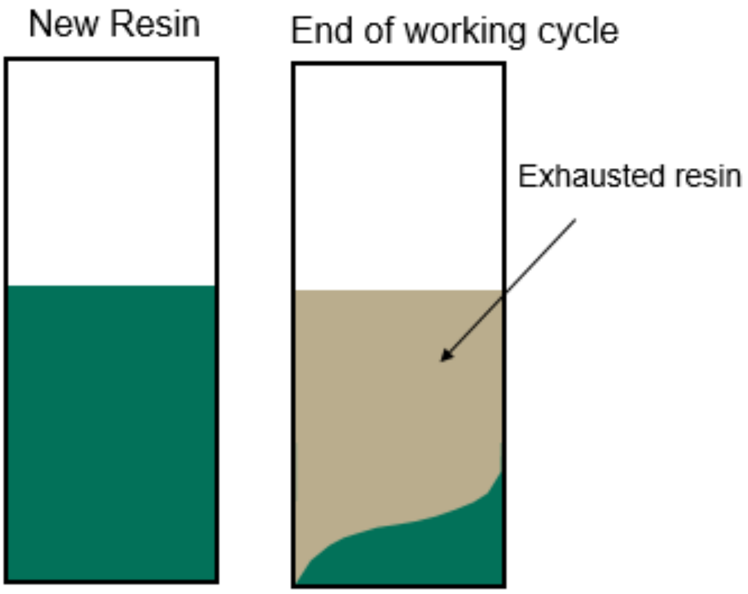

Fig. 2.6. The state of the resin at the beginning and at the end of the working cycle

Regeneration of ion-exchange resin can be carried out in co- and counter-flow mode **(Fig.2.7).**

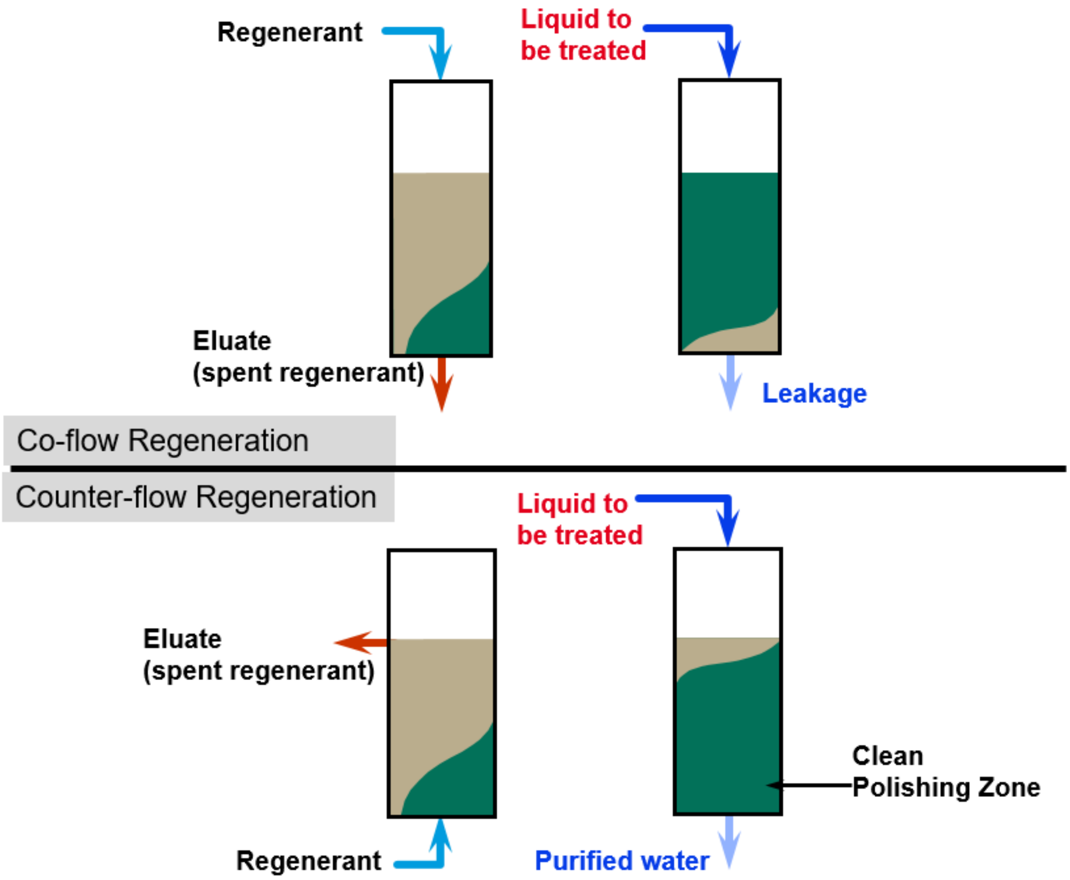

Fig. 2.7. Comparison of resin regeneration efficiency in co- and counter-flow mode

During co-flow regeneration, the regenerant is supplied in the same direction as the source water (from top to bottom), which leads to the formation of a layer of spent resin in the lower part of the column, which cannot be regenerated. In turn, when the source water is passed through such a column, an increased content of pollutants is observed in the first portions of purified water due to the leaching of the latter from the unregenerated resin layer.

During counter-flow regeneration, the regenerant is supplied in the opposite direction to the source water flow, which allows layer-by-layer regeneration of ionite from less polluted to more polluted, as a result, the resin is fully regenerated, and the layer of polluted resin remains in the upper part. During the next filter cycle, the source water is supplied to the ionite layer, which could not be fully regenerated, but this does not lead to a deterioration of the quality of purified water.

The counter-flow mode is more effective, allows to restore the capacity of the resin by 94-98%, with a lower consumption of regenerant, compared to co-flow mode (Table 2.1**).**

Table 2.1. **Comparison of resin capacity recovery efficiency during counter- flow and co-flow regeneration**

Process characteristics	Counter-flow	Co-flow
Water conductivity, µS/cm	0,1 - 1	3 – 30
Average SiO_2, ppb	5 – 20	30 – 200
Exceeding the output of counterions in the regenerant over stoichiometry, %	105 – 150	180 – 400
The degree of recovery of resin capacity, %	94 – 98	85 – 90

2.1.6. MAIN CHARACTERISTICS OF ION-EXCHANGE RESINS DETERMINED DURING QUALITY CONTROL

There are many manufacturers of ion exchange resins on the market, whose products can differ significantly in quality. For the correct selection of products and assessment of their quality, it is necessary to take into account the values of the main characteristics, namely:

Exchange capacity — is a quantitative characteristic showing the total amount of counterions (mg-eq) per unit of dry mass (mg-eq/g) or volume of swollen resin (mg-eq/cm^3).

Theoretically, this value should exactly correspond to the number of functional groups, but in practice, the capacity depends on a number of factors, which makes it difficult to unambiguously define this concept. In this regard, several capacity values are used, which primarily differ in physical content.

Full exchange capacity (FEC) is determined by the complete saturation of the ion exchange resin with respect to any counterion.

Operating exchange capacity (OEC) — part of the FEC that can be used in these working conditions.

The capacity of strongly acidic and strongly basic ionites is constant in a wide range of pH (1.5-12.5) and does not depend on the nature of the counterion. Weakly acidic cationites reach their maximum capacity only at high pH values, and weakly basic anionites — at low. The greater exchange capacity of ionite allows, other things being equal, to increase the duration of the filter cycle, reduce the number of regenerations, which facilitates the operation of the water treatment plant and reduces the amount of wastewater. It should be noted that in industrial water treatment processes, the value of FEC is of interest not so much as the value of **working dynamic exchange capacity (WDEC)**. This value depends both on the properties of the ionite (POE, divinylbenzene content, structure and particle size composition), and on the hydrodynamic conditions of the sorption process and the regeneration mode.

The swelling of ion-exchange resins ensures a rapid flow of ion exchange and significantly affects its character. Swelling of ion exchange resins is related to both the presence of fixed ions that can solvate and counterions capable of hydration, independent movement in the ionite, and mixing with solvent molecules. Thus, the ability of resins to swell is influenced, on the one hand, by the number and charge of functional groups, and on the other by the properties of the matrix, primarily the degree of its crosslinking.

The speed of water filtration through the layer of ion-exchange resin and the hydrodynamic conditions of the flow around the grains, which affect the quality of ion separation, depend on the size of the swollen grains and its homogeneity. During swelling, the grain size increases significantly, therefore, the technical characteristics of ion exchange resins should be calculated taking into account the **swelling coefficient (cm^3/g).**

Particle size distribution (mm) — the relative content of granules of different sizes (%). The particle size distribution is an important characteristic of ion exchangers, since the size and uniformity of the composition of the grains, as noted above, largely determine the efficiency of the sorption process. According to the particle size distribution, ion exchange resins are classified into **polydisperse** and **monodisperse** or **monospheric (Fig. 2.8).**

The use of monodisperse resins allows for higher quality water at lower operating costs, as such ion exchangers have excellent kinetics, high mechanical strength and are better separated when using mixtures of several resins, which allows for their more complete regeneration. Monodisperse resins are used in countercurrent ion exchange technologies, which helps to increase their efficiency.

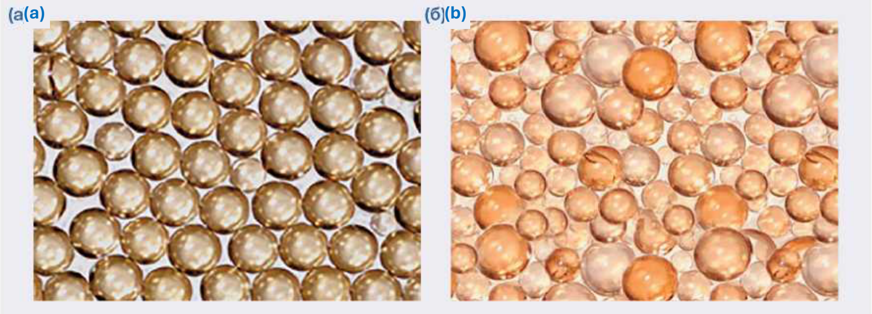

Fig. 2.8. Resins with monodisperse (a) and polydisperse (b) particle size distribution

Osmotic stability (%). The mechanical strength of the grains of ion exchange resins is quite high, which makes it possible to use them multiple times in the conditions of work in columns and even in a fluidized layer. However, during regeneration, a sharp change in the volume of granules occurs, which can lead to cracking of the grains due to osmotic shock. The ability of resins to resist this phenomenon is characterized by osmotic stability. Osmotic stability is defined as the proportion of grains destroyed and cracked because of 50 consecutive treatments of a weight of ionite with acid and alkali solutions from the total number of grains in the sample selected for analysis.

The higher the osmotic stability of ionite, the longer its service life. The value of osmotic stability is determined by the porous structure of the ionite, the content of the crosslinking agent in it, as well as the nature of the matrix and functional groups. Highly crosslinked resins and macroporous resins have higher osmotic stability than others. Osmotic stability, thermal and chemical stability of cationites increase with an increase in the content of

DVB. However, the kinetic characteristics deteriorate significantly. Usually, for cationites used in water treatment processes, the content of divinylbenzene is 6-8%. The term of effective operation of ion exchange resins depends on their mechanical, thermal, and chemical stability.

High **mechanical strength (%)** is necessary to reduce resin wear during its operation. Insufficient mechanical strength leads to the fact that ionite is partially crushed during operation, due to the friction of its grains with each other during loosening of the resin layer during regeneration. This leads to the gradual washing out of dust-like particles and to the irreversible loss of a certain amount of ionite. The high mechanical strength of ionite is especially important in the operation of large-sized installations, where the resins are subjected to significant mechanical loads.

Thermal stability of ion exchange resins requires attention, since at temperatures exceeding the permissible ones, decomposition and hydrolysis of functional groups can occur. Thus, strongly acidic cation exchangers are thermally stable up to 150 °C, and weakly acidic ones - up to 120 °C, in contrast to strongly basic anion exchangers, which are stable up to 40 °C, and weakly basic ones - up to 75 °C.

The service life of ionite, the quality of purified water and the types of substances that can be used for its regeneration depend on **chemical resistance**. Usually, ion exchange resins are stable in strongly acidic and alkaline environments, as well as in relation to organic solvents. There are varieties of resins with increased resistance to aggressive environments. However, the resins used in water treatment are unstable to the influence of oxidants, to active chlorine, in particular, ozone, hydrogen peroxide, etc. At the same time, stability strongly depends on the content of the crosslinking agent (DVB) in the resin.

The ability of ionites to get poisoned. In the processes of natural water conditioning, an important role is played by the resistance of ion-exchange resins to contamination by natural organic substances, in particular humic and fulvic acids, which tend to interact with ion-exchange resins, and above all, with anionites, through the ion-exchange mechanism and as a result of hydrophobic interaction with aromatic fragments of SDVB matrix. This interaction is partially irreversible, therefore, during operation, ionites accumulate natural organic substances, which affect their physicochemical and operational characteristics: the exchange capacity decreases, amphoteric properties begin to manifest, the consumption of regeneration solutions and service water increases. All this eventually reduces the economic efficiency of ion exchange demineralization of natural water.

2.1.7. FIELDS OF APPLICATION OF ION EXCHANGE

Ionites and ion exchange processes are used in hydrometallurgy and the chemical, food and pharmaceutical industries, in medicine, biochemistry and biotechnology, in analytical chemistry, in the nuclear industry and other industries. However, the main field of application of ionites was and remains water treatment — water softening and demineralization, as well as industrial wastewater treatment. Today, the largest industrial consumers of water that has undergone ion exchange conditioning are the power industry, the food industry (beverage production), the production of semiconductors and microelectronics, and pharmaceutical industries. However, in the field of drinking water preparation, various ion exchange materials are also widely used in local installations for various purposes and performance.

2.1.8. ADVANTAGES AND DISADVANTAGES OF USING ION-EXCHANGE PROCESSES IN WATER TREATMENT

Advantages	**Disadvantages**
Ability of deep softening and demineralization of water	High consumption of reagents for regeneration, which many times exceeds the stoichiometric amount, in the processes of desalination and water softening
Ability of chemical regeneration and multiple use of ion exchange materials	Inordinately large consumption of water for own needs, which reaches 15-20% of the volume of treated water
Ability to selectively remove impurities	Irreversible ionite poisoning during operation
A wide range of equipment for processes of different productivity, extensive operating experience and a high level of automation	Environmental problems arising from the disposal of spent regeneration solutions and washing waters.

2.2. ACTIVATED CARBON FOR WATER PREPARATION

2.2.1. TYPES OF ACTIVATED CARBON

In terms of shape and particle size, activated carbon (AC) can be powdery, granular (crushed or granulated) **(Fig. 2.9)**, and fibrous. Powdery AC have particle sizes less than 0.1 mm, granular ones have particle sizes from 0.5 to 5 mm, fibrous ones have particle sizes greater than 0.1 mm and lengths of several centimeters.

Powdered AC is mainly used for one-time water purification, for example, at municipal water treatment plants, where this process is called carbonization. Also, powdered coal can be used in some combined processes, for example, with ultrafiltration, to increase the efficiency of extraction of the low-molecular fraction of organic substances.

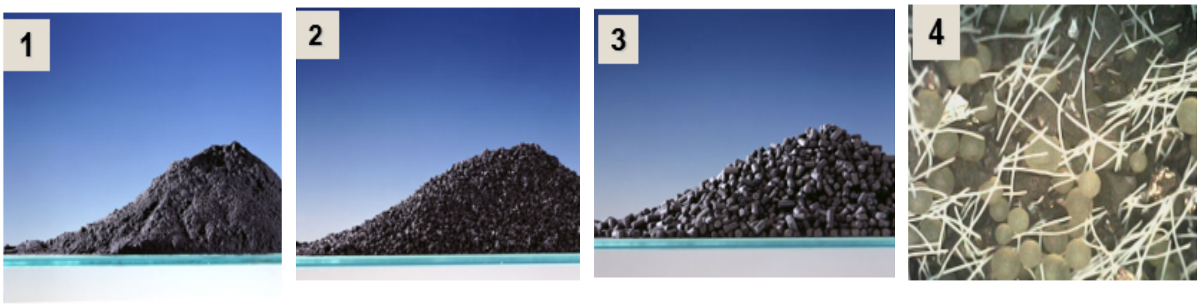

Fig. 2.9. Types of activated carbon: 1 – powdered (PAC); 2 – granulated (GAC) coconut; 3 – granular (GAC) bituminous reagglomerated; 4 – fibers

Granular or **granulated coal** (one of the most common forms of AC) is used for water purification by filtration in housings with a dense or moving sorbent layer, as well as in filling cartridges for household filters.

Fibrous carbon is mainly used in household filter cartridges.

2.2.2. RAW MATERIALS FOR ACTIVATED CARBON

Wood, coconut, hard coal or bituminous activated carbon and their mixtures are used in water treatment processes. Diverse types of wood, hard and bituminous coal, peat, coconut shell are used as raw materials for their production. Less often, animal bones, plant bones, paper pulp, and solid industrial waste can be used as raw materials. For the activation of coal, a thermal method can be used - pyrolysis followed by high-temperature activation in the presence of steam, or a chemical method - treatment of coal with salt or mineral acids at temperatures of 200-650 °C.

AC on a coal base, or they are also called bituminous AC, have much better hydraulic and mechanical characteristics than wooden ones, which allows them to be used as backfill in filter housings of any size, both with a fixed and a moving layer of filtering material. At the same time, the quality of bituminous coal strongly depends on the coal deposit used as raw material. The raw material for obtaining bituminous activated carbon can be hard and bituminous coal, as well as peat. Bituminous activated carbon is widely used to remove natural organic substances such as humic compounds from water, as well as to remove unpleasant odors and tastes from water, remove herbicides and pesticides.

There are two main types of bituminous or hard coal AC — direct activation and reagglomerated. To obtain bituminous AC of direct activation, raw materials are crushed and activated with oxygen and steam. To obtain bituminous coal of higher quality with a homogeneous structure, the reagglomeration method, first proposed by the Chemviron Carbon company (Belgium) is used. The essence of the method is that hard coal is crushed into powder, then under the action of binders it is agglomerated into briquettes, which are further crushed into granules of the desired size with subsequent activation with oxygen and steam. AC obtained in this way is characterized by high strength and balance of transport and sorption pores. The AC surface has a graphite-like structure and includes functional groups (**Fig. 2.10**), which are introduced because of activation, as well as heteroatoms (N), which allow sorption of organic polar molecules, can exhibit catalytic and oxidative properties, and give the surface amphoteric properties**.**

The AC surface is recharged depending on the pH of the medium.

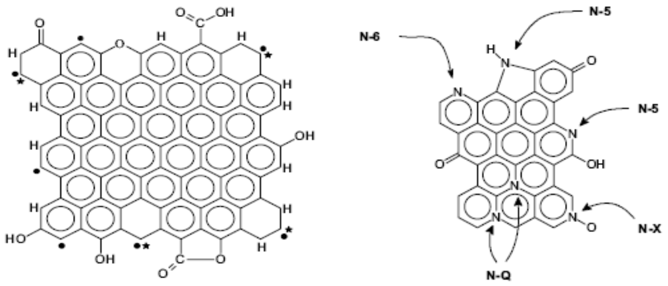

Fig. 2.10. Surface of activated carbon

In the structure of AC, three types of pores are distinguished **(Table 2.2)**.

Table 2.2. **Classification of AC pores**

	Pore radius, nm	Specific pore volume, cm^3/g	Specific surface area, m^2/g
Macropores	> 50	0.35	1
Mesopores	2-50	0.50	200
Micropores	0.4-2	0.25	1 000

Wooden AC is characterized by high porosity, a wide distribution of pores in size, a large specific surface and, as a result, high capacity. However, they have low mechanical strength. In addition, macropores prevail in the structure of wooden ACs, which makes them ineffective in removing the most common impurities, such as chlorine derivatives and organic compounds. In this regard, recently charcoal is rarely used in local water treatment systems.

Coal from coconut shells is extremely popular for water purification. **Coconut coal** is much cleaner than its counterparts due to the low content of inorganic ash. The nutshell is dense, has a fibrillar structure, which affects the strength and, accordingly, the resistance of the granules to destruction during processing, and also minimizes dust removal from the cartridge during its use. Coconut charcoal is known to have a significantly higher micropore volume than other types of activated carbon, which provides a large surface area and higher porosity of the granules. For example, it has 50% more micropores than bituminous activated carbon. Examples of the porous structure of various ACs are shown in **Figure 2.11.**

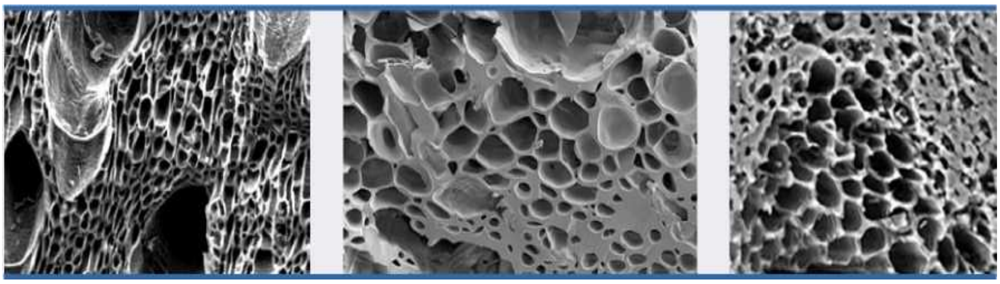

Fig. 2.11. Types of porous structure of activated carbon

The high concentration of micropores and high surface area provide coconut charcoal with the greatest efficiency in retaining substances that are particularly harmful to health, such as chlorine and its carcinogenic organic derivatives. According to their capacity characteristics in relation to natural organic substances, AC types can be placed in the following row: charcoal < coconut coal < anthracite coal < bituminous coal **(Table 2.3).**

Table 2.3. **Properties of activated carbon of different origin**

AC type	Porous structure	Effectiveness of cleaning from natural organic substances	Removal of chlorine and organic chlorine derivatives	Strength properties
Reagglomerated coal	Macro/mesa	Particularly good	Good	Good
Coconut direct activation	Micro	Average	Particularly good	Particularly good
Coal of direct activation	Macro	Good	Badly	Average
Based on brown coal	Macro	Good	Badly	Bad
Charcoal	Macro	Average	Badly	Bad

2.2.3. ACTIVATED CARBON REGENERATION

During the operation of granulated AC, its sorption capacity decreases and, at a certain moment, it becomes necessary to replace or regenerate it (restoration of adsorption capacity). Regeneration of pulverized and granulated AC can be conducted by chemical, thermal and biological methods, each of which has its own advantages and disadvantages. At the same time, thermal regeneration with steam at hot temperatures (800-900 °C) is the most common and economically feasible, which allows restoring the sorption capacity of coal by 80-90%.

It is worth noting that complete or partial replacement of spent coal is often more expedient than its regeneration. Powdered coal is not regenerated.

2.2.4. SORPTION MECHANISM ON ACTIVATED CARBON

There are **two main mechanisms** by which activated carbon (AC) removes impurities from water: **physical adsorption** and **chemisorption**. Physical adsorption is based on the forces of intermolecular interaction — this mechanism removes, for example, organic substances from water. Chemisorption is based on the principle of absorption with the formation of chemical compounds on the surface of a solid body because of chemical reactions. Thanks to chemisorption, chlorine, chloramine, ozone, and some other compounds are removed from water. Chemisorption, unlike physical adsorption, is an irreversible process.

Due to the developed internal surface, AC is capable of effectively removing organic compounds of various nature, as well as some inorganic substances, from water. This is due to its active use in water treatment for discoloration, elimination of unpleasant taste and smell, which can be caused by the presence in water of natural organic compounds, hydrogen sulfide, residual chlorine and its toxic by-products.

AC can also be used at the stage of preliminary preparation to remove impurities from water that are the cause of degradation of ion exchange resins and reverse osmosis membranes, namely, chlorine compounds and humic substances.

In addition, an important feature of AC is its high adsorption activity in relation to a wide range of toxic water pollutants, namely: dioxin, benzopyrene, polychlorinated and polyaromatic carbohydrates, phenol, pesticides, petroleum products, compounds of heavy metals, chlorinated organic substances, etc.

To perform the listed functions, there are a large number of several types of activated carbon. Let's consider the main ones.

Dechlorination of water using AC

The dechlorination process is a combination of reactions with the coal surface and catalysis.

Forms of chlorine presence in water:

$$Cl_2 + H_2O \rightarrow HClO + HCl$$

$$HClO = H^+ + ClO^-$$

Reaction with the coal surface:

$$C^* + HClO \rightarrow CO^* + H^+ + Cl^-$$

Factors influencing the process:

- Temperature - the process proceeds more efficiently when the temperature increases.
- pH - at a low pH, the process is more efficient.
- Organic substances can block the surface of AC.

2.2.5. ACTIVATED CARBON CHARACTERISTICS DETERMINED DURING ASSESSMENT OF PRODUCT QUALITY

Mechanical indicators:

Fractional composition - the classification of grains by size is measured in millimeters and mesh https://www.softwave.com.ua/uk/mesh-size-vugilya-ukr/. Sieve analysis are used to determine the fractional composition.

Bulk density (g/cm³) - the mass of loosely packed coal per unit volume.

Surface area (m²/g) - is the surface area of a solid body divided by its mass.

Mechanical strength (%) - the ability to withstand mechanical loads.

Chemical indicators:

Humidity (%) - the amount of moisture contained in activated carbon.

Ash content (%) - the amount of ash (sometimes considered only water-soluble) in activated carbon.

pH of the aqueous extract - the pH value of an aqueous solution after boiling a portion of activated carbon in it.

Adsorption characteristics:

Iodine index (iodine adsorption, iodine number) (mg/g) - characterizes the content of micropores.

Adsorption by methylene blue, (mg/g) - characterizes the content of mesopores.

Molasses number or index (mg/g) - characterizes the content of macropores.

2.2.6. USE OF ACTIVATED CARBON IN WATER TREATMENT

In water treatment, there are several primary areas of use of AC, namely: filtering water through granular coal, carbonization of water with powdered AC, as well as the use of AB for the production of household cartridges.

Water digestion is used in centralized water treatment or at industrial facilities, for example before the ultrafiltration stage. The process itself does not require large capital expenditures, but at the same time, it is characterized by a high consumption of powdered coal. Water digestion has a number of disadvantages that limit its use: difficulties associated with soaking and dosing coal, the need to have containers for contact of coal with water, as well as settling tanks.

Water filtration through granular coal is widely used both in centralized water treatment and in local. For centralized water treatment, there are two most common schemes for the application of granular AC: adsorption — at the final stage of water purification or post-filtration adsorption and adsorption at the stage of water filtration in fast mechanical filters.

In the case of post-filtration adsorption, filters with granular AC are located after the main stages of traditional water purification. This type of cleaning is used to remove disinfection products, dissolved organic compounds from water, as well as improve its organoleptic indicators. In such a scheme, water of the highest quality is supplied to the AC, which, of course, extends its service life. Regeneration of coal may be necessary only in case of its biological fouling. The use of granular AC in local water purification systems deserves special attention. In this case, AC can be used both in column-type filters of various dimensions and in compact cabinet-type filters.

Moreover, depending on the parameters of the source water, as well as the required quality of the purified water, in local systems of water filtration on AC can be combined with the stages of mechanical purification, softening or complex purification of water. AC is also actively used in household filters for water purification, where it serves as a filler for jug-type filter cartridges, as well as for flow-through filters and backwash systems, including for household reverse osmosis. In household reverse osmosis systems, two types of AC cartridges can be found at once, namely, backfill cartridges and carbon blocks.

2.2.7. CARBON BLOCKS

Recently, the use of **carbon block** cartridges in modern water treatment has become popular, as they have a number of advantages.:

- the carbon block is made of activated carbon granules, the size of which is 7-20 times smaller than in the filling cartridges. This allows you to significantly increase the surface of sorption, contact time with impurities, and, as a result, cleaning efficiency.
- granules in the carbon block are fixed by a binder, which allows you to maintain their stable position relative to each other, therefore the formation of longitudinal channels is physically impossible, and water flows evenly through the porous volume structure.
- certain brands of carbon block cartridges provide the ability to filter tiny particles from 0.5 microns to 10 microns in size. Such cartridges simultaneously purify water from a wide range of chemical pollutants, such as: chlorine, chloramines, pesticides, drugs, radionuclides, organic solvents, oil products, giardia cysts, mercury, lead and improve the organoleptic properties of water (unpleasant taste and smell, turbidity).

Carbon block – is a dense porous cylinder, the surface of which is protected by a layer of non-woven filter material, and plastic covers are provided on the top and bottom to organize the transverse flow of the filtered medium from the outside to the inside through the body of the cartridge and the removal of filtrate from the core through the outlet (**Fig. 2.12**).

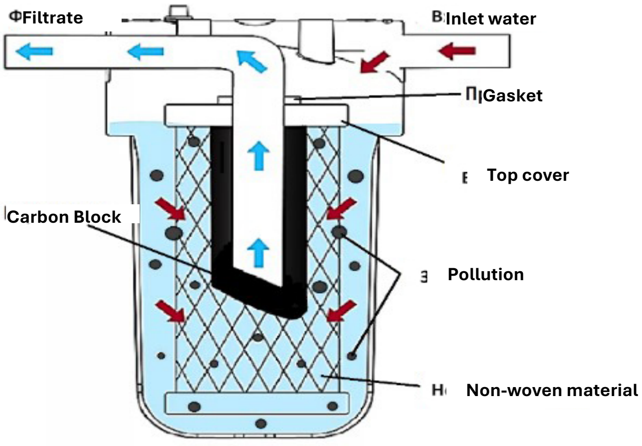

Fig. 2.12. Schematic diagram of the carbon block cartridge

The technology to produce carbon blocks is quite complex, as it requires a balance of various factors and competing processes, namely:

- properties and size of activated carbon particles,
- characteristics of the binder and its mass fraction in the mixture,
- production technology.

To produce carbon block cartridges, two methods are used, known as extrusion technology and compression molding.

In the extrusion technology, a mixture of small granules of activated carbon and a polymer binder, previously prepared in a mixer, is introduced into the loading zone of the worm extruder, where the binder, being transported by a screw along the working cylinder, melts, mixes with coal granules and is squeezed out through a cylindrical matrix. **Compression molding technology** uses a similar principle, namely: pre-mixing activated carbon granules and binder, loading the mixture into a mold, its temperature treatment with melting under pressure, cooling the mold, removing the blanks, trimming the ends if necessary, and assembling cartridge filters. The main advantage of compression molding is the ability to vary the size of the activated carbon granules and binder, as a result of which it is possible to provide different porosity of carbon blocks in the pore size range from 0.5 microns to 20 microns. This method allows the use of a diverse set of thermoplastic binders and finer activated carbon, as well as creating filters that can withstand higher pressure and have better performance and efficiency in water purification.

Considering the noted advantages of carbon block filters, their use in local water treatment is becoming more and more widespread, both as independent elements and those included in reverse osmosis installations.

2.3. CATALYTIC LOADS

Catalytic loadings are natural or artificial materials that contain an oxidation catalyst (in most cases, manganese dioxide - MnO_2) on the surface or in the porous structure of the granules, which creates a catalytic effect in oxidation-reduction reactions, significantly accelerating their course.

Water treatment using catalytic loads is one of the modern technological methods that provide three operations in one filter column with a programmable valve: **oxidation, sedimentation, and sediment filtration**. Most often, they are used to remove iron, manganese, and hydrogen sulfide mainly from water of underground sources.

Classical methods of deironing and demanganization of groundwater, based on aeration followed by filtration, have certain disadvantages in terms of reliability, manufacturability, economic feasibility, and ease of operation. The disadvantages of traditional technologies include limited scope of application (mainly industrial), significant fluctuations in the quality of purified water, large equipment dimensions, etc. These factors stimulated the active development of catalytic loads as the basis for creating fundamentally new efficient, high-performance, and compact water treatment systems.

In modern water treatment, a wide range of catalytic loads based on manganese dioxide is used, starting from natural pyrolusite, and ending with a number of artificial loads. The latest technological innovations make it possible to remove arsenic, radium, uranium, heavy metals, and radionuclides together with manganese, iron, and hydrogen sulfide.

2.3.1. TYPES OF MATERIALS

The most popular catalytic filter materials based on rather light matrices are aluminosilicates, dolomite, natural and artificial zeolites, activated carbon. Examples of such catalytic loads that provoke the rapid formation of an autocatalytic layer of iron and bind manganese (II) can be: Birm, GreenSand, Pyrolox (all manufactured by Clack Corporation, USA).

The main similarity of all these materials is the presence of 3- or 4-valent manganese oxides in their composition, and the advantage is the possibility of regeneration by a reverse flow of water simultaneously with their loosening, which allows you to effectively clean the grains of the load from accumulated contaminants almost throughout the entire height of the layer. Operating experience shows that the natural material pyrolyzite (**Pyrolox**), which consists of 65-85% manganese dioxide, has the best catalytic properties, but at the same time, it has the highest bulk density, and therefore requires a higher water consumption for washing. Materials such as **Greensand** and **Pyrolox** are able to remove hydrogen sulfide, but at high concentrations of the latter it is recommended to use special loads.

KDF-85 (produced by Oceanic Water Systems, USA), which consists of high purity copper-zinc granules, also belongs to catalytic filter loadings. **KDF-85** is a granular material designed to remove chlorine, iron, hydrogen sulfide, and heavy metals from water. It also has bactericidal properties. The difference of this material is its high specific density, which makes it difficult to wash. It is most effective to use it in combination with activated carbon, which allows you to significantly increase the degree of purification, reduce operating and capital costs for water treatment.

To remove iron, hydrogen sulfide and chloramines from water, catalytic granular **activated carbon Centaur** (manufacturer Chemviron Carbon, Belgium) is used. Its catalytic properties are ensured by a controlled activation process, during which all adsorption characteristics are preserved, and catalytic centers are formed.

2.3.2. FEATURES OF THE APPLICATION OF CATALYTIC LOADS

Catalytic loading, despite all the apparent simplicity of their use, is a complex tool for water treatment:

First, for their effective operation, the catalytic surface of the material must remain clean and accessible to polluting components. Therefore, treated water containing enormous amounts of suspended matter, slime-forming bacteria, clay, and large organic molecules must be pre-cleaned of these impurities.

Secondly, unstable groundwater can also inhibit the catalyst layer due to the deposition of hardness salts on it and "weld" the granules together, preventing the filtration and backwashing processes.

Thirdly, low or high pH values, as well as the complete absence of oxygen in deep water, can lead to leaching of the catalyst (as an oxygen donor) and its removal from the catalytic bed into the treated water.

Fourth, all systems that operate on the basis of catalytic oxidation, for example, of iron, with the participation of atmospheric oxygen, are ineffective against organic iron and iron bacteria; moreover, if any form of organic iron is present in the water, an organic film forms on the surface of the granules over time, isolating the access of ions to the catalyst.

In case of unfavorable water composition with high concentration of pollutants, catalytic loadings require technological reagent support by auxiliary oxidants. Therefore, catalytic materials are divided into reagent-free and reagent-based. When using a number of loadings, for example GreenSand, in the regeneration program of the filter column, in addition to backwashing and direct washing, a stage of loading treatment with 0.2-0.3% potassium permanganate solution is introduced. For this purpose, a hardware design of the process is provided, which includes a programmable valve and a tank where the solution is automatically prepared.

Reagent catalytic technologies have significant drawbacks:

- when using them, it is necessary to have not only a catalyst, but also an oxidant;
- they are ineffective against organic iron;
- they do not work at high iron content (more than 10-15 mg/dm^3);
- high linear flushing speeds and large service water flows are required.
- a toxic precursor — potassium permanganate — is used as a regenerating agent.
- the entry of potassium permanganate with wastewater into domestic sewage treatment plants leads to the death of microorganisms and disruption of the operation of septic tanks.
- possible entry of manganese into treated water.
- there are restrictions on the composition of the water being treated.

Returning to reagent-free loadings, it should be noted that treated water, which does not contain atmospheric oxygen and has a low pH, but contains large quantities of impurities such as suspended solids, clay and large organic molecules, hydrogen sulfide and petroleum products, organic iron, and iron bacteria, significantly reduces, and sometimes completely eliminates, the effectiveness of these loadings.

In any case, the choice of the optimal type of loading and the technology of its application, considering the specific composition of the water, depend, first of all, on the experience and qualifications of specialists.

2.4. COMPLEX WATER PURIFICATION

Traditional methods of water purification — filtering it through coal, catalytic sorbents, and ion exchange resin — provide a solution to one problem at one stage. So, passing water through a carbon filter, we remove extraneous odors, organic substances, chlorine; passing through filters with cation exchange material — we make water soft, and filtering it through catalytic loading — we remove iron, manganese, hydrogen sulfide. Each of these methods of water purification effectively copes with one problem. But the water after each of these filters, as a rule, does not become completely clean. If several impurities are found in the water, several filters must be installed. This option for solving the problem requires a lot of space, investments, and, of course, each of the filters in the scheme requires personal service.

That is why in the field of water treatment, filters for complex water purification with multifunctional filter loads have appeared and are becoming more and more in demand. Their use ensures the solution of several problems in one device, which allows, without losing cleaning efficiency, to reduce the dimensions of the installation and simplify its maintenance.

There are several different products right now designed to simultaneously remove a number of impurities (hardness compounds, iron, manganese, ammonium and organic matter) in a single filter that is regenerated with a sodium chloride solution.

These products can be conditionally divided into three groups:

- materials based on zeolites (Crystal Right, USA),
- materials that are **mixtures of standard ion exchange resins** produced by many different companies,
- materials based on modified ion exchange resins (**Ecomix**, LLC "Ecosoft" Ukraine).

Each group has its own characteristics:

Zeolites effectively soften water and remove dissolved and oxidized iron from but leave organic iron untouched. In addition, they do not remove organic substances, but are poisoned by them, just like by hydrogen sulfide. The service life of the material is 1-2 years. Consumption of sodium chloride for regeneration is 130 g per 1 liter of loading.

Materials based on standard ion exchange resins, which can consist of a mixture of different types of cations or cationite and anionite. They tend to soften water and remove iron, but quickly get poisoned. Usually, after 20-30 regenerations (about 6 months of operation), such materials lose up to 30% of their capacity and, therefore, the duration of the filter cycle. Their service life is no more than 2 years. To extend it, manufacturers recommend regularly washing the material with acid reagents. The removal of manganese by most of these materials is not efficient enough and threatens to increase its concentration at the end of the filter cycle to a level that exceeds the original. Consumption of sodium chloride for regeneration is 140-160 g per 1 liter of loading.

Ecomix — a multi-component filter material consisting of five original components that have ion exchange, sorption, and filtration properties **(Fig. 2.13).**

The material is intended for cleaning well and tap water. It effectively removes all forms of iron, manganese, and organic pollution from water, softens water and retains ammonium. All these processes occur simultaneously in one stage and in one filter **(Fig. 2.13)**. The material is easy to use — works in standard water softeners, is regenerated with a solution of tableted salt, and does not require special reagents or equipment. The service life of the material is 5-10 years. Consumption of sodium chloride for regeneration is 100 g per 1 liter of loading.

Fig. 2.13. Ecomix multi-component filter material

As can be seen from **Figure 2.13**, Ecomix includes a special sorbent based on modified Ferrosorb ionite for removing iron and manganese compounds **(Fig. 2.14)**.

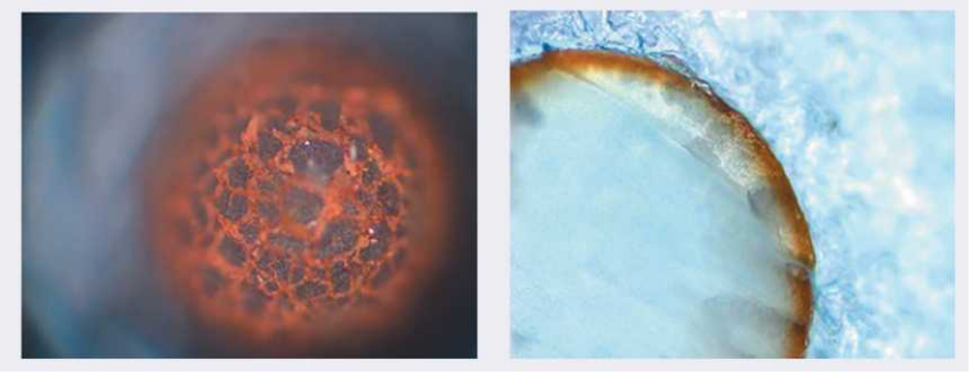

Fig. 2.14. Photomicrographs of granules of the Ferrosorb component

The presence of **Ferrosorb** in Ecomix provides effective removal of iron compounds throughout the service life. The permissible iron content for Ecomix in the source water is **15 mg/dm^3** — one of the highest materials for iron removal. Moreover, Ecomix is the only comprehensive loading to remove both dissolved inorganic and organically bound iron, as well as one of the most reliable materials for reducing manganese, which always accompanies iron in water.

To remove organic substances and reduce the color of water in Ecomix, modified ionite **Humisorb** is used **(Fig. 2.15).**

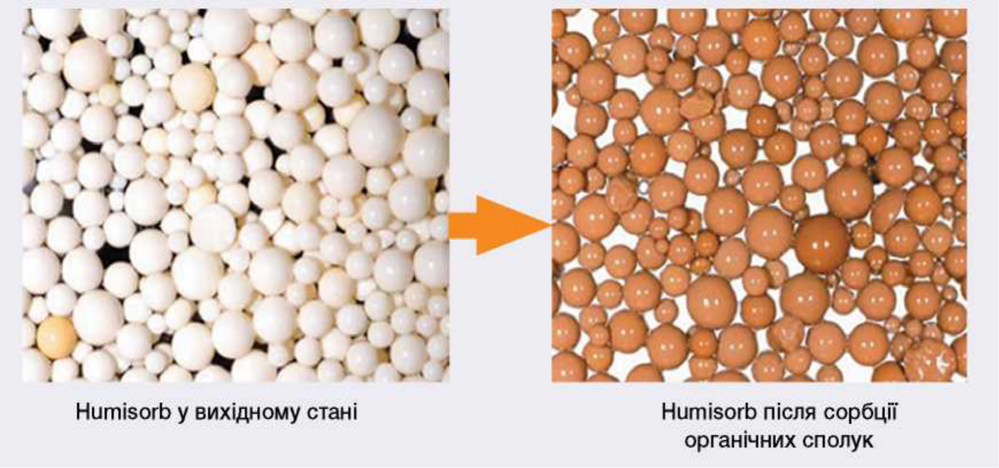

Fig. 2.15. Photomicrographs of Humisorb component granules

The Ecosoft company produces several brands of material for water purification with different contents of organic substances: **Ecomix A** (for water with an oxidizability of no more than 15 mgO_2/dm^3), **Ecomix C** (for water with an oxidizability of no more than 20 mgO_2/dm^3) and **Ecomix P** (for water with an oxidizability of no more than 3 mgO_2/dm^3). Depending on the required degree of oxidation reduction, the user chooses the required Ecomix brand. The effectiveness of reducing the values of other water quality indicators is

the same for Ecomix A, Ecomix C and Ecomix P.
It should be noted that all existing downloads for complex water treatment do not provide for the possibility of water disinfection, therefore they should be used only for additional treatment of tap water or water treatment from deep underground sources.