UDC 644.6:541.183 **DOI: 10.31652/2786-6033-2023-2(4)-33-37**

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THE USE OF SPENT SORPTION MATERIALS FOR THE TREATMENT OF FOOD INDUSTRY WASTEWATER

A significant number of sorbents used in the food industry are not reused due to the complexity of their regeneration and significant material costs. They are often stored on the territory of the enterprise or taken to landfills, usually without authorization. Today, it is important to study the regeneration and reuse of sorbents used in food production. It is promising to use sorbents previously used at the stage of water treatment or preparation of technological solutions and regenerated in wastewater treatment, in particular, in the same food production facilities and in other industries where wastewater contains organic substances.

The article investigates the reuse of a spent sorbent mixture consisting of activated carbon and kieselguhr for the treatment of wastewater from dairy processing enterprises. The results of experimental studies of the dynamics of ion exchange adsorption of lactic acid and alanine by mixed sorbent and spent sorbent under periodic conditions are given. According to the results of the study, the difference in cleaning efficiency for the two options is insignificant and amounts to about 3%, which is within the experimental error.

It is shown that the sorption of pollutant components of wastewater of milk processing enterprises by cheap sorbents, which include regenerated sorbents, is one of the most promising because of their high efficiency, low cost of treatment, and the possibility of further use of spent sorbents in agriculture.

Keywords: sorption, mixed sorbents, organic pollutants.

Introduction. The food industry is one of the largest water consumers. The preparation of food and drinks is inextricably linked to the use of clean water. The quality of water used in the food industry is subject to careful monitoring. Moreover, each area of the industry must operate on the basis of both industry standards and specific regulations. This is the only way to ensure the required taste, odor, appearance, and internal content. Water treatment technologies that are relevant to the food industry include settling, coagulation, flocculation, flotation and biochemical treatment, disinfection, and electrodialysis. Water treatment in food production may involve several stages. Adsorption is often used for water treatment, in particular, water softening. For example, in the production of soft drinks, activated carbon filters are used to treat water, which can reduce the content of organic compounds and inorganic salts in drinking water. In beer production, water is softened by adsorption on zeolites.

A lot of food additives of synthetic origin (e.g., sodium benzoate, citric acid) cause undesirable coloration or turbidity of the product. The production process does not always allow for boiling to eliminate this drawback, as this often results in a loss of food value. In this case, activated carbon adsorption is most often used.

Sorption processes are widely used in the food industry. The quality of food products and technological schemes of their production always have special requirements, which are clearly regulated by the relevant documents. Accordingly, the sorption materials used in food production have the highest quality parameters, the content of impurities in them is minimal, and therefore the cost of such materials is higher compared to adsorbents used in other industries.

The peculiarity of food production technologies is that the technological scheme always clearly stipulates not only the type of sorbent, but also its brand, dispersion, origin, and even the manufacturer. For example, sorbents are used to clarify sugar syrups, malt mixtures, refine edible oils, reduce acidity and eliminate unwanted color (Table 1). It is worth noting that activated carbon is most often used in food production, while a mixture of activated carbon and other, cheaper sorbents such as kieselguhr, zeolite, and glauconite is used to reduce the cost of the adsorption material.

Table 1

Characterization of individual adsorbents and their application in the food industry

Technological process	Adsorption material
Purification of water-sugar solutions in the beverage industry	Kieselguhr brands Bekogur 3500 and Bekogur 200 activated carbon, synthesized from wood (for example, Dekolar A)
Clarification of sugar syrup before concentration	Activated carbon synthesized from wood (for example, BAU-A) and thermally activated glauconite
Purification of edible oils	Activated carbon is synthesized from walnut shells (for example C WZ-22)
Reducing acidity of dairy products	Zeolite CPPS and thermally activated glauconite
Removal of unwanted color (whey, milk, low-alcohol beverages)	Activated carbon synthesized from coconut shells (for example, Norit DLC SUPER 30)
Softening of drinking water	Crushed stone and sand from natural zeolite of the Sokyrnytsky deposit

Among the conventional treatment methods, adsorption processes are widely used to achieve effective removal of dyes from industrial wastewater [1-4].

Adsorption processes are widely used in food technology, not only in the preparation of raw materials and water, but also in the treatment of wastewater. These processes are among the most effective methods of cleaning water from organic matter pollution.

Solid sorbents are used for various processes which differ in certain patterns. Such processes include physical adsorption, chemisorption, ion exchange, chromatography, etc. Various synthetic and natural solids sorbents are used for adsorption processes. Choice sorbent is determined by its sorption capacity, selectivity, and cost. Recently, natural and modified sorbents - zeolites, bentonites, kieselguhr and activated carbon were widely used [1,3] for wastewater treatment.

An important advantage of these methods is possibility of regeneration of sorbents and their reuse [2].

The use of traditional activated carbon (AB) is the most common in adsorption processes, but it is quite expensive. Many studies have been conducted to investigate the adsorption properties of low-cost adsorbents such as peat, bentonite, steel mill slag, porcelain clay, corn residues, wood chips, and silica [1]. However, these inexpensive adsorbents usually have low adsorption capacity and require large amounts of adsorbent to effectively treat wastewater. To date, in order to reduce the cost of AB, it is most often used in a mixture with clay natural or modified sorbents, or food industry waste [4].

Wastewater from food processing plants is a highly concentrated microbiological contaminant. The technical solutions used today to treat them are ineffective due to their low technical level, or they are costly and lead to a significant increase in production costs.

Wastewater from dairy processing plants is characterized by a high content of dissolved organic matter, characterized by COD (chemical oxygen demand) in the range of 2000 - 60,000 mg O_2/dm^3. Law prohibits disposal of such wastewater into sewerage networks, and its accumulation on filtration fields leads to the formation of toxic substances.

Currently, adsorption methods using natural and synthetic sorbents are widely used for wastewater treatment, which makes it possible to regenerate and reuse them. The availability of natural porous materials in our region that have filtering properties and are able to adsorb suspended and dissolved components in water with the pore surface makes it possible to use them effectively for wastewater treatment of dairy processing plants, which confirms the relevance of certain studies [5]. At the same time, the use of activated carbon is considered the most effective for removing organic matter from wastewater, but due to the high cost of such an adsorbent, its use for wastewater treatment is limited. A significant number of sorbents used in the food industry are not reused, due to the complexity of their regeneration and significant material costs. In addition, the reuse of used sorbents requires their biological treatment, which is due to the specifics of the adsorbed substances. Therefore, they are often stored on the territory of the enterprise or taken to landfills, usually without authorization. More promising is the use of such sorbents in wastewater treatment, in particular, in food production and other industries where wastewater contains organic substances.

The purpose of the research is to investigate the possibility of reusing a spent sorbent mixture for wastewater treatment at dairy processing plants.

Experimental part. The regeneration of the spent mixed sorbent, consisting of activated carbon (BAU-A) and kieselguhr (K) of Bekogur 200 grade in a mass ratio of 1 : 3, was carried out as follows:

- At the first stage, the regeneration of the mixed sorbent was carried out in a hydrodynamic mode at a mass ratio (sorbent): H_2O = 1 : 4, process temperature 50-60°C for 45-60 min.
- The mixed sorbent was boiled stepwise in a 1 % NaOH solution for 45-60 min and a 4 % HCl solution for 45-60 min, followed by filtration, washing with distilled water to pH = 7, and drying.

The efficiency of regeneration was determined by the ability of the spent sorbent to absorb the main pollutants of dairy wastewater.

The main pollutants of wastewater are:

- lactic acid (α-oxypropionic acid);
- milk proteins (mostly water-soluble, albumin)
- molasses;
- orphan;
- fats;
- lactose;
- synthetic organic substances that cause coloration of wastewater (sodium benzoate, salts of citric and malic acids, etc.);
- phosphorus half.

For the study, were used model solutions containing lactic acid at a concentration of 0.002 mg/dm^3 and alanine (modeling the content of water-soluble proteins) at a similar concentration. It was investigated the process of sorption of oxypropionic acid and alanine by regenerated mixed sorbent (variant 2), mixed sorbent consisting of activated carbon (BAU-A) and kieselguhr (K) of Bekogur 200 brand (variant 1). The study of the sorption process of α-oxypropionic acid and alanine by a mixed sorbent under dynamic conditions was carried out in a column-type apparatus. The work was carried out on an installation (Fig. 1), which operates according to the following scheme: the model solution flows from the separating funnel 1 into the adsorption column with zeolite filling 2. The sorbent is poured onto a grate 3 covered with low-density filter paper (black tape). The filtration rate is regulated by the tap 4 on the dividing funnel 1 and the tap of the column apparatus should be fully open. The filtrate was collected in a container 5 at regular intervals and analyzed. The minimum height of the sorbent layer was at least 7cm [6].

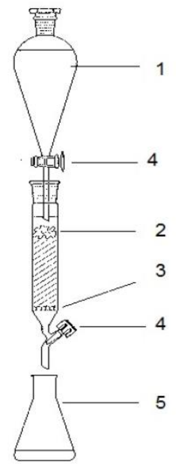

Figure 1. Schematic of the experimental setup:
1 – separating funnel with eluent;
2 – mixed sorbent;
3 – grate;
4 – faucet;
5 – receiver for collecting fractions

The lactic acid content was determined by potentiometric titration, and the amino acid content was determined by the photocolorimetric method based on the ability of peptide bonds (- CO-NH-), carboxyl and amino groups to form colored complex compounds with copper sulfate in alkaline medium. Solutions of amino acids and proteins give a blue-violet color [7].

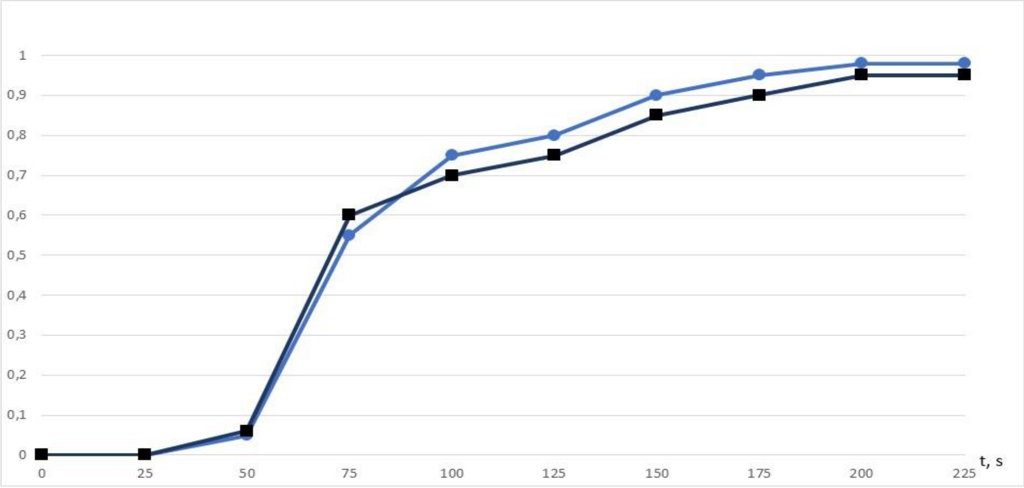

Figure 2. Sorption curves of α-oxypropionic acid depending on the sorbent:
● - fresh mixture of activated carbon and kieselguhr (variant 1)
■ - spent and regenerated mixture of activated carbon and kieselguhr (variant 2)

The curves of lactic acid sorption by the mixed sorbent are shown in Fig. 2. It is obvious from the data that under the conditions of this hydrodynamic regime of the adsorption process of α-oxypropionic acid on the selected sorbent, a mixed-diffusion adsorption mechanism takes place. We observe a plateau in the time space of 100-150 s. At the same time, the efficiency of the spent and regenerated sorbent practically does not differ from the fresh mixture of activated carbons of kieselguhr.

According to the results of the study, the maximum degree of purification for option 1 is somewhat higher; amounting to 98%, but the difference in the efficiency of purification for the two variants is insignificant, amounting to about 3%, which is within the error of the experiment. The maximum degree of purification for the home variants is achieved in the same time interval - in 200 seconds.

Experimental data on the kinetics of alanine adsorption are shown in Fig. 3. The plateauing at time >15 min of sorption indicates the transition of the adsorption process to the internal diffusion region and to the equilibrium state. At the same time, it is observed that the sorption efficiency is somewhat higher when using a fresh mixture of activated carbon and kieselguhr, but the difference in the purification efficiency for the two variants is insignificant (99% for variant 1 and 96% for variant 2), amounting to 3%, which is within the error of the experiment. The maximum degree of purification is achieved in the same time intervals for the home variants, it occurs after 175 seconds.

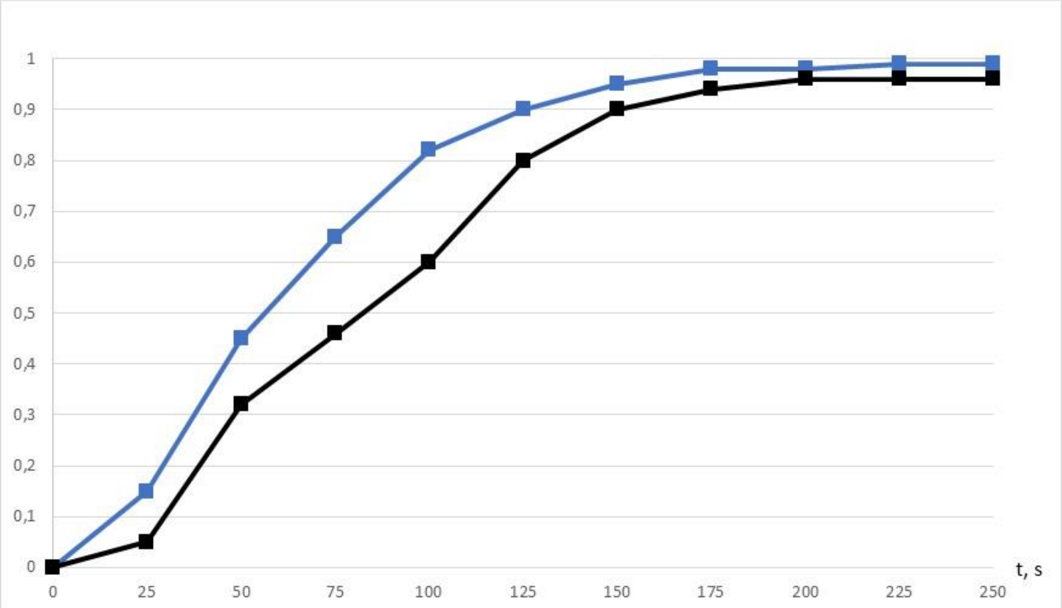

Figure 3. Sorption curves of alanine depending on the sorbent:
● - fresh mixture of activated carbon and kieselguhr (variant 1)
■ - spent and regenerated mixture of activated carbon and kieselguhr (variant 2)

Therefore, it can be argued that chemical regeneration of the spent sorbent mixture containing diatomaceous earth and activated carbon allows the use of waste materials at the stage of wastewater treatment of food production and provides the necessary extraction of pollutants of organic origin.

Conclusions. The effectiveness of regeneration of the spent mixed sorbent was determined, when it was sequentially purified from organic impurities after clarification of technological solutions by treating it with 1,25 % NaOH solution or sequential treatment with 1 % NaOH solution and 4 % HCl solution with the restoration of the sorption capacity of such a sorbent to 97-100 %. The activity of the regenerated mixed sorbent towards the main components of wastewater from dairy processing enterprises was investigated.

The research shows that the sorption of pollutant components of dairy processing enterprises by cheap sorbents, including regenerated sorbents, is one of the most promising due to their high efficiency, low cost of treatment, and the possibility of using spent mixed sorbents as fertilizers, soil structure improvers, and feed mixtures.

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Review received 31.05.2023