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REUSE OF THE SPENT SORBENT MIXTURE FOR WASTEWATER TREATMENT

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Abstract. Much of the sorbent used in the food industry is not re-used because it is difficult to regenerate and expensive. Also, the reuse of used sorbents involves their biological cleaning, which is due to the specificity of adsorbed materials. As a result, they are often stored off-site or disposed of in landfills, usually without authorization. It is more promising to use such sorbents in waste water treatment, especially in the same food industry and in other industries where wastewater contains bioorganic substances. Studies have been made on the reuse of a used sorbent mixture, consisting of activated carbon and kieselguhr, for the treatment of wastewater from food processing plants. It has been determined the efficiency of the regeneration of the used sorbents, when it is successively cleaned from organic impurities after purification of technological solutions by its successive treatment with an alkali solution and then with a solution of hydrochloric acid, with the recovery of the sorption capacity of such a sorbent to 97–100 %. The activity of the regenerated mixed sorbent with respect to the main components of the wastewater from dairy has been studied. The research results show that the mixture of sorbents has a higher sorption capacity regarding to lactic acid with a higher cleaning efficiency; however, when removing the protein pollutant, it is possible to pump more effluent before the first traces of the pollutant appear. It is shown that the sorption of components – pollutants of the milk processing industry by affordable sorbents, which include regenerated ones, is among the most promising due to their high efficiency, low cost of cleaning, and the possibility of further use of used sorbents in agriculture.

Keywords: sorption, mixed sorbents, activated carbon, kieselguhr, bioorganic pollutants.

1. Introduction

The relevance of the work is due to the need to dispose of waste materials for water treatment on the one hand, and to improve water purification technologies on the other hand, in particular by regenerating and reusing such materials. This, in turn, paves the way for the creation of sustainable, efficient and environmentally safe water purification technologies to provide the population with clean water for various needs and preserve water resources (Bordun et al., 2022).

Pollution of surface waters by organic substances and organic matter from wastewater from food production is a significant environmental risk. These substances enter water bodies, cause the development of disruption of the natural balance of water bodies, eutrophication and have a eutrophication, and have a negative impact on flora and fauna (Malovanyy et al., 2016).

Therefore, improvement and creation of conceptually new methods of water treatment and waste water treatment in the food industry is an urgent scientific task of today.

Water treatment in food production can involve several stages. Water treatment in food production

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(particularly dairy) can involve several stages. Adsorption is often used to treat drinking water, especially for its softening. Thus, in the production of soft drinks, filters with activated charcoal are used for water preparation, which can reduce the content of bioorganic compounds and inorganic salts in drinking water. In the production of beer, its adsorption on zeolites is used to soften water.

Many food additives of natural and synthetic origin (e.g., sodium benzoate, citric acid, caramel) cause unwanted color or turbidity of the product. The technological scheme of production does not always allow the application of boiling to eliminate this drawback, because very often then we lose the value of the food product. In this case, adsorption on charcoal is most often used.

The quality of food products and the technological schemes of their production are subject to specific requirements, which are set forth in relevant documents. In line with these specifications, the sorption materials used in food production are of the highest quality, with minimal impurity content. Consequently, the cost of such materials is higher than that of adsorbents used in other industries. (Tymchuk et al., 2020).

The most common substance used in adsorption is traditional activated carbon, of such industries, but it is quite expensive. Many studies have been conducted to investigate the properties of sorption of inexpensive adsorbents such as peat, bentonite, metallurgical slag, china clay, corn processing waste, wood shavings, and silica (Toth et al., 2022). However, these inexpensive adsorbents have, as a rule, have unsatisfactory adsorption capacity or require the use of a large amount of sorbent for effective wastewater treatment. Today, in order to reduce costs, activated charcoal is most often used in a sorbent mixture with natural clay or modified sorbents, or food industry waste.

A significant number of sorbents used in the food industry are not reused, largely due to the technical challenges associated with their regeneration and the high cost of the materials involved. Also, the reuse of spent sorbents involves their biological cleaning, which is due to the specificity of adsorbed substances. It is common practice to store these items outside the territory of the enterprise, or to take them to landfills without permission.

In this case, there is a demand in searching of such sorbents that would be economically attractive, synthesized from readily available raw materials, and at the same time possess high efficiency as adsorbents. The reuse of sorbents that were previously used at the stage of water treatment or preparation of process solutions may be promising, in particular, in the food industry, as well as in other industries where wastewater contains bioorganic substances (Soloviy et al., 2020). The main direction of the aquatic environment protection in industry is the transition of enterprises to work on a closed-loop water supply scheme, when the company after the treatment of its own wastewater reuses it in the technological cycle, and polluted and untreated wastewater does not enter reservoirs (Tymchuk et al., 2020).

The purpose of the work is to evaluate the effectiveness of the regeneration of mixed sorbents and their reuse for wastewater treatment of milk enterprises.

2. Materials and Methods

We proposed the regeneration of a used combination of sorbents consisting of activated carbon (BAU-A) and kieselguhr (Bekogur 200) in a mass ratio of 1:3. Previously, these two sorbents were used to purify sugar syrups in the industrial of soft drinks production. Purification is carried out by passing the syrup through four filters made of non-woven materials on which a monosorbent is applied. At the end of each cycle, the sorbents are replaced with fresh ones, and the resulting mixture is stored at a non-industrial site for disposal.

Regeneration of the mixture of sorbents was carried out as follows:

– At the first stage, washing was carried out in hydrodynamic mode at a mass ratio (mixture): water = 1:4, process temperature 40 °C for 60 minutes.

– The mixed sorbent was gradually boiled in NaOH or KOH solution for 60 min and HCl or HNO_3solution for 60 min, process temperature 40 °C. The next step is to perform filtration and washing with distilled water.

– If necessary, additionally washed with distilled water to pH = 7 and drying (Ranskiy et al., 2019).

The sorption capacity by methylene blue was determined according to the standard method of determining the limit of adsorption by the photometric method (λ= 640 nm) (Hyvljud et al., 2014). The relative sorption capacity was determined by preliminarily determining the 100 % sorption efficiency of activated charcoal (sample 2). The results of the research are presented in Table 1.

Table 1

Sorption capacity of mixed sorbents

Sample No.	Name of the sorbent	A_{max}, mg/g	Specific sorption capacity, %
1	Mixed sorbent: activated charcoal + kieselguhr	235.2	88.9
2	activated charcoal	280.2	100.0
3	kieselguhr	165.8	
4	Used mixed sorbent: activated charcoal + kieselguhr	85.5	30.5
5	Used and regenerated mixed sorbent: activated charcoal + kieselguhr	228.7	88.4

According to research results, the use of sorbent mixture (option 1), and even more so only kieselguhr (option 3), is less effective than activated carbon, but taking into account the economic factor, it is acceptable to use such a mixture for adsorption technological processes. In regeneration (sample 5) it is possible to achieve almost full initial sorption capacity, and considering that we are actually regenerating waste, the use of such products is quite promising for water treatment.

The sequential regeneration and activation of the spent a sorbent mixture was carried out by stepwise washing with water, alkali and mineral acid according to the defined conditions and reagents given in Table 2. This table also illustrates the maximum sorption capacity of each regeneration option (Sakalova et al., 2024).

Table 2

Conditions and results of mixed sorbent regeneration

Sample No.	Mass fraction of the solution, %												Specific sorption capacity, %
	KOH			NaOH			HCl			HNO_3			
	0.5	0.75	1.0	0.5	0.75	1.0	0.5	0.75	1.0	0.5	0.75	1.0	
1	–	–	–	–	+	–	–	+	–	–	–	–	88.4
2	+	–	–	–	–	–	–	–	–	+	–	–	87.7
3		–	–	–	+	–	–	–	–	–	+	–	92.0
4	+	–	–	–	–	–	–	–	+	–	–	–	88.4
5	–	+	–	–	–	–	–	–	+	–	–	–	90.6
6	–	–	+	–	–	–	–	–	–	+	–	–	92.1
7	–	–	+	–	–	–	–	–	–	–	+	–	95.3
8	–	–	–	+	–	–	–	–	+	–	–	–	88.4
9	–	–	–	–	–	+	+	–	–	–	–	–	91.9
10	–	–	–	–	–	+	–	+	–	–	–	–	92.0
11	–	–	+	–	–	–	–	–	+	–	–	–	99.0
12	–	–	–	–	–	+	–	–	+	–	–	–	98.5
13	–	–	+	–	–	–	–	–	–	–	–	+	100.0
14	–	–	–	–	–	+	–	–	–	–	–	+	100.0

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

The main polluting components of wastewater are:

– bioorganic substances: lactic acid (2-hydroxypropionic acid); milk proteins (mainly water-soluble, albumins); serum; fats; lactose;

– synthetic organic substances that cause the color of wastewater (sodium benzoate, salts of citric, malic acids, etc.);

– phosphorus compounds.

Model solutions containing lactic acid with a concentration of 0.002 mg/dm^3 and alanine (modeling the content of water-soluble proteins) with a similar concentration were used for the study. The process of sorption of lactic acid and alanine by a regenerated mixed sorbent (option 2), a mixed sorbent consisting of activated charcoal (BAU-A) and kieselguhr (Bekogur 200) (option 1) was investigated.

The study of the process of sorption of lactic acid and alanine by a mixed sorbent under dynamic conditions was carried out in a column-type apparatus. The work is carried out on the apparatus (Fig. 1), which works according to the following scheme: the model solution flows from the separatory vessel 1 into the adsorption column with the adsorbent 2. The sorbent is poured onto the grid 3, which is covered with low-density filter paper (black tape). The filtering speed is regulated by the tap 4 on the dividing funnel 1, and the tap of the column apparatus must be fully open. The filtrate was collected at specified time intervals in container 5 and analyzed. The minimum height of the sorbent layer was at least 7 cm (Soloviy et al., 2020).

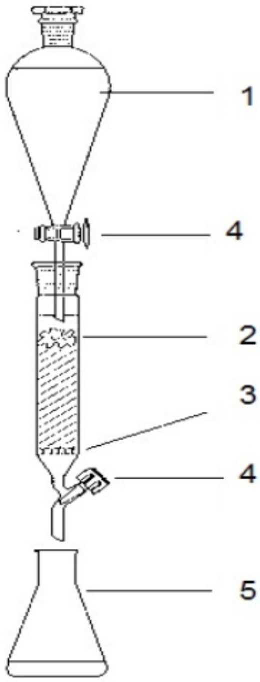

Fig. 1. Scheme of the experimental apparatus:
1 – separatory vessel with eluent;
2 – mixed sorbent;
3 – grid;
4 – tap;
5 – container for collection of fractions

Determination of the lactic acid content was carried out by the potentiometric titration method, and the amino acid content was determined by the photocolorimetric method, which is based on the ability of peptide bonds (–CO–NH–), carboxyl and amino groups to form colored complex compounds with copper sulfate in an alkaline medium. Solutions of amino acids and proteins give a blue-violet color (Hyvljud et al., 2019).

3. Results and Discussion

The sorption curves of lactic acid by the mixed sorbent are shown in Fig. 2. It can be seen from the given data that under the conditions of this hydrodynamic mode of the process of adsorption of *α*-oxypropionic acid on the selected sorbent, a mixed-diffusion mechanism of adsorption takes place. Reaching the plateau is observed in the time space of 100–150s. At the same time, the effectiveness of the used and regenerated sorbent practically does not differ from a fresh mixture of charcoal and kieselguhr.

According to the results of the study, according to option 1, the maximum degree of purification is slightly higher and is 98 %, but the difference in the efficiency of purification according to the two options is insignificant and is about 3 %, which is within the experimental error. The maximum degree of cleaning for both options is achieved in one time interval – in 200 seconds.

Experimental data on the kinetics of alanine adsorption are shown in Fig. 3. Reaching the plateau at τ>15 minutes of sorption indicates the transition of the adsorption process into the internal diffusion region and into the equilibrium state. At the same time, we observe a slightly higher sorption efficiency when using a fresh mixture of activated charcoal and kieselguhr, however, the difference in the purification efficiency according to the two options is insignificant (99 % according to option 1 and 96 % according to option 2), it is 3 %, which is within the experimental error. The maximum level of purification is achieved in the same time intervals according to both options, it occurs after 175 seconds.

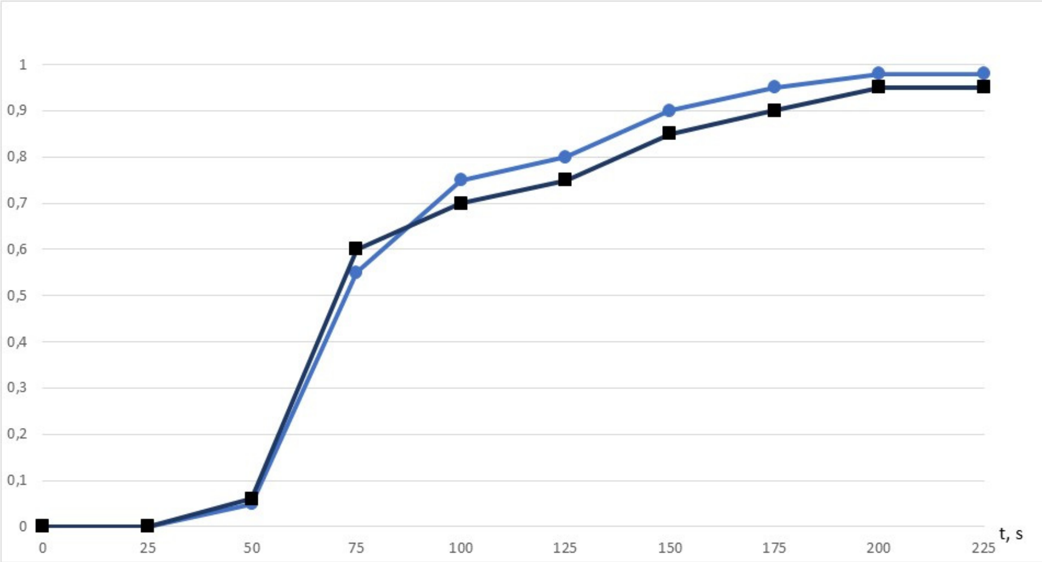

Fig. 2. Sorption curves of lactic acid depending on the sorbent:
● – fresh mixture of charcoal and kieselguhr (option 1);
■ – used and regenerated mixture of activated charcoal and kieselguhr (option 2)

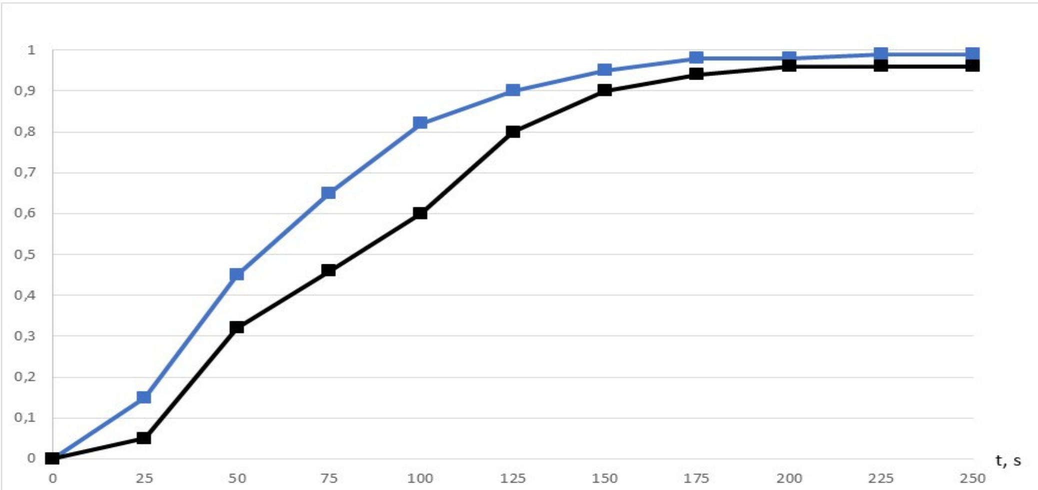

Fig. 3. Alanine sorption curves depending on the sorbent:
● – fresh mixture of charcoal and kieselguhr (option 1);
■ – used and regenerated mixture of activated charcoal and kieselguhr (option 2)

The calculated data of the adsorption efficiency of alanine and lactic acid by mixtures of sorbents are presented in Table 3. According to the option 1, a mixture of pure activated charcoal and kieselguhr in a mass ratio of 1:3 was used. According to option 2 the regenerated mixture was used.

The research results show that the mixture of sorbents has a higher sorption capacity for lactic acid with a higher purification efficiency; however, when removing the protein pollutant, it is possible to pump more effluent before the first traces of the pollutant appear. When comparing the efficiency of mixtures of options 1 and 2, it is worth noting that the efficiency of their use is almost the same, the deviation of the corresponding indicators in most cases is within the experimental error.

Thus, we can state that the chemical regeneration of the used mixture of sorbents containing kieselguhr and activated charcoal allows the use of used materials at the stage of wastewater treatment of food industries and ensures the necessary removal of pollutants of organic origin.

Table 3

Sorption efficiency indicators for different mixtures of sorbents

Sample No.	A_{max}, mg/g	*Specific sorption capacity, %	The first traces of the pollutant in the purified solution, sm^3/sm^3	Effective volume (V_{eff}), sm^3/sm^3	Dynamic exchange capacity (T)	α, %	
						a_{max}	$\bar{a}$
Lactic acid							
1	140	98	1.1	4.3	0.005	95.9	83.2
2	136	92	1.3	5.0	0.012	97.8	80.2
Alanine							
1	128	99	1.9	8.0	0.018	95.7	79.3
2	122	97	1.6	6.9	0.019	95.9	76.2

* The specific sorption capacity for individual pollutants was determined using pure activated charcoal BAU-A.

4. Conclusions

It has been determined the efficiency of the regeneration of the used mixed sorbent, when it is successively cleaned from organic impurities after purification of technological solutions by its successive treatment with an alkali solution (KOH or NaOH) and then an acid solution (HCl or HNO_3), with the recovery of the sorption capacity of such a sorbent by methylene blue to 97–100 %. The activity of the regenerated mixed sorbent regarding to the main components of wastewater of milk processing enterprises has been studied.

The work shows that the sorption of the components – pollutants of the milk industry enterprises with cheap sorbents, which include regenerated ones, is among the most promising due to their high efficiency, low cost of purification, the possibility of using used mixed sorbents as fertilizers, soil structure improvers and feed mixtures.

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