Physical and Chemical Features of Aqueous Media Treatment Process from Components of Cow Milk with a Milled Waste of Corn

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Abstract. The effluent treatment process for dairy waste water adopts physicochemical methods with adsorption playing a significant role in removing organic chemical contaminants. Corn waste, due to their abundance and large volumes, often attract the attention of environmental researchers. It is known that corn is an effective sorbent in the purification of aqueous media from oil products and dyes. In this work, there are researches of the physical and chemical characteristics of aqueous media treatment process from the components that are the part of the drainage of milk processing plants (lactic acid and asparagine) with ground thermal modified corn waste. It has been established that the obtained sorption material effectively extracts various components of sewage from milk processing plants. Extraction of asparagine occurs more efficiently than lactic acid, so for the amino acid, 91% efficiency is achieved, for lactic acid 78%. When the amount of pollutant in the range of COD values 305–320 mgO/dm³, the rational weight of the sorption material additive is 6 g/dm³.

1. Introduction

Milk is a very important food for mankind, so milk processing plants are distributed around the world. Dairy enterprises are one of the largest consumers of fresh water and sources of significant amounts of sewage. Specific consumption of drainages from dairy plants averages 5–7 m³ per 1 ton processed milk, but often, especially in factories with outdated technology, this indicator is much higher [1, 2].

The most common components of sewage of dairy enterprises are lactose, milk proteins (casein, β-lactoglobulin, α-lactalbumin), milk fat and their oxidation products [3–6].

In the table 1 range and average composition of dairy factory wastewater are presented [7].

In the table 2 the sources of dairy industry wastewaters are presented [7, 8].

Such drainages represent a great danger to water bodies. The organic components in dairy processing were very high biodegradable. In waterways, bacteria will consume the organic components of the waste. The active multiplication of microorganisms and the oxidation of sewage components by them lead to a sharp decrease in the level of dissolved oxygen in the water, which causes oxygen starvation in fish and other inhabitants of aquatic systems and is the occasion of their death. Common techniques for treating dairy industry wastewaters include grease traps, oil water...
separators for separation of floatable solids, equalization of flow, and clarifiers to remove suspended solids. Dairy wastewaters are generally treated using biological methods [9–11].

Table 1. Range and average composition of dairy factory wastewater.

| Component        | Range (mg/dm³) | Average (mg/dm³) |
|------------------|----------------|------------------|
| Suspended solids | 24–5,700       | –                |
| BOD5             | 450–4,790      | 1,885 *          |
| Nitrogen         | 15–180         | 76               |
| Phosphorus       | 11–160         | 50               |
| Sodium           | 60–807         | –                |
| Chloride         | 48–469         | 276              |
| Calcium          | 57–112         | –                |
| Magnesium        | 25–49          | –                |
| Potassium        | 11–160         | 67               |
| pH               | 4–12           | 7.1              |

*average yield loss (that is, wastage <2%)

Table 2. Sources of waterborne waste.

| Product processing stages | Sources of waste                  | Product processing stages | Sources of waste                  |
|--------------------------|-----------------------------------|--------------------------|-----------------------------------|
| Market milk              | ○ foaming                         | ○ Butter making          | ○ vacreation and salt use         |
|                          | ○ product washing                 |                         | ○ produce washing                 |
|                          | ○ cleaning operations             |                         | ○ cleaning operations             |
|                          | ○ overfilling                     |                         |                                  |
|                          | ○ poor drainage                   |                         |                                  |
|                          | ○ sludge removal from clarifiers/ Separators |               |                                  |
|                          | ○ leaks                           |                         |                                  |
|                          | ○ damaged milk packages           |                         |                                  |
|                          | ○ cleaning of filling machinery   |                         |                                  |
| Cheese making            | ○ overfilling vats                | ○ Powder manufacture    | ○ spills of powder handling       |
|                          | ○ incomplete separation of whey from curd |             | ○ start-up and shut-down          |
|                          | ○ using salt in cheese making     |                         | ○ plant malfunction               |
|                          | ○ spills and leaks                |                         | ○ stack losses                    |
|                          | ○ cleaning operations             |                         | ○ cleaning of evaporators and driers |
|                          |                                   |                         | ○ bagging losses                  |

However, large fluctuations in the composition and concentration of pollutants of sewage lead to failures and "breakthroughs" with the use of only biological methods of purification, so treatment of dairy drainages requires additional steps.

The effluent treatment process for dairy waste water adopts physicochemical methods with adsorption playing a significant role in removing organic chemical contaminants [9, 12]. Natural, low-cost adsorbents have been used to remove organic materials from dairy wastewaters, though some of the most-used adsorbents for this purpose are activated carbon [4, 8, 13–15].
Most often, milk processing enterprises are located in agricultural regions, where there is agriculture in addition to livestock. At the same time, a wide range of cellulose wastes are formed nearby which are not often used. The use of such waste for sewage treatment can be a rational solution, which is an example of a cycle of effective and rational nature management with minimizing anthropogenic damage to the environment.

Agricultural sorbents are cheap, efficient, environmentally friendly, and easy to deploy. However, efficiency is dependent on sorption capacity, density, wettability, retention rate and recyclability [16, 17].

There are a lot of studies in the world devoted to the use of various wastes in the role of sorption materials. In particular, studies are known on the use of the carbonation precipitate of sugar production, wastes of the felt-felting industry, tree waste, etc. [18–21].

Corn waste, due to their abundance and large volumes, often attract the attention of environmental researchers. Thus, it is known that corn is an effective sorbent in the purification of aqueous media from oil products [22] and dyes [23]. However, due to the huge variety of production processes existing in the modern world, and, consequently, the sewage that contains the widest range of pollutants in a wide variety of combinations, studies on the rationality of the use of sorption materials for the purification of sewage from specific industries are still relevant.

Sewage refers to multi-component colloid-dispersed systems with a pronounced force field of the interface. This can cause a change in the composition of the surface layer of dispersed particles. Adsorption layers on the surface of dispersive particles in the presence of a liquid disperse medium can significantly change the stability of the dispersive-colloidal system, what is very important in the conditions of sewage treatment of various origin and composition. Therefore, in order to improve the ability to manage the stability and properties of colloid-disperse systems, which include sewage, we conducted studies of the adsorption properties of modified corn cobs according to the relation sewage studied.

As representatives of pollutants, lactic acid and asparagine are chosen because they are a part of cow milk proteins. In addition, studies were carried out on the overall efficiency of purification of model sewage containing whole milk.

2. Materials and methods
Sorption material was prepared from dried in corn cobs room conditions. The agricultural waste was subjected to a temperature effect in a muffle furnace at 300°C. for 30 minutes to carbonize the surface, and then ground to a particle size D < 3 mm.

Model solutions of lactic acid and asparagine were prepared by dissolving the samples of substances in distilled water.

Model sewage simulating the drainage of milk processing enterprises was prepared by mixing the measured volume of pasteurized cow milk with tap water.

Purification of aqueous media was carried out as follows: 100 ml of the solution was placed in a conical flask, and then a sample of sorption material was added and mixed by electronic stirrer for 20 minutes. After 30 minutes from the beginning of the experiment, the contents of the flask were filtered through filter paper and the COD was determined in the filtrate.

The purification efficiency (E) was calculated according to the formula:

$$E = \frac{C_1 - C_2}{C_1} \times 100\%$$

where $C_1$ and $C_2$ – the concentrations of substances before and after of water purification, respectively.

3. Experiment
The amino acids of the proteins belong to the L-form amino acids and have the general formula $R-CH(NH_2)COOH$. 

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When dissolved in water, amino acids exist in the form of bipolar ions (Figure 1) [6].

Lactic acid has the formula $\text{CH}_3\text{CH(OH) COOH}$ and it is formed in sewage in several hours after their formation under the influence of microorganisms, with the further storage of sewage the amount of it increases.

In water, the carboxylic acids dissociate according to the scheme:

$$\text{R-COOH} \leftrightarrow \text{R-COO}^- + \text{H}^+$$

In the course of the research, data were obtained on the effect of the amount of sorption material added on the efficiency of extraction of the two above-mentioned sewage components of milk processing plants. The results are shown in Figures 2, 3.

![Figure 1. Aspartic amino acid at pH = 7.0.](image)

From the results obtained, it can be seen that the sorption material is more effective than the amino acid. This is probably due to the amphoteric properties of the amino acids, in connection with which they can interact with the active centers of the sorbent by several functional groups, whereas only carboxyl-\(\text{COO}^-\) is active in lactic acid.

Rational addition of the sorbent at the initial indexes of sewage, similar to the tested ones, is 6 g/dm$^3$, since with further increase in sorbent addition; the purification efficiency does not increase.

It is known that adsorption is an exothermic process, so an increase in temperature should cause a decrease in adsorption. This is actually observed under adsorbing gases and vapors. When adsorbing from solutions, however, the effect of the solubility of the substance plays no less important role. If the solubility of the adsorbent increases with increasing temperature the adsorption should decrease.
When the solubility drops with heating of the solution, adsorption will increase. The combination of these two factors (exothermicity of the process, adsorption and changes in the chemical potential of the solution with a change in the solubility of the selectively adsorbed component) determines the total effect of temperature on the balance upon adsorbing from solutions.

The solubility of most molecularly dissolved organic substances increases with increasing temperature, as a rise in temperature contributes to the destruction of the water structure. Only for a small number of molecularly dissolved substances in a certain temperature range does solubility decrease. On the other hand, according to the Van Gough rule, an increase in temperature should lead to an intensification of the process due to acceleration. Nevertheless, at a high temperature, Brownian motion of particles can start, which can complicate the sorption process.

In connection with the above factors, the determination of the nature of cleaning with increasing temperature is very important.

We conducted a series of experiments with model sewage with triplicate repetition to clarify the temperature range in which the purification efficiency is maximal. The results of the experiments are shown in Fig. 4.

![Figure 4. Dependence of purification efficiency on the temperature of model sewage.](image)

It has been established that the optimal temperature range for the process of water purification for the sorption material under investigation is 20–30°C, at which the purification efficiency is maximal and equal to 92% in the COD (sorbent mass = 6 g/dm³).

4. Conclusion
The obtained sorption material efficiently extracts various components of sewage from milk processing plants. Extraction of the amino acid that is part of the cow's milk protein (asparagine) occurs more efficiently than lactic acid. So, for the amino acid, 91% efficiency is achieved, for the acid 78% efficiency is achieved. When the amount of pollutant in the range of COD values is 305–320 mgO/dm³, the rational weight of the sorption material additive is 6 g/dm³.

It has been found that the preferred temperature range for treating sewage is 20–30°C.

Thus, modified corn wastes are an effective sorption material for post-treatment of milk-containing sewage, and it is preferable to purify waters that have not been subjected to long-term storage, since they will contain less lactic acid.

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