Automatic control of the methionine extraction process from food enterprises wastewater

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Abstract. The process of methionine extracting from food enterprises wastewater by ion exchange sorption was studied in work. The optimal conditions for conducting the process of sorption and desorption of methionine on polycondensation cation exchanger KU-5 were determined. The maximum coefficient of ion-exchange equilibrium from aqueous salt solutions in a strongly acidic medium (pH 2) at the sodium sulfate concentration in the equilibrium solution of 2.1 mg-Eq/ml was determined by the analysis of the isotherms of methionine sorption in the sodium form of the KU-5 cation exchanger. Methionine desorption was carried out with a 1% NaOH solution, which allowed crystalline methionine being extracted from the eluate at pH 6.5 at room temperature, this crystalline methionine meeting the requirements of regulatory documentation. An automatic control scheme where the adsorber operates in a closed cycle: sorption – acidic wastewater displacement – desorption and activation of cation exchanger – regenerating solution displacement – sorption, was proposed to optimize the process. The method allows additional measurement of the modes and changing the equipment parameters depending on the rational parameters of the sorption/desorption. This approach allows complete extraction of the target component from wastewater, as well as increases the sorbent use completeness and energy and resource-saving at the enterprise.

1. Introduction
The global trends in wastes treatment are increasing the level of their beneficial use, while the level of waste disposal remains low in Russia today. Even though in recent years increased attention has been paid to the problem of waste disposal in the country, Russia is noticeably behind the leading world powers in terms of useful components extracting from wastes. In 2018, the Industry Development Strategy for the treatment, recycling and disposal of wastes was approved. It focuses on industrial enterprises on reducing wastes amount, their reuse and recycling.

The food industry has a negative impact on water resources due to significant water pollution in the technological cycle and the content of a large number of pollutants of mineral and organic nature in it, which complicates the treatment of wastewater to the required standards. At the same time, wastewater of the food industry is a source of valuable components that can be extracted and used in various industries.
Voronezh region is one of the leading regions in the country in terms of agricultural production growth, including livestock. This circumstance makes it necessary to produce feed and premixes ensuring the healthy development of organisms and their rapid biomass increase, which is ensured by the obligatory introduction of amino acids into the feed [1, 2]. For meeting the growing needs of animal husbandry, it is required to export many essential amino acids from abroad, which does not contribute to the strengthening of domestic production as well as increases the production cost in the current political and economic situation.

Taking into account the above mentioned, the search for technological solutions that extract essential amino acids from wastewater from food production is of primary importance, which will not only ensure the extraction of valuable components from waste but reduce the negative impact on water bodies as well.

2. Materials and methods

The objects of research are industrial wastewater from the brewing industry. Sorption of methionine from wastewater was studied on cation exchanger in the sodium form KU-5. The concentration of methionine ions is determined by the photometric and iodometric method. The concentration of sodium ions was determined by the method of electrical conductivity, acidity using a potentiometer pH-340. The amount of sorbed methionine is determined by the difference in concentrations in the initial and equilibrium solutions, as well as by the results of the desorption of methionine from a resin of 0.2 n NaOH. Determination of the total exchange capacity of sulfocationite is carried out under dynamic conditions from methionine solutions with pH 1 ÷ 2 in the absence of Na + ions, and the selectivity coefficient of sorption of methionine ions was determined.

3. Results and discussion

The sorption process was studied on KU-5 cation exchanger with a swelling coefficient of 2.6 from solutions containing 0.01 ÷ 0.12 g-Eq / l of methionine, 0.2 ÷ 2.0 g-Eq / l of Na₂SO₄ at pH = 2, temperature 20 ÷ 65°C under static and dynamic conditions. The choice of cation exchanger was carried out according to the analysis of literature data on the selective amino acids extraction [3]. According to this analysis, an increased selectivity of methionine sorption on polycondensation cation exchanger KU-5 was noted in comparison with cation exchanger KU-2-8 and KU-23. This result is explained by the geometric structural features of the ion exchanger (its irregularity) and with the formation of additional bonds organic counterion-ion exchanger. The data on methionine selective sorption from aqueous salt solutions are shown in Table 1.

| Concentration of Na₂SO₄ 0.1n. | Concentration of Na₂SO₄ 1n. | Concentration of Na₂SO₄ 2n. |
|-------------------------------|-------------------------------|-------------------------------|
| $K_{Na^+}^{met^+}$ | $m_{met^+} / m_0$ | $K_{swell}$ | $K_{Na^+}^{met^+}$ | $m_{met^+} / m_0$ | $K_{swell}$ | $K_{Na^+}^{met^+}$ | $m_{met^+} / m_0$ | $K_{swell}$ |
| 0.2 | 2.40 | | 0.2 | 1.85 | | 0.25 | 1.80 |
| 5.8 | 0.60 | 2.30 | 23.4 | 0.60 | 2.80 | 31.4 | 0.40 | 1.80 |
| 0.90 | 2.20 | | 0.90 | 2.75 | | 0.65 | 1.70 |

The effect of the ionic strength of the solution and temperature on the sorption selectivity was noted. The effect of the ionic strength of solutions on the sorbents swelling was revealed: during methionine sorption from concentrated salt solutions, the swelling coefficients decrease. The increase in the methionine sorption selectivity with an increase in the ionic strength of the solution is consistent with the idea of the effect of swelling on selectivity due to a decrease in the activity of water in solutions with high ionic strength. The increase in selectivity can also be explained by the increased hydrophobicity of methionine ions in these solutions.
Methionine desorption was carried out with NaOH solutions in the concentration range 0.5 \( \div \) 10\%. Elution curves confirm the formation of various forms of methionine upon desorption by concentrated, and 1\% NaOH solution: in the first case methionate was formed, in the latter one – methionine. Confirmation is the pH values of the formed eluates given in Table 2.

**Table 2. Methionine desorption with 1\% NaOH solution containing 30 g / l methionine at 70 °C**

| Characteristics       | Eluate | Methionine |
|-----------------------|--------|------------|
|                       | pH     | Sample     | Methionine concentration in the eluate, g / l | Desorbed methionine, g | % of sorbed methionine | % of desorbed methionine |
| Acidic solution       | 3.5 \( \div \) 4 | 0.39 | 18.6 | 4.97 | 1.94 | 7.46 |
| Concentrated eluate   | 6.5    | 0.4  | 19.3 | 79.5 | 19.8 | 76.2 |
| Alkaline solution I   | 8.5 \( \div \) 9 | 0.2  | 9.6  | 42.5 | 2.5  | 9.62 |
| Alkaline solution II  | 10     | 0.1  | 4.7  | 33.3 | 0.33 | 1.27 |
| Alkaline solution III | 12     | 0.5  | 23.9 | 29.5 | -    | -    |
| 1\% solution NaOH     | 12     | 0.5  | 29.9 | 2.1  | 1.05 | 4.04 |
|                       |        |      |      |      |      |      |
| Total:                |        |      | 25.62 | 98.59 | 100  |

As we can see from the Table, a concentrated eluate is formed at pH = 6.5. Crystalline methionine corresponding to the technical conditions (TC) is released from the concentrated eluate at room temperature.

The purity of the isolated crystalline methionine was characterized by the content of the main product and sodium sulfate (according to the technical conditions for methionine [4]), as well as by the data obtained by elemental analysis of the product for carbon, sulfur and nitrogen.

The studies carried out allowed proposing a new method for the automatic control of the process of ion-exchange sorption of amino acids from wastewater in a continuous mode, which has many advantages over the analogues known today [5, 6, 7].

The method of automatic control of the process of ion-exchange sorption of amino acids from wastewater in a continuous mode, the scheme of which is shown in Figure 1, is as follows.

Wastewater containing the target component in the form of an amino acid (for example, methionine), various salts (for example, sodium sulfate) and other components are supplied to the tank 6. In the tank 6, the correction signal is transmitted from the microprocessor 83 to actuator 120 of the control valve 15. An acceptable source water level is maintained, controlled by sensor 46. The required level of acidity (e.g., pH 1 \( \div \) 2) is also monitored by sensor 54 and maintained by adding appropriate reagents (acids) to the tank 6.

From the tank 4 along line 27, the source water is supplied to the ion-exchange column 1 by transmitting the correction signal from the microprocessor 74 to the actuator 108 of the control valve 14. The ion-exchange column 1 is filled to the minimum allowable level (for example, 1.6 m) with sulfocathionite. Sulfocathionite has the highest selectivity, kinetic permeability and dynamic activity to the target component in the form of an amino acid (for example, KU-5 cation exchange resin of the polycondensation type which, when sorbed from aqueous salt solutions of industrial wastewater, has the highest selectivity to methionine).
Figure 1. Scheme of the method for automatic control of the process of ion exchange sorption of amino acids from wastewater: 1 – vertical type ion-exchange column (adsorber); 2 – sorption chamber; 3 – desorption chamber; 4 – refrigerator; 5 – separator; 6 – source water tank; 7 – regenerating solution container; 8 – containers for distillate; 9, 10 – heating elements; 11, 12 – engines; 13.14 – fans; 15-29 – control valves; 30 – a pipeline for supplying source water to the ion exchange column 1; 31 – wastewater removal pipeline; 32 – distillate feed pipeline to the ion exchange column 1; 33 – a pipeline for the removal of distillate from the ion exchange column 1; 34 – supply pipeline of the regenerating solution into the ion exchange column 1; 35 – a pipeline of the spent regenerating solution from the ion exchange column 1; 36, 37 – air supply pipelines to the refrigerator 4; 38 – pipeline for the excess air discharge from the separator; 39-43 – flow sensors; 44, 45 – sensors of the concentration of the target component in the source water and treated water at the outlet of the ion exchange column respectively; 46-51 – level sensors in the tanks of the source water 6, regenerating solution 7 and distillate 8 respectively; 52, 53 – temperature sensors of the regenerating solution in the tank 7 and the distillate in the tank 8 respectively; 54-56 – acidity sensors in the source water when it is supplied to the ion exchange column 1, in the spent regeneration solution from the ion exchange column 1 and acidic waters at the exit of the ion exchange column 1 respectively; 57-59 – speed sensors; 60, 61 – pressure sensors; 62-82 – secondary devices; 83 – microprocessor; 84-102 – digital-to-analogue converters; 103-121 – actuating units.
At the same time, using low sensor 39 in pipeline 30, the flow rate of the source water is controlled. Water is regulated by transmitting the correction signal from microprocessor 83 to the actuating unit 119 of the control valve 16 to ensure the optimum filtration rate during sorption (e.g., 3000 l/h • m²), controlled in the apparatus with a speed sensor 58. Water is filtered in the ion exchange column 1. The removal of wastewater, in this case, is carried out through pipeline 31 by transmitting a correction signal from microprocessor 83 to actuating unit 121 for switching control valve 17.

Upon reaching a certain residual concentration of the target component in the form of amino acid corresponding to the “breakthrough” point and controlled by the target component concentration sensor 45, the ion exchange column is refilled with cation exchanger to the maximum permissible level (e.g., 4 m), which ensures that the target component in the solution is absent in the form of amino acids at the outlet of the column, after which the sorption process is carried out until a residual concentration of the target component in the form of amino acids appears in the spent solution from the point corresponding to the “breakthrough” point and at this moment carrying out of the transmission of the correction signal from microprocessor 83 to the actuating unit 107 of control valve 28, for moving part of the cation exchanger from sorption chamber 2 for regeneration into desorption chamber 3 until it is completely filled to a level (e.g., 1.6 m) controlled by sensor 51, and the sorption chamber is refilled to the maximum permissible level (e.g., 4 m) from separator 5 subjected to regeneration with cation exchanger.

The regenerated cation exchanger is injected into separator 5 by air flows by blowers 13 and 14 from refrigerator 4 at a speed that ensures its movement (e.g., 0.069 m/s), by transmitting correction signals from microprocessor 83 to actuating units 115, 116 to turn on the engines respectively 11, 12.

For prevent clogging of the filters in the separator, the necessary pressure difference inside and at the exit of it is measured by pressure sensors 60, 61 respectively. The necessary pressure (0.8-1.5 kPa) is maintained by transmitting a correction signal from microprocessor 83 to actuating units 108, 113 and 114 for switching control valves 26, 24 and 25 that change the ratio of air flow in separator 5, controlled by flow sensors 42, 43.

To prevent contamination of the desorbed methionine with sodium sulfate, the acidic wastewater remaining in column 1 after sorption is displaced by supplying distillate from tank 8 to it by transmitting a correction signal from microprocessor 83 to actuating units 111 of the control valve 22. The distillate passes through a layer of cation exchanger and at the exit of the ion exchange column 1, acidity is measured therein with sensor 55. Then it is removed through pipeline 33.

The distillate is supplied into ion-exchange column 1 heated in tank 8, to the required temperature (70 °C), controlled by sensor 53 and maintained at a predetermined level, by transmitting a correction signal from microprocessor 83 to actuating unit 109 of heating element 10. In-tank 8, the required level of distillate is maintained and measured by sensor 48 by transmitting a correction signal from microprocessor 83 to actuating unit 109 of the control valve 21.

After the distillate is displaced from the system in the ion exchange column 1, a desorption solution is filtered (hot (t = 70 °C) 1% sodium hydroxide solution containing 25-30 g/l methionine), which has been previously heated in tank 7 by transmitting a correction signal from microprocessor 83 to actuating unit 104 of heating element 9 to a predetermined temperature level (50 °C). The required level of the desorption solution, measured by sensor 47, is maintained in tank 7 by transmitting a correction signal from microprocessor 83 to actuating unit 106 of the control valve 18.

The desorption solution is supplied to the ion exchange column 1 by transmitting the correction signal from microprocessor 83 to actuating unit 105 of the control valve 19. At the same time, the flow rate of the desorption solution, which is controlled by the transmission of the correction signal from microprocessor 83 to actuating unit 105 of the control valve 19, is controlled by flow sensor 41 at the exit of the ion exchange column 1 to ensure the optimal filtration rate during desorption (e.g., 2500 l/h • m²). After the solution passes through the ion-exchange column 1, it is selected in the form of an acidic concentrated eluate at a given acidity value, controlled by sensor 56, and by transmitting the correction signal from microprocessor 83 to actuating unit 117 of the control valve 23. Then it is removed into pipeline 35 from which crystalline target component in the form of an amino acid is
further separated after cooling to room temperature (e.g., methionine in an amount of 75 ÷ 80% of the adsorbed one).

The replacement of the regenerating solution is carried out by transmitting correction signals from microprocessor 83 to actuating unit 111 of the control valve 22 for distillate supplying to the ion exchange column 1.

At the end of the displacement of the neutral target component (methionine), the pH of the eluate increases sharply and quickly reaches its original value (for example, pH = 12 ÷ 12.5). In this case, the remaining methionine is desorbed and, together with the mother liquor obtained by filtration of crystalline methionine, is used for desorption in the next cycle. Simultaneously with desorption, methionine is regenerated (conversion to sodium form). The purity of the extracted crystalline methionine was characterized by the content of the main product and sodium sulfate (according to TC for methionine), as well as data obtained by elemental analysis of the product for the content of carbon, sulfur and nitrogen.

After regeneration, the cation exchanger is transferred to the refrigerator for its further reuse by transmitting the correction signal from microprocessor 83 to actuating unit 103 of the control valve 27.

Thus, the continuous operation mode of the ion exchange column 1 provides that when reaching the concentration of methionine 0.5 g / l at the adsorber exit 1, sorption chamber 3 is refilled with the cation exchanger. When reaching the concentration of methionine 0.5 g / l at adsorber exit 1 for the second time, the motion of the cation exchanger part for regeneration in desorption chamber 3 for the subsequent stages of displacement and desorption is carried out. Thus adsorber works in a closed cycle: sorption – acidic sewage displacement – desorption and cation exchanger activation – displacement of the regenerating solution - sorption.

In this case, the information about the flow of ion exchange sorption of amino acids from wastewater is transmitted from the sensors through secondary devices 62-82 to microprocessor 83, which generates correction signals through digital-to-analogue converters 84-102 to actuating units 103-121 to change the parameters of the equipment depending on the criteria chosen.

This method of automatic control of the process of ion-exchange sorption of amino acids from wastewater in continuous mode has advantages because the additional measurement of modes and changing the parameters of the equipment depending on the rational parameters of the process allows improving the accuracy of control and minimize energy and material costs. Consistent placement in the sorption chamber and the sorbent refill and subsequent timely removal of its part from the chamber provides its fullest use to extract the target component.

4. Conclusion
The regularities of the process of ion exchange sorption of methionine on the polycondensation cation exchanger KU-5 were studied, the optimal conditions for conducting sorption and desorption of amino acids were identified in work.

The method of automatic control of the process of ion-exchange sorption of amino acids from wastewater in a continuous mode was proposed according to the regularities studied. The advantage of the method proposed is provided by the fact that the additional measurement of modes and changing the parameters of the equipment, depending on the rational parameters of the process allows increasing the accuracy of control and minimizing energy and material costs. The described method of automatic control of the sorption process allows the complete use of the sorbent for selective extraction of amino acid by sequential placement and refill in the sorption chamber and subsequent timely removal of its part from the chamber.

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