Research of surface-active properties and sizes of pectin molecules after post-alcohol grain distillery dreg

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Abstract. From the multicomponent composition of biologically active substances contained in wheat post-alcohol grain distillery dreg, the leading role in the manifestation of surface-active properties is presumably played by pectins. Therefore, the purpose of the work was to isolate pectins from the distillery dreg, study their surface-active properties and determine the size of molecules in the saturated adsorption layer to justify the possibility of using pectins in pharmaceutical practice as auxiliary substances. The physical and chemical characteristics of pectins isolated by the technology of complex processing of distillery dreg were studied: pH of 0.5% aqueous solution (4.25), average molar mass (1650•10^3 kg/mol), degree of polymerization (10), binding capacity to lead (II) ions (282.29 mg/g of pectin). According to a series of pectin solutions with a concentration of 0.5-6.1 mol/m^3 the following parameters were determined and calculated experimentally at a temperature of 293 K: surface tension (51.96•10^{-3}-67.55•10^{-3} N/m), surface activity (7.54), marginal surface excess (6.25•10^{-5} mol/m^2), critical micelle formation concentration (1.48 mol/m^3 or 0.24%). The found characteristics of the surface properties of the calculated size of the pectin molecule in a saturated adsorption layer: cross-sectional area (2,658 Å^2), weight of pectin per unit area (1,031•10^{-4} kg/m^2), the length of the molecule (1026 Å), the volume of the molecule (Å^3 2727), the radius of the cross section of the molecule (0.920 Å), the cross-sectional diameter of the molecule (1,840 Å). The calculated size of the pectin molecule from distillery dreg in a saturated adsorption layer, comparable to the parameters of analogues (beet pectin, polygalacturonic acid, sodium alginate), indicate the biological availability of the tested pectins and creates the prospect of their pharmaceutical use in drug technology.

1. Introduction

Taking into account diversity of the composition of biologically active compounds contained in the post-alcohol distillery dreg: proteins and amino acids, neutral and acidic carbon-water, higher fatty acids, polyphenolic compounds, biogenic elements [1], we need to confirm the assumption that the leading role in the manifestation of dreg is surface-active properties belong to pectins. A prerequisite for this is the versatile study of pectins as adsorbents [2], and therefore it seems appropriate to study the surface activity of pectins isolated from other components of dreg.

The goal of the research is to study the surface-active properties of pectins isolated from the post-alcohol distillery dreg and determining the size of its molecules in a saturated adsorption layer.
The object of the research is pectin fraction extracted from the post-alcohol wheat distillery dreg produced by the distilleries “Cossack” (Kazachye), “Suvorovsky” of the Stavropol Territory [3, 4], according to the technology of complex processing of grain dreg [5].

2. Materials and methods

The isolation of the pectin fraction from wheat post-alcohol distillery dreg, in accordance with the technology of complex processing of distillery dreg [5], is based on their extraction with a solution of ammonium oxalate, concentration and subsequent processing of the extract with ethyl alcohol, purification of the target product by reprecipitation from aqueous solutions with various solvents.

The following physicochemical characteristics of the isolated pectins were established: pH of a 0.5% aqueous solution (potentiometric method [6]) is 4.25, average molar mass (viscometric method [7]) is $1650 \times 10^{-3}$ kg / mol the degree of polymerization is 10, binding ability (compleximetric titration method [8]) is 282.29 mg of lead (II) ions per 1 g of pectin, which is 30% higher than the similar activity of the known antidote - beet pectin [2].

The surface-active properties of the isolated pectins were studied by a method of the highest pressure of air bubbles using the Rebinder device [10], which was performed according to the algorithm described for the post-alcohol distillery dreg. For the study, we used a series of solutions with a pectin concentration of 0.5 ÷ 6.1 mol / m$^3$ by successively diluting with water a stock solution with a pectin concentration of 6.1 mol / m$^3$. The pressure drops (p, mm) for the solvent and solutions were measured at a temperature (T) of 293 K, followed by the calculation of the surface tension ($\sigma$, N / m) of the solutions according to the well-known formula [9].

The surface activity (g), as a derivative of the surface tension with respect to the concentration of pectins (C, mol / m$^3$) [10] at a constant temperature (293 K), was determined using the surface tension isotherm of aqueous solutions with respect to the tangent of an inclination angle of the curve (picture 1) (Figure 1).

![Figure 1. Isotherm of surface tension of water solutions of pectins](image)

The surface excess (G, mol / m$^2$) of the investigated solutions was calculated from the found surface activity using the Gibbs equation (1) [10]:
\[ G = \frac{\Delta \sigma \cdot C}{\Delta C \cdot R \cdot T} \]  

(1)

where \( R \) is the universal gas constant equal to \( 8.314 \text{ J} / (\text{mol} \cdot \text{K}) \).

According to the graph of the relationship between the reciprocal of surface excess and concentration, according to the Langmuir adsorption isotherm, the segment cut off on the ordinate axis is numerically equal to the limiting surface excess \( (G^\infty, \text{mol} / \text{m}^2) \) [10] (Figure 2).

![Figure 2. Pectin adsorption isotherm](image)

According to the graph of dependence of the decimal logarithm of surface tension on the decimal logarithm of the concentration of pectins (Figure 3), the bend point of the curve obtained, which corresponds to the abscissa, is an antilogarithm of the critical micelle concentration (CMC) [9].

![Figure 3. Dependence of surface tension on the concentration of pectins](image)

Using the ideas of Langmuir on the structure of the surface layer, we calculated the sizes of pectins in the saturated adsorption layer.
The product of the maximum surface excess by the Avogadro constant determines the number of molecules that occupies a unit area. The cross-sectional area of the pectin molecule \( S, \text{m}^2 \) in the saturated adsorption layer was calculated according to equation (2) [10]:

\[
S = \frac{1}{G_\infty \cdot N_A}
\]

where: \( N_A \) is the Avogadro constant \((6.02 \cdot 10^{23} \text{ mol}^{-1})\).

The product of the maximum surface excess by the average molar mass of pectin \( M, \text{kg} / \text{mol} \) is the mass of pectin \( m, \text{kg} \) per unit surface \( \text{m}^2 \) of the saturated adsorption layer (3) [10]:

\[
m = G_\infty \cdot M
\]

The length of the pectin molecule in the saturated adsorption layer equal to the thickness of this layer \( l, \text{m} \) was calculated according to equation (4) [10]:

\[
l = \frac{m}{\rho} = \frac{G_\infty \cdot M}{\rho}
\]

where: \( \rho \) is the density of pectin, \( \text{kg} / \text{m}^3 \).

The volume occupied by the pectin molecule in the adsorption layer \( V, \text{m}^3 \) is the product of the cross-sectional area of the pectin molecule by the length of its molecule (equation 5) [10]:

\[
V = S \cdot l
\]

The radius \( r, \text{m} \) and the diameter \( d, \text{m} \) of the cross section of the pectin molecule are determined based on the formula for calculating the area of a circle (equation 6):

\[
S = \pi r^2
\]

3. Results and its discussion

The experimental and calculated indicators of the surface-active properties of pectins are shown in table 1.

The surface activity of pectin from wheat stillage determined graphically by surface tension isotherm (Figure 3) was 7.54, which is 2.5-8 times higher than that of beet pectin, but 1.5-3 times lower the activity of sodium alginate and polygalacturonic acid [2]. According to the isotherm, the molecules of the studied pectins go entirely to the surface.

The pectin adsorption isotherm (Figure 1) indicates that the ordinate segment from the origin of the coordinate axis to its intersection with the straight line is numerically equal \( 1 / G_\infty = 1.6 \cdot 10^4 \text{ m}^2 / \text{mol} \), i.e. the limiting surface excess of distillery pectin pectin is \( 6.25 \cdot 10^{-5} \text{ mol} / \text{m}^2 \), which is 4 times higher than that for sodium alginate, 7.5-44 times higher than beet pectin, and 5.6 times higher than polygalacturonic acid [2].

With an increase in the concentration of pectins in solution, the number of molecules in the surface layer increases. As a result, a saturated monomolecular adsorption layer is formed on the boundary surface, where the pectin molecules are extremely oriented.

When the equilibrium in the “true solution ↔ colloidal solution” system shifts towards the formation of a colloidal solution, the size and number of kinetically active particles change, as shown in the graph “Surface Tension - Pectin Concentration” (Figure 3), the break point (log \( C = 0.17 \)), corresponding to a critical micelle concentration of \( 1.48 \text{ mol} / \text{m}^3 \) (or 0.24%).

The calculations of the sizes of pectin molecules in the saturated adsorption layer according to the above equations made it possible to obtain the following data:

- cross-sectional area of a pectin molecule:
  \( S = 1 / (6,02 \cdot 10^{23} \text{ mol}^{-1} \cdot 6,25 \cdot 10^{-5} \text{ mol/m}^2) = 2,658 \cdot 10^{-20} \text{ m}^2 \) (or 2,658 Å²)
- mass of pectin per unit surface:
  \( m = 6,25 \cdot 10^{-5} \text{ mol/m}^2 \cdot 1650 \cdot 10^{-3} \text{ kg/mol} = 1,031 \cdot 10^4 \text{ kg} \)
- pectin molecule length:
  \( l = (6,25 \cdot 10^{-5} \text{ mol/m}^2 \cdot 1650 \cdot 10^{-3} \text{ kg/mol}) / 1,005 \cdot 10^3 \text{ kg/m}^3 = 1,026 \cdot 10^{-7} \text{ m} \) (or 1026 Å).
• volume occupied by the pectin molecule:
  \[ V = 1,026 \cdot 10^{-7} \text{ m} \cdot 2,658 \cdot 10^{20} \text{ m}^2 = 2,727 \cdot 10^{-27} \text{ m}^3 \text{ (or 2727 Å)} \]
• radius of the cross section of the pectin molecule:
  \[ r = \sqrt{(2,658 \cdot 10^{20} \text{ m}^2/3,14)} = 9,20 \cdot 10^{-11} \text{ m (or 0,920 Å)} \]
• diameter of the cross section of the pectin molecule \( d = 2 \times r = 1,84 \cdot 10^{-10} \text{ m (or 1,840 Å)} \).

### Table 1. Indicators of surface-active properties of pectins

| solution No. | C pectins, mol / m³ | P, mm | \( \sigma \), N/m | \( G \), mol/m² | \( \lg C \) [mol/m³] |
|-------------|---------------------|------|-----------------|----------------|------------------|
| 1           | 6,1                 | 30   | 51,96 \cdot 10^{-3} | 32,54 \cdot 10^6 | 0,785            |
| 2           | 4,5                 | 33   | 57,16 \cdot 10^{-3} | 19,20 \cdot 10^6 | 0,653            |
| 3           | 3,0                 | 34   | 58,89 \cdot 10^{-3} | 24,38 \cdot 10^6 | 0,477            |
| 4           | 2,3                 | 35   | 60,63 \cdot 10^{-3} | 14,30 \cdot 10^6 | 0,362            |
| 5           | 1,5                 | 36   | 62,36 \cdot 10^{-3} | 21,33 \cdot 10^6 | 0,176            |
| 6           | 1,2                 | 37   | 64,09 \cdot 10^{-3} | 10,67 \cdot 10^6 | 0,079            |
| 7           | 0,8                 | 38   | 65,82 \cdot 10^{-3} | 7,59 \cdot 10^6  | -0,097           |
| 8           | 0,5                 | 39   | 67,55 \cdot 10^{-3} | 2,13 \cdot 10^6  | -0,301           |
| H₂O         | -                   | 42   | 72,75 \cdot 10^{-3} | -              | -                |

Comparison of wheat dreg pectin with other natural polysaccharides [2] used in drug technology (Table 2) showed some differences: the dreg pectin molecule in the saturated adsorption layer has a minimum area, radius, and cross-sectional diameter and the smallest volume; it is characterized by the largest mass per unit surface and length. Taking into account the pore diameter of biological membranes \( (3.5–4) \cdot 10^{-10} \text{ m} \), pectin molecules from dreg and sodium alginate molecules can pass through them from all polyuronides, which favors to a certain extent bioavailability of pectin isolated from bards.

### Table 2. Comparative characteristics of polysaccharides by the size of molecules in a saturated adsorption layer

| M, kg/mol | S, m² | m, kg | l, m | \( V \), m³ | \( r \), m | \( d \), m |
|-----------|-------|-------|------|------------|-----------|----------|
| Pectin from dreg: |       |       |      |            |           |          |
| 1650 \cdot 10^{-3} | 2,658 \cdot 10^{20} | 1,031 \cdot 10^{-4} | 1,026 \cdot 10^{-7} | 2,727 \cdot 10^{-27} | 9.9 \cdot 10^{-10} | 1,8 \cdot 10^{-10} |
| Beet pectin (Krasnodar): |       |       |      |            |           |          |
| 6570 \cdot 10^{-3} | 19,9 \cdot 10^{-30} | 0,547 \cdot 10^{-4} | 0,538 \cdot 10^{-7} | 10,736 \cdot 10^{-27} | 25,0 \cdot 10^{-10} | 5,0 \cdot 10^{-10} |
| Beet Pectin (Nalchik): |       |       |      |            |           |          |
| 3200 \cdot 10^{-3} | 116,2 \cdot 10^{-20} | 0,046 \cdot 10^{-4} | 0,045 \cdot 10^{-7} | 5,262 \cdot 10^{-27} | 6,1 \cdot 10^{-10} | 12,2 \cdot 10^{-10} |
| Polygalacturonic acid: |       |       |      |            |           |          |
| 3000 \cdot 10^{-3} | 15 \cdot 10^{-20} | 0,333 \cdot 10^{-4} | 0,330 \cdot 10^{-7} | 4,935 \cdot 10^{-27} | 2,2 \cdot 10^{-10} | 4,4 \cdot 10^{-10} |
| Sodium Alginate: |       |       |      |            |           |          |
| 89700 \cdot 10^{-30} | 10 \cdot 10^{-20} | 15,0 \cdot 10^{-4} | 14,722 \cdot 10^{-7} | 146,630 \cdot 10^{-27} | 1,8 \cdot 10^{-10} | 3,6 \cdot 10^{-10} |

### 4. Conclusion

Pectins, isolated from wheat post-alcohol stillage, are surface-active substances. Their surface activity is 7.54, the maximum surface excess is \( 6.25 \cdot 10^{-5} \text{ mol / m²} \), CMC - 1.48 mol / m³ (or 0.24%). The article determined sizes of pectin molecules from dreg in the saturated adsorption layer, which slightly differed from the known polysaccharides by a smaller area, radius, cross-sectional diameter and volume with a larger mass per surface unit and length. Comparability with natural analogs of dreg pectins creates the prospect of their pharmaceutical use in making drugs.
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