Research of surface-active properties of post-alcohol grain distillery dreg

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Abstract. The concentration of low-molecular pectins (6.67 mol/m3) in the liquid phase of wheat post-alcohol grain distillery dreg is relatively high. That is why the aim of the work was to study the surface-active properties of distillery dreg by the method of the highest pressure of air bubbles to assess the possibility of its use in pharmacy as an auxiliary aid. Also, the prospects for using distillery dreg as a pharmaceutical raw material are due to the rich composition of biologically active substances, multi-tonnage production, and affordability. According to a series of solutions of the liquid phase, distillery dreg with a concentration of pectins of 0.06÷6.67 mol/m3 were determined and calculated indicators at a temperature of 293 K: surface tension (58.89•10-3-72.75•10-3 N/m), surface activity (11.67), surface excess (1.28•10-5 mol/m2), maximal surface excess (1.28•10-5 mol/m2), critical micelle concentration (1.32 mol/m3 or 0.22%). Sequentially Gibbs equation and graphical method (using the surface tension and Langmuir adsorption isotherms) were used in the experiment. According to these characteristics, distillery dreg is comparable to known tension-active polysaccharide (sodium alginate, polygalacturonic acid). They are used in drug technology as substances that increase the viscosity, which is used to stabilize liquid and soft dosage forms: emulsions, ointments, suppository bases and suspensions, and, consequently, changes in the rate of release and absorption of drugs, improving the conduct of technological processes.

1. Introduction

Post-alcohol distillery dreg is the most voluminous industrial waste in Russia: about 10 million m3 per year [1, 2]; on average, 1 m3 of alcohol produced accounts for 13 m3 of stillage [3, 4]. Among the various wastes of alcohol production (concentrate of head impurities of ethyl alcohol, fermentation gases, alfalfa water, fusel oil), dreg accounts for 85% [3, 4].

The distillery dreg content of natural compounds: proteins and amino acids (20-46% in the liquid phase, 2.0-2.5% in the solid phase), reducing sugars (13.0-17.5% in the liquid phase, 1.6-2.1% in the solid phase), pectins (0.8-1.4% in the liquid phase, 3.4-5.3% in the solid phase), fatty oil (8.4-11.1%), flavonoids (0.4-0.9%), vitamins (3.4-11.4 mg%), nutrients [5], as well as practical non-toxicity [6] made it possible to consider dregs as a secondary raw material resource of pharmaceutical use. One of the most important adsorption characteristics of substances that determine their properties and areas of pharmaceutical application is surface activity. Research in the field of chemistry of surface phenomena...
is inextricably linked with issues of rational technology, stabilization, storage, and increasing the effectiveness of the therapeutic effect of drugs. In this regard, the establishment of the surface activity of the stillage would make it possible to substantiate its use as an adjuvant in the technology of dosage forms.

The goal of the research is to study the surface-active properties of post-alcohol distillery dreg to assess the possibility of its use in pharmacy as an adjuvant.

The object of the study is the liquid phase of the post-alcohol wheat distillery dreg produced by typical alcohol enterprises “Cossack” (Kazachye) and “Suvorovsky” in the Stavropol Territory, using hydroenzymatic processing of grain in alcohol technologies [3, 4]. The choice of the liquid phase is conditioned by its significant share in the dreg (approximately 90%), the choice of the grain source — wheat — is associated with its most frequent use in alcohol production [3, 4].

2. Materials and methods

Given the evidence of the surface-active properties of pectins [7], the content of which in the liquid phase of wheat stillage is 6.67 mol / m$^3$ (or 1.1%), a study of the surface activity of dreg is carried out considering the concentration of pectins. In addition, the low molar mass of pectins contained in dreg ($1650 \cdot 10^{-3}$ kg / mol [5]), along with other factors, favors the high bioavailability of dreg.

The surface activity of a series of solutions with a pectin concentration of 0.06–6.67 mol / m$^3$ prepared by diluting the liquid phase of the stillage with water was studied by the method of the highest pressure of air bubbles using the Rebinder device [8]. Using the differential pressure values measured for the solvent and each solution at a temperature of 293 K, the surface tension of the solutions was calculated using the following equation (1) [8]:

$$\sigma_2 = \frac{\sigma_1 \cdot p_2}{p_1}$$

where $\sigma_1$ and $\sigma_2$ are the surface tension of water and solution, respectively, N / m; $p_1$ and $p_2$ — pressure drop for water and solution, respectively, mm.

A measure of surface activity is the first derivative of surface tension considering the concentration of the solute, taken with the minus sign (2) [9]:

$$g = \frac{d\sigma}{dC}$$

where $g$ is surface activity;
$C$ is the concentration of solute, mol / m$^3$.

Therefore, the surface activity at a constant temperature (293 K) was determined using the surface tension isotherm of aqueous solutions — dependence of surface tension on solute concentration, as tangent of the inclination angle to the obtained curve (Figure 1).
Figure 1. Isotherm of the surface tension of aqueous solutions of the liquid phase of distillery dreg

Based on the found surface activity value using the well-known Gibbs equation (3) [9], the surface excess ($G$, mol / m$^2$) of the studied solutions was calculated:

$$G = \frac{\Delta \sigma \cdot C}{\Delta C \cdot R \cdot T}$$

where $R$ is the universal gas constant equal to 8.314 J / (mol · K).

The graphical relationship between the reciprocal of the surface excess and concentration, according to the Langmuir adsorption isotherm, is the equation of a straight line running parallel to the abscissa axis and cutting off a segment numerically equal to the limiting surface excess ($G_\infty$, mol / m$^2$) [9] (figure 2).

Moreover, in the graphical system, the dependence of the decimal logarithm of surface tension on the decimal logarithm of the concentration of the dissolved substance (Figure 3) is found at the bend point of the curve corresponding to the abscissa axis, the antilogarithm of which is the critical micelle formation concentration (CMC) [8].

3. Results and its discussion

The experimentally found and calculated indicators of the surface-active properties of the liquid phase of wheat stillage are shown in the table.

| Table 1. Indicators of surface-active properties of the liquid phase of millet distillery dreg |
| solution No. | C pectins, mol / m$^3$ | $P$, mm | $\sigma$, N/m | $G$, mol / m$^2$ | $\lg C$, [mol/m$^3$] |
|-------------|-----------------------|--------|--------------|----------------|---------------------|
| 1           | 6.67                  | 34     | $58.89 \cdot 10^{-3}$ | $11.36 \cdot 10^{-6}$ | 0.82                |
| 2           | 3.33                  | 34     | $58.89 \cdot 10^{-3}$ | $11.62 \cdot 10^{-6}$ | 0.52                |
| 3           | 1.70                  | 34     | $58.89 \cdot 10^{-3}$ | $11.38 \cdot 10^{-6}$ | 0.23                |
| 4           | 0.85                  | 36     | $62.36 \cdot 10^{-3}$ | $8.43 \cdot 10^{-6}$  | -0.07               |
| 5           | 0.42                  | 38     | $65.82 \cdot 10^{-3}$ | $6.64 \cdot 10^{-6}$  | -0.38               |
| 6           | 0.24                  | 39     | $67.55 \cdot 10^{-3}$ | $4.27 \cdot 10^{-6}$  | -0.62               |
| 7           | 0.12                  | 40     | $69.29 \cdot 10^{-3}$ | $2.84 \cdot 10^{-6}$  | -0.92               |
| 8           | 0.06                  | 42     | $72.75 \cdot 10^{-3}$ | -               | -1.22               |
| H$_2$O      | -                     | 42     | $72.75 \cdot 10^{-3}$ | -               | -                   |

In accordance with the surface tension isotherm shown in Figure 1, the surface activity of the liquid phase of wheat stillage was 11.67. Compared with other polysaccharides (sodium alginate, polygalacturonic acid), whose molecules completely surface [7], the activity of wheat stillage is less pro-
nounced: a monomolecular layer on the water surface is formed at high concentrations. It should be noted that the distillery dreg, which is a multicomponent system, in addition to reducing the surface, can lower the Gibbs surface energy by redistributing the solute between the phase volume and the surface (boundary) layer.

The distillery waste adsorption isotherm (Figure 2) indicates that the ordinate segment from the origin of the coordinate axes to its intersection with the straight line is numerically equal to $\frac{1}{G_\infty} = 7.8 \cdot 10^4 \text{ m}^2 / \text{mol}$, i.e. the value of the limiting surface excess of the distillery dreg liquid phase is $1.28 \cdot 10^{-5} \text{ mol} / \text{m}^2$, which is comparable with the known polyuronides: sodium alginate ($1.67 \cdot 10^{-5} \text{ mol} / \text{m}^2$) and polygalacturonic acid ($1.11 \cdot 10^{-5} \text{ mol} / \text{m}^2$) [7].

Thus, as the concentration of pectins in solution increases, increases the number of molecules in the surface layer. This leads to the formation on the boundary surface of a saturated monomolecular adsorption layer in which the pectin molecules are extremely oriented.

During the transition of the true solution, the colloidal solution changes the size of kinetically active particles (ions, molecules, micelles) and their number. Therefore, there is a break point ($\log C = 0.12$), on the graph of the dependence “Surface Tension - Concentration of pectins in the liquid phase of dreg” (Figure 3), corresponding to a critical micelle concentration of 1.32 mol / m³ (or 0.22%).

![Figure 2. Adsorption isotherm of the liquid phase of distillery dreg](image1)

![Figure 3. Dependence of surface tension on the concentration of pectins in the liquid phase of distillery dreg](image2)
4. Conclusion
The liquid phase of wheat post-alcohol distillery dreg containing 6.67 mol / m³ of pectin has surface-active properties: the surface activity is 11.67, the maximum surface excess is 1.28 · 10^-5 mol / m², CMC - 1.32 mol / m³ (or 0.22%). According to the indicated characteristics, the distillery dreg is comparable with the known surface-active polysaccharides (sodium alginate, polygalacturonic acid) used as auxiliary agents in drugs production.

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