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ПОВЫШЕНИЕ КАЧЕСТВА ТЕХНИЧЕСКОЙ И ПИТЬЕВОЙ ВОДЫ, ОБУСЛОВЛЕННОЕ ОБРАЗОВАНИЕМ КОМПЛЕКСОВ АМИНОКИСЛОТ С ИОНАМИ КАЛЬЦИЯ И МАГНИЯ

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Системы отопления домов и предприятий пищевой промышленности требуют использования воды высокой очистки. С целью повышения качества технической и питьевой воды проводились эксперименты по изменению жесткости воды, отобранной в четырех районах г. Казани, с помощью добавления к ней β-аланина и l-аспарагина, как агентов образования комплексов с ионами кальция и магния. Полученные результаты показали, что выбранные аминокислоты в экспериментальных условиях способны снижать жесткость и увеличивать качество воды в 1,1-1.2 раза. Эти данные довольно хорошо согласуются со стехиометрическим взаимодействием ионов металлов и аминокислотой. Следовательно, дальнейшего понижения жесткости можно достичь увеличением добавки аминокислоты. Вычисленные теплоты сжигания и образования комплексов кальция и магния с β-аланином и l-аспарагином подтвердили экспериментальные результаты относительно их стабильности. Такие экспериментальные результаты побудили нас к вычислению теплоты сгорания ($\Delta_c H°$) и образования ($\Delta_f H°$) комплексов кальция и магния с вышеуказанными аминокислотами [металл(аминокислота)$_2$, $\Delta_c H°$, $\Delta_f H°$ (kJ mol^{-1}± 0.5 % соответственно), число валентных электронов (N-g)] в соответствии со схемой термохимических исследований. На основании анализа термодинамических расчетов был сделан вывод о стабильности комплексов аминокислота – металл, т.е. об эффективном связывании аминокислотами катионов щелочноземельных металлов. Было предложено использовать вышеуказанные аминокислоты или синтезированные на их основе малые пептиды, прикрепленные к сорбционным фильтрам в процессе водоподготовки либо непосредственно, либо на длинных «ножках». Тогда катионы будут задерживаться на фильтрах, а сами фильтры можно будет регенерировать подобно ионообменным материалам.

Ключевые слова: техническая вода, питьевая вода, жесткость воды, аланин, аспарагин, кальций, магний, теплота сгорания, теплота образования

QUALITY INCREASING OF TECHNICAL AND POTABLE WATER DUE TO COMPLEXATION BETWEEN AMINO ACIDS AND Ca AND Mg SALTS

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The home heating systems as well as the food industry require a high degree of water purification. In the aims of the increasing of the quality of technical and potable water the experiments on the determination of the rigidity of water have been carried out in the fourth districts of Kazan after the addition to the water samples of β-alanine and l-asparagine as the agents for the complex formation with calcium and magnesium salts. The obtained results showed that the chosen amino acids able to reduce the rigidity and increase the quality of waters in 1.10-1.22 time. The calculated heats of combustion and formation of complexes of calcium and magnesium with alanine and asparagine confirm the conducted experimental results on their stability. Such experimental results prompted us to calculate the heat of combustion ($\Delta_cH°$) and formation ($\Delta_fH°$) of complexes of calcium and magnesium with the mentioned above amino acids [Met(amino acid)$_2$, $\Delta_cH°$, $\Delta_fH°$ (kJ mol^{-1}± 0.5 % , respectively), number of valence electrons (N-g)] in according to the scheme of thermochemical research. It has been suggested to introduce the above mentioned amino acids or synthesized on their base little peptides into sorption-filters at the water preparation process.

Keywords: technical water, potable, water rigidity, alanine, asparagines, calcium, magnesium, combustion heat, formation heat

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INTRODUCTION

The home heating systems as well as the food industry require a high degree of water purification. The general rigidity of water is characterized by the total contents of the calcium and magnesium cations and expressed in mmol l^{-1}. The rigidity sub-divide on the soft (1.5-4.0 mmol l^{-1}), middle (4.0-8.0 mmol l^{-1}) and very rigid (8.0-12.0 mmol l^{-1}). The top limit of the rigidity of the potable water in the systems of the water supply on operating the sanitary norms should not exceed 7 mmol l^{-1} [1-3].

To make the water suitable for the use in various industries and especially in the potable it subject to the softening. In the system of the water-preparation for the struggle against the water rigidity often use the reagent, ion-exchanging, thermal and other methods of the softening [1,2].

There is an internet-information, that NuFresh Water System Company suggested to use alanine as "a water softener ... non-toxic and biodegradable ... to introduce it as water softener to combat skin roughness and dull hair" [4].

Taking into account the above mentioned information [4], we chose not expensive and non-toxic *β*-alanine and *l*-asparagine as the means for the receiving of the water softness due to the interaction via complex formation between titled amino acids and Ca and Mg salts in technical and potable waters. Such assertion requires the determinations of the rigidity of technical and potable waters.

METHODS AND EXPERIMENTS

The definition of the rigidity of technical and potable water.

In a conic flask on 250 ml it has been placed of 100.0 ml of the selected technical and potable water, it has been added the 5-7 drops of the indicator "erichrom-black" and it have been titrated with trilon B with normality N is equal 0.05 until the change of the paint from red up to dark blue [3]. An average volume of trilon B, necessary for the definition of the general rigidity of water, defined by three experiments with a mistake ± 0.05 ml. The general rigidity of potable water (R_g) counted on the formula (1),

$$Rg = \frac{(N \cdot F \cdot Vtr)}{Vtest} \cdot 1000 \text{ mmol} \cdot l^{-1}, \qquad (1)$$

were *N* is concentration of trilon B, *F* is coefficient, as usually, equal to 1, *Vtr* is a middle volume of trilon B, which was used on the titration, *Vtest* is a volume of water, which was used for the analysis.

Thermochemical calculations.

To be assured, that the use of chosen amino acids can be successful for this aim necessary to do the calculation of such thermochemical parameters as the heat of combustion and formation metal-amino acid, which can witness the trustworthy the above suggestion.

The heats of combustion (D_cH^o) of all complexes Met(amino acid)$_2$ is occurs accordingly to the equation (2), in which introduced a solid (s), liquid (l) and gas (g) reagents and products of combustion.

$$C_aH_bN_cO_dMet(s) + nO_2\,(g) \rightarrow xCO_2(g) + yH_2O(l) + zN_2(g) + dMetO(s) + \Delta_cH^\circ \quad (2)$$

The heats of combustion were calculated with the use of computer program [5], in which have been included the equation (3), because of it received on the experimental values of Δ_cH° of twenty amino acids. The *N* parameter is the number of valence electrons from which is subtracted g is a number of lone electron pairs of heteroatoms in amino acids [6]

$$D_cH^o = 25.0 - 105.3\,(N - g) \quad (3)$$

The heats of formation (Δ_fH°) of all complexes were calculated with the use of Hess-law (Eq. 4), which contains the heats of formation of all values of products (Eq. 2)

$$D_cH^\circ = \Sigma\, n_i\Delta_fH^\circ_{products} - \Sigma n_j\Delta_fH^\circ_{reagents} \quad (4)$$

RESULTS AND DISCUSSION

The all mentioned above prompt us to use an ecologically safe amino acids *β*-alanine and *l*-asparagine as the means for the softness of technical and potable water. It is known that amino acids form the stable complexes with some metals [7], but there is not information about their use for the softness of water. All waters have been taking from the different districts of Kazan and three times were undergoing to the analysis on the rigidity by the method represented in experimental part. The obtained results represented itself the next:

1. The calculated on formula (1) the general rigidity of technical-potable water of Novo-Savinovsky district is 4.9 mmol·l^{-1} (*Vtr* is 9.8 ml). After the addition of 0.021 g·l^{-1} *β*-alanine the general rigidity was 4.4 mmol·l^{-1} (*Vtr* is 8.9 ml) and was reduced in 1.10 time.

2. The potable water of Sovetsky district undergo to the titration with the trilon B (*Vtr* is 11.0 ml, the rigidity is 5.5 mmol·l^{-1}). After the addition of 0.020 g·l^{-1} *β*-alanine (*Vtr* is 8.9 ml) the rigidity (4.5 mmol·l^{-1}) was reduced in 1.22 time.

After the addition of 0.021 g·l^{-1} *l*-asparagine (*Vtr* is 8.9 ml) in the next probe the rigidity (4.9 mmol·l^{-1}) was reduced in 1.12 time.

3. The technical water of Laishevo district undergo to the titration without of trilon B (*Vtr* is 12.9 ml, the rigidity is 5.9 mmol·l^{-1}). After the addition of 0.020 g·l^{-1} *β*-alanine (*Vtr* is 9.9 ml) the rigidity (4.9 mmol·l^{-1}) was reduced in 1.20 time.

4. The technical-potable water of Derbyshky district undergo to the titration without of trilon B (*Vtr* is 11.9 ml, the rigidity is 5.9 mmol·l^{-1}). After the addition of 0.020 g·l^{-1} *β*-alanine (*Vtr* is 9.9 ml) the rigidity (4.9 mmol·l^{-1}) reduced in 1.20 time.

However necessary to add to these experiments the next explanation. The general quantity of Ca and Mg salts in the extracts is equal ~0.5 mmol and the stechiometric relation between metal and amino acid in complexes is equal 1:2. Consequently, only 0.11 mmol or about 20% of metal is connected with amino acid. Necessary to increase the amount of amino acid for the else more lowering rigidity of water.

Necessary to note that the receiving results on the softness as technical so potable water are not so impressive compared to industrial results [1,2], but from the ecological and spending points of view they seem acceptable.

Such experimental results prompted us to calculate the heat of combustion (Δ_cH°) and formation (Δ_fH°) of complexes of calcium and magnesium with the mentioned above amino acids [Met(*amino acid*)$_2$, formula, Δ_cH°, Δ_fH° (kJ·mol^{-1}±0.5% correspondingly), number of valence electrons (*N-g*)] in accord with the scheme of thermochemical research (Eqs. 2 and 3) suggested in the previous part. The calculated magnitudes are: for Ca(*β-alanine*)$_2$, $C_6H_{12}N_2O_4Ca$, -3327.9±16.6, -1383.5±6.9, 32; for Ca(*l-asparagine*)$_2$, $C_8H_{14}N_4O_6Ca$, -4170.3±20.8, -1614.0±8.1, 40; for Mg(*β-alanine*)$_2$, $C_6H_{12}N_2O_4Mg$, -3327.9±16.6, -1349.6±6.7, 32; for Mg(*l-asparagine*)$_2$, $C_8H_{14}N_4O_6Mg$, -4170.3±20.8, -997.0±5.0, 40.

The received thermochemical data are corresponded to the representation about a high stability of calcium and magnesium-amino acids formation and are proved the suggestion on their use as the softness means for any water.

The technical solution of this question can be the next: the introduction of the previously synthesized little peptides [8-10] or the introduction of alanine or asparagine into the filters in the time of the water preparation. In both cases the formed metal-amino acid complexes will remain in the filters or the sorption columns.

CONCLUSION

The received experimental results on the determination of the technical and potable rigidity of water allow to conclude, that alanine and asparagine can do a technical and potable water more soft into 1.10-1.22 times.

The increasing of the amount of amino acid must lead to the more sensitive lowering of the water rigidity. The chosen amino acids could be introduced into the sorption-filters for the preparation process of any water.

The calcium and magnesium salts form a stable complexes with the mentioned amino acids, but accordingly to thermochemical calculations, *l*-asparagine is more active in this process.

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