

Вологоутримуюча здатність (ВУЗ) є однією з найважливіших функціонально-технологічних властивостей. Харчова добавка "Магнетофуд» має комплексну дію, в тому числі ВУЗ. Тому важливим є вивчення механізму ВУЗ "Магнетофуд». Встановлено механізм взаємодії наночастинок (НЧ) харчової добавки "Магнетофуд» з функціональними групами біополімерів вуглеводного комплексу житньо-пшеничного борошна. Запропоновано "кластерно-капілярна» модель ВУЗ "Магнетофуд» з вуглеводами тіста. Молекули води спочатку адсорбуються, зокрема, на поверхні зерен крохмалю і в мікрокапілярах. НЧ "Магнетофуд», завдяки нанорозмірів, активної і іонізованої поверхні, біосумісності з полімерними молекулами вуглеводів, легко проникають в пори (мікрокапіляри). НЧ "Магнетофуд» мають високий хімічний потенціал, тому вони активують, наприклад, поверхню крохмальних зерен і внутрішню поверхню капілярів. Наночастинки "Магнетофуд» утворюють комплекси з ОН-групами і ефірними Оксигенами амілози і амілопектину крохмалю за рахунок координаційних зв'язків. Виникають супрамолекулярні ансамблі "Магнетофуд»-вуглевод" типу "кластерів». НЧ "Магнетофуд» також електростатично взаємодіють з диполями води. Виникають міцні аквакомплекси. Далі молекули H_2O проникають всередину – в найменш організовані ділянки ланцюгів макромолекул полісахаридів. Де утримуються водневими зв'язками з диполями "Магнетофуд» і іонногенними групами вуглеводів: атомами Гідрогену і Оксигену ОН-груп D-глюкопіранозних залишків. Навколо НЧ "Магнетофуд» виникають аквакомплекси, а в "кластерах» – сольватасоціації. Полімерні ланцюги розсуваються і поліпшується проникнення диполів H_2O всередину вуглеводу. Така абсорбція води послаблює міжмакромолекулярні зв'язки в щільних шарах полісахариду і сприяє проникненню в них вологи. Експериментально встановлено, що харчова добавка "Магнетофуд» володіє комплексною дією: сорбційним, комплексоутворюючим, волого- і жируотримуючим. А це призводить до збільшення виходу і поліпшення якості хлібобулочної продукції.

З цієї точки зору результати досліджень становлять інтерес не тільки для України, але і для наукового світу інших країн

Ключові слова: поліфункціональна харчова добавка, вуглеводний комплекс борошна, механізм взаємодії, "кластерно-капілярна» модель

SUBSTANTIATION OF THE MECHANISM OF INTERACTION BETWEEN THE CARBOHYDRATES OF RYE-WHEAT FLOUR AND NANOPARTICLES OF THE POLYFUNCTIONAL FOOD ADDITIVE "MAGNETOFOOD

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1. Introduction

Bread is an indispensable product in the daily diet of our compatriots, which is why adding useful components to its composition can significantly affect people's health. Bread satisfies 30 % of the need for protein and calories, 50 % – for vitamins of group B, salts of iron, phosphorus, carbohydrates, and dietary fibers [1, 2].

Dough and baked bread are complex hydrophilic colloidal systems, whose state depends on the properties of raw materials that are used for baking, parameters of the techno-

logical process, and the changes that occur when baking and storing bread. Thus, the state of moisture in dough and bread represents not only theoretical, but practical interest as well [3, 4]. Moisture-retaining capacity (MRC) is an important functional-technological property of the carbohydrate-containing raw materials and finished products. MRC is characterized by the degree of water absorption. MRC is equal to the mass of water retained by 1 g of dry matter under certain conditions [4].

The carbohydrate complex of flour is dominated by higher polysaccharides – hydrocolloids (starch, fiber (cellulose),

hemicellulose, pentosane). Flour contains a small amount of sugar-like polysaccharides (di- and trisaccharides) and simple sugars (glucose, fructose).

When baking bread, polysaccharides partially gelatinize and split into dextrin hydrolytically. In addition, storing bakery products "deteriorates" the nanostructure of gelatinized starch and bread becomes stale as a result. In order to stabilize the nanostructure of starch and polysaccharide solvato associates in the carbohydrate complex of flour, we suggest using the nanoparticles of the food additive "Magnetofood". "Magnetofood" is a polyfunctional food additive with a comprehensive effect, which is a finely-dispersed powder with particles the size ~ 78 nm [5–7].

Structural elements with particles the size of up to 100 nm possess a qualitatively new range of properties: mechanical, magnetic, thermal and electro-conducting, optical, chemical, and biological. The specificity of the nanoparticles properties manifests itself through quantum-mechanical effects [8, 9]:

- reduction of crystalline lattice parameters for ferrites of Fe_3O_4 type when the size of particles is less than 100 nm. This is accompanied by its transition from transition from the cubic to octahedral, as well as an increase in the share of surface active reactive atoms [10, 11];

- increase in the surface area, which is the place of accumulation of crystalline defects that lead to changes in chemical potential and reactivity;

- very small size of the structural units, or a high dispersion of nanoparticles and the large number of phase boundaries and the developed specific surface. That all has a decisive role in the formation of unusual physical-chemical properties of nanoparticles: high reactivity and surface activity, pronounced sorption activity [12];

- the excess free energy of nanoparticles, which determines predisposition to nucleation, solvation, and aggregation with the formation of supramolecular ensembles, solvato complexes, agglomerates [13].

Nanoparticles of the food additive "Magnetofood" possess great potential and high biocompatibility with biopolymers, particularly carbohydrates. Thus, they promise a variety of important fundamental discoveries, new functional and technological properties, and advanced technological applications [8, 10]. Non-covalent adsorption of polymeric molecules, H_2O dipoles, occurs at the surface of the magnetic nanoparticles of "Magnetofood". The process of adsorption of polysaccharides and water is mainly determined by the ionic, van der Waals, hydrogen, and hydrophobic types of interactions. These interplays occur between the surface of the nanoparticles and the adsorbing molecules and lead to a change in the Gibbs free energy. There form supramolecular ensembles, which significantly influence the functional and technological properties of raw materials and semi-finished products, as well as the quality of the finished products.

Certain scientific efforts are required to elucidate the mechanism of MRC of nanoparticles (NP) of the food additive "Magnetofood" and the mechanism of interaction between the "Magnetofood" NP and the polysaccharides of carbohydrate complex of flour. First, one needs to understand the nature and strength of interaction between the "Magnetofood" nanoparticles and water. Second, it is necessary to understand the nature of interaction between the "Magnetofood" NP and respective substrates [14, 15].

2. Literature review and problem statement

An analysis of the scientific literature [3, 4, 16–40] reveals that a variety of raw ingredients have been applied in order to adjust bread baking properties, specifically the water-absorbing capacity of flour and moisture-retaining capacity of dough systems. However, there are no data on the patterns of interaction between the nanoparticles of metal oxides and carbohydrates of flour and other food ingredients.

The main components that bind water in dough are proteins and *starch*. Scientific papers [3, 4] report that 82–85 % of all the water introduced to dough is absorbed by starch and proteins.

Starch is the most important carbohydrate in flour; it is in the form of grains the size from 0.002 to 0.15 mm. The size, shape, the ability to swell and gelatinize of starch grains are different for different kinds of flour. Starch (Fig. 1) is a mixture of 2 homopolysaccharides: linear – amylose, and branched – amylopectin, whose general formula is $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. The ratio of amylose to amylopectin is equal to 1:4 [16, 17]. Starch is both a *strong* and very *labile* formation. The *strength* of the structure of the starch grain is predetermined by the presence of several bonds ("bridges") in it that bind together the macromolecules residing side by side. Thus, a large number of the OH-groups present in starch predetermines the existence of a hydrogen bond. The phosphate acid contained in starch also participates in the formation of "bridges", producing the ethereal connections between the adjacent chains of macromolecules. In addition, strengthening the structure of starch can occur due to its low molecular fractions. The *lability* of starch manifests itself in its extreme sensitivity to various external influences, sometimes very weak. Starch easily changes its structure. Moreover, depending on the nature and power of influence on the starch grain, certain bonds will break while other types of links may remain unchanged. All that makes starch extremely volatile (*labile*) chemically, as well as colloiddally-chemically [16–19].

The *adsorption of water* occurs mainly at the surface of starch grains and in micro-capillaries. Moisture in micro-capillaries can be associated with the inner surface of the capillaries of carbohydrates mechanically and physically-chemically. Adsorptive moisture is the easiest to remove. The amount of adsorbed water is directly proportional to the surface of starch grains or inversely proportional to the average size. The *absorption of water inside the grains of starch* occurs mostly in the active centers, located in the amorphous regions. The amount of absorbed water is inversely proportional to the degree of biopolymer crystallinity and is associated with the inner structure of starch grains [20, 21].

Starch from different plants differs by the hydrophilicity and strength of the micellar structure. Thus, rye starch swells easier and better peptizes (dissolves) than that of wheat [20, 22].

One of the most important properties of the native starch is the capability of its grains to *swell* in water with increasing temperature, yielding a viscous colloidal solution (gel). In the process of swelling and gelatinization part of the polysaccharides dissolves and remains in the grain void (granules), with part of macromolecules passes into solution. The temperature at which such a change in the starch grain occurs is called the temperature of gelatinization. Gelatinization temperature of wheat starch is 54–62 °C, rye starch – 50–55 °C.

Structure-forming phase in the rye-wheat dough consists of a gluten "frame" and swollen starch granules. When baking bread, polysaccharides partially gelatinize and split into dextrin hydrolytically. Over time, storing the bakery products "deteriorates" the nanostructure of the gelatinized starch; bread stales as a result [20, 23, 24].

Technological splitting of starch granules is carried out under conditions of an elevated temperature and under the action of hydrolytic enzymes (Fig. 1) [23]:

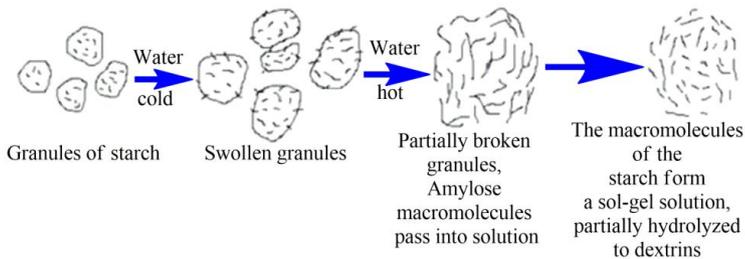


Fig. 1. Schematic of technological changes in starch grains

Disruption of the aggregative stability of dispersed systems leads to the division into macro-phases or to the emergence in the volume of the system of spatial fractal structures and to the transition of a freely-dispersed system (*sol*) into the bound dispersed gel nanostructure. The gel system, based on the starch macromolecules, consequently acquires a complex of new structural-mechanical (rheological) properties, which include strength, resiliency, elasticity, etc. *Gel* forming is predetermined by the emergence of a spatial "frame", which prevents fluidity [23, 24].

A variety of technological treatment techniques (physical, chemical, biological) for native starch make it possible to greatly change the structure and properties, which include primarily hydrophilicity (specifically the capability to dissolve in cold water), the ability to gelatinize and form gel, resistance to heat and action of acids, etc.

To stabilize the structure and moisture-retaining ability of polysaccharides in food masses, particularly in the rye-wheat dough semi-finished product, we suggest applying the polyfunctional food additive "Magnetofood". During hydration of carbohydrates in the presence of nanoparticles (NP) of the food additive "Magnetofood", *polysaccharides* form supramolecular ensembles with the system of hydrogen, hydrophobic, electrostatic, coordinating bonds and a mixture of polymer molecules.

To improve the water-absorbing capacity (WAC) of flour and the moisture-retaining capacity (MRC) of dough masses, the technologies of bread baking employ mineral compounds (ammonium salts of orthophosphate acid, sodium orthophosphates, potassium orthophosphates) [25]. The shortcoming of these additives is the insufficient functionality in terms of specific volume, porosity and shape stability of bread; the mechanism of interaction between the carbohydrates of food raw materials, flour and other ingredients remains unclear.

It is possible to very effectively enhance the MRC of dough and the actual yield of bakery products by applying the specialized compositions of the enzymes DSM for the non-starch polysaccharides of flour [26]. Their drawbacks are their narrow focus of application; the absence of an integrated effect and a lack of the moisture-retaining capacity model.

Improving the moisture-retaining capacity (MRC) of dough can be achieved by the enrichment with the biologically active substances of vegetable, fruit [27], and herbal supplements [28]. The shortcomings of supplements is the low functionality in terms of texture and physical-chemical properties of baked products; the mechanism of interaction between the carbohydrates of powder-like food raw materials is not substantiated.

Widespread at present are various polysaccharides: citrus fibers; hydrocolloids of plant origin, ethers of cellulose. *Hydrocolloids*: banana and apple powders; buckthorn meal; guar and xanthan gums; polydextrose is a polysaccharide composed of glucose polymers with low molecular weight [29]. *Citrus fibers* are the source of useful health fiber. Their content of dietary fiber ranges from 88 to 93 %, including about 20 % soluble [30]. However, their influence on the technological parameters of dough semi-finished products and finished products is not significant. The antioxidant, bacteriostatic effects are missing, there is no any model of moisture-retaining capacity; high cost.

In order to enhance water-absorbing capacity (WAC) of flour, it is proposed to use natural powder-like ingredients. These compounds are obtained by drying the dairy [31] and egg products [32]: natural fat-free yoghurt, low-fat natural cheese, fat-free milk, egg yolk, etc. Their shortcomings include the lack of polyfunctionality and mechanism of interaction between carbohydrates of flour and an insufficient output of finished products.

Recently, food technologies have exploited, in order to enhance the moisture-retaining capacity, a variety of functional ingredients obtained from industrial by-products: skin, hoof, feathers [33]; offal [34]; grains, bran [35]; serum [36]. The general drawback is the narrow focus of application, insufficient moisture-retaining capacity and the lack of an integrated effect; the mechanism of interaction with the carbohydrates of food raw materials and dough systems is not substantiated.

The bread baking technologies use wheat-based bio-supplements to improve the MRC of dough [37]. However, neither yield, no structural-mechanical parameters of finished products improved; still lacking is the model of a moisture-retaining capacity.

To enhance the water-absorbing capability of flour and the moisture-retaining capacity of dough, bread making also uses bio-supplements of various chemical composition: soybean, chickpea [38]; enzymes, microalgae [39]. The disadvantages of soy bean and chickpea is their insufficient functionality in terms of specific volume, porosity, and shape stability of bread. And for enzymes and microalgae – a high cost and insufficient yield of finished products. However, the mechanism of interaction with the carbohydrates of flour and dough systems was not considered.

In recent years, bread making has exploited, in order to enhance the MRC of flour and dough, phenol-derivative compounds of plant origin [40]. The disadvantages of these dietary supplements are the insufficient output; shelf life of the finished products; the model of moisture-retaining capacity is not substantiated.

Analysis of information sources [3, 4, 16–40] reveals the lack of data on the use of nanopowdered additives-improvers in bread making technology, and the model of

interaction with polymeric matrices of the carbohydrate complex of flour. To create new functional and technological properties and to substantiate the mechanism of moisture-retaining capacity, particularly in the rye-wheat dough system, we suggest using the polyfunctional food additive "Magnetofood". The "Magnetofood" nanoparticles of the food systems "Magnetofood" demonstrate sorption, complexing, emulsifying, moisture-retaining, fat-retaining, moisture-binding properties, as well as contribute to the stabilization of indicators of semi-finished products and finished products in the process of manufacturing and storing and helps receive bakery products with high consumer characteristics [5–7, 14, 15].

3. The aim and objectives of the study

The aim of present study is to substantiate the mechanism of interaction between the carbohydrates of rye-wheat flour and nanoparticles (NP) of the food additive "Magnetofood" in order to improve the moisture-retaining capacity of dough.

To accomplish the aim, the following tasks have been set:

- to substantiate the mechanism of interaction between nanoparticles (NP) of the food additive "Magnetofood" and the functional groups of biopolymers of the carbohydrate complex of rye-wheat flour;
- to establish the mechanism of NP influence of the food additive "Magnetofood" on the binding of moisture by biopolymers of the carbohydrate complex of rye-wheat dough;
- to substantiate the mechanism of interaction between nanoparticles of the food additive "Magnetofood" and biopolymers of the carbohydrate complex of rye-wheat dough and to elucidate its moisture-retaining capacity.

4. Materials and methods to study the food additive "Magnetofood"

4. 1. Examined materials and equipment used in the experiment

We examined the impact of NP of the polyfunctional food additive "Magnetofood" on the technological properties, specifically moisture-retaining capacity, of rye-wheat dough.

Object to study: technology of rye-wheat bread.

Subjects to study:

- sample 1 control – dry rye-wheat starch, which is a mixture of rye starch, first grade [TU 10.62.11-668-37676459-2017. Packed starch. Scientific-industrial center "Agroprom"], and wheat starch of high grade [RST UkrSSR 1490-90 Starch of wheat. Technical specifications]. The ratio of rye to wheat starch is 60:40;
- sample 2 – dry rye-wheat starch with the polyfunctional food additive "Magnetofood" in the amount of 0.10 % by weight of starch in the form of a powder [6];
- sample 3 – dry rye-wheat starch with the polyfunctional food additive "Magnetofood" in the amount of 0.15 % by weight of starch in the form of a powder [6];
- sample 4 – dry rye-wheat starch with the polyfunctional food additive "Magnetofood" in the amount of 0.20 % by weight of starch in the form of a powder [6];
- sample 5 control – rye-wheat flour in line with DSTU-P 4583:2006. The ratio of raw rye flour to wheat flour, first

grade, is 60:40, according to the base formulation of the rye-wheat bread "Darnytski" [42];

- sample 6 – rye-wheat flour with the polyfunctional food additive "Magnetofood" in the amount of 0.10 % by weight of flour in the form of a powder [6];

- sample 7 – rye-wheat flour with the polyfunctional food additive "Magnetofood" in the amount of 0.15 % by weight of flour in the form of a powder [6];

- sample 8 – rye-wheat flour with the polyfunctional food additive "Magnetofood" in the amount of 0.20 % by weight of flour in the form of a powder [6].

The examined materials, equipment, and procedures applied in the experiment, are described in detail in paper [41].

5. Results of studying the mechanism of interaction between the food additive "Magnetofood" and the carbohydrates of rye-wheat flour

We investigated influence of the polyfunctional food additive "Magnetofood" on swelling, as well as the viscosity of suspensions with water, the moisture-retaining capacity, using model systems. The polyfunctional food additive "Magnetofood" was introduced in a dry form when preparing the test samples of starch and rye-wheat flour in the amount of 0.10–0.20 % by weight of starch or flour in the form of a powder [6].

The properties of starch, flour and dough, and the bread, baked using it, depends on the state of water that they contain, the ratio of moisture that is in the free and associated state. To clarify the mechanism of influence of the food additive "Magnetofood" on ingredients of the carbohydrate complex of rye-wheat dough, we examined during our study the amount of bound and free moisture in the tested samples of rye-wheat starch.

Our previous studies [14, 15] considered the processes of water adsorption at the NP surface of the food additive "Magnetofood" in detail. The mechanisms of interactions that occur between the "Magnetofood" NP and ionogenic groups of carbohydrates were also tackled.

To explain the increase in the moisture-retaining capacity (MRC) of dough made from the rye-wheat flour containing the "Magnetofood" NP, we suggest using a "cluster-capillary" model, which explains the formation of bonds between the food additive "Magnetofood", the moisture and carbohydrates of dough.

According to Bushuk, out of the total amount of water that is absorbed by a flour semi-finished product, 31.1 % is sorbed by protein; 45.5 % – by starch, and 23.4 % – by pentosanes [3].

Starch is very labile and sensitive to chemical reagents, specifically those that contain a metal. Especially strong effect on starch is exerted by electrolytes, particularly on the processes of swelling and starch gelatinization.

The nanoparticles (NP) of "Magnetofood" modify starch, changing its structure, helping to enhance the solubility and swelling even in cold water. NPs of the food additive "Magnetofood" interact with polysaccharides through the non-covalent coordination.

Fig. 2 shows the internal molecular complex of the "Magnetofood" NP with the main chain of amylose (or amylopectin) of starch.

Polarized nanoparticles (NP) of the food additive "Magnetofood" penetrate the micro capillaries and, by interact-

ing with ionogenic groups of biopolymers, activate starch, contributing to its swelling. Fig. 3 shows results of the interaction between NP of the food additive "Magnetofood" and water and a fragment of the main chain of amylose (or amylopectin).

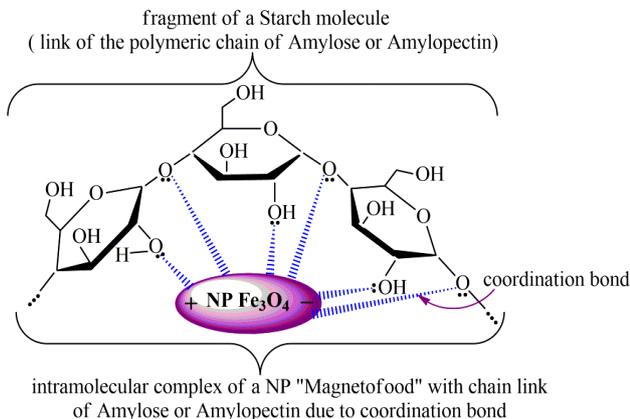


Fig. 2. Intramolecular complex formed by NP of the food additive "Magnetofood" and the link of the main chain of amylose (or amylopectin)

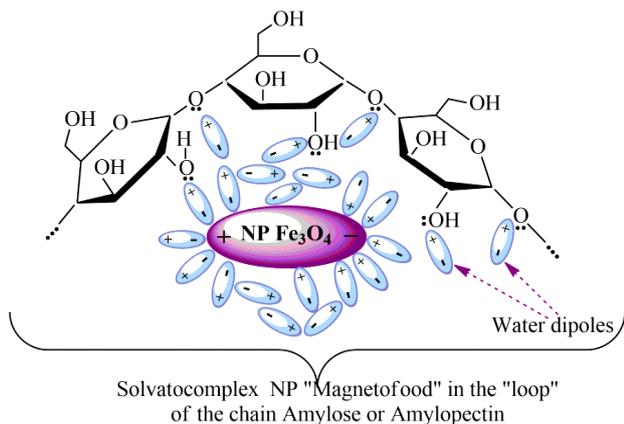


Fig. 3. Solvato complex inside the micro capillary whose internal wall are created by links of the main chain of amylose (or amylopectin)

Fig. 4, 5 illustrate intra- and intermolecular complexes of the "Magnetofood" NP with a link of the chain of amylopectin (Fig. 4) and links of the two main chains of amylopectin (or amylose) (Fig. 5).

It follows from data in Fig. 4, 5 that the coordinating interactions occur between nanoparticles of the additive "Magnetofood" and the oxygen (etheric, pyranose, and hydroxyl) of the D-glucopyranose remnants.

Fig. 6, 7 show the distribution of water dipoles in the "clusters" of links of the solvated polymeric chains of amylopectin and amylose.

Fig. 6, 7 show that an increase in the degree of branching of polymeric chains of amylopectin and amylose improves the penetration of H₂O inside starch.

Such an absorption of H₂O weakens the intramolecular bonds in dense layers and contributes the penetration of moisture in the most crystal layers. The result is the improved swelling, water-absorbing and moisture-retaining capacity of starch.

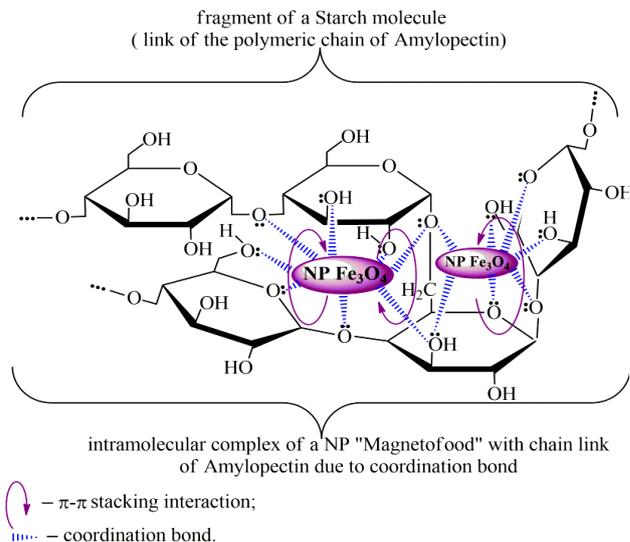


Fig. 4. Intra-molecular complex formed by the food additive "Magnetofood" NP and a link of the chain of amylopectin

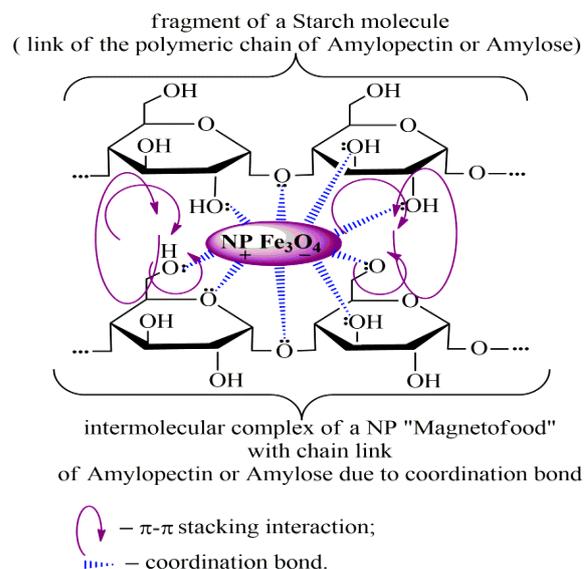


Fig. 5. Intermolecular complex formed by the food additive "Magnetofood" NP and links of the two main chains of amylopectin (or amylose)

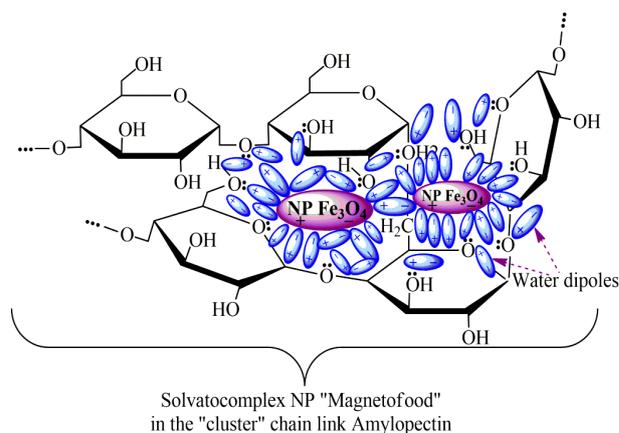


Fig. 6. Distribution of water dipoles in the "clusters" of link of the solvated polymeric chain of amylopectin

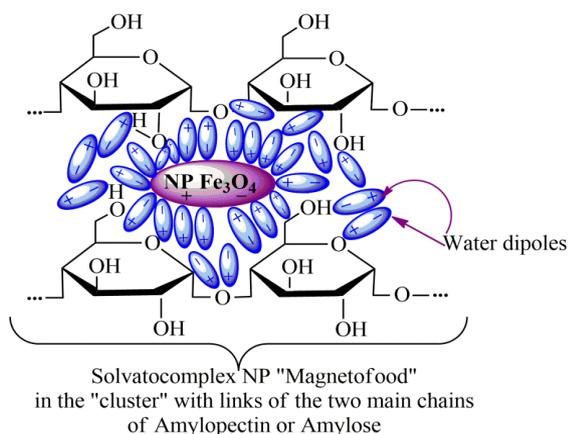


Fig. 7. Distribution of water dipoles in the "clusters" of links of two solvated polymeric chains of amylose and amylopectin

Essential role in the formation of functional and technological properties of rye-wheat flour belongs to structural polysaccharides, such as *cellulose* and *hemicellulose*.

When the food additive "Magnetofood" is added to the formulation of rye-wheat dough, structural carbohydrates are also exposed to its action. That is why we shall further consider the mechanisms of interaction between the "Magnetofood" NP and cellulose, hemicellulose. We shall investigate effect of the additive "Magnetofood" on their water-absorbing and moisture-retaining capacity.

Fig. 8 shows the mechanism of interaction between the food additive "Magnetofood" NP and a link of chain of cellulose.

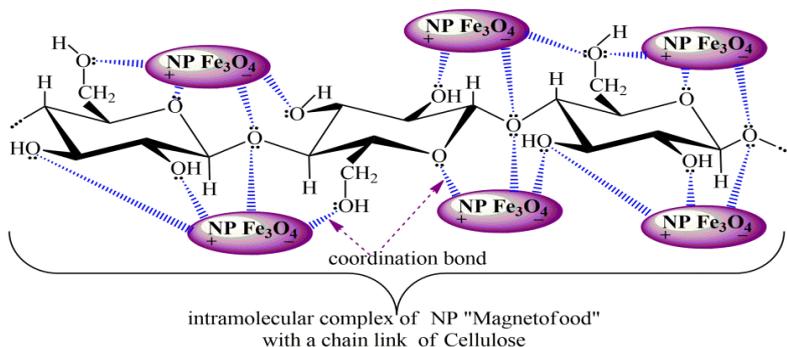


Fig. 8. Intra-molecular complex formed by the food additive "Magnetofood" NP and a link of the chain of cellulose

Fig. 9 shows the distribution of H₂O dipoles in a link of the cellulose chain

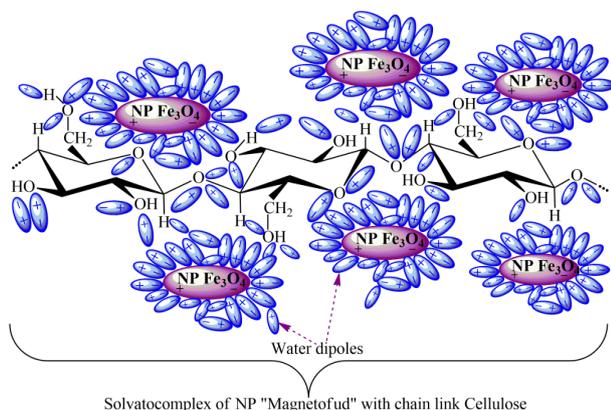


Fig. 9. Distribution of water dipoles in a link of the cellulose chain

It follows from data in Fig. 8, 9 that solvato associates are formed due to the open (linearly non-branched) structure of cellulose and the accessibility of hydrophilicity centers (NP of "Magnetofood", OH-groups, etc.).

The result is the improved absorption of moisture at the hydrophilic centers at the expense of hydrogen bonds. That, along with the finely-shredded texture, contributes to better swelling of the flour cellulose (Fig. 10).

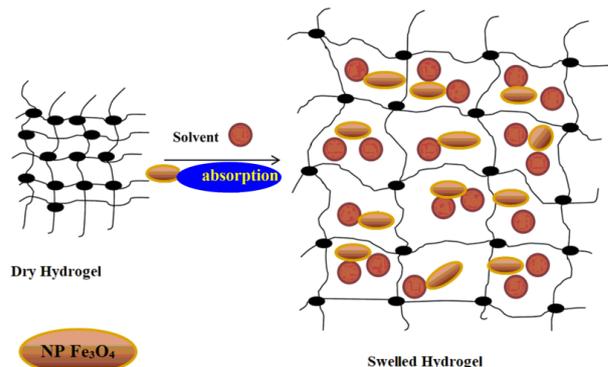


Fig. 10. Swelling process of a hydrocolloid

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The result is the improved absorption of moisture at the hydrophilic centers at the expense of hydrogen bonds. That, along with the finely-shredded texture, contributes to better swelling of the flour cellulose (Fig. 10).

Most *hemicelluloses* have an irregular structure and contain branched regions. Hemicelluloses, similar to cellulose, relate to the category of hydrophilic colloids, whose hydration is predetermined by electrostatic forces. That is why it is possible to use for hemicelluloses the "cluster-capillary" model of hydration under the influence of the food additive "Magnetofood".

Let us consider effect of the food additive "Magnetofood" NP on the structure of macromolecules of hemicellulose and the mechanisms of interaction between the additive "Magnetofood" and the ionogenic groups of macromolecules of a polymer and the polarized molecules of water. These mechanisms for glucomannan are similar to cellulose (Fig. 8, 9). Fig. 11 shows the self-organization into an electrostatic complex of the food additive "Magnetofood" NP with a link of the chain of xylan.

Data in Fig. 11 demonstrate how the electrostatic complexes between the "Magnetofood" NP and xylan are formed.

Fig. 12 shows the distribution of water dipoles in a link of the xylan chain.

It follows from Fig. 11, 12 that the influence of the "Magnetofood" NP increases the degree of branching of macromolecules and the number of available hydrophilic centers; there emerge the "clusters" in which the free and bound moisture is retained in the form of molecules of water and solvato complexes.

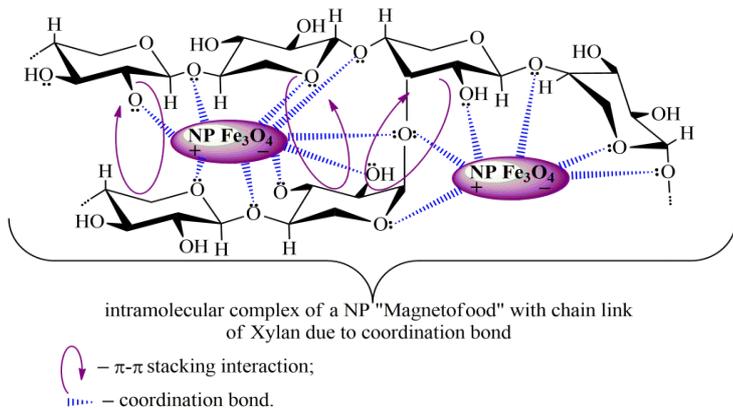


Fig. 11. Self-organization into an electrostatic complex of the food additive "Magnetofood" NP with a link of the chain of xylan

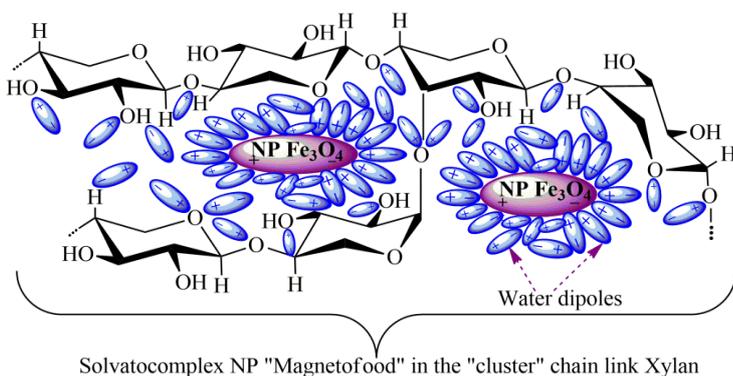


Fig. 12. Solvato complexes in the "clusters" of a link of the xylan chain

6. Discussion of results of studying the influence of the food additive "Magnetofood" on the moisture-retaining capacity of rye-wheat dough

Analysis of experimental data (Fig. 2) shows that there is an electrostatic complex emerging between the "Magnetofood" NP and the main chain of amylose (or amylopectin). This agglomerate forms at the expense of six intra-molecular coordination bonds between the "Magnetofood" NP and the atoms of Oxygen of glucose pyranose cycles.

An analysis of data from Fig. 3 reveals that in the pores (micro-capillaries) of starch the "Magnetofood" NP are the centers of hydrophilicity. NP of the food additives "Magnetofood" enter the dipole-dipole and ion-dipole interactions with the polarized water molecules. Solvato complexes thereby form.

Thus, during contact between water and starch its molecules originally *adsorb at the surface of starch grains and in micro-capillaries*. Next, water molecules penetrate starch forming the hydrogen bonds in the least organized sections of the chain of macromolecules. The formations emerge: "Magnetofood"-carbohydrate of the "cluster" type.

Data in Fig. 4, 5 show that the coordinating bonds reinforce the π - π stacking interaction between pyranose cycles of the "plane-to-plane" type. In the amylopectin molecule (or amylose), the π - π stacking interaction is pre-determined by the electrostatic forces: hydrophobic forces and the London dispersion forces between the remnants of glucopyranose. All that contributes to: first, increasing the degree of branching of the main chain of amylopectin (or

amylose); second, the emergence of formations of the "cluster" type.

In other words, under the influence of the food additive "Magnetofood" NP, intra- and intermolecular associates form in starch. The result is the emergence of formations of the "cluster" type; the interweaving of highly branching molecules of amylopectin and spiral chains of amylose in a complex network (mesh or lattice) of interconnected polymeric molecules. The "Magnetofood" NP are the centers of hydrophilicity; the "clusters" are the formations that connect and retain moisture.

The more branched structure facilitates the interaction between starch and water. Nanoparticles of the food additive "Magnetofood" affect the chain structure of starch, increasing the degree of branching (Fig. 6, 7) and improving the penetration of H₂O into starch. Hydrogen bonds form between the dipoles of water and the "Magnetofood" NP dipoles, as well as between the atoms of Hydrogen and Oxygen of the OH-groups of D-glucopyranose residues of starch. Aqua complexes form around the "Magnetofood" NP; solvato associates form in the "clusters". That spreads the polymeric chains and improves water penetration into starch.

Such an absorption of H₂O weakens the intra-molecular bonds in dense layers and contributes to the penetration of moisture in the most crystal layers. The result is the improved swelling, water-adsorbing and moisture-retaining capacity of starch.

Thus, the micro-porous structure of starch grains and the polarized nanoparticles of "Magnetofood" with large specific surface predetermine the high sorption capacity of the starch-magnetofood mixture. Owing to the hydrophilic properties of the food additive "Magnetofood" NP and the macromolecules of amylose and amylopectin, starch granules that are enriched with the additive "Magnetofood" are very hygroscopic.

We propose a "cluster-capillary" model of the moisture-retaining capacity of the food additive "Magnetofood" with carbohydrates of rye-wheat dough. Its essence implies the following (we shall consider it using starch as an example). At contact between the carbohydrate-magnetofood mixture and water, its molecules originally *adsorb at the surface of starch grains and in micro-capillaries*. In the absence of the "Magnetofood" NP, moisture binds to the surface of grains and the inner surface of capillaries in a mechanical and physical-chemical fashion. Enriching starch with the food additive "Magnetofood" improves its water-adsorbing and moisture-retaining capacity. The "Magnetofood" NP, due to nano dimensions (78 nm), active and ionized surface, biocompatibility with carbohydrates, easily penetrate the pores (micro capillaries) of starch. The "Magnetofood" NP possess a high chemical potential, which is why they activate the surface of starch grains and the inner surface of capillaries. Nanoparticles of the additive "Magnetofood" form complexes with the OH-groups and essential Oxygens of amylose and amylopectin at the expense of coordination bonds. In this case, the "Magnetofood" NP also enter the electrostatic interactions with water dipoles. Solvato complexes thereby form. Solvato complexes retain water better compared with the mechanically and physically-chemically bound moisture.

Next, water molecules penetrate starch forming the hydrogen bonds in the least organized sections of the chain of macro molecules and forming a "Magnetofood"-carbohydrate of the "clusters" type. Hydrogen bonds also form between the dipoles of water and dipoles of the "Magnetofood" NP, as well as hydrogen atoms and oxygen of the OH-groups of D-glucopyranose residues of starch. Aqua complexes form around the "Magnetofood" NP; solvato associates form in the "clusters". This spreads polymeric chains and improves water penetration into starch. Such an absorption of water weakens the intramolecular bonds in dense layers and contributes to the penetration of moisture in the most crystal layers. The molecules of water, sorbed in the volume of starch grains, are in three states in the following form:

- 1) molecules, dissolved (free) in the matrix;
- 2) initially sorbed (strongly bound) at the active centers of the "Magnetofood" NP and the molecules of a given polysaccharide;
- 3) twice sorbed at the active centers of (clustered) molecules.

This process passes a stage of gel forming when starch grains swell and enhance in volume owing to the forces of cohesion between macromolecules.

It follows from data in Fig. 8 that the intra-molecular complex in the cellulose molecule forms through the coordination interaction between the nanoparticles of "Magnetofood" and the atoms of Oxygen (hydroxyl, ether, and pyranose). Each nano particle of "Magnetofood" coordinates around it at least 3–4 atoms of Oxygen.

The "Magnetofood" NP and the hydrophilic components of cellulose (OH-groups, atoms of Oxygen – essential and pyranose) are capable of entering electrostatic interactions and can form hydrogen bonds with the polarized molecules of H₂O.

An analysis of Fig. 8, 9 shows that the high reactive and complexing capacity of the food additive "Magnetofood" NP contributes to an increase in the energy potential of hydrophilic components of cellulose, thereby improving:

- 1) the adsorption of H₂O dipoles in micro-capillaries, built in a three-dimensional mesh structure;
- 2) the penetration of the H₂O polarized molecules inside cellulose through the spreading of polymeric chains and the weakening of intra-molecular bonds in dense layers.

The result is the improved absorption of moisture at the hydrophilic centers at the expense of hydrogen bonds. That, together with the finely shredded texture, contributes to the better swelling of flour cellulose (Fig. 10).

Data in Fig. 11 show that each "Magnetofood" NP enters 6 or more coordination interactions with the atoms of Oxygen (hydroxyl, ether, pyranose) of xylan. The electrostatic complexes thereby form. These, along with the hydrophobic "plane-to-plane" interactions of pyranose cycles, increase the degree of branching of polymeric chains and give rise to the emergence of formations of the "cluster" type.

It follows from Fig. 11, 12 that the influence of the "Magnetofood" NP increases the degree of branching of the macromolecules of xylan, specifically, there appear side chains that push the main chains apart. The result is the increased quantity of available hydrophilic centers. There also appear the "clusters", which retain both free and bound moisture in the form of water molecules and solvato complexes.

When solvato complexes form, there are shells forming at the surface of colloidal particles of polysaccharides, in particular xylan, due to electric charges arising as a result of ionization; the shells are composed of the dipoles of water, oriented,

depending on the sign of the charge of high-molecular compounds, by their positive or negative end. Similarly formed is the solvato complex on the ionized "Magnetofood" NP. The result is the improved hydration and swelling. That explains better hygroscopicity, water-adsorbing and moisture-retaining capacity of hemicellulose compared with cellulose.

The limitation of this study is that the proposed "cluster-capillary" model of the interaction between the food additive "Magnetofood" and polysaccharides of rye-wheat flour was considered only for one type of a dough system – rye-wheat. It is also not known how a given additive would affect technological indicators of dough semi-finished products with a different formulation (from other types and varieties of flour).

The merit is that we proposed a model of interaction between the food additive "Magnetofood" NP and polysaccharides. This model could be used to study the functional and technological indicators, specifically MRC, carbohydrate complexes of other food systems (meat, dairy, etc.).

7. Conclusions

1. We have established the mechanism of interaction between nanoparticles (NP) of the food additive "Magnetofood" and the functional groups of biopolymers of the carbohydrate complex of rye-wheat flour: starch (amylose and amylopectin), cellulose, hemicellulose, in particular xylan. Polysaccharides form with the nanoparticles (NP) of the food additive "Magnetofood" supramolecular ensembles with a system of chemical bonds and electrostatic interactions.

2. We have established the mechanism of influence of the food additive "Magnetofood" NP on binding the moisture by biopolymers of the carbohydrate complex of rye-wheat dough. During hydration of carbohydrates, the "Magnetofood" NP interact with the biopolymers of the carbohydrate complex. This gives rise to the system of hydrogen, hydrophobic, electrostatic, coordination bonds; the interweaving of polymeric molecules. Clathrates, cavitates, clusters, aqua complexes, and solvato associates thereby form.

3. We propose a "cluster-capillary" model of the moisture-retaining capacity of the food additive "Magnetofood" with the carbohydrates of rye-wheat dough. At a contact between carbohydrate-magnetofood mixture and water, its molecules initially *adsorb at the surface of starch grains and in micro-capillaries*. In the absence of the "Magnetofood" NP, moisture binds to the surface of the grains and the inner surface of capillaries mechanically and physically-chemically. The food additive "Magnetofood" NP form complexes with the OH-groups and essential Oxygens of the carbohydrate. They also enter electrostatic interactions with the dipoles of water. Solvato complexes thereby form. Solvato complexes better retain water in comparison with the mechanically and physically-chemically bound moisture.

The molecules of H₂O penetrate then the least organized sections of the chain of macromolecules, particularly starch. There emerge the hydrogen bonds and the formation of a "Magnetofood"-carbohydrate of the "clusters" type. Hydrogen bonds occur between the dipoles water and the dipoles of the "Magnetofood" NP. In addition, between the atoms of Hydrogen and Oxygen of the OH-groups of D- glucopyranose residues of starch. Aqua complexes form around the "Magnetofood" NP; solvato associates form in the "clusters". This improves water penetration into the biopolymeric matrix. The hydration and water-retaining capacity of the carbohydrate improve.

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