Combined food additive based on iron oxide nanoparticles and кombu in a rye-wheat bread technology

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Abstract

Introduction. The aim of the study was to develop a technology for rye-wheat bread with a combined food additive (CFA) consisting of iron oxide nanoparticles (IONPs) and powder of dried brown algae *Laminaria japonica* L. (kombu) to improve baking performance and the nutritional value of the end-product.

Materials and methods. The synthesized IONPs and kombu powder were used to prepare a combined food additive that was added in the amounts of 1.0, 1.5, and 2.0% of the flour weight during the manufacturing of rye-wheat bread. Physical and textural characteristics of dough and bread were evaluated using standard methods. Sensory analysis of bread was performed to compare it with a traditional one.

Results and discussion. Preliminary treatment of kombu powder by hydration for 10 min and boiling in water for 5 minutes allowed reducing the iodine content by 78.9% to avoid the risks to exceed the recommended iodine daily intake. The inclusion of the CFA in the amounts of 1.0, 1.5, and 2.0% of the flour weight reduces the dough spreadability index from 4.6 to 11.4%, increases the accumulation of carbon dioxide in the dough from 6 to 11% and the specific volume of the dough from 6 to 13%, while reducing the dough formation time by 8.0±1.5 min. Rye-wheat bread with CFA had an increased specific volume by 17 to 33%, crumb porosity by 16 to 37%, shape stability by 19 to 59% compared to the control bread. A comparative analysis of physicochemical characteristics and sensory indicators determined the optimal amount of CFA 1.5% as for inclusion as an ingredient in rye-wheat bread formulation. The calculation of the biological value indicates an improvement in the nutritional value of the developed rye-wheat bread. Fortification of bread at a level of 55±10 μg/100 g of product with iodine allows recommending it to consumers with iodine deficiency diseases.

Conclusion. Combined food additive based on iron oxide nanoparticles and kombu powder can be used as an ingredient in the formulation of rye-wheat bread to stabilize its structure and improve the textural characteristics. The presence of valuable nutrients in its composition allows it to enhance the nutritional profile of rye-wheat bread.

Introduction

One of the modern trends in food production is application of novel natural additives is the development of functional foods with health-promoting properties (Ivanov et al., 2021). Among them, edible seaweeds (macroalgae) attract attention as supplements to the different traditional food products to increase their nutritional value and shelf life (Healy et al., 2023; Kryzhova et al., 2021; Polat et al., 2023; Stabnikova et al., 2021). Seaweeds are considered to be one of the most promising food resources due to their remarkable adaptability and short development period (Adeyemi and Fawole, 2023; Buschmann et al., 2017). This is evidenced by the steady increase in seaweed production, which has more than tripled worldwide over the past 20 years, according to the Food and Agriculture Organization (FAO, 2022).

Brown algae (*Phaeophyceae*) are among the most consumed seaweeds in human nutrition (Leandro et al., 2020). There are a number of reasons for this:

- high content of valuable nutrients such as sulfated polysaccharides, minerals, vitamins, dietary fibers, fatty acids, pigments, polyphenols, and polyunsaturated fatty acids (Biancarosa et al., 2018; Costa et al., 2021);
- specific technological functions allowing their use for stabilization and thickening in the food production;
- their use as nutraceuticals and pharmaceutical preparations due to the presence of bioactive compounds that exhibit various medical activities (Tagliapietra and Clerici, 2023).

Kombu (*Saccharina japonica*, formerly *Laminaria japonica*), a very popular brown seaweeds, can be classified as a valuable dietary product due to its low energy value, low content of fat and sugar (Mahadevan, 2015; Mohammed et al., 2021; Salido et al., 2024). These algae contain iodine in the form of iodides and iodates, as well as iodinated amino acids (Blikra et al., 2022; Romarís-Hortas et al., 2011), being one of the important natural sources of iodine and its organic compounds in human nutrition (Healy et al., 2023; Matos et al., 2024; Salido et al., 2024; Smyth, 2021). As is known, iodine is important for human health due to its fundamental role in the functioning of the thyroid gland and the associated production of thyroid hormones (Wells et al., 2017). Therefore, the use of algae-enriched products can be considered as a way to prevent iodine deficiency disorders (Matos et al., 2024). The content of this microelement in kombu significantly depends on growing conditions and time of harvesting and can change widely from 2500 to 10,000 μg/g dry weight (dw) (Smyth, 2021). At the same time, much lower number of 241 μg/g dw was presented in the review (Blikra et al., 2022). The iodine content in commercially available kombu powders varied from 3940 to 7430 μg/g dw depending on the batch of product purchased at different times (Gubskyi et al., 2015). This fact must be taken into account when fortifying food products and control of the iodine content in the finished product must be strictly observed. Consuming iodine in food in amounts exceeding the recommended daily allowance (RDA) of 150 μg (NIH, 2023) and especially the tolerable upper intake level (UL) of 600 μg/day for adults established in Europe (WHO, 2007) may have negative effects on human health (Correia et al., 2021; Roleda et al., 2018).

Another recent trend in food production is the implementation of nanotechnologies (Ameta et al., 2020; Sanguansri and Augustin, 2006). Unique and new functional properties of nanomaterials can find applications in food preparation, including improvement of the sensory characteristics of finished products and extension of their shelf life. All this fully applies to metal and metal oxide nanoparticles, which have a huge potential for use in the food industry, both in the development of innovative food products and in food packaging (Adeyemi and Fawole, 2023; Joshi et al., 2024).

Bread is one of the most widely consumed staple food throughout the world. Thus, it has significant potential for fortification with many functional ingredients and rapid dissemination of the developed functional foods with improved nutritional properties to the general population (Aabel et al., 2023). However, the addition of certain fortifying agents, including seaweeds, can have a significant impact on the textural and sensory properties of baked goods.

Despite the rich chemical composition of seaweeds, their traditional use in wheat or rye bread technologies has been limited (Polat et al., 2023). Meanwhile, there has been an increase in the research on this topic recently, especially for wheat flour products (Aabel et al., 2023). It was noted that the inclusion of seaweed in bread creates a number of new problems and complexities with significant changes in textural properties, sensory acceptability, and overall quality of the bread. Other studies have reported significant effects on the textural characteristics of bread, such as increased firmness and chewiness with decreased final porosity, and a consistent decrease in overall consumer ratings in sensory analysis (Arufe et al., 2018; Mamat et al., 2023; Sasue et al., 2023). The authors note that these effects increase with increasing amounts of seaweed powder added to the product formulation. However, some studies have shown consumer acceptability of bakery products containing up to 6% seaweed (Jönsson et al., 2024; Lamont and McSweeney, 2021; Mamat et al., 2023). All of these arguments support the conclusion of the review authors (Aabel et al., 2023) that the inclusion of seaweed as an ingredient in bread formulation requires careful balance and precise formulation to ensure that the desired characteristics are maintained.

The possibility of using iron oxide nanoparticles (IONPs) as a food additive with certain functional and technological properties was shown (Tsykhanovska et al., 2020; 2021; 2022a, b). The inclusion of IONPs into bread formulation improved its functional and technological properties during storage.

An analysis of the literature confirmed the lack of research on the simultaneous use of algae and nanoparticles in bread technologies. Therefore, the purpose of the present research was to study the possibility of using a combined food additive based on iron oxide nanoparticles and kombu powder in the technology of rye-wheat bread. This improvement should occur by taking advantage of both ingredients, namely kombu as a natural source of bioactive substances, and the unique properties of iron oxide nanoparticles.

Materials and methods

Chemicals and raw materials

All reagents used in the synthesis of iron oxide nanoparticles and analysis were provided by Merck (Darmstadt, Germany). Kombu (kelp powder, food grade, moisture less than 12%, crude protein 11.4%) was purchased from Fuzhou Beautiful Agricultural Development Co., Ltd (Fujian, China). Commercial grade wheat and rye flour, table salt, and pressed baker's yeast were bought in local markets in Kharkov, Ukraine. Natural concentrated rye sourdough "Sapore Othello" in powder form was purchased from Puratos, Belgium.

Preparation of combined food additive

The general flow chart of the CFA preparation and the wheat-rye bread, as well as their analysis using standard methods, is shown in Figure 1.

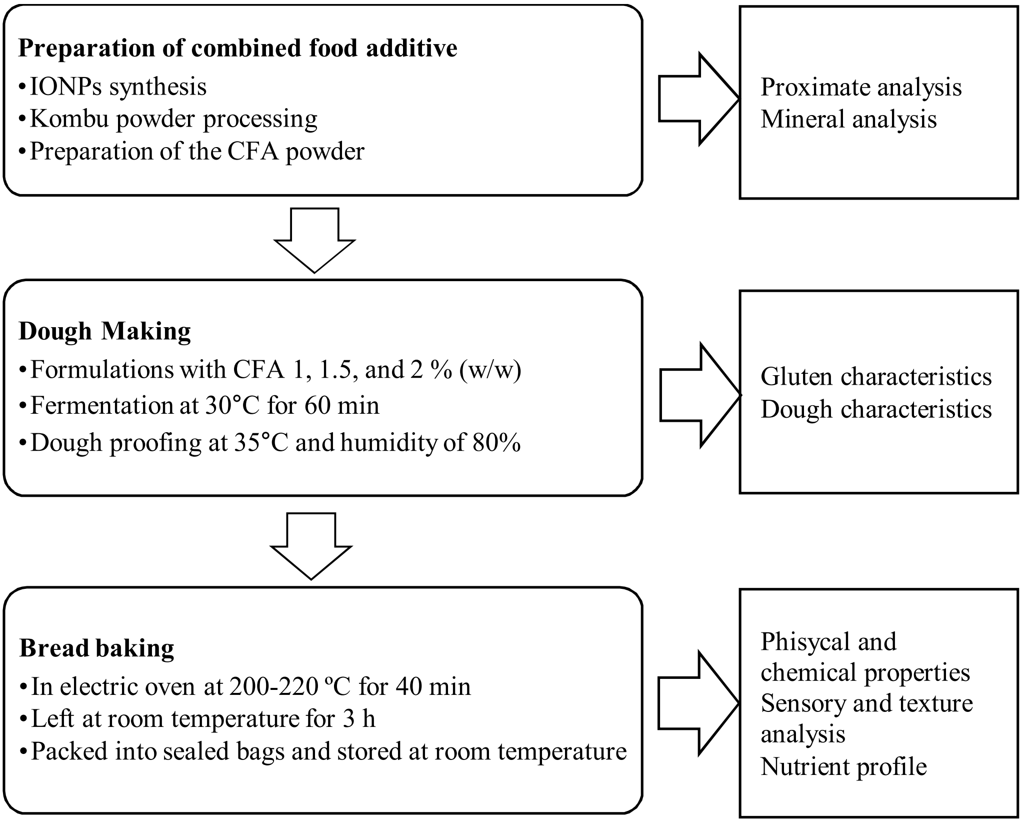

Figure 1. A chart flow of the research

Nanoparticles IONPs were obtained by precipitation of iron (II) and (III) salts with ammonia solution. The precipitate was washed with distilled water and dried at 100 ºC for 60 minutes. The obtained dark brown powder is a mixture of iron oxides FeO and Fe_2O_3 with an iron content of at least 90% and about 10% moisture. An average particle size was 75±10 nm with a zeta potential in aqueous suspensions 40±5 mV. The synthesized nanoparticles are stable to the action of external factors and oxidation.

Considering the significant iodine content in seaweed, kombu powder was pre-treated by rehydration and boiling according to the method (Correia et al., 2021) with slight modifications. Dry kombu powder was rehydrated for 10 min using tap water (ratio by 1:10 w/w) at room temperature. Then water was drained, and the rehydrated kombu was placed into boiling water and boiled for 5 min. Water was drained, and the seaweed biomass was dried in an oven at 40 °C for 12 hours. Finally, a dehydrated kombu was ground using a household coffee grinder Bosch TSM6A013B (BSH Hausgeräte GmbH, Germany) for 2–3 min to obtain a homogeneous fine powder. The average volume diameter of powder particles measured by laser diffraction on a PSA 1190 particle size analyzer (Anton Paar, Austria) was about 200±15 µm.

Next, the crushed kombu powder was ground in a mortar with IONPs for 3–5 minutes and the mixture was dried at 105 °C to a moisture content of no more than 5%. The complex food supplement prepared in this way contained 15% (w/w) iron oxide nanoparticles and 85% (w/w) kombu powder and was used as the ingredient in the formulation of rye-wheat bread.

Bread production

To prepare rye-wheat bread, a formulation with peeled rye flour, 60 g; wheat flour first grade, 40 g; dry rye sourdough, 3.0 g; table salt, 1.4 g, and water, 45 g, was used as a control called BC. In the developed bread, the formulation included a combined food additive in the amount of 1.0, 1.5, and 2.0% w/w of the total amount of flour, and these samples were named B1, B2, and B3, respectively. The dough was kneaded in a kitchen machine Tefal Bake Essential QB160138 (Tefal, France) for 20 min. The homogeneous dough was subjected to fermentation at a temperature of 30±2°C for 60 min. After giving the final shape to dough manually, it was allowed to be proofed at 35±2°C and humidity of 80±5%. Baking was performed in an oven KIY-V ShZh-3 (KYI-V, Ukraine) at temperature 200–220°C for 40 min. The breads were left at room temperature for 3 h. The samples were then packed into sealed bags and stored at room temperature for sensory analysis.

Proximate analysis

Protein content was determined by the Kjeldahl method (ISO 1871:2009, 2009) and a conversion factor of 6.25 was used for protein calculation. Fat content was determined by the Soxhlet extraction method (ISO 11085:2015, 2015), the fat was extracted with petroleum ether boiling range of 40–60°C and determined gravimetrically. The moisture and ash content of the samples was determined according to the official procedures 44-16.01 humidity-air-oven (aluminum plate) and 08-01.01 ash-basic method, respectively (AACC, 2000). The results were presented on a dry weight basis (dw).

Mineral analysis

The mineral contents of bread samples were determined with an inductively coupled plasma atomic-emission spectrometer Thermo iCAP 6300 Duo ICP-AES Spectrometer (Thermo Scientific, USA) with the operating parameters as in (Yurchenko et al., 2020). Sample preparation was performed according to (Bilgiçli and İbanoğlu, 2015) without modification. Determination of iodine content in the samples was carried out by galvanostatic coulometric titration using equipment (Gubsky, 2023) according to the procedure (Gubskyi et al., 2015). Preliminarily studied samples were subjected to mineralization using the method of dry alkaline ashing to convert all chemical forms of iodine into iodide.

Dough characterization

The effect of the combined food additive on gluten was assessed by the amount of raw gluten, its compressebility and extensibility, which were determined using standard methods according to Drobot (2015).

The titratable acidity of the dough was determined by the volumetric titrimetric method with a 0.1 M sodium hydroxide solution as titrant in the presence of phenolphthalein as an indicator. The result was expressed in degrees (Neumann). For the dough, two acidity values were determined as the initial acidity at the beginning immediately after the preparation of the bread dough and as the final acidity at the end of fermentation

Dough development and gas production were carried out using rheofermentometer CHOPIN Technologies Rheo F4 (KPM Analytics, USA). From the dough development and gas release curves, which were recorded in real time, the total volume of carbon dioxide released Vt in mL, value of maximum dough height Hm in mm, dough height at the end of the measurement h in mm, decline in dough development (Hm-h)/Hm in % and time to maximum dough development T1 in min were quantified.

Specific volume of dough was determined from the data on the initial volume of the dough and its change during fermentation according to the methodology (Drobot, 2015). In the experiment, a sample weighing 50 g was placed in a 250 ml cylinder and kept in a thermostat at a temperature of 30°C.

Dough spreading was determined by observing the change in the diameter of a dough ball weighing 100 g during its fermentation at a temperature of 30°C for 180 min (Drobot, 2015). When calculating the yield stress in Pa, data on the degree of penetration determined by the Labor penetrometer (LABOR machine s.r.o., Czech Republic) were used.

Bread quality assessment

The total titratable acidity, moisture content, specific volume and porosity were estimated by standard methods according to Drobot (2015). The total titratable acidity of the bread was determined by the titrimetric method with a 0.1 M sodium hydroxide solution as titrant in the presence of phenolphthalein as an indicator. Briefly, freshly crushed bread weighing 25±0.01 g was placed in a 500 ml flask. Then add 50 ml of distilled water and grind the bread into pulp. 200 ml of water was added to the resulting mixture and the flask with the sample was shaken for 5 minutes. It was allowed to settle for 30 minutes and filtered. The supernatant was titrated with alkali solution and the result was expressed in degrees.

Bread moisture was determined by drying 5 g of ground bread crumbs in an OlisLab 4300 drying oven (Chizhova's device) (Olis, Ukraine). The weight and volume of bread were measured after baking. Specific volume was calculated as weight/volume. The mass of the bread by weighing with the help of Certus Balance CBA-300-0,05 scales (Certus, Ukraine) and the volume of the bread (ml) were measured according to the principle of measuring the volume of loose filler (fine grain) squeezed out of the bread, using the device RZ-BIO (Laboratorna Technika, Ukraine). The porosity of rye-wheat bread in (%) was determined using the UOP-01 (Zhuravleva) device (ThermoLab, Ukraine) and calculated according to the expression

$$\text{Porosity} = \frac{V_x - (\frac{m_B}{\rho_M})}{V_x}$$

where V_x is total volume of the bread recess in ml;

m_B is the mass of the recesses in g;

ρ_M is the density of the non-porous crumb mass in g/ml.

The shape stability of rye-wheat bread (F in the standard edition) was determined by expression

$$F = \frac{H}{D}$$

where H is the bread height in cm;

D is the bread diameter in cm.

The effect of the additive on the shelf life of bread freshness was studied by crumbliness of the crumb determined after 72 hours of storage. For this purpose, two parallelepiped-shaped pieces weighing 5 g each were cut out of the crumb and placed in a 250 ml conical flask that was moved on a vibrating mixer for 5 min. The crumbs formed as a result of friction of the two pieces were collected and weighed on a scale with an accuracy of 0.01 g (Drobot, 2015). The crumbliness index X in % of the crumb weight was determined by the expression

$$X = \frac{G_1}{G_2} 100$$

where G_1 is the crumb weight in g;

G_2 is the weight of the bread sample in g.

Analysis of the crumb texture profile of rye-wheat bread samples was evaluated using a TA.HDplusC Texture Analyzer (Stable Microsystems, UK) with a cylindrical probe (P/25) at a compression ratio of 25% at a speed of 1 mm/s according to the method (Bourne et al., 1978). Ten different parts for three different batches were pre-selected. The samples were cut from the center of the product into squares of 2.0×2.0 cm and kept for 2.0 hours at 20±2ºC and relative air humidity of 45–50% before conducting the test for standardization of water absorption. The analysis was carried out on such textural properties as hardness in g, cohesiveness in g, springiness in g, chewennes in %, elasticity in g according to Szczesniak (2002).

Indicators of the biological value of proteins were evaluated within the framework of approach (Mitchelll and Block, 1978) in the form of the unbalance coefficient of the amino acid composition UCAAC in %, the coefficient of biological value BV in % and the coefficient of utilitarianism CU in the magnitude ranges from 0 to 1 according to the methodology presented in the study (Sokolovskaya et al., 2020)

$$UCAAC = \sum_i \frac{(SCORE_i - SCORE_L)}{8}$$

$$BV = 100 - UCAAC$$

$$CU = \frac{SCORE_{min} \times \sum_i^8 AAC_{st}}{\sum_i^8 AAC_s}$$

where $SCORE_i$ is the *i*th essential amino acid score in %;

$SCORE_L$ is the limiting essential amino acid score in %;

$SCORE_{min}$ is the minimum of the score's of essential amino acids in %;

AAC_{st} is the total content of essential amino acids in the reference protein in mg/g of protein;

AAC_s is the total content of essential amino acids in the sample protein in mg/g of protein.

The sensory properties of bread were determined by scoring the quality of baked goods (Drobot, 2015). A preliminary acceptance test was used to evaluate the following attributes in the bread samples: crust surface, crust and crumb color, bakedness, porosity, chewiness and elasticity of crumb, taste, and odor by the ISO's methods (ISO, 2012, 2016). The sensory analysis was performed at State Biotechnological University (Kharkiv, Ukraine) as in (Aksonova et al., 2022). The panelists stayed in the room with temperature 25±2 ˚C and the relative humidity 55±3%. The samples were prepared 1 h before the evaluation. Samples were kept in coded plates covered with aluminium foil. Ten trained panellists were selected to guarantee the evaluation accuracy. The intensity of each sensory characteristic was recorded on a 5-point hedonic scale after 1 h orientation sessions. In this session, the panelists had specified the terminology and anchor points on the scale. The coded samples were shown simultaneously and evaluated in random order.

Statistical analysis

A one-factor analysis (ANOVA) for a series of parallel measurements (at least 3) was used. The data in tables represents the mean±standard deviation. Value of $p < 0.05$ was considered statistically significant. The Tukey's HSD test was used to determine significant differences between means. Basic statistics and ANOVA were performed using the statistical software package Minitab ver. 18.1 (Minitab Inc., USA).

Results and discussion

Combined food additive characteristics

Combined food additive was a finely dispersed uniform dry powder with a mean volume particle size of 197±15 µm (Figure 2). The powder has a greenish-brown color and a characteristic taste and odor for algae.

Figure 2. Combined food additive

An experimental study of the proximate composition of the developed additive was conducted. The water content in the additive powder was 4.12±0.04%. A characteristic feature of the additive was a significant protein content of 11.6±0.4%, while the lipid level was 1.75%.

Significant fluctuations in the iodine content in raw materials and the requirement regarding the limiting indicators of RDA and UL necessitate a quantitative assessment of the iodine content in the additive. This indicator may be a limiting factor in determining the maximum possible amount of CFA additive to be included in the recipe for rye-wheat bread. The initial iodine content in the manufacturer's kombu powder was 1012±25 µg/g. This value is within the range of iodine content in kombu discussed above. After appropriate treatment of the powder by hydration and boiling, the iodine content was reduced to 213±15 µg/g by dry weight of the additive. This decrease accounts for 78.9% of iodine loss. This value agrees well with the results for *Laminria digitite* in the study (Correia et al., 2021). According to the authors, the applied processes significantly reduce the iodine content because of its water-soluble form, which is extracted from the raw material. In addition to the decrease in iodine content, it should be noted that the sodium and potassium contents decreased to 47 and 55 mg/g (dw), which amounted to a decrease of 40 and 50%, respectively.

Particular attention was paid to the quantitative determination of algae polysaccharides in the additive, taking into account their positive effect on the quality of bakery products (Fu et al., 2021; Jönsson et al., 2024; Koh et al., 2020). The content of the main polysaccharides of the CFA, namely laminarin, fucoidan and alginic acid, was 3.35, 3.45 and 28.55%, respectively. Thus, CFA is a valuable source of dietary fiber to provide the recommended daily intake of 25-35 g for adults (Stephen et al., 2017). On the other hand, the said polysaccharides have important functional and technological properties. For example, alginic acid and its derivatives have gelling, structure-forming and emulsifying properties.

With regard to rye-wheat bread, the presence of the specified polysaccharides in the additive is a factor in improving the functional and physical properties of both the dough and the bread as a final product. This conclusion is based on some experience in studies related to the use of algae in the bakery products formulation. Thus, the inclusion of algae polysaccharides for partial replacement of 0-1.5% of the wheat flour in the bread recipe slowed down the process of starch retrogradation from amorphous to a more structured form (Fu et al., 2021). As a result, the bread prepared from frozen dough with 1% of *Laminaria japonica* L. polysaccharides had increased specific volume, water content and texture quality, while stalling processes during the storage were reduced.

Another study examined the effect of sulfated polysaccharide fucoidan as a fortifying agent at a concentration of 0.4 g and 0.80 g per 100 g of flour. Fortification of flour with fucoidan improved the gluten structure and gas-forming capacity of yeast, and the baked bread had a significantly higher specific volume and softer breadcrumbs. In addition, fucoidan-fortified bread was found to retain both antioxidant and anticancer activities *in vitro* (Koh et al., 2020).

Dough characteristics

An important technological factor in the formation of the quality of rye-wheat bread is the properties of wheat flour gluten. During hydration of gluten proteins, glutenin and gliadin interact with the formation of a viscoelastic three-dimensional matrix (Wrigley et al., 2006). The quantity and quality of gluten largely determines the texture of the dough and its ability to hold carbon dioxide. Effect of combined food addition on gluten characteristics is presented in Table 1.

Table 1

Gluten characteristics

Indicator	Dough sample			
	BC	B1	B2	B3
Wet gluten, %	26.8±0.3^{a}	27.9±0.5^{b}	28.6±0.4^{bc}	29.4±0.3^{c}
Compressibility, CU	78±2^{a}	73±1^{b}	70±2^{c}	66±2^{cd}
Extensibility, cm	15.0±0.6^{a}	14.0±0.5^{b}	12.5±0.3^{c}	11.0±0.4^{d}

$^{a\text{-}d}$ Means within the same row with different superscripts are significantly different at $p < 0.05$.

The analysis of the data in Table 1 allows confirming the improvement of the quantity and quality of gluten with the inclusion of CFA in the bread formulation compared to the control, regardless of the added amount. Thus, there is a statistically significant increase from 4% to 10% of the wet gluten quantity ($p < 0.05$). The inclusion of the additive increased the compressibility by 7-18% and decreased extensibility by 7-36% of gluten, corresponding to samples B1-B3. The probable cause of these facts is the ability of iron oxide nanoparticles of additives to form protein-ligand complexes (Tsykhanovska et al., 2022c, 2023) with protein molecules and, in particular, with gluten proteins (Tsykhanovska et al., 2018). An additional factor may be the interaction between wheat flour proteins and algal polysaccharides (Fu et al., 2021). In general, it can be assumed that the combined food additive forms bonds between molecules of proteins and carbohydrates with the formation of a spatially stable matrix.

The positive effect of CFA on physical-chemical and rheological characteristics of rye-wheat dough was established because of rheofermentometer measures. The inclusion of the additive in the recipe of bread had a positive effect on the improvement of the gas-forming ability in rye-wheat dough (Figure 3).

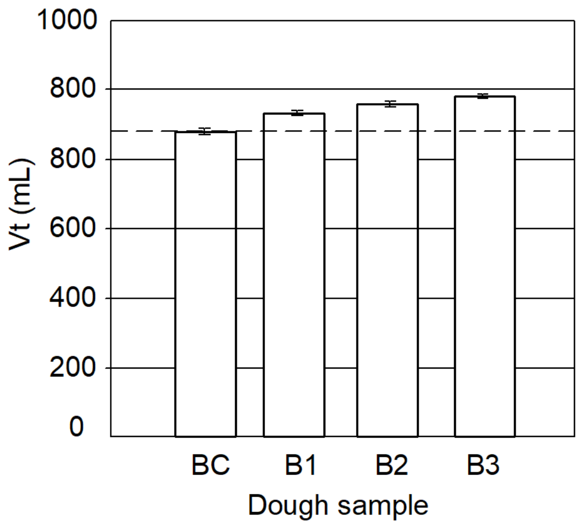

Figure 3. Total amount of CO_2 produced in the dough samples

Thus, the amount of carbon dioxide released from the gaseous release curve during the fermentation period of the experimental dough increased by 6-11% ($p<0.05$) compared to the control, depending on the sample. Intensification of alcoholic fermentation in the dough can occur due to the activation of yeast cells in the presence of additive's bioactive compounds. According to the dough development time curve, with increasing addition content in the bread formulation, the time to maximum dough development T1 decreases (Figure 4). The maximum dough height Hm and dough height h at the end of fermentation period are by 8.5-19.0% and by 10.5-26.0% higher compared to the control sample (Figure 5).

A decrease in decline in dough development (Hm-h)/Hm is also observed in samples B1-B3 as the amount of additive increases. These parameters are caused both by an increase in the gas-retaining capacity of test samples as a result of the discussed gluten strengthening, and by the acceleration of gas formation in it, as was said above.

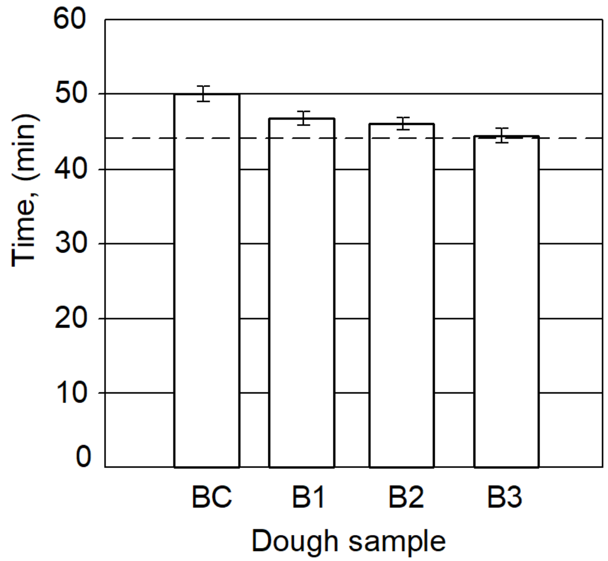

Figure 4. Time to maximum dough development T_1

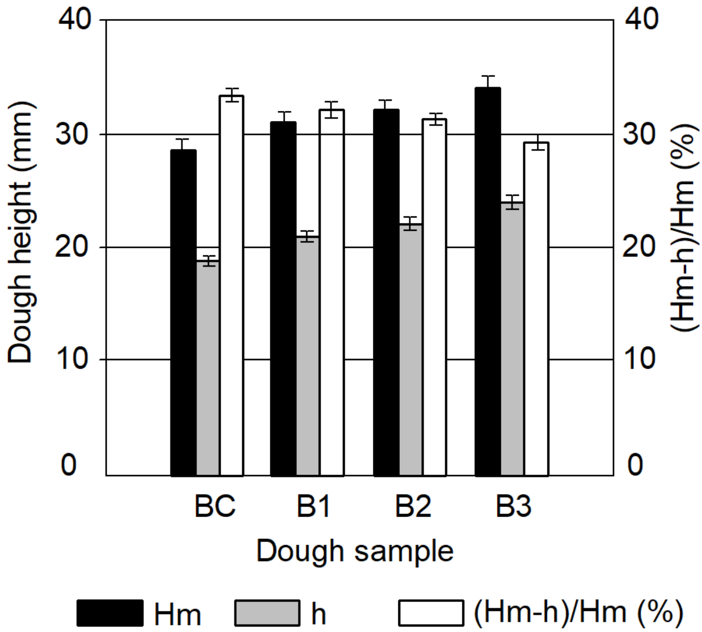

Figure 5. Magnitudes of maximum dough height Hm, dough height h at the end of the measurement after 3 hour and decline in dough development (Hm-h)/Hm of the dough samples

The inclusion of CFA in the formulation of rye-wheat dough leads to a slight decrease in both the initial and final acidity by 0.1–0.3 grades, which may be a consequence of the amphoteric properties of iron nanoparticles (Table 2).

Table 2

Physicochemical and rheological characteristics of rye-wheat dough

Indicator	Dough sample			
	BC	**B1**	**B2**	**B3**
Initial acidity, grades	$6.9{\pm}0.1^{a}$	$6.8{\pm}0.3^{a}$	$6.7{\pm}0.3^{a}$	$6.6{\pm}0.2^{a}$
Final acidity, grades	$8.0{\pm}0.4^{a}$	$7.9{\pm}0.3^{a}$	$7.9{\pm}0.2^{a}$	$7.8{\pm}0.3^{a}$
Spreading, mm	$88.0{\pm}1.2^{a}$	$84.0{\pm}1.1^{b}$	$81.0{\pm}1.0^{c}$	$78.0{\pm}1.0^{d}$
Specific volume, ml/g	$2.48{\pm}0.1^{a}$	$2.64{\pm}0.11^{b}$	$2.72{\pm}0.11^{c}$	$2.80{\pm}0.12^{d}$
Yield stress, Pa	$452{\pm}8^{a}$	$478{\pm}9^{b}$	$492{\pm}9^{c}$	$508{\pm}7^{d}$
Adhesive strength*, kPa	$2.3{\pm}0.1^{a}$	$2.0{\pm}0.2^{b}$	$1.8{\pm}0.2^{c}$	$1.7{\pm}0.2^{cd}$

[a-d] Means within the same row with different superscripts are significantly different at $p < 0.05$.
*The value is determined using steel plates

However, the observed decrease is statistically insignificant (p>0.05) and thus requires additional research. An increase of the additive content when moving from sample B1 to B3 changes some of the physical properties of the dough. The data in Table 2 indicate a decrease in the spreading index of rye-wheat dough from 11 to 13% (p<0.05). This fact is caused to the strengthening of wheat gluten and the increase in the water-retaining capacity of the dough. There is also an increase in the specific volume of the dough from 6 to 13% (p<0.05), which confirms the data shown in Figures 4 and 5. This parameter is caused both by an increase in the gas-retaining capacity of test samples as a result of the discussed gluten strengthening, and by the acceleration of gas formation in it, as was said above.
A study of the rheological properties of rye-wheat dough with the addition of an additive indicates an increase in yield stress from 6 to 12% (p<0.05). This fact shows the water-binding ability of the additive components and is the reason for the reduction in adhesion strength (to steel as the platinum material for research) by 15-35% (p<0.05). There results are consistent with the data of other research (Różyło et al., 2017; Tsykhanovska et al., 2022a).

Rye-wheat bread samples characteristics

The produced samples of rye-wheat bread were subjected to physicochemical analysis for moisture content and acidity (Table 3).

These results indicate that the inclusion of the additive in the bread formulation contributes to an increase in bread moisture due to the greater water-holding and water-absorbing capacity of the CFA. The amphoteric properties of the iron-containing component of the complex food additive slightly reduce the acidity of bread by 0.1–0.3 degrees. However, the observed decrease is not statistically significant (p>0.05).

Table 3

Characteristics of rye-wheat bread

Characteristics	Bread sample			
	BC	B1	B2	B3
Moisture content, %	47.0±0.2^{a}	47.8±0.1^{b}	48.2±0.3^{bc}	48.6±0.2^{c}
Acidity, degrees	7.4±0.3^{a}	7.3±0.2^{a}	7.2±0.q^{a}	7.1±0.2^{a}
Specific volume, ml/g	1.7±0.1^{a}	1.8±0.1^{ab}	2.0±0.1^{bc}	2.1±0.1^{cd}
Porosity, %	58±1^{a}	61±1^{b}	63±1^{c}	65±1^{d}
Shape stability, H/D	0.32±0.02^{a}	0.35±0.01^{b}	0.37±0.01^{bc}	0.40±0.02^{c}
Crumbliness after baking, %	4.7±0.2^{a}	4.3±0.3^{ab}	4.0±0.2^{b}	3.8±0.2^{bc}
Crumbliness after storage*, %	6.1±0.4^{a}	5,5±0.3^{ab}	4.9±0.2^{c}	4.6±0.3^{cd}

$^{a-d}$ Means within the same row with different superscripts are significantly different at $p < 0.05$.
* The value is determined after 72 h storage

The inclusion of CFA had an effect on changing some of the physical properties of rye-wheat bread compared to the control sample. Due to the improvement of the dough structure, its gas-forming and gas-retaining capacity (Figure 3), there was an increase in the specific volume from 6 to 24% and the crumb porosity from 5 to 12%, and the shape stability from 9 to 25% with an increase in the additive content in samples B1-B3. At the same time, a decrease in crumbliness was observed from 9 to 24% immediately after baking and from 11 to 33% after 72 hours of storage.

As mentioned above, this analysis was carried out on a 5-point scale, taking into account the contribution factors of each quality indicator. Recipients ranging from 4.5 to 5.0 rated the proposed quality indicators. Therefore, for better visualization, Figure 6 presents the results of the ratings on the minimum rating-maximum rating scale. The use of a combined food additive had a positive effect on the taste, aroma and surface of the crust of products. Sensory analysis of rye-wheat bread samples with different amounts of addition compared to the control sample is shown in Figure 6.

The elasticity, volume, porosity of products and chewiness increased, which is consistent with the data on the improvement of the physical and chemical properties of bread with the additive (Table 3). However, the addition of more than 2% of the additive leads to the appearance of a specific taste and smell of algae in the bread, which led to a decrease in these indicators.

Inclusion of the complex food additive, 1.0, 1.5, and 2.0%, to the formulation of rye-wheat bread resulted in improving of the sensory characteristics in comparison with control bread without CFA, namely, the average score increased by 1.06; 1.08, and 1.07 times, respectively. Based on a comparative analysis of physicochemical, rheological and sensory indicators, it was concluded that the optimal amount of inclusion of a combined food additive in the formulation of rye-wheat bread as an ingredient is 1.5%. This bread sample was subjected to further quality assessment called BD (bread development).

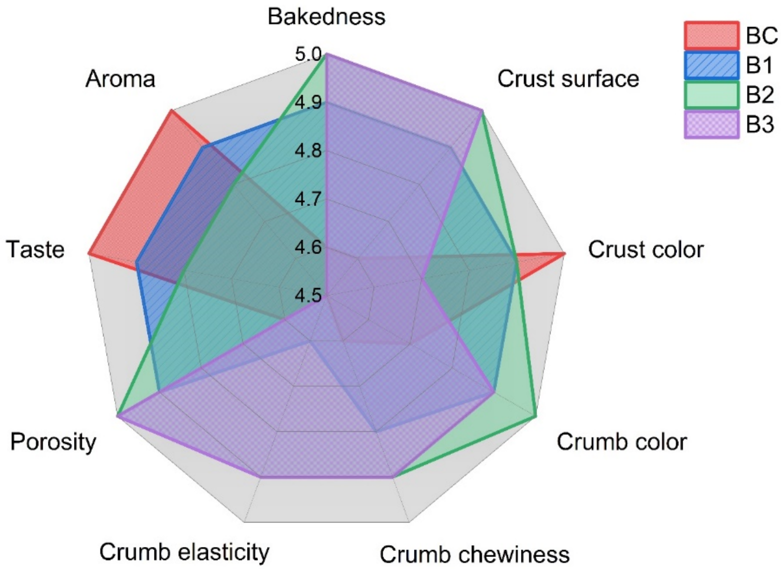

Figure 6. Spider diagram of sensory characteristics of bread samples

Bread quality assessment

One of the important factors influencing consumer preference for a food product, in addition to its appearance, aroma and taste, is its texture. Formed because of the interaction of the main components such as proteins, polysaccharides, and lipids, it should promote their release from the food matrix to reach the corresponding taste buds. The development of taste is closely related to both the destruction of the initial texture of the food product in the mouth and its changes during chewing. An experimental study of the texture of the bread under development with the inclusion of CFA in an amount of 1.5% by weight of flour compared to the control is shown in Table 4.

Table 4

Texture properties of bread samples

Characteristic	Bread sample	
	BC	BD
Hardness, g	714.2±1.8[a]	667.1±1.7[b]
Cohesiveness, g	0.343±0.001[a]	0.369±0.001[b]
Elasticity, g	0.48±0.01[a]	0.51±0.01[b]
Chewiness, %	75.1±0.9[a]	77.8±0.8[b]
Springiness, g	0.064±0.00[a]	0.069±0.00[b]

[a-d] Means within the same row with different superscripts are significantly different at $p < 0.05$.

The data in Table 4 indicate a significant (p<0.05) decrease in bread hardness by 6.6% and an increase in elasticity by 6.7%). A higher loaf specific volume (Table 3) results in lower hardness due to a less dense crumb and less compact cells (Table 4) (de la Hera et al., 2014). It was found that the inclusion of CFA in BD sample formulation contributes to a significant (p<0.05) decrease in bread hardness by 6.9% and an increase in elasticity by 6.68% compared to the control (Table 4). This is associated with a higher mass fraction of moisture (Table 3) and the plasticizing ability of water molecules. At the same time, springiness and cohesiveness of bread with CFA increased compared to the control by 7.3% and 7.1%, respectively, due to strengthening and stabilizing the structure through intermolecular interactions of biopolymer molecules (proteins, fats, and carbohydrates). The consequence of the higher cohesiveness of the bread with CFA (1.5%) compared to the control is an increase in the chewing index by 2.7% and an improvement in the chewing ability of the product.

Analysis of the nutrient profile and value of samples of rye-wheat bread shows an improvement in the nutritional value of the BD compared to the control (Table 5).

Table 5

Nutrient profile and value of rye-wheat bread

Nutrient or indicator	**Bread**	
	BC	**BD**
Macronutrients, g/100 g dw		
Protein	7.5±0.2^{a}	7.9±0.3^{b}
Fat	0.90±0.01^{a}	0.91±0.02^{a}
Starch	39.2±0.3^{a}	40.6±0.4^{b}
Fiber	0.40±0.01^{a}	0.46±0.01^{b}
Minerals, mg/100 g dw		
Sodium	343.5±0.9^{a}	349.3±1.1^{b}
Potassium	98.6±0.7^{a}	101.0±0.8^{b}
Iodine	nd**	0.055±0.010
Nutrition value		
UCAAC, %	28.75±0.04^{a}	19.50±0.04^{b}
BV, %	71.25±0.87^{a}	80.50±0.92^{b}
UC	0.54±0.02^{a}	0.62±0.02^{b}

$^{a\text{-}d}$ Means within the same row with different superscripts are significantly different at p < 0.05.

*nd is not detected.

Analysis of the nutrient profile and value of rye-wheat bread samples shows an improvement in the nutritional value of the BD compared to BC (Table 5). The data in Table 5 indicate a significant increase in the content of protein, starch, dietary fiber, and some minerals (p < 0.05). Kombu was characterized above as a natural source of iodine. The control sample did not contain iodine. The inclusion of the additive in the bread formulation made it possible to obtain a final product fortified with iodine with a content of 55±10 μm/100 g of bread. This magnitude allows calculating the daily consumption of the developed bread without exceeding the RDA value.

To assess the biological value of rye-wheat bread according to the Mitchell-Block method (Block and Mitchell, 1946), the protein content was preliminarily determined, and the amino acid score was estimated. The limited amino acid in both samples is lysine, but in the BD sample, this indicator is improved by 37.5% compared to the control. The score of other essential amino acids also increases in the range from 4.75 to 20.05% compared to the control. Data on the amino acid composition were used to calculate the coefficient of imbalance of the amino acid composition according to formula (1). The obtained values of this indicator for both BC and BD samples are 32.8 and 28.2%, respectively, which indicate a satisfactory biological value of the samples. This conclusion is confirmed by calculating the value of the balance of essential amino acids in relation to the physiologically necessary norm as a coefficient of utility. The calculated values of this coefficient are 0.54 and 0.62 for the BC and BD samples, respectively, which testify to the improvement of the balance of essential amino acids in the developed sample of rye-wheat bread. Thus, fortification of rye-wheat bread with a combined additive made it possible to improve its food value.

Conclusions

1. Iron oxide nanoparticles with an iron content of at least 90% and an average particle size of 75±10 nm were synthesized.
2. Commercial kombu powder was treated by hydration for 10 min and boiling in water for 5 minutes, which reduced the iodine content in the sample from 1012±25 µg/g to 213±15 µg/g dw.
3. Dry powders of nanoparticles of iron oxide and kombu in a ratio of 15:85 (w/w) were used to develop a combined food additive (CFA) as an improver of technological properties and a fortifying agent when included in the formulation of rye-wheat bread as an ingredient.
4. The inclusion of the additive in the amount of 1.0, 1.5, and 2.0% of the flour weight (bread samples B1, B2, and B3) improves the quality of gluten. This is confirmed by a statistically significant increase in raw gluten by 4% to 10%, increased compressibility by 7–18% and decreased extensibility by 7–36% of gluten for bread samples B1-B3.
5. The gas formation curves showed an increased release of carbon dioxide during the fermentation period of the experimental dough by 6–11% ($p<0.05$) compared to the control, depending on the sample, due to the activation of yeast cells in the presence of biologically active compounds of the additive.
6. According to the curve of dough development time, with an increase in the content of the additive in the bread recipe, the time of maximum dough development decreases, and the maximum height of the dough and the height of the dough at the end of the fermentation period are 8.5–19.0% and 10.5–26.0% higher compared to the control sample.
7. Analysis of the physicochemical properties and sensory characteristics of rye-wheat bread samples allowed to determine the optimal level of fortification of rye-wheat bread with CFA at a level of 1.5% dw.
8. The inclusion of a combined food additive in the rye-wheat bread formulation increased its nutritional value, as evidenced by an increase in the unitarity index from 0.54 to 0.62.
9. Fortification of rye-wheat bread with iodine at a level of 55±10 µg/100 g allows it to be considered as a functional product for the prevention of iodine deficiency diseases.

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