Applicability of mineral raw materials in the food industry and agriculture as nanomaterials – A review

Az ásványi nyersanyagok nanoanyagként való alkalmazhatósága az élelmiszeriparban és a mezőgazdaságban – áttekintés

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There are thousands of minerals on Earth, and some of them are used in various fields of industry. Nanomaterials have unique application properties, mainly related to their dimensional properties. These materials have a much larger surface area than the full-size version of the same materials. Clay minerals can change their physical and chemical properties through adsorption and desorption of various ions. Because of these properties, nanomaterials are widely used in industry and agriculture. The food industry and agricultural sector are increasingly using these materials. Bentonite, zeolite and illite are already used in the cosmetics industry and are also widely used as packaging materials. On the other hand, the direct application of nanomaterials in the food industry isn't yet widespread; rather, these materials are used to facilitate one stage of the processing process. Nanomaterials, including clay minerals, are likely to play an important role in the development of the food industry. With this in mind, the aim of our work was to review and summarize the current applications. In the first part of our study, we summarize the main features of dispersed systems and the characteristic properties of clay minerals that can be considered significant from the point of view of applicability in agriculture and the food industry. We present the main types of nanoclays used in food and their typical uses, and finally summarize the possible future directions of use.

Több ezer ásványi anyag létezik a Földön, és ezek egy részét az ipar különböző területein hasznosítják. A nanoanyagok egyedi alkalmazási jellemzőkkel rendelkeznek, amelyek elsősorban méretbeli tulajdonságaikhoz köthetők. Ezek az anyagok sokkal nagyobb felülettel rendelkeznek, mint ugyanezen anyagok normál méretintervallumú változata. Az agyagásványok különböző ionok adszorpcióján és deszorpcióján keresztül képesek megváltoztatni a fizikai és kémiai tulajdonságaikat. E tulajdonságok miatt a nanoanyagokat széles körben használják az iparban és a mezőgazdaságban. Az élelmiszeripar és az agrárszektor egyre nagyobb mértékben használja ezeket az anyagokat. Bentonitot, zeolitot és illitet már használnak a kozmetikai iparban és csomagolóanyagként is elterjedt. Másrészt a nanoanyagok közvetlen alkalmazása az élelmiszeriparban még nem elterjedt, inkább a feldolgozási folyamat valamely szakaszának elősegítése érdekében alkalmazzák ezeket az anyagokat. Valószínűleg a nanoanyagok, köztük az agyagásványok, fontos szerepet fognak játszani az élelmiszeripar fejlődésében. Mindezeket figyelembe véve, munkánk célja a jelenlegi alkalmazások áttekintése és összefoglalása volt. Tanulmányunk első részében összefoglaljuk a diszperz rendszerek főbb jellemzőit, továbbá az agyagásványok jellegzetes tulajdonságait, melyek az agrár és élelmiszeripari alkalmazhatóság szempontjából jelentősnek mondhatók. Bemutatjuk a nanoagyagok élelmiszerben alkalmazott főbb típusait és a jellegzetes felhasználásokat, végül összegezzük a jövőbeli lehetséges felhasználási irányokat.

Introduction

The term 'nano' itself refers to the particles in the 10^{-9} m interval. However, practically particles below 100 nm can be considered nanomaterials. The exact particle size restrictions can be regionally different and vary in different fields of science. The European Commission accepted the recommendation about the definition of nanomaterials on 18 October 2011 [1]. According to this recommendation, nanomaterials are:

- Natural or unintentionally synthesized or produced materials which contain particles in the unbound state, as an aggregate or agglomerate, where at least 50 per cent of the particles are in the 1–100 nm size interval.
- In special cases and when concerns regarding the environment, health, security or competitiveness make it reasonable, the 50 per cent of the number particle size distribution threshold value can be replaced by a threshold value between 1 and 50 per cent.
- Besides, fullerenes, graphene platelets and single-wall carbon nanotubes, if one or more dimensions are under 1 nm, can also be considered nanomaterials.

Short characterization of dispersed systems

A dispersed system is a material system in which one component is distributed in the other component. The distributed component, which is present in a smaller amount, is called dispersed material, while the other component, the matrix, is called continuous medium. In colloid or submicroscopic systems, the particle size of the distributed material ranges from 1 nm to 500–1000 nm, while in coarse dispersed or microheterogeneous systems, the particle size is over 1 µm: they can be seen with a microscope. The degree of dispersion is an important property of the disperse system. There is no sharp boundary line between the three size intervals: the detergents, colouring matters, and humic substances are at the lower limit of the colloid dimension, while the upper limit is the size of the soil particles. The fine disperse systems contain particles between 1µm – 1 nm. They are called colloid solutions or sols. While coarse solid particles are dispersed in the liquid medium, the system is called coarse dispersion or suspension. The main difference between the two types of systems is that in coarse dispersions, the phase separation takes place by gravitational forces, and the particles are sedimenting.

Stability of dispersed systems

There are differences between the sedimentation (kinetic) and aggregative stability of a dispersed system. Sedimentation stability is the stability against gravitational force, i.e. a system is stable if the particles are not sedimenting in time. The fine dispersions with a high degree of dispersion are kinetically stable; they can be characterized by a diffusion–sedimentation equilibrium. Cease of the kinetic stability can be attributed to a) the sedimentation of particles in coarse dispersions, b) the phenomenon that the light particles (droplets) are buoying up to the interface, c) the isothermic evaporation of the small particles onto the surface of the bigger particles (which also causes sedimentation) d) it can also be the consequence of the cease of the aggregative stability (bigger aggregates are formed and sedimentation occurs then).

Aggregative stability is the stability against association and compaction. The particles tend to stick to each other during their motion and collision if the attractive forces are higher than the repulsive forces. Therefore, aggregates are formed, and this process is called coagulation. It can be perikinetic (as a result of Brownian motion) and ortokinetic (enhanced by stirring, flowing or sedimentation). If the particles can partially maintain their separateness, the droplets grow together slowly; the process is called coalescence.

The stability of a colloid system is determined by the magnitude and resultant of the repulsive and attractive forces of the particles. During the Brownian motion, the following forces act between the particles.

Attractive forces are:
1. van der Waals attractive forces (universal forces, they are present between all particles),
2. attraction of hydrophobic surfaces (for instance, as a result of surfactant molecule adsorption),
3. polymer bridge type bonding between particles.

Repulsive forces are:
1. electrostatic repulsion (as a result of the overlapping of electric double layers),
2. formation of sub-surface hydrate layers (their overlapping results in repulsion),
3. steric stabilization (the macromolecules adsorbed on the surface of the particles interact, and repulsion evolves).

In the classic case (hydrophobic, charged particles), the main interacting forces are the van der Waals forces and the electrostatic repulsive forces [2–5]. The magnitude of the van der Waals forces depends on the particle size and the nature of the particles. The magnitude of the electrostatic repulsive forces depends on the effective Hamaker constant of the particles. The electrostatic repulsive forces evolve as a result of the overlapping of the electric double layer on the surface. Their magnitude is determined by the structure of the electric double layer, mainly by their thickness (which can be controlled by adding electrolytes), but also by their surface or Stern potential.

For these systems, the physical theory of colloid stability developed by Derjaguin–Landau–Verwey–Overbeek [2–4] is valid (DLVO theory). According to this, the distance dependence of the resultant of the repulsive and attractive forces between the particles is shown in *Fig. 1*.

As the magnitude of the van der Waals attractive forces are inversely proportional to the square or the
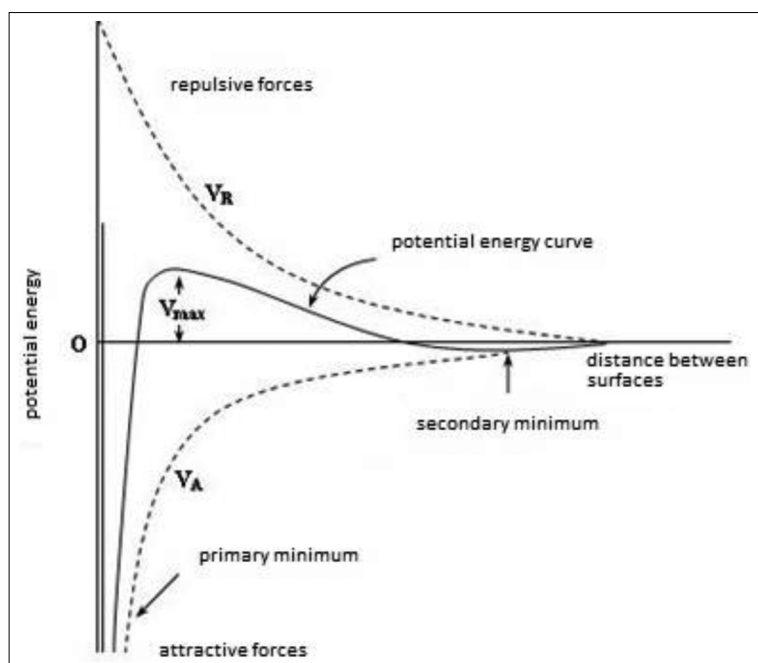
Fig. 1. *Potential energy curve of two colloid particles, V_R – repulsive forces, V_A – attractive forces, V_{max} – change of their results as a function of the distance between surfaces* [6]

cube of the distance between the surface of the particles and the electrostatic repulsive forces are decreasing exponentially as a function of the distance, at medium distances, a barrier appears on the interaction forces vs distance function. This energy barrier prevents the particles from approaching each other (by Brownian motion) to distances where the attractive forces are dominant. Calculation of these forces takes place by several methods in the scientific literature [2–5, 7, 8].

By adding electrolytes, the electric double layer can be shrunk, which results in the drop of the surface potential, and the potential barrier can be lowered; at a specific concentration, it can be abolished. At this condition, the particles aggregate fast. The critical coagulation concentration (ccc) is the concentration where this fast aggregation occurs, or more precisely, the minimum concentration whose increase does not accelerate the aggregation. If this aggregation results from the shrinking of the EDL, the process is called concentration coagulation (1-1, 2-1 electrolytes), ccc is inversely proportional to the sixth power of the valence of the counterions (z), while if it is caused by the decrease of the Stern potential (in the presence of high valence cations or surfactant ions), ccc $\sim 1/z^2$.

In the case of hydrophilic particles and if surfactant or polymer adsorption also occurs, so-called non-DLVO forces are also present (listed above, attractive and repulsive forces 2–3). The effect mechanism of these are discussed in the scientific literature [2–5, 7–9]. The destabilization of the hydrophilic colloids occurs if the surface hydrate layers are destructed (for

instance, the rise of the temperature) or if dehydrolyzing ions (for instance, sulphate) or organic solvents (alcohols) are added.

Role of colloidal stability in food industry applications

In order to capitalize on the beneficial effects of nanoparticles used in the food industry, their colloidal state should be retained, or in other words, their colloidal stability is of utmost importance.

There are several recent studies in the scientific literature where the aim of the research is to keep or increase the colloidal stability of the system. Nanoscale zein (a protein extracted from maize) particles can be used as carriers. It has high coating capacity, biocompatibility and biodegradability. Therefore, it can be used to enhance the delivery of enzymes, drugs and essential oils. However, low colloidal stability of such dispersions was reported. In order to increase their colloidal stability, the encapsulation of zein nanoparticles was found to be an effective solution [10].

There is a similar concern regarding resveratrol, a polyphenolic compound used in pharmacology due to its anti-cancer, anti-inflammatory, and antioxidant effects. Poor solubility and low colloidal stability hinder its application in the industry. However, it was found that the clinical effectiveness of resveratrol can be improved by encapsulating it into a food industry product, namely into soy protein isolate nanoparticles: their solubility, stability and bioavailability can be improved by this method [11].

The colloidal stability of whey protein concentrate was investigated [12] in the presence of green tea polyphenols. It was found that polyphenol concentration and pH play an important role in the colloidal stability of the mixture. Over a threshold concentration, the complexes become insoluble, and precipitation is formed. Green tea polyphenols can be considered protein cluster size modifiers. Moreover, they can affect not only the colloidal stability of the mixture but also the gelation process of the whey protein concentrates. At a proper polyphenol concentration, both the colloidal stability of the mixture and the health-promoting effects of green tea can be preserved.

A recent study [13] summarized the beneficial effects of the nanoencapsulation of bioactive compounds (polyphenols, carotenoids, vitamins) used in nano-delivery systems for agriculture. Chitosan, gum arabic, soya bean polysaccharides, zein, starch, whey

protein isolates, soy protein and fish oil, were mentioned as potential nature-derived polymers for encapsulation. It is stated that the polymer nanoencapsulation of most of the bioactive compounds improves solubility, cell uptake and bioavailability. In some cases (curcumin encapsulated in chitosan and gum arabic, lutein encapsulated in starch, folate B9 encapsulated in whey protein isolate and resistant starch), the nanoencapsulation also resulted in the improved stability of the bioactive compound.

Food industry nanoemulsions also occur: an ultrasound-assisted water-in palm oil nanoemulsion was developed [14], and the optimized composition was determined by taking the effects of polyglycerol polyricinoleate and sodium chloride on the stability into account.

Application of nanoparticles in food and products related to food

Nanoparticles have several food and agriculture application fields. The food industry and the agrarian sector are using these materials to an increasing extent [15, 16]. The development of nanocomposite pesticides, chemical fertilizers and other agrochemical materials takes place in the field of primary production (agriculture). The application of nanoparticles led to innovative packing materials, which improved the safety and storability of the products. Nanoparticles are developed to prevent the microbial decay of packed food, improve the colours, tastes, and texture and enhance the biological availability of vitamins and minerals [17].
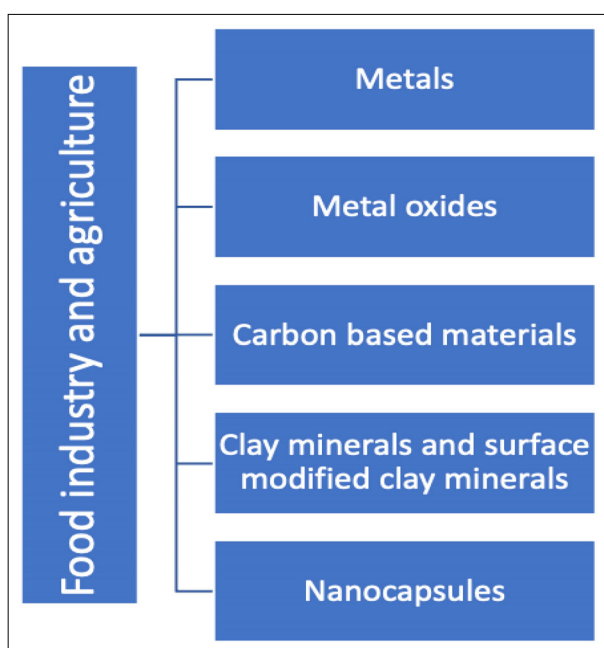
Generally, nanoparticles can be divided into three categories: inorganic nanoparticles and combined organic/inorganic (surface-modified) nanoparticles. Inorganic nanoparticles are usually metals and metal oxides; they are mainly used due to their antimicrobial characteristics [18–20]. Surface-modified nanoparticles add some functionality to the matrix, for instance, antimicrobial activity or preservative (as a result of oxygen absorption) – they are generally clay minerals, which are a subject of interest nowadays. Groups of nanomaterials used in the food industry are shown in *Fig. 2*.

Evaluation of the overview of the scientific literature showed that more than two third of the publications are related to the usage in foods, and only a small percentage discusses agricultural or forage applications. Only a few (6) nano-products are identified in the agricultural sector. Many nano-products are currently being developed. However, only a few exist at the moment [21]. Approximately half of the applied nanomaterials are inorganic, including metals, metal oxides, completely carbon-based materials (mainly carbon nanotubes, some fullerenes and soot) and clay. The nanocomposites are mainly (bio) polymers containing clay or other surface-modified materials. Another huge part of the publications deals with the application of nanocapsules [22–24], which can be called nanocapsules, nanocarriers, nanoemulsions or micelles [25]. In summary, it can be stated that a few nanomaterials give the majority of the materials applied in this field: silver, titanium dioxide and silicon dioxide are most frequently used in nanocapsules.

Fig. 2. Types of nanomaterials used in the food industry and agriculture
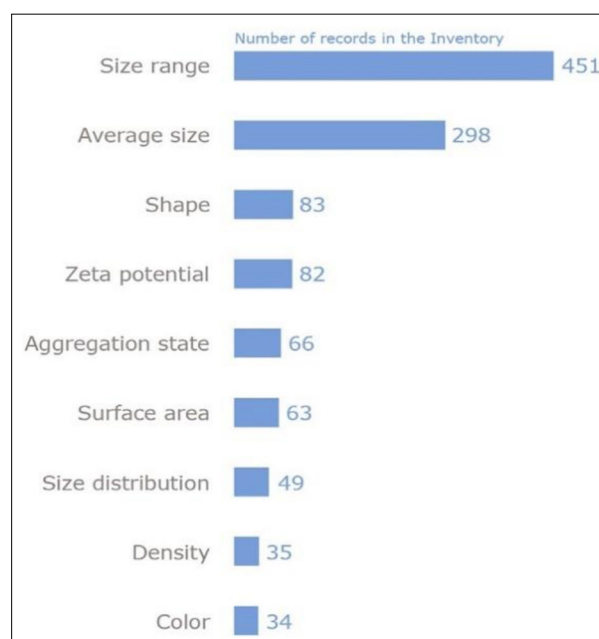

Fig. 3. Physical-chemical characteristics of NM types in the agriculture/forage/food sector. The number indicates the number of uses in the collected scientific literature [26]

Most of the analyzed studies focus on the application in the products. *Figure 3* summarizes the most important physical-chemical characteristics which are contained in these papers. The size interval or the average particle size of the nanomaterials is the most frequently examined. Only a small part of the publications describe other important physical-chemical properties like shape, zeta potential, aggregation state and particle size distribution.

Clay minerals

Out of the above-listed nanomaterials, the surface characteristics of the clay minerals are summarized in this chapter. Besides, the typical parameters of the Hungarian bentonite and kaolin occurrences are introduced. Studying the surface properties introduced here can affect the applicability of these clay minerals as nanomaterials to a great extent, among others, in the fields of the agrarian economy and the food industry.

Clays are consolidated or unconsolidated sedimentary rocks, while rocks which contain more than 25–30 per cent of grains under 1 micron and whose carbonate content does not exceed 15 per cent are called clay [27].

The structure of clay minerals can be characterized by the following. The size of the silicate tetrahedron (T) unit is 0.456 nm × 0.795 nm. The silicate tetrahedron sheets are connected by sheets of octahedra (O) between them, with cations located in their centre. The octahedral structures can be trioctahedral or dioctahedral, depending on the valence (divalent or trivalent) of the cation in the centre of the octahedra. Thus, the fundamental unit of the structure is the tetrahedral and octahedral sheets, where the tetrahedra are usually SiO_4 tetrahedra, in which often $Si \rightarrow Al$ (Fe^{3+}) substitution occurs, while in the octahedral layers, the cation is usually Al, Mg, Fe (Fe^{2+}, Fe^{3+}), or rarely: Li, Ti, V, Cr, Mn, Co, Ni, Cu, Zn; the anion: at two vertices OH^-, at other vertices O^{2-}. The tetrahedra are connected to each other via a mutual O^{2-} ion. The T and the O sheets, along with the mutual O^{2-} ion, construct a profile which is of the hexagonal cross-section. The divalent cations are connected to the silicate tetrahedron chains with $MgO_4(OH)_2$ octahedra. The octahedra continuously fill the octahedron sheet there. These are the trioctahedral structures. On the contrary, in the case of trivalent cations, in the tetrahedron and octahedron sheets, every third octahedron is empty in the octahedron chains that construct the sheets. These structures are called dioctahedral structures. Thus, the general structure of layer silicate minerals is the alteration of tetrahedron and octahedron sheets. The structure order can be categorized into two types: TO and TOT.

In TO(1:1) structures, the alteration of tetrahedron and octahedron sheets occurs. In TOT(2:1) type structures, there is an octahedron sheet between two tetrahedron sheets, and this three-unit block is the main unit of the lattice.

Their general feature is that the Si:Al and Al:Mg ratio in the lattice and their substitution are altering. Their other characteristics are water intrusion between the layers, good adsorption properties, ion exchange in the surface, in the inner layers and along the edges, low permeability, huge specific surface, and swelling capacity.

Formation of surface charges

Solid surfaces can bear charges in two different ways:
- permanently: the solid structure itself contains lattice charge defect sites,
- temporarily: as a result of the surface functional groups reaction (for instance, vH^+ association or dissociation) [6].

The charges of the permanently charged particles (for instance, montmorillonite, illite, zeolite) are the charge defect sites, which are at fixed spots in the lattice. Thus, there is a permanent charge density on the surface. In the crystal lattice of the Al^{3+} and the Si^{4+} ions, the surface charge density, which can be associated with a non-stoichiometric charge deficit originating from isomorphous substitution, evolved during the formation of the particles, is constant *(Fig. 4)*.
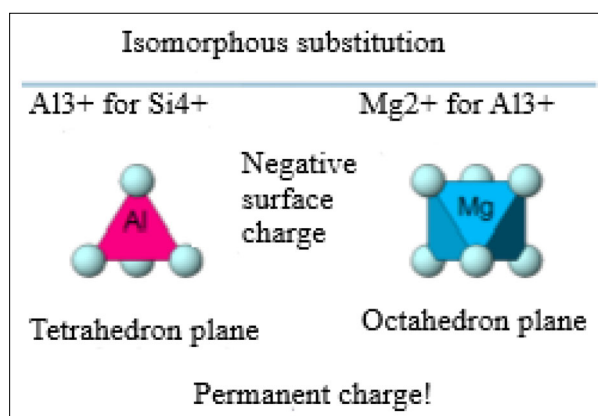

Fig. 4. *Scheme of isomorphous substitution in silicates* [28]

The formation of temporary charges *(Fig. 5)* implies chemical reactions occurring at solid/water interface layers. Therefore, for each system, the unique material characteristics, i.e. the chemical properties of the potentially charged solid and dissolved materials, should be taken into account. Besides the chemical quality of the surface (for instance, the quality and density of the active spots), on temporarily charged particle surfaces, the solution's composition also de-
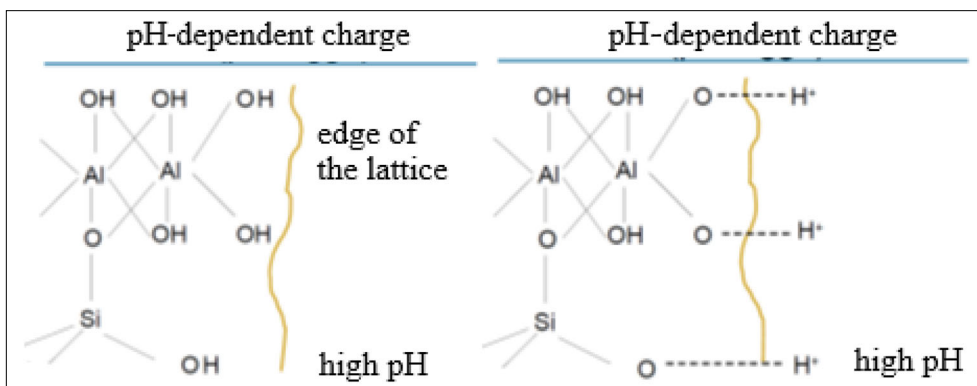
Fig. 5. Mechanism of formation of surface charges between clay mineral particles besides the formation of changeable (pH-dependent) charges [28]

termines the charges' formation. An electric double layer evolves around the particles due to the ion distribution between the charged solid/water interface and the aqueous bulk phase.

In the studies of Tombácz and Szekeres [29] and Tombácz et al. [30], the effect of pH change on the surface charge of particles in the case of montmorillonite 2:1 and kaolin 1:1 suspensions was studied. It was found that the point of zero charges (PZC) is at pH ~ 6.5 for OH groups located at the edges of montmorillonite lamellae. According to calculations made for protonation and deprotonation reactions of different OH groups, it can be said that this PZC value is less basic than Al-OH and less acidic than Si-OH. At the edges of montmorillonite pHPZC ~ 6,5, while at the surface of Al_2O_3 pHPZC ~ 8 and in the case of SiO_2 pHPZC < 4. Therefore under pH = 6.5, as a result of the protonation of the Al-OH groups located at the edge of clay minerals, positive charges appear. On the basis of these, it was assumed that these charges, which are oppositely charged sites related to the surface, can only appear in an acidic medium, and approximately under pH = 4, the number of positive charges at the edges can reach as much as 1 per cent of the total charge of the surface. There are also similar results obtained for kaolin during comparative investigations [31].

Kaolin

Kaolin consists mainly of kaolinite and illite. Kaolinite belongs to the group of clay minerals within the class of phyllosilicates. It consists of two sheets: a hydrargillite structured, octahedral $Al(OH)_3$ sheet is bound to a tetrahedral $[Si_4O_{10}]$ silicate plane. The altering sheets are bound by a hydrogen bond (via O^- and OH^- ions), which leads to different structural variations (kaolinite, dickite, nakrite).

Bentonite

Bentonite is a mineral formed via weathering of silicates whose montmorillonite content is a minimum of 75 per cent [27]. Montmorillonite is a dioctahedral structure, where from each of three octahedral positions, two are occupied by trivalent cations (primarily Al^{3+}), while the remaining uncompensated negative charge is occupied by cations with ion exchange potential [27]. An important characteristic of bentonites is the fine grains and their dimensions. The size of bentonite particles is in colloidal, i.e. they are between

Table 2. Data for bentonite from Mád [32]

Colour	Ochre
Chemical composition after drying at 140 °C	%
SiO_2	62.53
Al_2O_3	25.23
Fe_2O_3	1.5-2.34
TiO_2	0.23
CaO	1.57
MgO	1.77
Na_2O	0.54
K_2O	1.09
Lost of ignition (LOI)	8.15
Cation exchange capacity	mg eq./100 g
Ca^{2+}	37.5
Mg^{2+}	24.3
Na^+	3
K^+	2.7
H^+	1.7

Table 1. Data of bentonite and kaolin suspensions [32]

	Bentonite	Kaolin
Concentration	1.3 g/L	1.4 g/L
pH (at 23 °C)	7.8	6.4
Electric conductance	93.9 mS/cm	2.54 mS/cm

Table 3. Data for kaolin from Mád [32]

Colour	White
Chemical composition after drying at 140°C	%
SiO_2	72.23
Al_2O_3	18.53
Fe_2O_3	1.2
TiO_2	0.19
CaO	1.37
MgO	1.22
Na_2O	0.37
K_2O	0.62
Lost of ignition (LOI)	0.13

the 500 nm – 1 μm interval. The thickness of the bentonite lattice sheets is between 1.5–100 microns, while their diameter is around 30–200 microns. There are significant differences in size, which fact explains the differences between the basic characteristics of bentonites. Thus, it is very important to know the grain dimensions of bentonites before investigations.

The suspension of bentonite from Mád can be characterized by the following data *(Tables 1–3)* measured earlier by [32].

By studying *Fig. 6,* it can be observed that the particle size of bentonite ranges between 1–100 μm, with most of the particles in the 5–100 μm interval.

Applications in the agricultural production

Nano pesticides and other nanosize agrochemical materials are applied during agricultural production to improve their effectiveness [34]. It can be reached by reducing the particle size of the chemical agents to the nano interval; they are mixed into nanoemulsions or nanodispersions or built into solid lipid or polymer capsules [35]. The chitosan-based nanocapsules (polysaccharides from chitin) have multiple agrochemical uses. Solid lipid and polymer capsules filled with carbendazim and tebuconazole are considered to be novel fungicides. According to the scientific literature, the nanocapsules have good endurance, the fungicide agents are released from them gradually, and their harmful effects on the growth of plants are lower than those of present commercially available products [36]. Porous silicon oxide of the cavernous structure was investigated in the aspect of controlled release of validicine and 2,4-dichloro-phenoxyacetate herbicide. The surfactant-based nanoemulsions were investigated as beta-cipermetrin insecticide penetration systems [37]. Nanogels containing pheromone-methyl-eugenol are proved to be cheap solutions as much less amount was needed than the dosage at normal application. Natural nanosized ashes and inorganic metal nanoparticles were investigated as an insecticide, antimicrobial or antifungal agents. Apart from the protection of plants and food industry products from pests, nanotechnology also improves the quality of
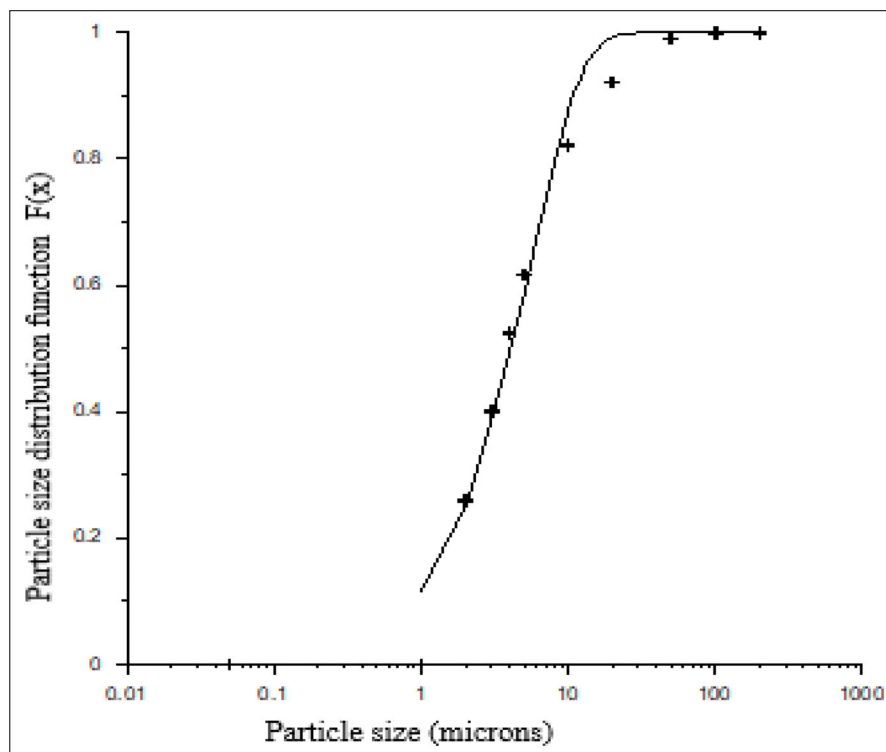

Fig. 6. *Particle size distribution of commercially available bentonite from Mád, Hungary, where F(x) is the cumulative mass fraction [33]*

plant production, potentially decreasing the amount of the needed chemical fertilizer as it influences both the nutrition uptake of the root and the water transport in the soil [38].

Forage applications

Only a few nanomaterial applications are available as forage additives; they are rather under development. Besides, there is no significant information about the applicability of some food additives like vitamin or nutrient capsules as forage additives. Most development and tests aim to enhance the digestion of forage by the adsorption of bacteria and toxins. Probably the antibacterial nanomaterials act like conventional antibiotics and can be added to the drinking water of animals [39]. The mycotoxin pollution of animal forage is a worldwide problem; it can cause serious illnesses in livestock. It was found that clay minerals (like montmorillonite-based nanomaterials) or other nanomaterials (for instance, polystyrene-based particles) adsorb mycotoxins [40]. Decreasing particle size to nanosize may increase the absorption of nutrients, as was shown by iron [41] and selenium: they improved the forage digestion of sheep substantially. Nano forms of selenium as micro-nutrients also showed increased bioavailability in fish [42] and livestock [43]. When no forage was used, the addition of copper nanoparticles or injection of copper sulphate into chicken eggs increased the conversion rate of forage as a result of muscle growth in the end period of breeding, and it also decreased the mortality[44]. Finally, bioconjugated nanoparticles (capsules) were investigated in forage and animal medicine products in the aspect of slow release of used nutrients or active substances [45].

Applications in the food industry

Applications in food additives and food supplements

Nanotechnology applications in food production involve food additives which improve the stability of food during processing and storage, improve the product characteristics or enhance the bioavailability of the nutrients. There are several such food additives in the scientific literature; the most important of them is synthetic amorphous silicon dioxide (SAS). It can be used as a cleaning agent for beverages or an anti-caking and texturing agent in many powdered food products (E551), in which they are at least partially in nano size [46]. Other anti-caking agents are used as well, including calcium silicate, sodium aluminosilicate, calcium phosphate, sodium ferrocyanide and microcrystalline cellulose. In the scientific literature, there is no available information on whether these materials are (partially) in the nanosize interval.

Another important food additive is titanium dioxide (E171). It is used as pigments in some foods to enhance their white colour, for instance, in dairy products and sweets. TiO_2, known for its whitening effect, cannot be considered a novel material, but it can contain nanosized particles during production [47]. It is also used as a flavour enhancer in different foods like dried vegetables, nuts, seeds, leaves and mustard, but also in beer and wine. TiO_2 in foods is of growing interest, and one recent study reports that 5–36 per cent of the titanium dioxide in ordinary foods is in the nanosize interval [48]. Nano-form titanium dioxide is also used as an antimicrobial agent to inactivate the disease-causative agents, sometimes combined with other compounds like nickel oxide or cobalt [49].

Iron oxide is mainly used as a food colourant. There is no information about the size of the particles. However, it can be assumed that they are in the micrometre size interval as they are produced by the grinding of larger particles. Iron nanoparticles are considered as health preserving food supplements since iron deficiency is one of the most frequent micronutrient deficiencies throughout the world. Solubility and bioavailability of the iron compounds can be improved by decreasing the primary particle size, which also results in the growth of the specific surface. The nanostructured iron compounds can also be useful in increasing the iron content of some foods [50].

Apart from the additives which improve the food itself or the taste of the product, nano-injection systems are also applied to increase the bioavailability of the nutrients. Nano-encapsulating involves the infiltration, absorption or dispersion into the vesicles or their surface, preserving the bioactive substances from biodegradation and improving the stability and solubility (for instance, solubilization of a hydrophilic substance into hydrophobic matrixes and vice versa).

Applications in materials in contact with food

Nano additives and nanotechnology have applications in different materials which are in contact with food. These are food packaging, food storage boxes, cooking machines, dishes, panels of devices, and nano sieves/membranes.

In the food industry, the application of nanomaterials in packages and food storage boxes is the most important type of application of nanotechnology to increase the storage time while the products can remain fresh [51]. The so-called nanocomposites decrease the oxygen permeability of the food packaging materials and also the carbon dioxide emission [52]. There are thermosoftening polymers containing nanosize inclusions. These inclusions are primarily clay minerals (2 wt%) added to polypropylene-based nanocomposites or polyamide plastic foils (for instance,

Durethan® meat package) [53]. Other examples of filling materials are carbon nanotubes, metals, metal oxides, cellulose, polymer resins or nanoparticles of fibres. The clay minerals also improve the ultimate tensile strength and thermal properties. Therefore, polymer-clay nanocomposites can be considered new food package materials. The polyamides layered by silicate barriers can have other beneficial characteristics like thermal buffering [54]. In low-density polyethene foils, the hybridization of nano-clays contributes to the lowering of the diffusion rate. Thus, it might be capable of retaining the antibacterial and antimycotic volatile oils as well [55]. Nanocomposite films enriched with silicate nanoparticles or nanocrystals can be used for plastic beer bottles, for instance, Nanocor [56], as it was reported in the USA. Carbon nanotubes can be used to improve heat and mechanical characteristics and to introduce antimicrobial effects. Nanomaterials can be built into packages of biodegradable food. For instance, TiO_2 nanoparticles in biodegradable polylactide (PLA) composite foils improved the heat and mechanical properties; on the other hand, they increased the photo degradability of the package as a result of UV adsorption. Phase shift agents built-in nano and micro-size polycaprolactone or polystyrene beads contribute to the thermal buffer capacity increase of the food package systems, and they also improve the cold chain preservability [26].

Summary, future trends

The application of nanotechnology has been attracting more and more attraction in the food industry as well. Therefore, it is useful to summarize the recent trends regarding this topic.

It is very important that a nanomaterial should be colloidally stable to preserve its beneficial properties. In our review paper, first, the fundamentals of colloidal stability are discussed. Subsequently, the possibilities of enhancing colloidal stability are introduced with some recent examples from the food industry. It can be said that the nanoencapsulation method of less soluble compounds is the most frequently used stability enhancement in the food industry. Concentration, pH and salt content can also influence the stability of the nanosystem.

Research of new products and application of nanomaterials in agriculture/forage/food are of growing interest and variety.

Although nanotechnology offers great possibilities for developing vegetable fertilizer products, only a few have been patented so far [57]. On the other hand, several companies (for instance, Syngenta, Bayer, Monsanto, Sumitomo, BASF and Dow Agro Sciences) issued patents for the manufacturing and application of encapsulated products available for producing nano pesticides. Some nano-products are already in the market (mainly in the USA), like Nanocid®-based pesticides and Chitosan. In the EU, there are only a few reported nano-products. Thus, it can be expected that the nano-agrochemical materials emerging in the EU market will not be based on new nanomaterials; they will be composed primarily of nanoemulsions/dispersions of earlier registered agents.

Nanomaterial applications in animal forages are mainly aimed at enhanced (selective) bioavailability of micro-nutrients, and it also ensures a treatment possibility of harmful levels of mycotoxins. Though it can be expected that some food processing agents would be applied in forage production [15], we could not find any paper focusing exactly on this application. Titanium dioxide, which can also have nanosize fractions, has become a forage and food additive in the EU [58].

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