VEGETABLE OIL CONVERSION INTO CORE-SHELL BIOPRODUCTS FOR STORED GRAIN PROTECTION

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Abstract

The paper presented a possibility for the eco-efficient valorisation of vegetable oils, a precious renewable natural resource from Romanian wild and cultivated flora, cheap and abundant raw materials for conversion into value added bioproducts for plant protection in organic agriculture systems and great importance for bioeconomy. An original technical solution was proposed for the stored grains protection against pests and diseases transferred from agricultural field to warehouses after the harvest time. Based on the validated properties of insecticidal diatomaceous earth and antimicrobial essential oils extracted from aromatic plants, an eco-friendly bioproduct was conceived and produced using a clean technology of green chemistry inspired by cold saponification process of natural fats followed by the microencapsulation of the essential oil in the soft potassium soap. One variant of the plant protection bioproduct was obtained by conversion of cold pressed rapeseed oil and essential thyme oil into a core-shell formulation obtained by granulation of the concentrated oil emulsion with fine powdered diatomaceous earth thus improving the controlled release of bioactive principles from the organomineral structure. The significant repellence potential against Sitophilus granaries insect adults and strong fungicidal action of thyme essential oil coupled with insecticidal effects and mycotoxin absorbent capacity of diatomite recommended the new product with a wide spectrum of action for a long preventive protection against biological contamination of warehouses.

Key words: vegetable oils, essential oils, stored grain protection, cold saponification.

INTRODUCTION

The most important risk factors regarding the contamination of stored grains are the pests and diseases transferred from agricultural field to storage at the time of harvest. Insects hatching inside the stored cereal grains release metabolites which promote microbial growth in favorable conditions of temperature and humidity. The most dangerous pathogens are fungal strains producing mycotoxins, metabolic products which reduce the quality of grains contaminating agro-products for feed or food processing and seriously affecting the health of animals and humans. Most agrochemicals currently used to control pests and diseases of stored grains are organophosphoric fumigants very soon under ban due to their high toxicity for mammals and environment. Present tendency of scientific research to discover and develop environmental friendly products, with high efficiency and low toxicity for users, led to the reconsideration of renewable natural resources, rich in bioactive principles for the protection of stored grains against pests and diseases.

Diatomaceous earth used as mineral vehicle for solid agrochemicals was considered the most effective mechanical insecticide for controlling insects damaging cereal seeds, the mechanisms of action being the rapid dehydration of the cuticle by contact and probably blocking the digestive system after ingestion (Lupu C., Manole T., 2015). Diatomite was also used to limit the contamination produced by micotoxigenic fungi growing on cereals, acting as an absorbent for mycotoxins.

Several essential oils extracted from wild or cultivated aromatic plants with antioxidant and antimicrobial effects have been used against fungal toxigenic growth on grains during storage. Essential oils extracted from leaves of eucalyptus and cupressus by hydrodistillation proved an excellent insecticidal and repellent action against stored grain insects when applied by fumigation (Bett Philip K. & al., 2016).
Volatile oils of thuya unpeeled fruit, eucalyptus and peppermint have proven fumigant effect against adult *Sitophilus granaries* in the storage of wheat (Hamza Ali F. & al., 2015). Bio-based plant protection products should be formulated by microencapsulation for stabilization and controlled release of bioactive principles. In order to reduce the use of chemical pesticides, seed treatment should become the preferred application technique of protection within integrated management systems (Matyjaszczyk E., Pieczyńska A., 2015). Bioproducts based on essential oils are relatively non-toxic to vertebrates, fulfills the criterion for low-risk pesticides and should be included in organic farming (Krimer Malešević V. & al., 2016). They are valuable alternatives to synthetic pesticides applicable in agriculture, beekeeping, food and medicine, offering limitless opportunity for scientific research to find new directions and possibilities of application in the future (Sparagano O. & al., 2016).

Present work proposed a technical solution for the simultaneously protection of stored grains against pests and diseases with an eco-friendly product obtained through a simple clean technology of "green chemistry" (Popescu M., Oancea F., Desliu-Avram M., 2015).

**MATERIALS AND METHODS**

The eco-friendly product proposed for stored grain protection was made using the following materials: a vegetable oil, potassium hydroxide, one or more bioactive essential oils, powdered diatomite, acetic acid, water. Nonvolatile oil can be any type of cooking oil, waste oil from fast-food or restaurants, waste oil from industrial processing of vegetable oils, preferable vegetable oils extracted from seeds of oilseed plants such as rapeseed, camelina, castor, and mustard containing biofumigant active principles. Volatile essential oils were selected based on fungicide and insecticide bioassays specific for pests and diseases of warehouses, from essential oils of thyme, thuja, sage, basil, oregano, rosemary, cloves, cinnamon, coriander, pine.

The first experimental sample was prepared using cold pressed rapeseed oil (Luna Sola Romania), KOH (89.3 % purity scales, produced by Lach - Ner, Czech Republic), essential oil of thyme (Solaris, Romania) by more than 42 % thymol active substance (Figure 1), and diatomaceous earth (Figure 2).

Diatomite rocks purchased from Romanian holdings Adamclisi Urluia, Pătârlagele and Adamclisi Fabrica were finely ground, dried and tested to establish the water activity value (Aw) with a portable device LabSwift-aw (Novasina). The relative humidity RH (%) = w x 100 was under 17% for products resistant to fungal contamination in stored grains or feed.

The process for preparing the oil-based product involved several experimental steps: a) cold saponification of vegetable oil with potassium hydroxide in aqueous solution with stirring at 52°C; b) neutralization the excess of potassium hydroxide with acetic acid to pH=9; c) encapsulation of the volatile oil into the soft soap texture; d) entrapping the oily core in diatomite coating using a rotating drum or a fluid bed granulator; e) drying the granules to air under ambient temperature and pressure; f) shifting the granules on different size meshes to packaging. Essential oil retention in the core was determined by extracting the crushed granules with methanol and identifying the major constituents of essential oils using a
RESULTS AND DISCUSSIONS

Experimental for active ingredient selection
The most suitable type of diatomite was selected as function of their special features.
1. Pătârlagele: 14.4% rh (26.9°C)
2. Adamclisi Urloaia: 15.9% rh (27.2°C)
3. Adamclisi Fabrica: 15.8% rh (27.4°C)

Diatomaceous earth have the relative density of 320-430 kg/m³, specific surface area 10-30 m²/g, Mohs hardness 4.5-5, and liquid absorption capacity of at least 150%.

The dose of 900 ppm (900 g/ton seeds) of diatomaceous earth used to control the attack of S. granarius in the cereal storage was effective after 21 days of exposure, as compared with an untreated control and a standard diatomaceous earth supplemented with a natural pyrethroid. The mortality of individuals of harmful population was significant after 14 days of application, recording values between 83.33% (source Urloaia and Adamclisi) and 100% for diatomite from Pătârlagele which blocked the development of insect reproduction after 60 days from the application (Lupu C., Manole T., Chiriloaie A., 2016).

A preliminary study conducted in laboratory conditions had been tested insect S. granarius behavior to thyme, thuya and oregano oils, individuals of this species showing a strong repellent reaction to Thymus vulgaris oil (Manole T., Fatu V., 2016). Administered in small doses in cereal stocks, thyme essential oil induced to harmful individuals a changing of feeding rhythm and disturbance of motility and mobility, allowing closer and faster contact with nearby diatomaceous earth.

Experimental cold saponification
A laboratory system composed of glass flask of 1 liter capacity, fitted with reflux cooler, mechanical stirrer, thermometer and dropping funnel (Figure 3) was loaded with 150 grams of cold pressed rapeseed oil which was heated at 55-60°C, then 75 ml aqueous KOH 25% was added dropwise with stirring and saponification reaction was completed after 2.5 hours. The pH of the resulting mixture was adjusted to 8.5-9 with acetic acid. A portion of 15 g of thyme essential oil were added dropwise with stirring, and more mixing for another 30 minutes obtaining a concentrated emulsion.

Experimental formulation and packaging
A 70 grams portion of the fluid obtained from the concentrated oil emulsion were added dropwise into a laboratory rotating metal drum (Figure 4), loaded with a fine powder obtained from ground diatomaceous earth and 120 grams were retained on the surface of the granules. Maintaining about 24 hours the obtained wet granules in open air at ambient temperature and pressure, 160 grams of dry product were obtained and sieved to yield granules with 2 mm, 1.6 mm and 1.02 mm grains (Figure 4).

Characterization of final product
The vegetable oil-based product for stored grain protection against pests and diseases resulted as gray-brown granules (Figure 5), with porous aspect, pleasant smell, and chemical composition: 15-25 % of potassium soap of rapeseed oil, 3-5 % potassium acetate, 1.5-3 % glycerin, 1.5-5% thyme oil, 40-65% of diatomaceous earth, 1.5-2% unsaponifiable matter and water up to 100%. The ability of the granules to retain the volatile oil by internal pores of diatomaceous earth and by oily core
(about 65% thymol) was shown by GC-MS analysis (Figure 5).

When a similar composition was formulated using a fluidized bed granulator, the efficacy of essential oil encapsulation was ten times lower than with the rotating drum, due to the volatile oil drive with the air flow (Figure 6).

After our knowledge, there is no scientific evidence regarding such an innovative (micro) encapsulated vegetable oil-based product into bioactive mineral core-shell granules conceived to ensure slow-release of active ingredients for simultaneous protection against storage insects and mycotoxigenic fungi.

CONCLUSIONS

Bio-based products for stored grain protection should be considered one of the most important means for agri-food chain decontamination and health safety areas of bioeconomy. Vegetable oils are one of the most available, cheap and versatile raw materials from natural renewable resources. Microencapsulation of antimicrobial essential oils into insecticidal salts of fatty acids from special plant oils and formulation as biodegradable granules into bioactive mineral shell represent modern and clean technologies for slow-release plant protection products against pests and diseases easy to obtain with a simple rotating granulator and use by organic farmers for stored grain long term preserving.

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REFERENCES


