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A nanosised oxygen scavenger: Preparation and antioxidant application to roasted sunflower seeds and walnuts

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ABSTRACT

A novel oxygen scavenger using iron nanoparticle was produced and evaluated as a potential oxygen scavenger. Iron nanoparticle was prepared by liquid phase reduction method in microemulsion systems. The absorption capacity of different kinds of oxygen scavengers was measured as a function of time, and the absorption rate constant was evaluated at 25 °C. The absorption kinetic analysis showed that the absorption process followed a first-order reaction. The absorption rate constant of nanosised and conventional oxygen scavenger were $0.45 \pm 0.044\ h^{-1}$ and $0.05 \pm 0.006\ h^{-1}$, respectively. Successful application of the nanosised oxygen scavenger on roasted sunflower seed and walnut demonstrated its ability to inhibit lipid oxidation in lipid-containing food. Roasted nut treated with nanosised oxygen scavenger possessed the lowest PV and AnV in all treatments after 120 days of storage. Therefore, it has the potential for broad application as an active packaging in a variety of oxygen-sensitive foods.

1. Introduction

Oxygen is responsible for many degradation reactions in food such as lipid oxidation, micro-organism growth, enzymatic browning and nutrition loss (Ayranci & Tunc, 2003), causing significant reductions in the shelf life of oxygen-sensitive food. Lipid oxidation in a series of free radical chain reactions destroys unsaturated fatty acids and produces toxic compounds and oxidised polymers. Oxidative processes also cause the degradation of proteins, pigments and vitamin, which limits the shelf life (Lee, Shin, & Han, 2004; Liu, Dai, Zhu, & Li, 2010). In order to protect oxygen-sensitive foods from oxidation, many technologies have been developed to eliminate or reduce the levels of oxygen inside packs. These include modified atmosphere packaging (MAP), vacuum packaging and oxygen scavenger sachet. For instance, some viable spores had been used as an active oxygen scavenger and incorporated in polymer packaging materials to remove residual oxygen in packaging (Anthierens, Ragaert, Verbrugghe, Ouchchen, & Devlieghere, 2011). Oxygen scavenger, also called oxygen absorber or deoxidiser, has been widely underutilised to protect packaged foods from proliferation of bacteria, colour change, loss of nutritive value, insect damage and loss of quality, such as oxidation in olive oil (Del, Ambrosino, Sacchi, & Masi, 2003), rancidity problems in hazelnut (Mexis, Badeka, Riganakos, & Kontominas, 2010) and spoilage of rainbow trout (Mexis, Chouliara, & Kontominas, 2009).

Based on the material components, there are two major types of oxygen scavengers: inorganic and organic. For instance Fe(0) and Fe(II) are inorganic, while ascorbic acid and vitamin E belong to the organic category of oxygen scavengers. Because of low cost, easily attainable raw materials, efficiency in eliminating oxygen and safety, the majority of oxygen scavengers presently available is iron-based systems. The working mechanism of the ferrous oxygen scavenging is the reaction of iron with oxygen in the container to form ferric oxides. The influences of the efficiency of oxygen scavenging are classified into extrinsic and intrinsic factors. Extrinsic factors include temperature, relative humidity and oxygen partial pressure in the package, which depend on the internal environment of food packaging. Intrinsic factors are determined by the properties of iron powder, such as the particle size and specific surface area (Polyakov & Miltz, 2010; Tewari, Jayas, Jeremiah, & Holley, 2002). So, increasing the reaction activity of iron powder is the most important thing to improve the oxygen absorption capacity of oxygen scavengers. Nanosised materials exhibit novel and significant material properties, including quantum size effect on photochemistry, magnetic properties and catalytic activities in comparison with their analogous larger-sized materials. For the iron nanoparticle, the activity increased largely due to the increase in density of reactive sites. Compared with conventional iron powder, the specific surface area of nanosised iron powder is much greater (Sun, Lia, Cao, Zhang, & Wang, 2006). This physical characteristic results in excellent adsorption properties and high reduction activities. In recent years, iron nanoparticles have been used for abiotic dechlorination of chlorinated compounds (Wang & Zhang, 1997; Zhong, Zhao, & Pan, 2007), and sorption of arsenic

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(Kanel, Greneche, & Choi, 2006). Thus the aim of this study was to investigate the possibility of utilising iron nanoparticles instead of conventional iron powder as the active agent in oxygen scavenger. To the best of our knowledge there was no information in the literature on the use of nanosised iron for oxygen scavenging.

During the last few years, many methods have been developed to prepare nanomaterials. Among these methods water-in-oil (w/o) microemulsion method is a versatile preparation technique which enables control of particle properties such as size, geometry, morphology, homogeneity and surface area (Anton, Benoit, & Saulnier, 2008). In this study, the nanosised iron particles were synthesised with a microemulsion formed by an iso-octane/ Span80-Tween60/ n-butanol system. Then O_2 adsorption ability and lipid antioxidant properties of the novel oxygen scavenger were studied. The nanosised oxygen scavenger was demonstrated to exhibit a remarkable antioxidant effect on roasted nut products and proven to be a promising application on preserving other oxygen-sensitive food.

2. Experimental and methods

2.1. Chemicals and materials

$FeSO_4$, $NaBH_4$, KI, iso-octane, n-butanol Span80 and Tween60 were purchased from Shanghai Chemical Reagent Company, Shanghai, China. All other chemicals and solvents used were of analytical grade. Double distilled and deionized water was used throughout the experiment. Roasted sunflower seed and walnut were purchased from Yao Shengji Company, Hangzhou, China.

2.2. Preparation of iron nanoparticles

In this Work, nanoscale iron particles were prepared in microemulsion solutions by the reduction of ferrous iron (II) with sodium borohydride following the method of Liu, Li, Jin, Gong, and Zang (2007) with some modifications. The synthesis route of iron nanoparticles was carried out according to the following Eq. 1:

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe + 2B(OH)_3 + 7H_2 \quad (1)$$

Mixed Span 80-Tween 60 (1:4) surfactant (4.0 g) were added into the iso-octane (8.0 g) and n-butanol (2.0 g) solution. Then the oil phase (iso-octane), surfactant and cosurfactant were mixed ultrasonically until the mixture became transparent. Two microemulsions were prepared as follows: microemulsion A was prepared by adding 4.5 mL 0.15 mol/L $FeSO_4$ solution into the solution mentioned above. Microemulsion B was prepared by adding 4.5 mL 0.5 mol/L $NaBH_4$ solutions into the same starting solution. Then microemulsion A and B were mixed and mechanically stirred at 500 rpm for 15 min at room temperature while flushing with N_2. The black powder which precipitated was repeatedly washed using deionised water and ethanol/acetone. The precipitates were then dried under N_2 at room temperature to obtain the iron nanoparticles.

2.3. Characterisation of Fe nanoparticles

Micrographs of Fe nanoparticles were obtained with a transmission electron microscope (H7000, Hitachi, Tokyo, Japan). The samples were prepared by placing a few drops of the iron dispersion on a copper grid, which was allowed to dry before observation under the microscope. The dynamic particle size distribution of the iron nanoparticles in aqueous solution were measured using Zetasizer Nano ZS (Malvern Instruments Ltd., UK) at a measurement angle of 90° with a He–Ne laser beam at 633 nm. An average value was obtained from three repeated measurements for each sample. X-ray powder diffraction (XRD) patterns of the silicas were recorded on a Dmax-2500 (Rigaka) X-ray powder diffractometer using Cu Kα (λ = 0.1542 nm, 40 kv/100 mA) radiation. Iron nanoparticles were placed in a glass holder and scanned from 30° to 90°. The scanning rate was set at 2.0°/min.

2.4. Preparation and absorption kinetics of oxygen scavenger

Fe nanoparticles, activated carbon, NaCl and $CaCl_2$ were mixed at a 1:1:1:0.2 weight ratios in an environment of N_2 to prepare the nanosised oxygen scavenger. Then, a mass of the mixture was placed inside a sachet, which was then sealed. The sachets were vacuum packaged to prevent contact with oxygen from the air before performing tests. The conventional oxygen scavenger was prepared by the same way mentioned above, in which the reduced iron powder was used instead of Fe nanoparticles. The size of reduced iron powder was ca. 20 μm. The reduced iron powder was treated with 0.5 mol/L HCl 30 min to activate before used. Individual oxygen scavenger sachet (containing 0.5 g iron powder) was placed in flask which was sealed with a rubber plug at 25 °C. The RH inside the glass containers was generated by saturated solutions of NaCl, which corresponds to 75.3% of RH. The headspace gas composition was measured by gas sampling at regular intervals. Oxygen concentration was detected by gas chromatography (SP-6890, Ruihong Instruments Ltd., Shandong, China). (chromatographic conditions: column temperature: 90 °C; detector: TCD, bridge current flow: 70 mA, carrier gas: N_2).

2.5. Lipid antioxidant activity of nanosised oxygen scavenger

2.5.1. Storage conditions

Two fifty grams roasted nuts were packaged in polyester/polyethylene (PET/PE) pouches, 70 μm in thickness, with nanosised oxygen scavenger 2 g (Fe nanoparticles: activated carbon: NaCl: $CaCl_2$ = 1:1:1:0.2) or conventional oxygen scavenger 2 g (Fe nanoparticles: activated carbon: NaCl: H_2O = 1:1:1:0.2). Then all the samples were stored in dark at 25 °C. Control sample without oxygen scavenger was also maintained under the same storage conditions. After 0, 20, 40, 60, 80, 100 and 120 days of storage, three pouches were withdrawn from each treatment for peroxide value (PV) and p-anisidine value (AnV) analysis.

2.5.2. PV and AnV determinations

The oil was extracted from ground nut sample (10 g) with 100 mL petroleum ether in the dark for 12 h. the solvent was separated by filtration over anhydrous sodium sulphate. Oil sample was concentrated by removing petroleum ether with a rotary evaporator at 40 °C.

The peroxide value (PV) of all samples was measured according to GB/T 5009.37–2003 (2003). Oil samples (2 g) were dissolved in 30 ml of chloroform: glacial acetic acid (3:2, v/v). Then 1 ml saturated solution of KI was added. The mixture was shaken shaken manually for 0.5 min and was then kept in the dark for 3 min. After the addition of 75 ml distilled water, the mixture was titrated against sodium thiosulphate (0.002 M) until the yellow colour almost disappeared. Then about 0.5 ml of starch indicator (1%) solution was added. Titration was continued until the blue colour just disappeared. The blank was also analysed under similar conditions.

The p-anisidine value (AnV) was determined according to Zhang, Yang, Zu, Chen, and Wang (2010). Oil samples (2 g) were dissolved in 25 ml isooctane and absorbance of this fat solution was measured at 350 nm using a spectrophotometer (UV-2550, GBC). Five millilitres of the above mixture was mixed with 1 ml 0.25% p-anisidine in acetic acid (w/v) and after 10 min standing, absorbance was read at 350 nm using a spectrophotometer.