

STUDIES ON ZEOLITE CONTRIBUTION TO THE SUN PROTECTION PROPERTIES OF PLANT OIL LOTION RICH IN VITAMIN E

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Abstract. Sunscreen lotions rich in vitamin E provide benefit in preventing and treating sunburns. The sun protection capacity of vitamin E's lotion formulations decrease with time of light exposure. The zeolite microparticles with previously absorbed vitamin E and added after to sun protection oil lotion could be used as reservoir for replacing UV photodegraded vitamin E. In the research, the vitamin E absorption capacities of zeolite microparticles of concentration of 0.2 % w/v in plant oil mixture (Olea Europea Oil, Sunflower oil) have been studied by UV-Vis spectrophotometry. The sedimentation and laser diffraction measurements gave broad distribution on size of the zeolite microparticles (1 μm to 15 μm) without interparticle interactions in the solution. The results showed ten-fold decrease in UV absorbance at wavelength of 292 nm in the first 30 minutes of vitamin E absorption to zeolite microparticles and a flat of release in the sunscreen lotion.

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1. INTRODUCTION

The sun emits ultraviolet (UV) radiation in the wavelength range of 200 – 400 nm. The most of the harmful UV-C (200–280 nm) and the most of UV-B (280–320 nm) radiation is absorbed in the stratospheric ozone layer. The UV-A (320 – 400 nm) radiation is not affected by the stratospheric ozone layer. In the last few decades it has been found that the stratospheric ozone layer is depleted and the amount of harmful short wave UV radiation reaching the earth's surface is increasing [1]. Besides, people are exposed to UV radiation by outdoor activities and by the use of artificial sun tanning equipment that increases the risks of harmful UV effects, such as photoaging, sunburn, immune suppression and skin cancer induction [2]. When the UV-A radiation penetrates into the skin it provokes several damages such as immediate and delayed tanning reactions, loss of collagen, decrease of the quantity of blood vessels, skin photosensitization, and alteration of the connective tissue in the dermis. The main absorbers of UV-A radiation in the skin are hemoglobin and melanin. The UV-B region is responsible for the skin tanning and direct damage to the skin, which results mainly in sunburn [2]. Most significantly, UV-B radiation results in direct damage of DNA by formation of free radicals in skin cells.

Sunscreen formulations use has been promoted as a way to prevent the harmful consequences of skin exposure to UV. Sunscreen formulations mainly protect against sunburn (expressed through the sun protection factor, SPF). However, in recent decades several pathways are founded to protect immune suppression, free radicals reduction and other biological consequences of

UV radiation through incorporating proper ingredients and skin delivery mechanism [3]. The protective effects of sunscreen formulations depend on the way it is applied. Reapplication to the skin increases the protective effect, especially during swimming or sweating. Also, SPF and the thickness define the protection [3]. Most sunscreens may contain: a) organic chemical substance (chemical blockers) with UV light absorbing capability (such as oxybenzone, octyl-methoxy-cinnamate, avobenzone, alpha-tocopherol); b) opaque nanoparticles (physical blockers) that reflects light (such as titanium dioxide, zinc oxide); c) herbal spices (aloe, green tee); d) and combination of them [4]. Today, a various sunscreen formulations are available at the market: lotions, creams, emulsions, dispersions, gels, milks, sprays, tonics and others.

Photodegradation of sun protection molecules under exposure to outdoor UV radiation generates submolecules (of which some are free radicals) that are harmful for the skin. Reduction of photo degradation of active sun protective molecules (such as alpha-tocopherol) is possible through several techniques: a) substances that absorb UV radiation at specific wavelength; b) combining different sun protective molecules in same sunscreen formulation in order to achieve synergistic effect; c) complexing, encapsulating or entrapping of sun protective molecules that protect the molecules from UV radiation during the process of their release from the carrier materials such as gels, hydrogels, polymer dispersions and nano or micro porous particles (such as zeolites). The following properties of the ideal sunscreen formulation should be manifested [4]: light absorption in the range 280 – 320 nm; stability to heat, light degradation and perspiration; non-irritant and nontoxic characteristics; slow skin absorption; solubility and incorporation capability in carrier vehicles.

Alpha-tocopherol (vitamin E) is very effective against UV-B free radical damage [5]. It has a synergistic effect when combined in sunscreens with ascorbic acid (vitamin C). Vitamin E absorbs strongly in the UV-B region of 280-320 nm. Therefore it can act as a photoprotective sunscreen in skin cell membranes. Alpha-tocopherol and its acetate derivative have been shown to act as UV sunscreen photoprotectants by a scavenging mechanism of free radicals reduction [5]. Skin cells are photosensitive to damage due to generation of radical oxygen molecules. These include singlet oxygen ($^1\text{O}_2^*$), free radicals such as superoxide anion radical O_2^* , perhydroxyl radical HO_2^* , protonated form of O_2^* , and hydroxyl radical $^*\text{OH}$, that destroy the structural integrity of cellular lipid membranes. Vitamin E acts in two ways: as a physical quencher of oxygen free radicals and as a chemical scavenger of photogenerated radicals. One molecule of a-tocopherol is able in average to deactivate up to 100 molecules of $^1\text{O}_2$ before itself being photodegraded. In addition, it has been shown that a-tocopherol could itself be converted in its radical form, a-chromanoxyl radical, by absorbing UV-B radiation. Vitamin E acts well together with other antioxidant (Vitamin C) because, in the absence of other antioxidant, it is depleted rapidly [6]. Recently, this conflict between the radical scavenging role of a-tocopherol as skin cells protector and the endogenous influence of its photodegraded radical form needs to be further investigated and resolved.

Another sunscreen formulation ingredient, as a part of this research, was octyl-methoxy-cinnamate (OMC). OMC is widely used as UV-B sunscreen protection substance. OMC photoisomerization processes take place under UV exposure [5]. When exposed to sunlight, this UV-B filter substance changes from octyl-p-methoxy-trans-cinnamate (E-OMC) to octyl-p-methoxy-cis-cinnamate (Z-OMC) with change in only 1 nm shift of the maximum UV absorption wavelength of n-hexane solution. The studies on OMC photostability show that no other degradation products, such as free radical submolecules, were detected when OMC was exposed to sunlight.

Entrapping of Vitamin E and OMC in some nano or microporous carrier particles could preserve defined amount of the sun protection molecules from photodegradation. After deterioration of the amount of the sun protective molecules under UV radiation exposure, a required quantity of in carrier preserved molecules could be released on defined pathways (for example, diffusion, pressure, heating) and thus replacing the deteriorated molecules to desired concentration for effective sun protection. One carrier material that can serve in that way is natural zeolite in its clinoptilolite mineral form.

The aim of this research is to investigate the loading capacity of vitamin E and OMC as sun protection molecules to zeolite's microparticles. Natural zeolite can slowly or cannot adsorb molecules at all depending on the size of the openings (pores), thus functioning as molecular sieves. The electrical charge and polarity of the adsorbed molecules defines the adsorption ability of zeolites [6]. Clinoptilolite is a member of the natural zeolites. Clinoptilolite has distinctive framework topology and Si/Al ratio less than 4. Its approximate chemical composition may be expressed as follows: $(K_2, Na_2, Ca)_3[(Al_6Si_{30} O_{72}) \cdot 24 \cdot H_2O]$. Three independent components are present in the clinoptilolite structure: the aluminosilicate framework, zeolite water and exchangeable cations. This clinoptilolite mineral contains three channels embraced by tetrahedral rings (Fig.1). The quantity of zeolite water depends on the distribution and type of cations, because cations in the channels and cavities are surrounded by both water molecules and oxygen atoms.

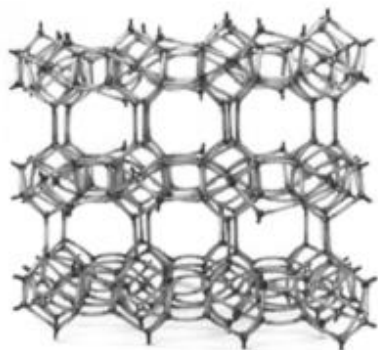


Fig.1. Zeolite framework structure.

Cations are bound to the zeolite structure more strongly by water oxygen than by oxygen atoms in the zeolite framework [6]. Water molecules present in the zeolite occupies the internal voids. Access of outer molecules to the zeolites voids and cavities occurs through rings composed of Al/Si and O atoms. The size of the pore (window) for zeolites with smaller rings that contain six Al/Si sites or less is 0.2 nm, and for larger rings the size is 0.8 - 0.85 nm. The internal structure of zeolites consists of interconnected cages or channels through the whole volume, which can have dimensionalities of one to three. The total pore volume usually is in the range of 0.10 to 0.35 cm³/g.

2. EXPERIMENTS

Natural zeolite in its clinoptilolite mineral form was purchased from Bulgaria. Before use the zeolite powder was subjected for 6 hours at temperature of 100 °C in an oven under pressure of $1 \cdot 10^4$ Pa in order to evaporate the zeolite water. The laser diffraction measurement (Laser Fraunhofer, Germany) gave broad distribution on zeolite particles size in the range from 1 μm to 15 μm. The average pore size of 0.85 nm of the zeolite particles was determined by water diffusion method and relative total pore volume of 30 % has been calculated. The density of the particles of 2.30 g/cm³ was determined by the gravimetric method. In order to investigate possible interactions, conglomeration or aggregation of zeolite particles Sunprotection oil (SPO) in solution, sedimentation experiments were conducted on the tensiometer model DACT 31, DataPhysics, Germany. UV-Vis spectrophotometry experiments were conducted on Ultrospec 5300 pro UV/Visible Spectrophotometer, GE, USA. The sedimentation experiments, UV-Vis spectroscopy studies and preparation of the investigated solutions were conducted at room temperature. Sunprotection oil used in the research was a commercial grade product consisted of the following ingredients: parafinum liquidum, olea europea oil, sunflower oil, ethylmethoxy-cinnamate, alpha-tocopherol, Perfume.

3. RESULT AND DISCUSSION

Sedimentation experiments were conducted with a cone holder immersed in a glass cup full of 20 cm² of 0.2 % w/v zeolite in 0.2 v/v SPO in n-hexane at 20 °C and the tension force on the cone attached to the measurement unit of the tensiometer was measured in period of 2500 s. As the sedimentation of zeolite particles occurs, the cone holder becomes more filled and tension force of the cone increased with time. The sedimentation rate was determined and the results are shown on fig.2. The results show linear decrease of the sedimentation rate that is an indication for no interparticle interaction in n-hexane, conglomeration or other aggregation processes of zeolite particles in SPO.

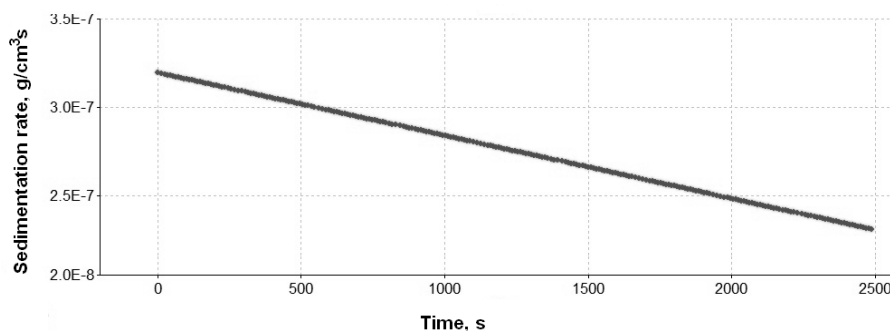


Fig.2. Sedimentation rate of 0.2 % w/v zeolite in 0.2 % SPO in n-hexane.

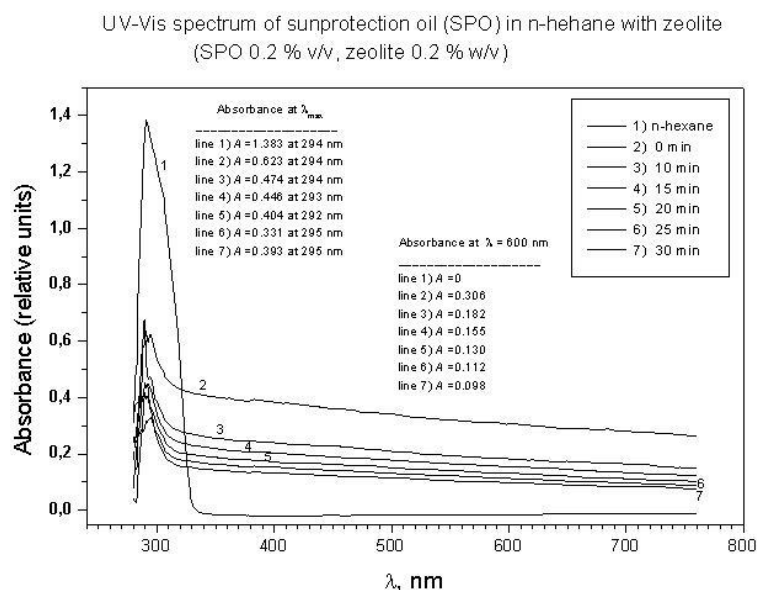


Fig.3. UV-Vis spectra of SPO in hexane with zeolite powder.

The investigation of the adsorption capacity of zeolite particles to SPO and thus to Vitamin E (alpha-tocopherol) and OMC as sunscreen active molecules were conducted on solution of 0.2 % v/v SPO in n-hexane with 0.2 % w/v zeolite powder (clinoptilolite form). UV-Vis spectrophotometer model Varian 2000 has been used with quartz glass cells. UV-Vis scans in the wavelength range 280 – 900 nm with resolution of 1 nm have been made on the investigated solution. As a reference substance, n-hexane has been used. Before subjecting the investigated solution to UV-Vis spectrophotometry, the solution of 0.2 % v/v SPO in n-hexane with 0.2 % w/v zeolite powder was slowly stirred for 2 hours. UV-Vis scans have been made on every 5 minutes up to 30 minutes after placing the solution in the spectrophotometer. Decrease of the absorbance A of the SPO at the wavelength of maximum absorption (≈ 292 nm) has been detected over time (fig.3). That was an indication that zeolite particles are adsorbing active molecules from the SPO (Vitamin E and OMC) that have maximum absorption in the same wavelength region [7].

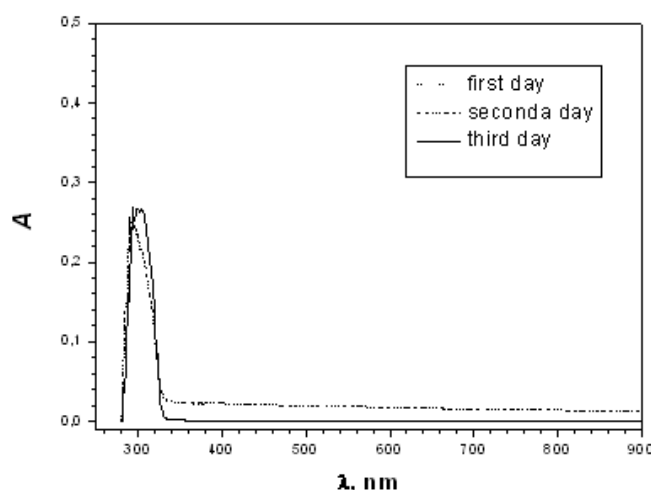


Fig.4. UV-Vis spectra of SPO with zeolite powder after one, two and three days of steering.

The maximum SPO loading capacity of the zeolite powder has been determined after providing some preconditions. Namely, solution of 0.2 % v/v SPO in n-hexane with 0.2 % w/v zeolite powder (clinoptilolite form) was constantly steered during three days. After 24 hours, 48 hours and 72 hours from the beginning, solution samples were put into the spectrophotometer and V-Vis spectra were obtained (fig.4). It is noticeable from fig. 4 that after two days of adsorption there is no difference between the UV-Vis spectra for the second and the third day. The maximum absorbance at 292 nm is around 0.25 which is three times smaller than at the beginning (line 2, fig.3). This is evidence that zeolite powder can adsorb Vitamin E and OMC as sunprotection molecules and thus can serve as a reservoir for replacing photodegraded molecules during outdoor light exposure.

CONCLUSIONS

The research on the time dependence of the UV-Vis spectra of 0.2 % v/v SPO in n-hexane with 0.2 % w/v zeolite powder after preparation of the investigated solution showed that clinoptilolite, a natural form of zeolite, has a capacity for adsorption of Vitamin E and octyl-methoxy-cinnamate as active sunprotection molecules. Sedimentation studies showed that there is no interparticle interaction and aggregation of zeolite particles in non-polar solution that could lead to particles sticking and thus lowering the adsorption capacity.

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