Nanoparticles of Activated Natural Zeolite on Textiles for Protection and Therapy

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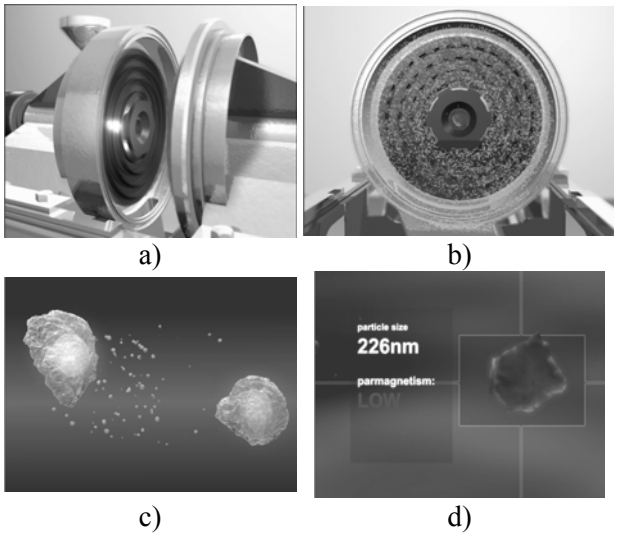
Abstract: Activated natural zeolite *clinoptilolite* is microporous hydrated aluminosilicates crystals with well-defined structures containing AlO_4 and SiO_4 tetrahedral linked through the common oxygen atoms. It is to point out that zeolites act as strong adsorbents and ion-exchangers but having many other useful properties. Zeolites are nontoxic substance, excellent for UVR and microbes protection, for proteins and small molecules such as glucose adsorption. Due to its cationexchange ability, zeolites have catalytic properties and for that multiple uses in medicine and industry, agriculture, water purification and detergents.
The present paper is an attempt to modify cotton and polyester fabrics for summer clothing with addition of natural zeolite nanoparticles for achieving UV and antibacterial protective textiles. For this purpose cotton fabrics were mercerized and polyester fabrics modified by alkaline hydrolysis and by EDA (ethylenediamine) aminolysis. Zeolite in this paper refers to activated particles of clinoptilolite, with some fraction of nanoparticles produced by tribomechanical processing in the patented machine.

Key-Words: zeolite, cotton, polyester, summer cloths, UVR protection, antibacterial protection

1 Introduction

Zeolites are hydrated natural or synthetic micro porous crystals with defined structures based on AlO_4 and SiO_4 tetrahedral building blocks connected through oxygen atoms. Zeolites have a variety of uses, they are employed as adsorbents, ion~~ic~~ exchangers, catalysts and detergent builders in industry, agriculture, veterinary medicine, health care and environmental protection.[1,2] Natural zeolites are rock-forming, micro porous silicate minerals. A mineral of the natural zeolite, clinoptilolite, has a crystalline configuration, tetrahedron structure. It has a lattice structure with long channels comprising water molecules and alkaline earth ions. As these do not occupy fixed positions, these ions may shift within the lattice. They can be easily released and exchanged without changing the character of crystal lattice, enabling clinoptilolite to have strong ion exchange properties[1,2], as an example clinoptilolite bonds heavy metals. Many researchers report that clinoptilolite absorbs toxins and mould.[3]
Clinoptilolite can be grinded by a certain tribomechanical processing in a patented machine (Patent: PCT/1B99/00757) yielding particles on a sumicron level (micro and nanoparticles) this process leads to an increased specific surface which amongst others yields a higher activity with respect to the above mentioned properties. Nanoparticles of one gram of micronized clinoptilolite have an inner surface of 50,000 m^2 50 million micro channels representing exceptionally powerful micro filters.



a) b) c) d)

Fig. 1. Tribomechanical activation (TMA) – a)

TMA machine, b) TMA machine with particles, c) input of clinoptilolite particles, d) nanoparticles of clinoptilolite

Due to the increased total surface area and an increased accessibility of the micro-channels the activity of the zeolite is increased several hundred times. Activated natural zeolite has multiple uses in industry and agriculture, while the broad spectrum of medical[3]. Its positive effect on the metabolism of living organisms has been confirmed in case of human application. Most recent research conducted basically over the last ten years proves its anticancerogenic and antimetastatic effect[8, 12,13], its strong antiviral activity and an assistance of metabolic processes. Scientists define it as the most powerful natural imunostimulator and antioxidant [7]. Zeolites could be now considered to be full-fledged mineral commodities, the use of which promise to expand even more in the near future[1, 2].

When applied externally in powder form, it has been found to quicken the healing of wounds and surgical incisions, and act as proven bactericides and fungicides as well. Applied on textile, clinoptilolite increases the active surface area. If added to azalides in textile finishing, they increase the efficiency of antimicrobial action. Zeolite gives a contribution to UV protection by scattering UV radiation unlike other agents which absorb this radiation preventing their transmission. Treated textiles achieved high level of UV protection.[4,5].

2 Activated Zeolite in Diverse Biological Activities

Amongst other useful properties and application activated zeolite posses diverse biological activities previous successfully used as vaccine adjuvant and for the treatment of diarrhea. Activated zeolite plays an important role in regulation of immune system containing high portion of silica that can be found in Hecht, Hecht-Savoley[1] Silica, silicates and aluminosilicates act as non-sapecific immunostimulators like superantigens. Superantigens (SAG) are a class of immunostimulators and disease causing proteins of bacterial and viral origin with the ability to activate a relatively large fraction of T cell population. Where immunity is reduced, zeolite activates B and T cells populations. In the disease of autoimmune system, it lowers the cancer marker CD 56[9].

It is well known that protein kinase stimulates oncogenes which results in mutation of DNA and creation of malignant cells. Activated zeolite inhibits protein kinase B (c-Act) to other kinase included in the apoptosis process and provokes of cancer. In this way it prevents the creation of malignant cells[10]. Zeolite has antibacterial, antioxidative and immunostimulatory property. Loccal application of such elite to animal skin cancers effectively reduced tumor formation and growth. It was shown that it might affect cancer growth by attenuating survival signals and inducing tumor suppressor genes in treated cells. Having antiviral properties activated zeolite locally, on the skin, has therapeutically application against herpes virus infection or orally in the cases of adenovirus or enter virus infections. It is to point out that virus are very small and on nonsocial level, from 65 -80 nm for adenoviruses and enter viruses to 100 - 200nm for herpes viruses. Antiviral effects of activated zeolite can be explained by incorporation of virus particles into the pores of such crystals that can be found in[10].

2.1 Antioxidative effects

Activated zeolite has very strong antioxidative properties that could affect oxidative stress in cancer and diabetes patients. Additionally, *diabetes mellitus* patients can use zeolite for the reason of its glucose high absorbance. Free radicals are the main factors of many pathological changes in organisms. It was found that around 90% of various diseases are results of disturbances in cell function or cell damage caused directly or indirectly by the activity of oxygen free radicals. Free radicals derived from oxygen have been implicated in numerous pathological processes including inflammation, reperfusion injury, hemorrhagic shock, autoimmune diseases, neurological disorders, *diabetes mellitus* and cancer. That can be found in Ivkovic and Zabcic (2002- I). It is confirmed that activated zeolite acts against disease *Psoriasis vulgaris* on the base of antioxidative activity. That can be found in Schulz, Gulbin, Gulbin, Ivkovic and Bendzko (2005).

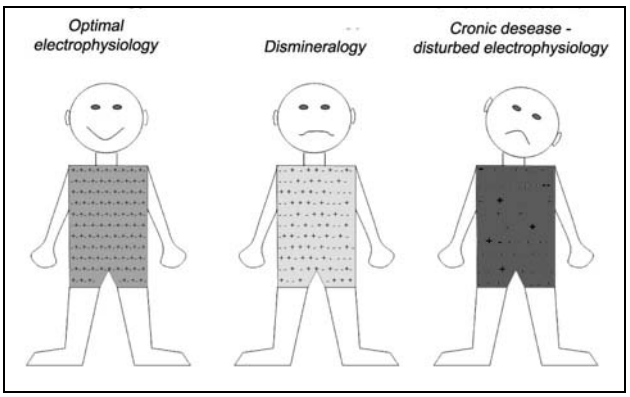


Fig. 2 - Human body is electric charged with examples of models for optimal electrolytic regulation and its dissordes[1]. Total Antioxidant

Status (TAS) measures the concentration of antioxidants in the organisms. From many results it is shown that activated zeolite influenced an increase in TAS value more than 26% which is in comparison to known antioxidants (A, C, and E vitamines, flaovoinouds, melatonin etc.) tenth time effective. That can be found in Ivkovic and Zabcic[7].

Currently, various antioxidants are under clinical investigation as an adjunct to standard and experimental cancer therapies.

Anticancer activity of antioxidants may not only be attributed to their radical scavenger properties, but also to direct modulation of cellular signal transduction pathways, resulting in growth arrest and apoptosis of cancer cells.

Recently, it has been shown that 4 weeks of oral supplementation with activated zeolite resulted in restoration of previously increased antioxidant levels (Randox Total Antioxidant Status) and decreases of free radicals (d-ROM-s Free Radical Analytical System) in plasma of cancer patients.

Beside its antioxidant capacity, activated zeolite demonstrated anticancer activity in vitro tissue cultures by inhibition of protein kinase B (c-Act) and induction of expression of tumor suppressor proteins, independently from p53 protein. Blockade of cell growth has been shown in several cancer cell lines (Fig. 3).

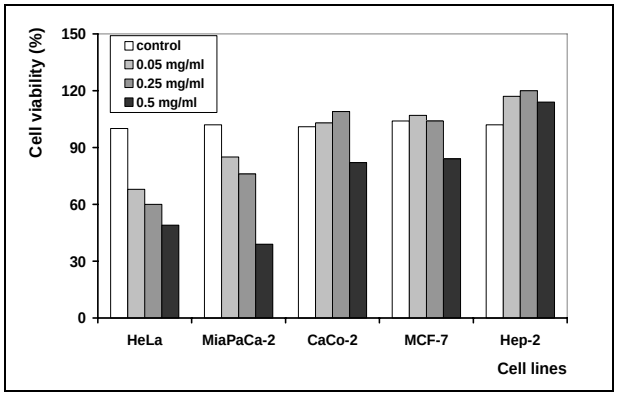


Fig. 3. The effect of activated zeolite treatment on growth of different human cell lines. The results are represented as a percentage of growth control cells. Legend: HeLa - cervical carcinoma; MiaPa-Ca-2 - pancreatic carcinoma; CaCo-2 - colon carcinoma; MCF-7 - breast cancer; Hep-2 - laryngeal carcinoma.

The effect of activated zeolite on cell proliferation in vitro was studied on several human cell lines.

The cell viability was determined using MTT assay (from Sigma) which detects dehydrogenase activity in viable cells.

In the Fig. 5 it can be shown the effect of this zeolite on the growth of next human cell lines: HeLa-cervical carcinoma; MiaPaCa-2-pancreatic carcinoma; CaCo-2 - colon carcinoma; MCF-7 - breast cancer; Hep-2 - laryngeal carcinoma. The high inhibitory effects of zeolite are obtained with two cell lines, HeLa and MiaPaCa-2 what confirmed the recently results about zeolite inhibition of protein kinase B (c-Act).

Additionally, the combination of activated zeolite with doxorubicin for the treatment of mammary carcinoma-bearing mice was significantly more effective in reducing the number pulmonary metastases when compared to doxorubicin mono-therapy[7]. That can be found in Pavelić et al. (2001).

2.2 TMAZ in Healing Wounds

In the wound healing there are five important requirements: moist environment, antimicrobial, non-toxic to human cells, hypoallergenic and continuous debridement. Activated zeolite just follows these requirements having for such a reason favorable effects on the healing process in the next superficial skin wounds:

Acute skin problems - mechanical skin damage, thermal burns, abrasions, insect bites, post-operative wound treatment, herpes simplex and herpes zoster.

Chronic skin problems - various skin infections, allergic reaction, degenerative diseases, neurodermitis, ulcer cruris, decubitus ulcers, etc.

3 Nanoparticles of a natural zeolite (clinoptilolite) applied on textiles

Nanoparticles of a natural zeolite (clinoptilolite) applied on textiles are following the tendency for new textile applications as materials for human performance, such are medical, protective and sports application. During last few years these tendencies led to rapid growth of different protective finishes, material modification and application of nanoparticles, as well. Textile and clothing is a human's second skin, therefore it is the most suitable interface between environment and human body. It is ideal tool for personal protection and safety[8] .

3.1 UV Protection

A good fabric UV protection is a guaranty that clothing will have the ability to protect the skin from incident solar energy. In addition to some beneficial effects of UV radiation (UV-R, from 100 nm to 400 nm) on skin it may cause skin damage such as sunburn, allergies, skin aging and even skin cancer especially during the summer time. The UV-C radiation (from 100 nm to 280 nm) get absorbed

by atmosphere, but UV-B (from 280 nm to 320 nm) and UV-A (from 320 nm to 400 nm) rays reach the Earth and cause known skin aging and recently the formation of skin malignant neoplasm. Diminishing of the ozone layer raised this risk, what have resulted with large investigation of fabric UV protection. It is well known that garment provides some UV protection. Fabric can reflect, absorb and scatter solar wavelengths, but in the most cases it does not provide full sun screening properties. UV protection highly depends on a large number of factors, such are type of fiber, porosity, density, moisture content, type and conc. of dye, UV-B protective agents, and fluorescence whitening agents (FWA) in the case of white textiles, if applied. Nanoparticles of a natural zeolite (clinoptilolite) applied on textile material it scatters the light, resulting in UV protection[4,5].
Therefore, for the purpose of this paper, sun screening properties of cotton (C) and polyester (poly(ethylene-terephtalate), PET) fabric after standard surface modifications – cotton mercerization and PET alkaline hydrolysis; and after treatment with zeolite nanoparticles and FWA's were shown. Fabric labels and treatments are collected in Table 2.

Table 2. Fabric labels and treatments

Label	Treatment
CB	Bleached cotton fabric with H_2O_2
CBM	Bleached mercerized cotton fabric in 24 % NaOH
CBZ	Bleached cotton fabric impregnated with 5/g l zeolite
CBMZ	Bleached mercerized cotton fabric impregnated with 5 g/l zeolite
PET	Untreated polyester fabric
PETH	Hydrolized polyester fabric in 1,5 mol/l naOH
PETZ	Polyester fabric impregnated with 5 g/l zeolite
PETHZ	Hydrolized polyester fabric impregnated with 5 g/l zeolite

UV protection was determined through Ultraviolet protection factor (UPF) using transmission spectrophotometer Cary 50 Solar-screen (Varian) according AS/NZS 4399:1996 Sun Protective Clothing: evaluation and classification. UPF indicates how much longer the person can stay in the sun with the fabric covering the skin as compared with the uncovered skin to obtain same erythemal response.

Results of UV protection expressed through mean UPF values shown on Fig. 4.

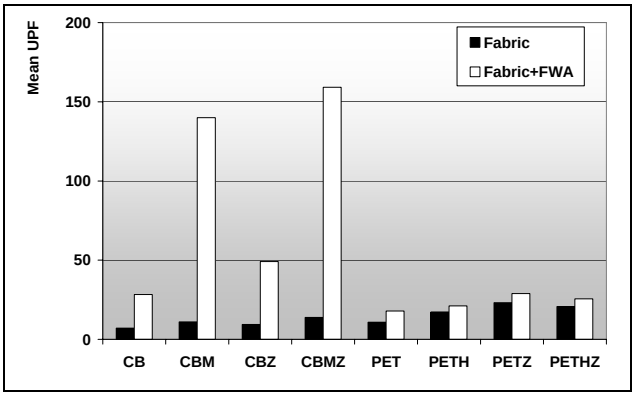


Fig. 4. Mean UPF values of cotton and polyester fabrics after surface modification and treatment with zeolite and FWA's

Fig. 4. indicates that polyester fabric give off better UV protection than cotton fabric after surface modification and treatment with nanoparticles of zeolite due to polyester chemical constitution. Polyester fiber has double bonds in polymer chain which can absorb small amounts of UV-R. Nevertheless, small amounts of UV-R are reflected from polyester multifilament. After FWA treatment it is evident that cotton fabric absorbs higher amounts of FWA. Bleached cotton is non-rateable for UV protection. Mercerization, as standard cotton modification, results in higher cotton absorbility and little increment of UPF, because fabric shrinks.
Nanoparticles of zeolite on fabric surface scatter UV-R resulting in better UV protection. Additionally, zeolite increase fabric surface area resulting in higher adsorption of FWA. Therefore, mercerized and zeolite treated cotton fabrics give off excellent UV protection after FWA.
UPF values for polyester fabric show similar behavior as for cotton fabric. Modification of polyester fabric results in little better UV protection, while treatment with nanoparticles of zeolite results in good UV protection. FWA treatment of polyester results in good protection as well. Meanwhile, FWA treatment to polyester fabric with zeolite results in very good UV protection.

3.2 Antimicrobial protection

Clothing and textile materials are carriers of microorganisms such as pathogenic and odor-generating bacteria, and mold fungi because of the adhesion of these organisms on fabric surface. Current vogue that promotes a healthier and active lifestyle led in last few years to rapid growth of antimicrobial finishes which results in textile

material to impart durable freshness and a feeling of safety and wellbeing of consumers. Azalides are subclass of macrolide antibiotics. Azithromycin, the most famous azalide with brand names Zithromax® (Pfizer) and Sumamed® (Pliva), is derived from erythromycin by adding a nitrogen atom into the lactone ring of erythromycin A, thus making the lactone ring 15-membered. Azithromycin is used for the treatment of respiratory-tract, soft-tissue and genitourinary infections. It prevents bacteria from growing by interfering with their protein synthesis. Therefore it is of great interest to research its antibacterial ability on textiles – nonwoven that can be used as protection masks and clothing in hospitals, woven for laundry and shits in hotels and hospitals and knitted for summer clothing, socks and underwear. Although its mechanism of action and susceptibility to resistance are similar to those of the macrolide antibiotics, azithromycin's extended spectrum of activity includes Gram positive and Gram negative organisms, as well as atypical pathogens.

Therefore, for the purpose of this paper, other set of cotton fabrics were impregnated with 5 g/l of zeolite nanoparticles and than antimicrobially treated with azlide by exhaution method in Linitest (Original, Hanau). at pH 5.5, T = 60 °C for t = 20 min with 3 % owf of the AZI 25 % water solution.

Table 2. Fabric labels and treatments

Label	Treatment
B	Bleached
BM	Bleached mercerized
...Z	Impregnated with zeolite nanoparticles
...A	AZI by exhaustion method

Fabric antimicrobial activity was determined according to EN ISO 20645. The results are collected in Table 3.

Results clearly show that traditionally pretreated cotton fabrics – bleached and mercerized have no antimicrobial activity. Impregnation with zeolite (BMZ) results in antimicrobial activity to both, Gram positive as well as Gram negative *Klebsiella pneumoniae* bacteria.

Azalide compound had shown excellent antimicrobial activity on Gram positive as well as Gram negative bacteria. It is evident that zeolite treated fabrics, and treated with AZI show off the best results. Therefore, synergism between zeolite and azalide is confirmed.

Table 3. Antimicrobial activity of treated woven fabrics on Gram positive *Staphylococcus aureus* and Gram negative *Klebsiella pneumoniae*

Sample	*Staphylococus aureus*	
	D [mm]	*activity*
B	24	no
BA	42	high
BM	24	no
BMA	44,5	high
BZ	25	small
BZA	42	high
BMZ	34,5	high
BMZA	48	high
	Klebsiella pneumoniae	
B	24	no
BA	30	high
BM	24	no
BMA	39,5	high
BZ	24	no
BZA	37	high
BMZ	29	small
BMZA	42	high

After the washing all fabrics treated with antimicrobial agent, azalide (AZI) still show antibacterial activity, but in lesser quantity.

All fabrics treated with zeolite and azalide have great antimicrobial activity even after washing treatment, therefore all of them give excellent antimicrobial protection.

4 Conclusion

Surface modification of textile materials – cotton mercerization and alkaline polyester hydrolysis slightly increase fabric UV protection. Nanoparticles of zeolite applied to fabric surface result in good UV protection. FWA treatment leads to excellent UV protection for cotton and very good protection for polyester. Even though natural zeolites are yellowish do not affect fabric whiteness significantly. It is to point out that nanoparticles of zeolite and FWA give off synergistic effect in fabric UV protection.

Activated nanoparticles of zeolite have important role in increasing antimicrobial and UV protection of cotton fabrics regardless of the fabric structure or the applying treatment. The high antimicrobial activity against Gram positive as well as Gram negative bacteria achieved in previous our paper with azalide compounds is better when cotton fabric is additionally finished with zeolite. It is to point out very high and unexpected synergistic effect of activated zeolite and azalide compound for achieving UV protection. It is to conclude that cotton fabrics treated with nanoparticles of zeolite

show high synergistic protection of cotton fabrics ever after washing.

Based on small part of presented biological properties it is to conclude that textile and clothing with activated zeolite can protect the skin, showing effects on the healing process in the skin wounds and therapy effect against different shin diseases like, psoriasis, cancer. Achieved UV protection in textile finishing means antioxidative protection, as well.

On the base of wide described zeolite properties as its high adsorbance, microporous structures, microclimate condition, antioxidative effects, UV protection, antimicrobial and antiviral protection, it is to conclude that activated zeolite:

1. adsorbs sweat and stops unpleasant odors
2. cleans the skin from oxidants and free radicals
3. protects the body against harmful UV emission
4. protects the body from microorganisms and prevents its access and activity
5. constantly holds the body temperature
6. increase energy levels of entire body
7. protects of rheumatic problems
8. enhances exchanges of substances in the body and helps the skin "breath"
9. has favorable effects on the healing process in the skin wounds
10. regulates the pH values of skin and
11. is very comfortable to wear.

Tribomechanical activated zeolite on textiles promises multifunctional properties and different biological effects in the near future what requires further research work.

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