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Innovazione e ricerca

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La sonochimica applicata alla funzionalizzazione delle superfici tessili

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Como, 5 giugno 2013

AICTC
Associazione Italiana di
Chimica Tessile e Coloristica



AICTC
Italian Association of
Textile Chemists and Colourists



Le presentazioni

PL12 - The Sonochemical Coating of Textiles with Antibacterial Nanoparticles. A. Gedanken, Bar-Ilan University, Israel

O01 - Simultaneous Deposition of Chitosan and ZnO **NP's on Textiles via One**-step Sonochemical Reaction. I. Perelshtein et al., Bar-Ilan University, Israel

O02 - Simultaneous Sonochemical-enzymatic Coating Of Textiles With Antimicrobial Nanoparticles. P. Petkova et al., Universitat Politècnica de Catalunya, Spain

O03 - Environmental and Economic Sustainability of Novel Enhanced Antibacterial Nanotechnology Finishing Based on Ultrasound Processes. M.Perucca and G.M.Piacenza, Environment Park s.p.a, Italy

O13 - Antibacterial Efficiency of The Sonochemical Coating with CuO Nanoparticles, Produced in situ, versus CuO Nanoparticles from Throwing Stones Method. M. Blanes et al., AITEX, Spain

P42 - Coating Antibacterial Nanoparticles on Textiles: Towards the Future Hospital in which all the Textiles will be Antibacterial. I. Perelshtein et al., Bar-Ilan University, Israel

P43 - Self-cleaning and Antimicrobial Finishing of Textiles with TiO₂ Nanoparticles by Sonochemistry. N. Perkas et al., Bar-Ilan University, Israel



Il progetto europeo SONO

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SONO



www.fp7-sono.eu

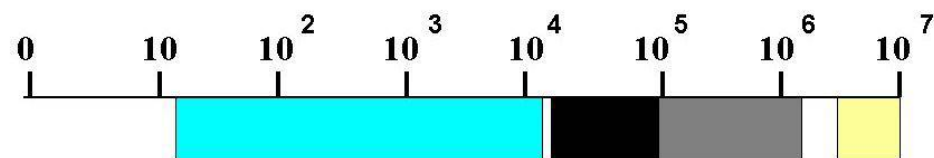
www.sonochemistry.info

Gli ultrasuoni

Gli ultrasuoni sono delle onde meccaniche sonore.

Le frequenze sono superiori a quelle mediamente udibili da un orecchio umano.

La frequenza convenzionalmente utilizzata per discriminare onde sonore da onde ultrasoniche è fissata in 20 kHz.



Human hearing



16Hz - 18kHz

Conventional power ultrasound



20kHz - 100kHz

Extended range for sonochemistry

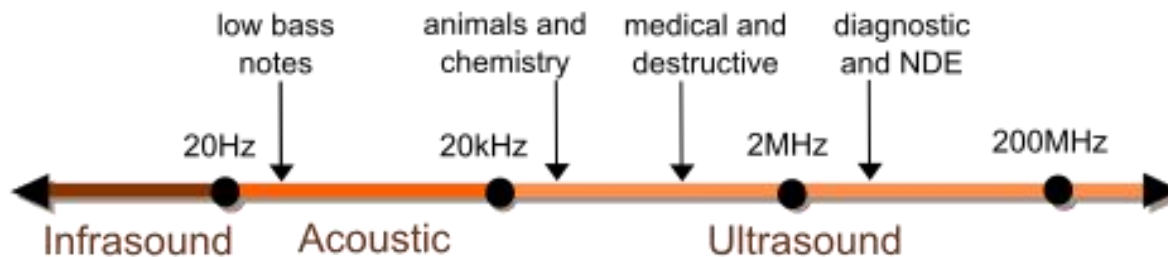


20kHz - 2MHz

Diagnostic ultrasound



5MHz - 10MHz



Gli ultrasuoni: applicazioni

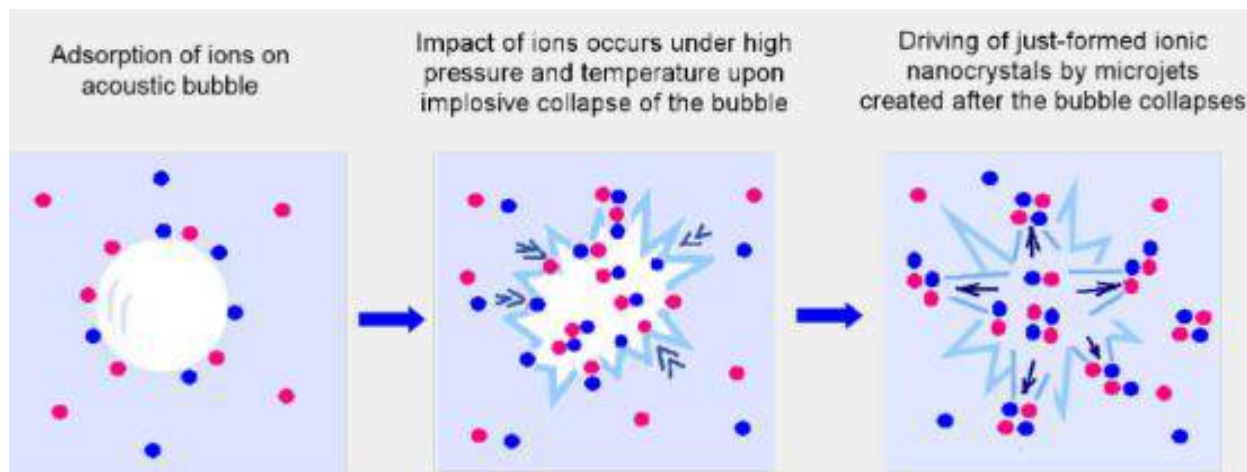
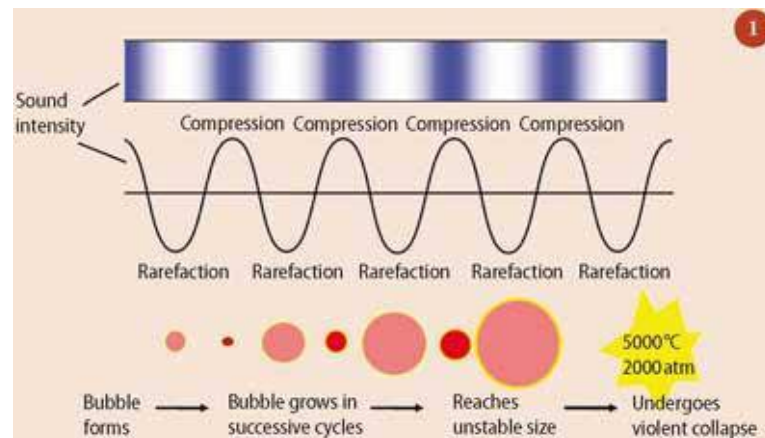


La sonochimica

La sonochimica si occupa dello studio degli effetti delle onde acustiche sui sistemi chimici.

Ultrasuoni: onde capaci di generare fenomeni quali la sonoluminescenza, la cavitazione sonora, la sonolisi e la sonocatalisi.

La cavitazione consiste nella formazione e successivo collasso di bolle per implosione. Il collasso della bolla è capace di generare altissime quantità di energia. La compressione delle bolle è molto più rapida del trasporto termico per cui si generano zone di calore localizzate e di breve durata.

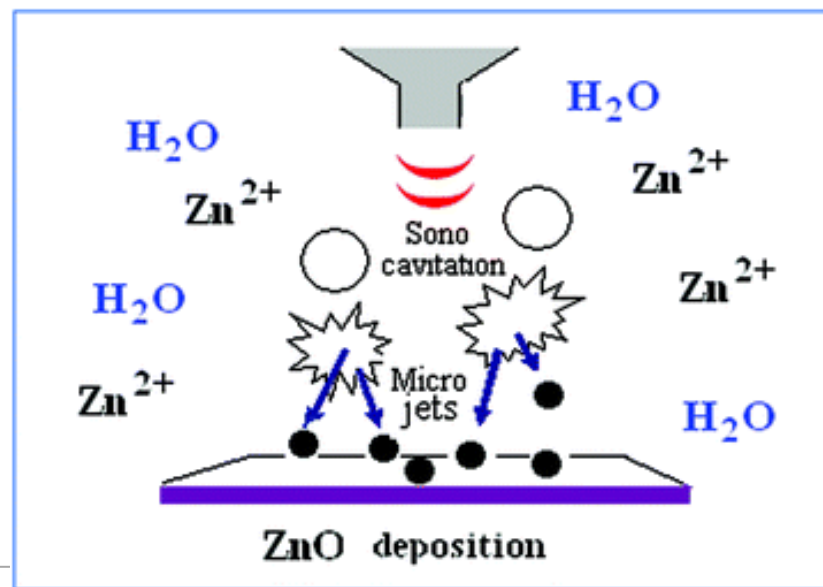
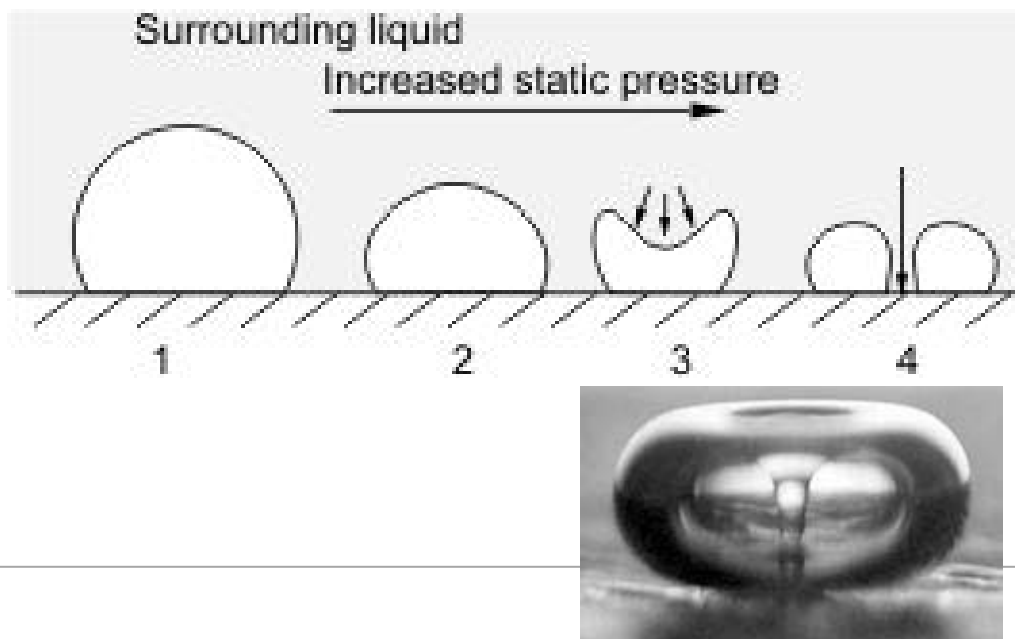


La sonochimica: sistemi eterogenei

Sistema eterogeneo: liquido contenente un solido.

Se la cavitazione avviene in vicinanza di una superficie il collasso della bolla non ha geometria sferica e genera la formazione di un getto di liquido ad alta energia e velocità verso la superficie stessa. Se sono presenti particelle in sospensione, queste possono collidere tra loro e/o essere sparate ad alta velocità verso la superficie.

La collisione genera modificazioni superficiali fino alla degradazione della superficie stessa.



Il progetto SONO

Concept

Le infezioni acquisite nel corso dell'ospedalizzazione:

- hanno una frequenza di 1/10 pazienti
- causano la morte di circa 3 milioni di persone per anno (nel mondo)
- comportano elevati costi umani e sociali



Scopo

- Sviluppare una linea pilota per la produzione di tessuti medicali ad attività antimicrobica forte e persistente mediante lo scale up del processo sonochimico (brevetto) per la deposizione di nanoparticelle (NP) di ossidi metallici su tessuti

Partners

- 17, da 10 paesi, 2 italiano (Klopman, Environment Park)

La chimica

- NP di Ag: riserve espresse da FDA
- NP a base di ZnO, CuO, MgO

I substrati tessili

- Cotone e cotone/PES

Il processo

- “in situ” (one step)
- “ex situ” (throwing stones)

Le tecnologie

- Trasduttore piezoelettrico
- **Trasduttore “magnetistrictive”**

La macchina (1)

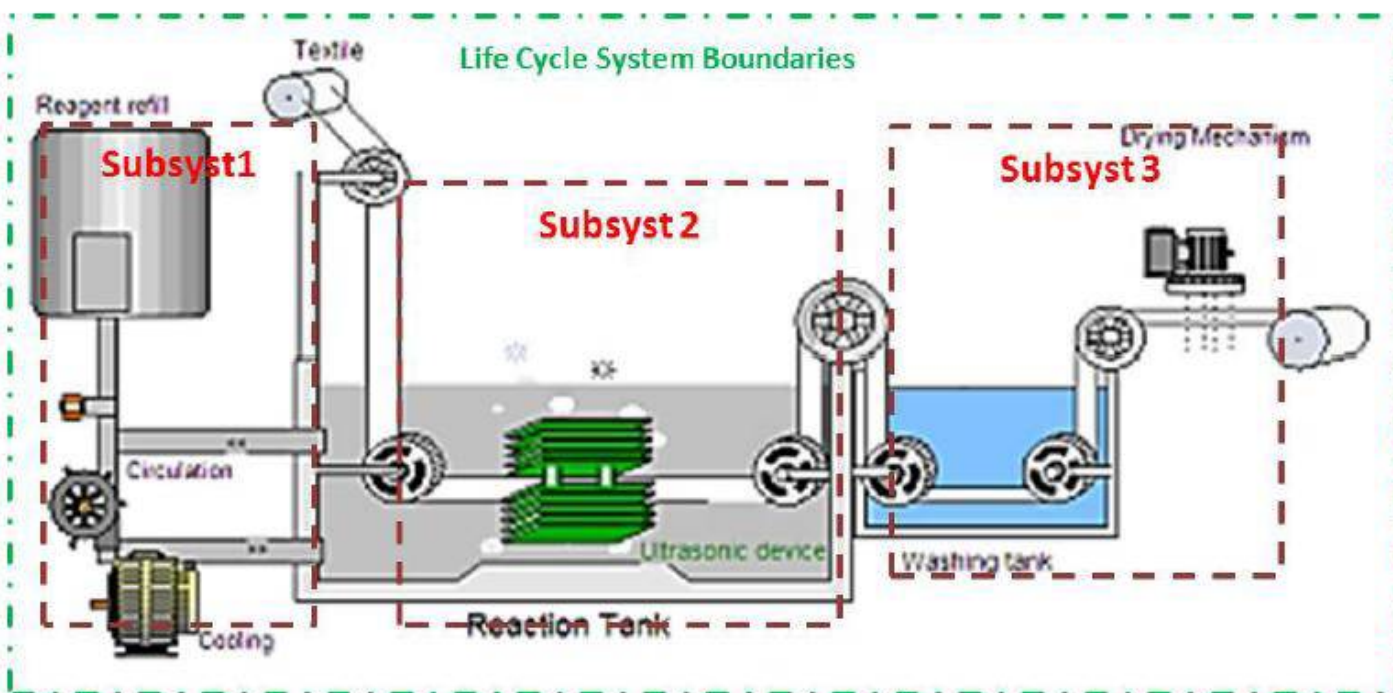


Figure 2. Schematics of PZ and MG processes flow chart. The external dashed line represents the system boundaries, the internal dashed lines the three subsystems. The monitoring and control system (subsystem n.4) is included in the functional system but has been excluded from the LCA due to its negligible impact

La macchina (2)

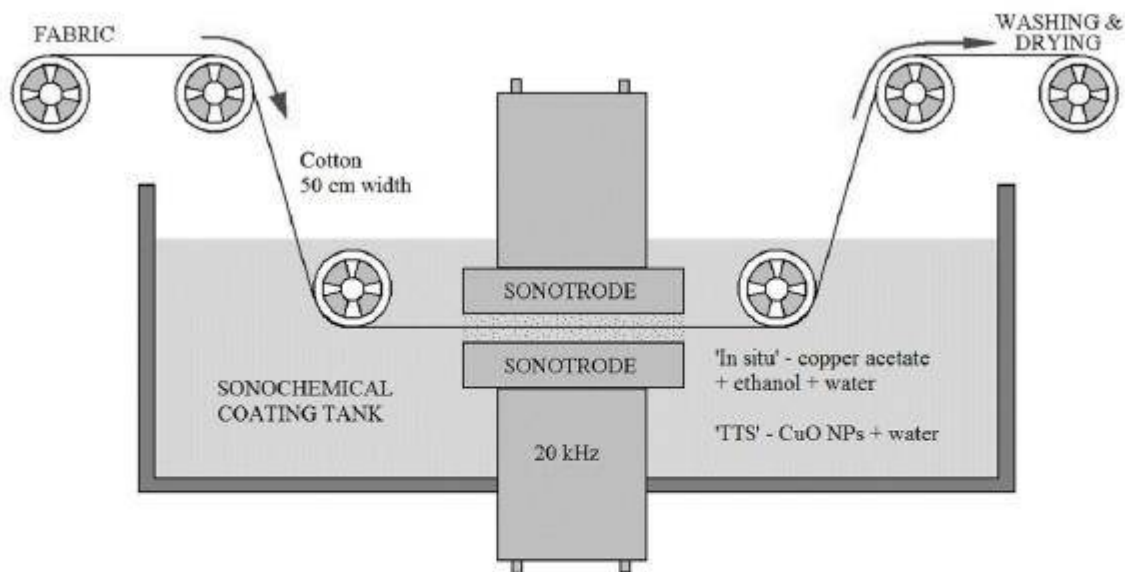


Figure 1. Schematic of sonochemical impregnation tank. Fabrics are fed on a roll through a tank containing either the reagents for CuO NP formation or a suspension of pre-made CuO NPs. Ultrasonic cavitation between the sonotrodes convert the soluble reagents in to insoluble NPs. The collapse of cavitation bubbles at the surface of fabric impacts NPs at high velocity in to the fibres thus impregnating the fabric with the NPs (either produced in situ or added in suspension).

Presentazione O13

Antibacterial activity of sonochemical coatings with CuO NPs:

- in situ (90% ethanol)
- ex situ (100% water)



Figure 2. Photographs of cotton fabric impregnated with CuO NPs via the ‘in situ’ method (LHS) and the ‘TTS’ method (RHS)

Presentazione O13

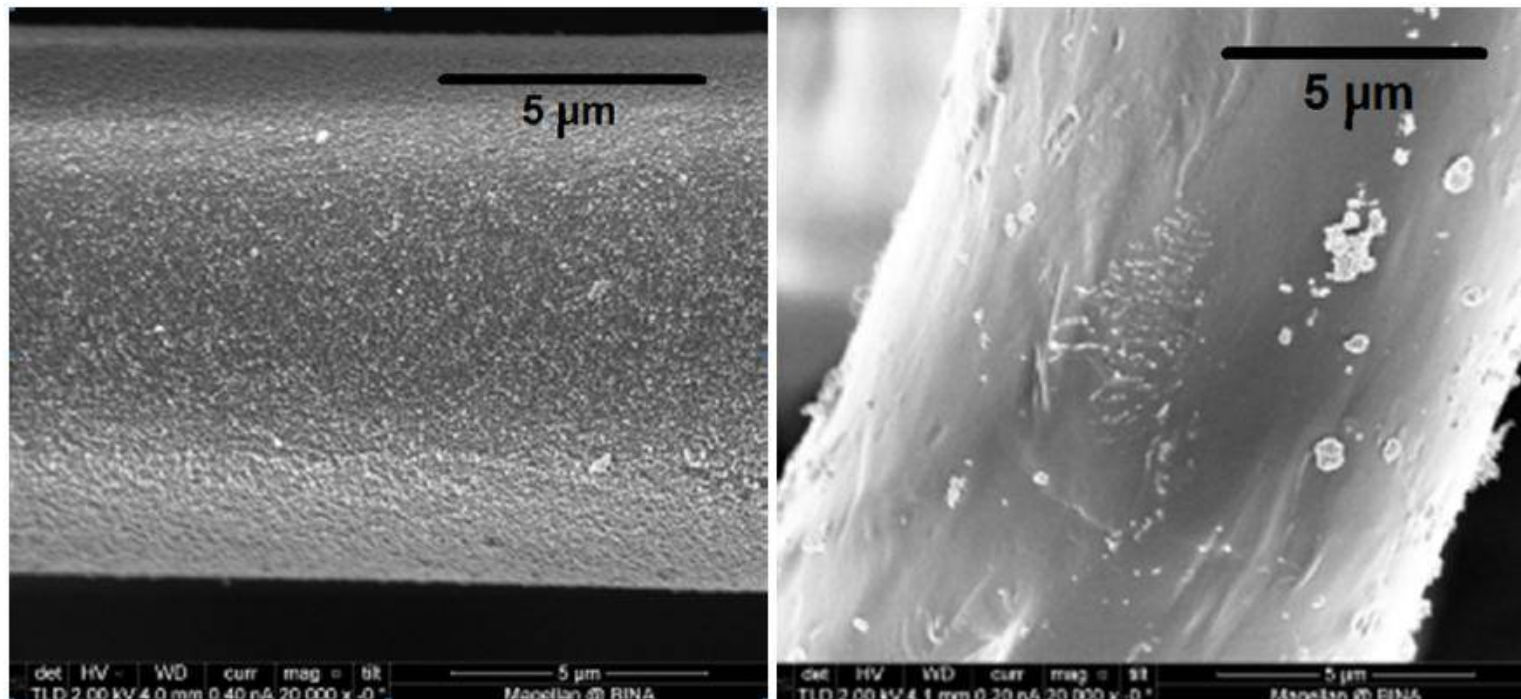


Figure 2. Scanning electron microscope images of cotton fabrics impregnated with CuO NPs via the ‘in situ’ method (LHS) and the ‘TTS’ method (RHS). The black scale bar is equal to 5 µm.

Levels of CuO = 0.9 % w/w

More homogeneous layer of nanoparticles (60 and 80 nm) for in situ sonochemical generation

Presentazione O13

Resistance to washing of NPs

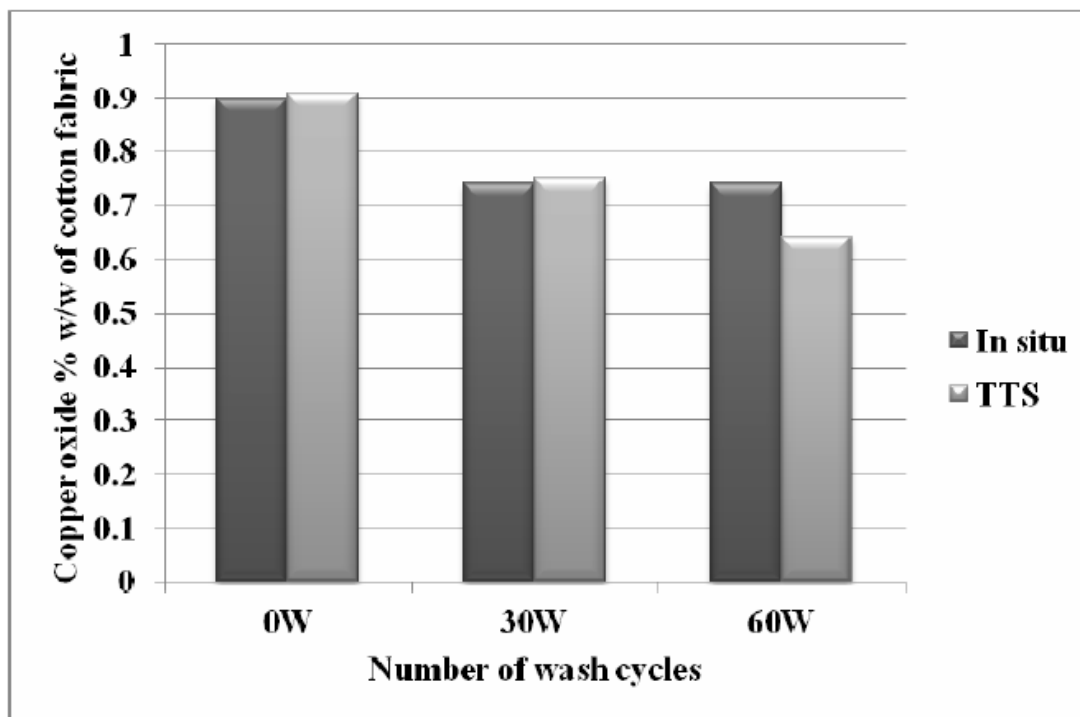


Figure 5. CuO content as percentage weight by weight of impregnated fabrics after washing. 0.5 M nitric acid was used to dissolve the copper oxide nanoparticles for the ICP analysis.

Presentazione O13

Antimicrobial activity against:

- Gram negative: *Acinetobacter baumannii*, *Escherichia coli*, *Pseudomonas aeruginosa*,
- Gram positive: *Methicillinresistant Staphylococcus aureus (MRSA)*

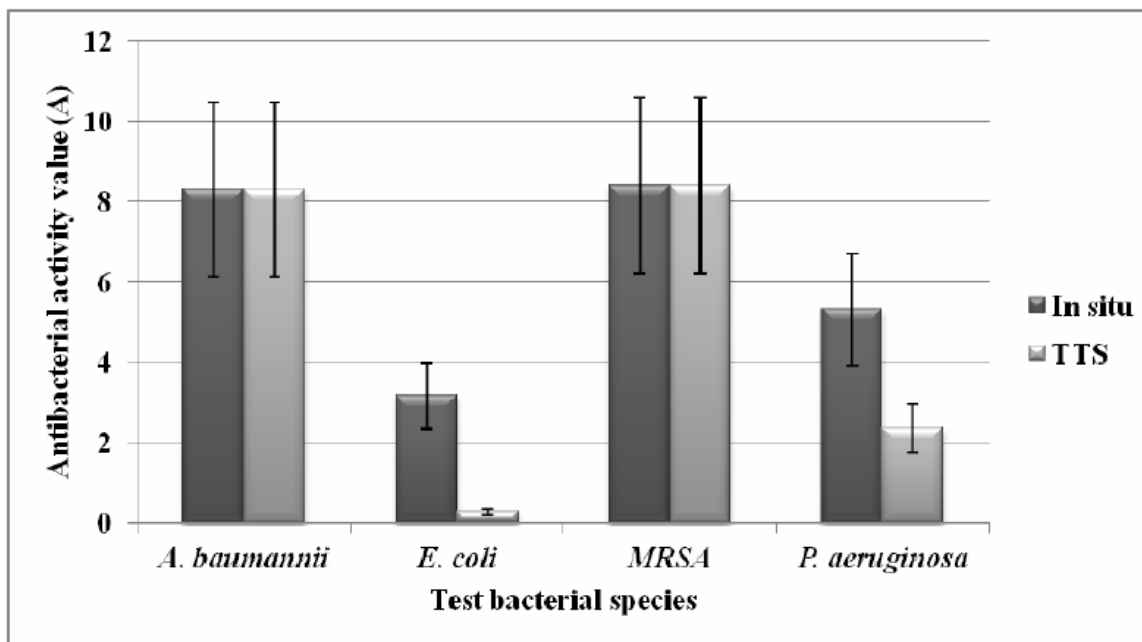


Figure 3. Antibacterial activity values of cotton fabric impregnated with CuO NPs. Comparison of results for *Acinetobacter baumannii*, *Escherichia coli*, MRSA and *Pseudomonas aeruginosa* with the two CuO NP impregnation techniques – ‘in situ’ and throwing the stones (TTS).

Presentazione O13

Resistance to washing (65°C) of antimicrobial activity

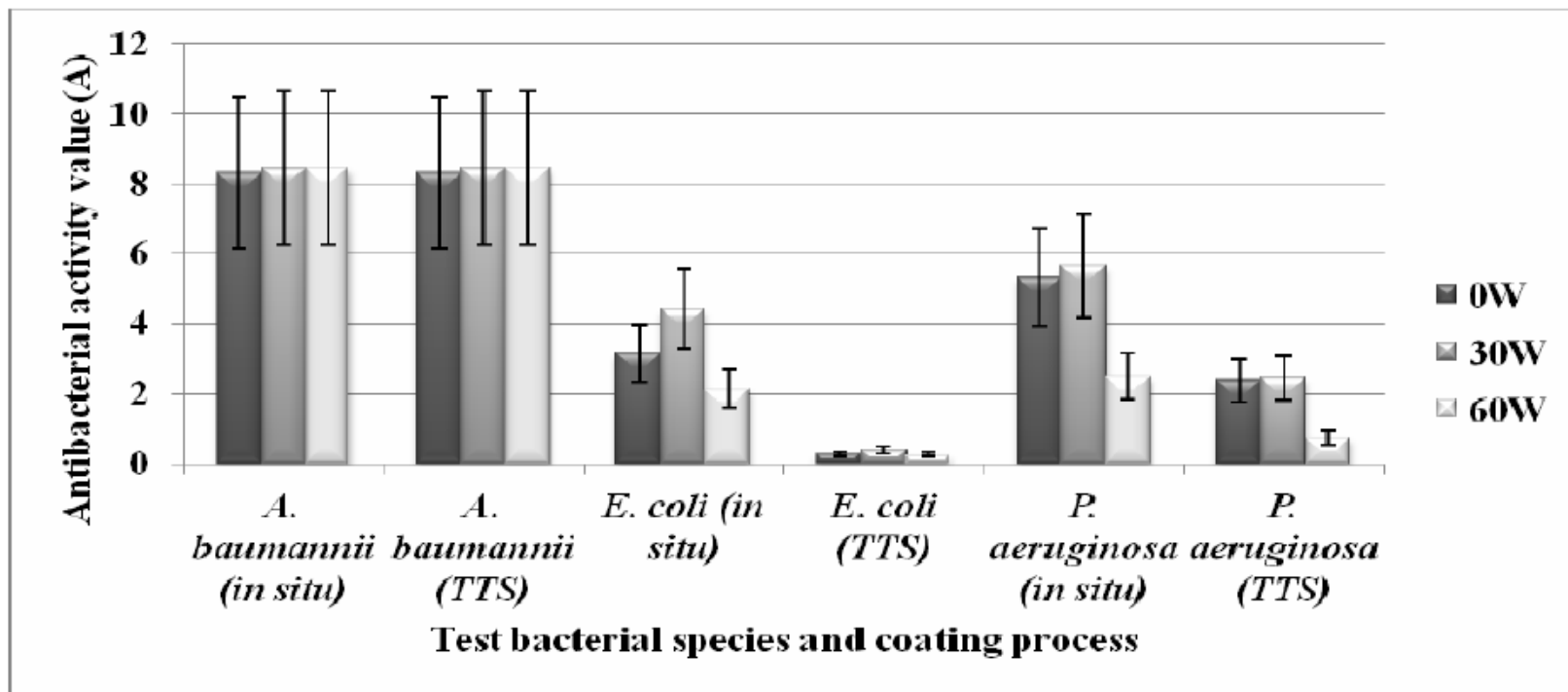


Figure 4. Antibacterial activity after washing of cotton fabric impregnated with CuO NPs via the in-situ and TTS methods.



Presentazione O13

Cotton fabrics sonochemically impregnated with CuO NPs have been shown to display very good levels of antibacterial activity against a range of bacteria associated with hospital acquired infections

The CuO NPs produced sonochemically in situ showed a better range of antibacterial activity than the CuO from throwing stones method using pre-made CuO NPs.

These results are related with the uniformity of CuO NPs dispersion on the fibres.

Presentazione P42

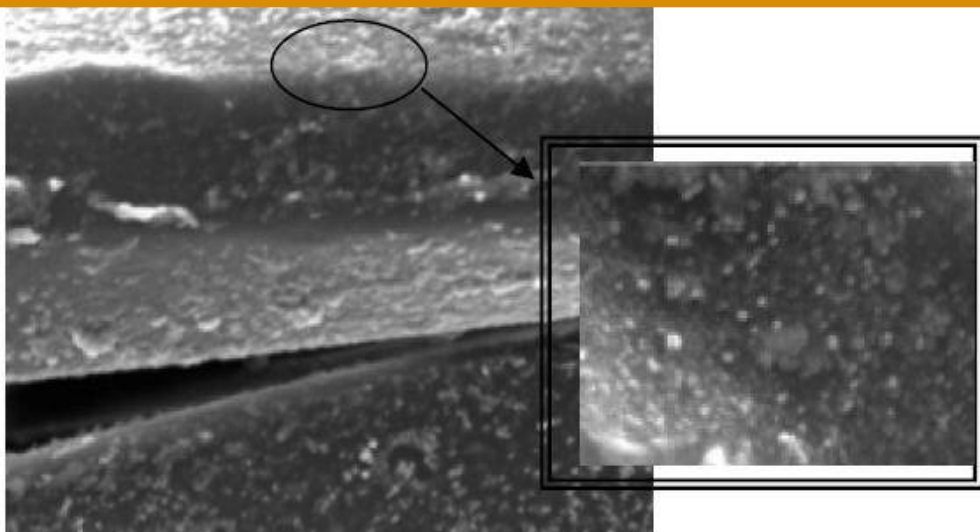


Figure 1. SEM of CuO coated cotton following 65 wash cycles

- Pilot plant for roll to roll coating a fabrics in a width of 50 cm and in a speed of 3 m/min
- Fabrics coated with CuO NP's (in situ; brown color of the fabric) and then washed for 65 cycles, using industrial washing machine
- Homogeneous mono-dispersed coating is observed with particles ranging in size from 20 to 50 nm
- The antibacterial properties of the washed fabrics were very high

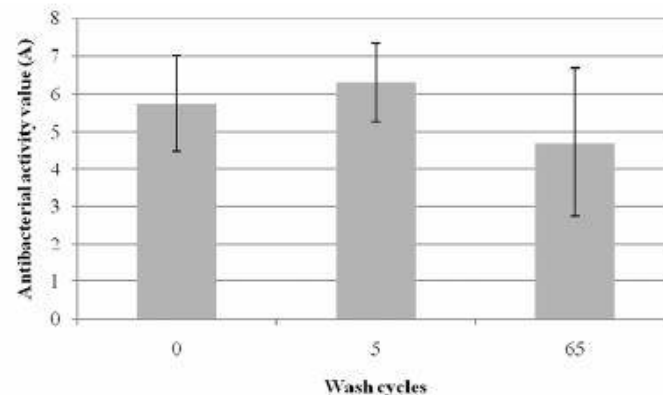


Figure 2. Antibacterial activity values of washed CuO coated fabrics against *Staphylococcus aureus* (ATCC 6538). Testing was carried out according to the absorption method from BS EN ISO 20743:2007.

Presentazione P43

TiO₂ NPs in two crystalline forms, anatase and rutile, were synthesized and deposited onto the surface of cotton fabrics by using ultrasonic irradiation (in situ)
The antimicrobial and self-cleaning properties were tested

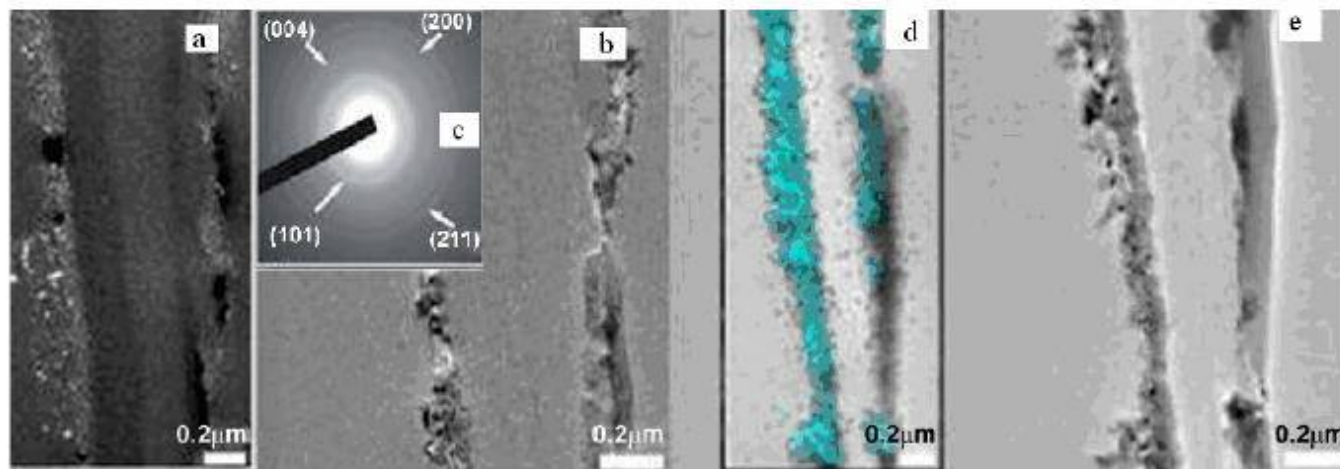
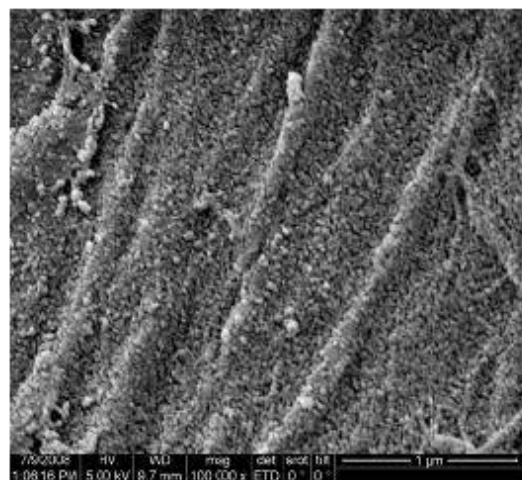


Fig. 1. HRSEM image of TiO₂-cotton composite.

Fig. 2. HRTEM images of TiO₂-cotton composite: a) dark-field; b) bright-field; c) diffraction pattern; d, e) STEM mode (Ti is shown as blue dots).

TiO₂ content: 2-3 wt%
Particles size: 10- 15 nm

Presentazione P43

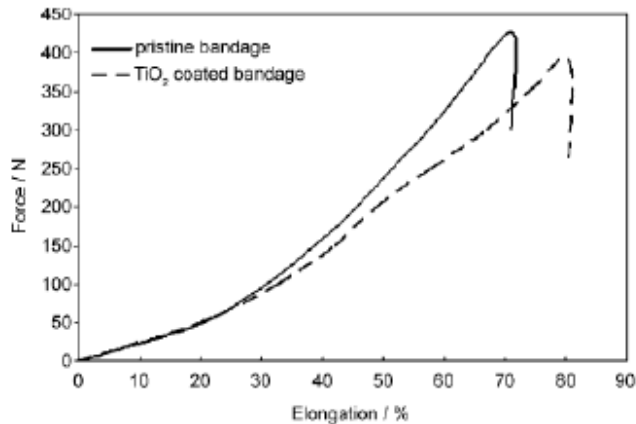


Fig. 3. Mechanical properties of the cotton bandages.

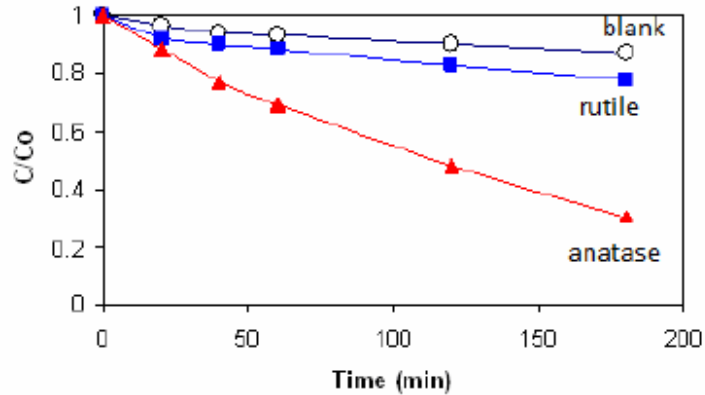


Fig. 4. Photodegradation of MB on TiO₂-cotton.

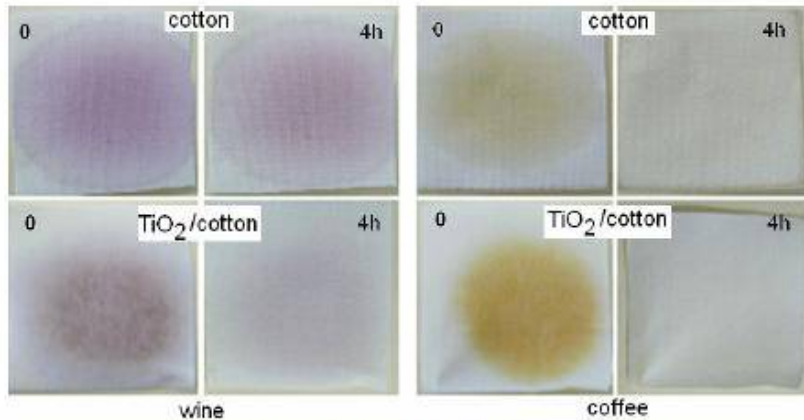


Fig. 5. Stains degradation test.

The tensile strength was about 10% less than that of the pristine cotton

Self-cleaning property of the titania (anatase) coating were tested by the degradation of organic dirt such as red wine and coffee stains under UV irradiation

Presentazione P43

Antimicrobial activities of the TiO₂-cotton composites were estimated against Gram-negative and Gram-positive strains, as well as against *Candida albicans*

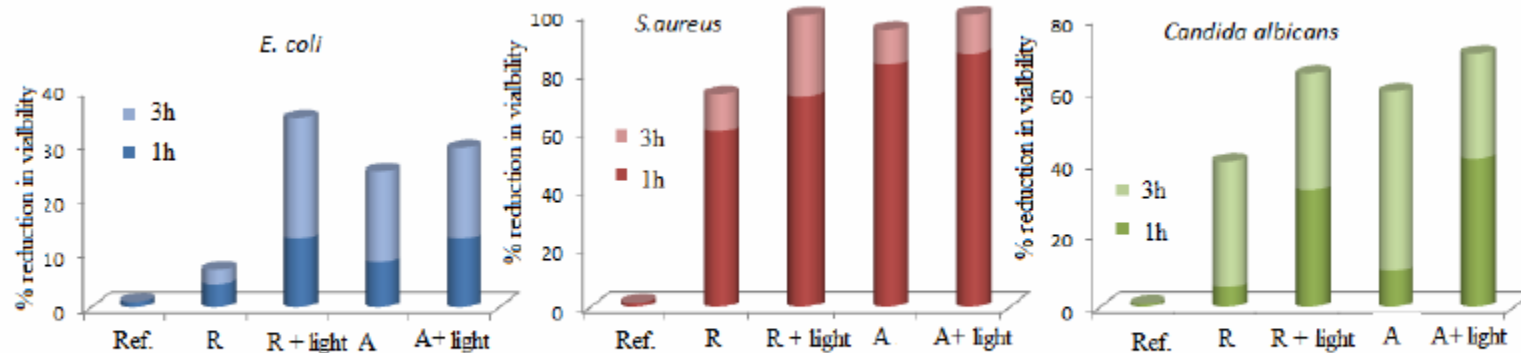


Fig. 6. Antibacterial activity of TiO₂-cotton composites: (A-anatase, R-rutile).

- The antimicrobial actions of both anatase- and rutile-coated cotton were improved through visible light mediation (450 nm, 100 mW cm⁻², light-emitting diode)
- Anatase was more effective than rutile against the bacteria and candida
- Illumination enhanced the antimicrobial activity of rutile more effectively than that of anatase.



Presentazioni O01 e O02

O01 - Simultaneous Deposition of Chitosan and ZnO **NP's on Textiles via One-step Sonochemical Reaction**. I. Perelshtein et al., Bar-Ilan University, Israel

The combination of CS with inorganic nanoparticles (NPs) was an efficient approach to produce antibacterial materials with improved functional properties. The aim of the present work is to demonstrate the feasibility of the sonochemical coating of textiles with CS NPs and a CS–Zn nanocomposite in a single-step process without the use of any binding agents. Two approaches have been developed for applying chitosan simultaneously with ZnO NPs: 1) in-situ and 2) ex situ modes. More than two-fold increase of the antibacterial activity of ZnO-CS NP coated textiles was detected as compared to the fabrics treated with the sonochemically synthesized CS NPs alone

O02 - Simultaneous Sonochemical-enzymatic Coating Of Textiles With Antimicrobial Nanoparticles. P. Petkova et al., Universitat Politècnica de Catalunya, Spain

In the present work, we developed an antimicrobial coating of ZnO NPs, either commercial or **synthesized “in situ”, using simultaneously ultrasound and enzymes. Under these conditions a uniform and stable NPs coating was deposited on the cotton surface, resulting in excellent antibacterial activity though using low concentration of ZnO**

Presentazione O03

LCA/LCC analysis

The comparisons among the processes are made for several scenarios and parameters such as process throughput, process speed, power input, labour intensity, time horizon, geographical location of finishing plant

The two pre-industrial scale finishing units are based on ultrasound technology employing different transducers:

- the Magnetostrictive transducers unit (MG) developed by VIATECH Ltd. (Moscow, Russia) and installed at DAVO STAR IMPEX SRL in Bucharest, Romania
- the Piezoelectric transducers unit (PZ) developed by CEDRAT TECH (Grenoble, France) and installed at KLOPMANN International S.p.A in Frosinone, Italy.

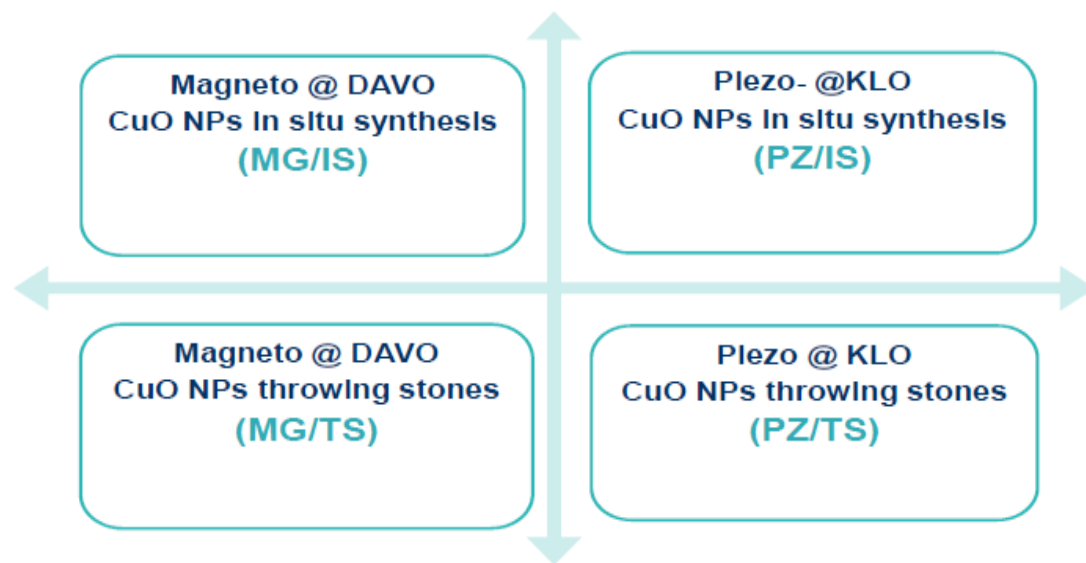


Figure 1. Experimental scenarios for comparative analysis

Presentazione O03

LCA analysis

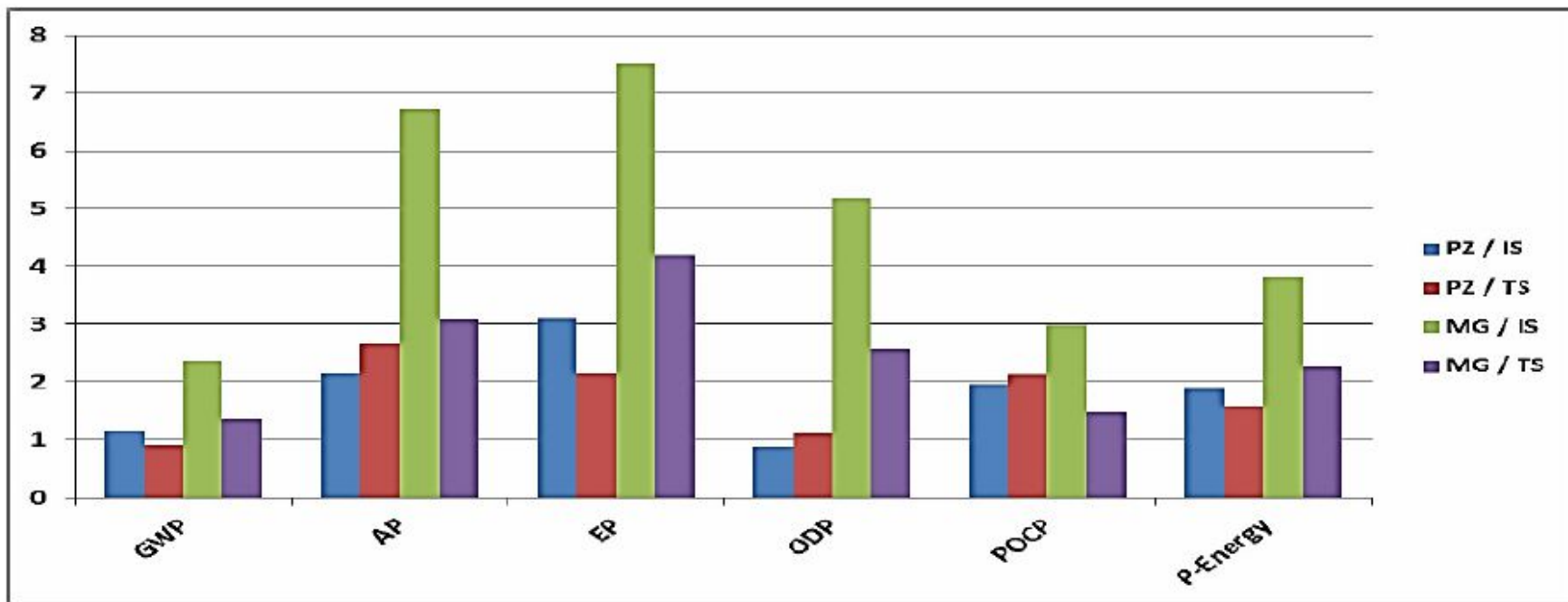


Figure 5 Environmental impact categories for the FFC1 studied at 60% US power cases.

Presentazione O03

LCC analysis

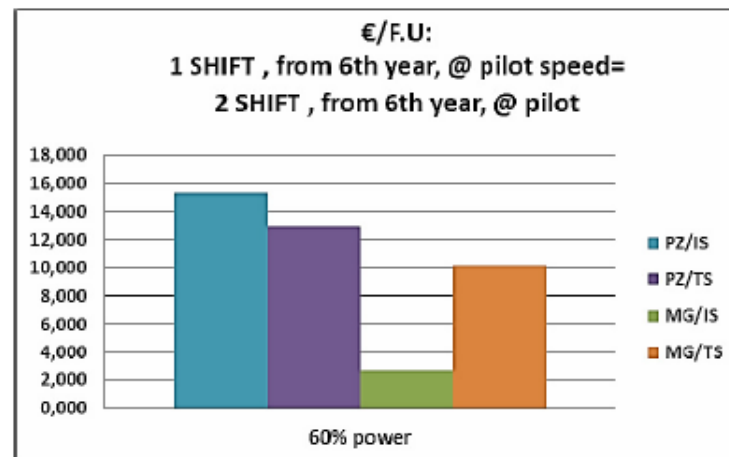
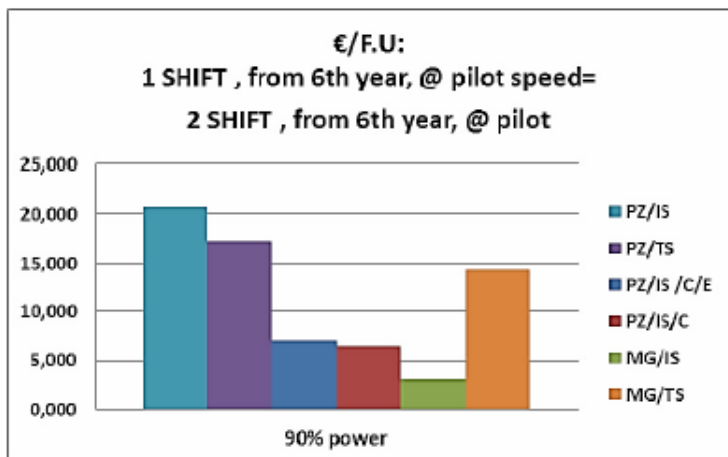


Figure 7. Cost impacts: FFC1 processes at 90% and 60% US power in case of 2 shifts per day from sixth year on, respectively. When the impact of RTD and initial investment has been amortised the cost are reduced to constant values. From the 6th year, the 2 shifts scenario costs are equal to the 1 shift costs.



Presentazione O03

Concluding remarks

LCA:

- All PZ processes are characterised by lower primary energy demand with respect to the MG ones
- Ozone Depletion Potential is negligible for all the scenarios considered
- Potential impact to water pollution (Acidification Potential and Eutrophication potential) are minor and comparable for both PZ and MG treatment systems
- The IS process yields a larger impact than the TS (almost double for GWP and EP), due to the
- employment of metal-organics precursors and ethanol

LCC:

- Data referred to PZ and MG units are including geographical dependence due production lines location, mainly impacted by labour, energy and reagent cost
- Considering location and technology, the MG processes are always the best competitive ones in terms of process specific costs, for instance MG/IS is about 50% cheaper than PZ/TS
- MG/TS is more expensive than MG/IS due to the intrinsic cost of procured MeO NPs
- As a general comment on cost impacts it may be concluded that at industrial scale the throughput increase by process speed enhancement may benefit to cost reduction but the right balance has to be found with initial investment cost that may hamper competitiveness for the first five years production



Presentazione O14

O14 - Ultrasonic Washing Process After Reactive Printing. G. Özcan, Istanbul Technical University, Turkey

We have conducted comprehensive research of real after-treatment conditions of reactive printing line and ultrasonic technology adaptation.

In the literature, high frequencies (30-47 kHz with 230 W power output) are used for scouring or washing process of textile materials. The washing processes were carried out in Intersonic washing machine which has 26 kHz frequency and 120 Watt power. Washing ratio for Red Panama Fabric was 1:62 in the real washing line whereas it was 1: 63 in our ultrasonic bath.

At the end of the study we could obtain the desired color fastness value with our new model. The temperature is reduced from 95°C to 60°C. Chemical consumption is also reduced from 4g/l to 3 g/l gaining 25% chemical costs. Moreover, because the number of washing bath is reduced, the redundant washing tanks and rollers are not required. These results show that our new model is also environmentally friendly design.



Presentazione O15

O15 - The Effect of Low-frequency Ultrasound on The Activity and Efficiency of a Hydrolytic Enzyme.
O. Szabó and E. Csiszár, Budapest University of Technology and Economics

In this study a commercial cellulase enzyme complex was used in order to characterize the effect of sonication on the enzyme activity.

The ultrasonic experiments were carried out using an ultrasonic horn type reactor (Sonics & Materials, Model: Vibra-Cell VCX500). The system was thermostated to 50 ± 2 °C.

In spite of the fact that the applied sonication depressed the activity of the cellulase enzyme, the outcome of the enzyme catalysed hydrolysis in the model reaction was always positive, implying that the advantageous effects of sonication impressed on the heterogeneous cellulose-cellulase reaction always overcome the undesirable, enzyme modifying effect of the ultrasound.



Presentazione P17

P17 - Evaluation of Actual Dyestuff Penetration in Ultrasonic-assisted Wool Dyeing. M. Giansetti et al., Politecnico di Torino, Italy

The main goal of the present work is to define the amount of absorbed dyestuff inside wool fibres, either after dyeing or rinsing, in order to evaluate the mass transfer intensification due to US effect.

The US transducer is a flat SONOPLATE® emitting device (Weber Ultrasonics GmbH), positioned at the bottom of the vessel and constituted of 8 cone-shaped transducers, mounted on a stainless steel plate. It works at a fixed frequency of 25 kHz and is supplied with a 600 W power generator.

Dye-bath exhaustion profiles were calculated for all tests but they do not give significant information since it seems that values close to 100% of final exhaustion are reached in all tests, independently from the dyeing temperature and presence of US.

At low temperature (60°C) the US effect is remarkable, even if the conventional dyeing at 98°C still reaches the best results.

US seem to influence the penetration, and subsequently fixation, of the dyestuff, as the amount lost during the rinsing step is lower than the other tests.



Presentazione P63

P63 - Washing Intensification by Ultrasounds. R.Peila et al., Politecnico di Torino, Italy

In the present study the ultrasound technology was applied to wool fabrics washing processes. Two ultrasounds frequency ranges were studied, 25 and 46 kHz. The temperature and ultrasounds contact time of the samples were varied in order to optimize the washing process.

The samples were washed in a stainless steel vessel, equipped with a centrifugal pump and an electrical resistance to implement the bath circulation and heating. A flat SONOPLATE® emitting device constituted by 8 cone-shaped ultrasound transducers was placed at the vessel bottom to produce the ultrasound waves. The transducers worked at 25 kHz frequency and were supplied with a 600 W power. The samples were washed in 10L bath with 2 g/L commercial detergent concentration at 20, 40 and 60°C. The ultrasound contact time was varied from 1, 3 and 5 min. at each temperature.

A higher US frequency allows to obtain better washing results if compared with those obtained without US.