UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

SOCIETÀ ITALIANA DI IGIENE

il Gruppo di Lavoro Salute e Ambiente
presenta
Convegno Nazionale
Climate Change & Public Health

Thermal water and climate change: innovative treatments and water recycling chain

Federica Valeriani & Vincenzo Romano Spica

Università degli Studi di Roma "Foro Italico"

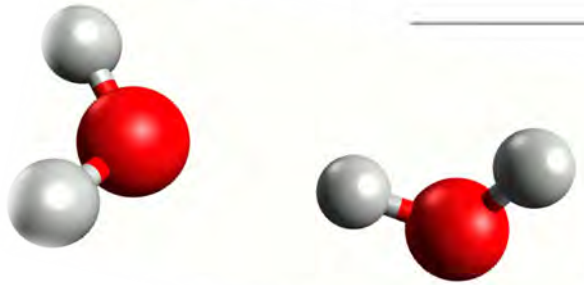
INTRODUZIONE

Le acque termali naturali sono utilizzate per scopi ricreativi o applicazioni per il benessere e sono disponibili a livello globale. L'uso improprio e mutevoli condizioni climatiche aggravano il rischio di esaurimento di queste preziose risorse idrotermali e possono alterare le proprietà fisico-chimiche e microbiche per le quali sono rinomate.

Tuttavia, queste acque sorgive dovrebbero essere lasciate non trattate per garantire la loro composizione specifica, mantenendo le proprietà originali e i potenziali benefici per la salute durante la balneoterapia.

Table 1. Classification of natural mineral waters based on fixed residue at 180 °C and chemical composition, according the 2009/54/EC Directive [43].

Classification of Mineral Waters	
Classification according to fixed residue at 180°	**Classification according to chemical composition**
Very low mineral content waters (Fixed residue <50 mg/L)	Bicarbonate waters (>600 mg/L)
Low mineral content waters (Fixed residue 50–500 mg/L)	Calcic waters (>150 mg/L)
Medium mineral content waters (Fixed residue 500–1500 mg/L)	Chloride waters (>200 mg/L)
Rich mineral content water (Fixed residue <1500 mg/L)	Ferrous waters (>1 mg/L)
	Fluorurate waters (>1 mg/L)
	Magnesiac waters (>50 mg/L)
	Sulphated waters (>200 mg/L)
	Sodium-Rich waters (>200 mg/L)



La questione della "intoccabilità" delle acque naturali termali e terapeutiche e l'incompatibilità con i tradizionali processi di disinfezione sono state affrontate in diverse normative

INTRODUZIONE

Sono necessarie tecnologie adeguate e convenienti per il riciclo dell'acqua termale, poiché la maggior parte delle tecnologie di trattamento modifica la qualità dell'acqua o non resiste alla corrosività delle acque

International Journal of *Environmental Research and Public Health*

MDPI

Review

Recreational Use of Spa Thermal Waters: Criticisms and Perspectives for Innovative Treatments

Federica Valeriani, Lory Marika Margarucci and Vincenzo Romano Spica *

Public Health Unit, University of Rome "Foro Italico", Rome 00135, Italy; federica.valeriani@uniroma4.it (F.V.); lory.margarucci@tiscali.it (L.M.M.)

* Correspondence: vincenzo.romanospica@uniroma4.it

Received: 26 October 2018; Accepted: 23 November 2018; Published: 27 November 2018

check for updates

Abstract: Natural spa springs are diffused all over the world and their use in pools is known since ancient times. This review underlines the cultural and social spa context focusing on hygiene issues, public health guidelines and emerging concerns regarding water management in wellness or recreational settings. The question of the "untouchability" of therapeutic natural waters and their incompatibility with traditional disinfection processes is addressed considering the demand for effective treatments that would respect the natural properties. Available strategies and innovative treatments are reviewed, highlighting potentials and limits for a sustainable management. Alternative approaches comprise nanotechnologies, photocatalysis systems, advanced filtration. State of the art and promising perspectives are reported considering the chemical-physical component and the biological natural complexity of the spa water microbiota.

Keywords: recreational water; spa; thermal water; innovative treatment

Table 2. Several types of antimicrobial agents and their candidate applications in SPA pools: main advantages and limits for swimming pool uses.

Disinfection Solution	Advantages	Limits	SPA Pool Applications	References
Chlorine-based disinfectant	Inexpensive and relatively convenient to produce, store, transport and use. Provides rapid and long-lasting disinfection effects. Residual disinfectant activity in pool.	The formation of potentially toxic DBPs, such as THMs, HAAs, HANs, THAs and CAMs. Presence of chlorine-resistant microorganisms such as *Cryptosporidium parvum* and *Giardia lamblia*.	In hot tubs, acceptable free chlorine levels tend to be higher than in swimming pools. Moreover, due the chemical characteristics of thermal water, the reaction between chemical compound and disinfection agents can lead the increase the potentially toxic DBPs.	[22,25,65,72–80]
Ozone	Highly effective, no smell. Can reduced the formation of potentially toxic disinfection by-products (DBPs).	Toxic and explosive; heavier than air. Risks and adverse health effects for the operator. Lack of residual disinfection proprieties; (usually joined with chlorine). Production of activated compounds suitable for THMs formation in the post-chlorination step.	AOPs have recently shown successes in the treatment of organic pollutants in aquatic environments, involving the generation of non-specific OH radicals. A de-ozonization step is needed.	[61,81]
Ultraviolet (UV) irradiation	Physical treatment without adding chemicals to the water. Effective for the control of resistant microorganisms including protozoa such as *Cryptosporidium parvum* and *Giardia lamblia*.	The formation of nitrogenous-based DBPs (HANs) Lack of residual disinfection proprieties.	UV radiation can be proposed to reduce the risk of infection by dermatophytes eventually present in swimming pools that use thermal water. Cost-competitive with chlorine to improve the quality of swimming pool water.	[61,81–83]
Bromine-based disinfectant	Inexpensive and relatively convenient to apply. Provides rapid and long-lasting disinfection effects.	It is difficult to dissolve and must be inserted into the pool through an automatic feeder. DBP There are reports that is associated with eye and skin irritation.	The use of bromine-based disinfectants is generally not practical for outdoor pools and spas because the bromine residual is depleted rapidly in sunlight.	[25,61,92]
Stabilised silver/copper	Copper/silver ionization was proposed for treatment of swimming pool water: protocols and devices are available. No pH adjustment is required.	Low effectiveness Limited information on toxicity of ion forms and interaction with other chemicals.	Silver is a broad-spectrum disinfectant usually supplied as a solution to be dosed or added to the spa-pool system. Higher concentrations may be required depending on the condition of the facility.	[25,61,92]
Hydrogen peroxide	Effective Low pollution on water.	With hydrogen peroxide the by-products are not problematic but it can generate toxic radical compounds.	Hydrogen peroxide can be used with silver and copper ions (low levels of the silver and copper): proper consideration to replacement of water for preventing excessive build-up of the ions.	[25,93]

Note: Disinfection byproducts (DBPs); Hypochlorous acid (HOCl); Trihalomethanes (THMs); Haloacetonitriles (HANs); Hydroxyl radical (OH); Advanced oxidation processes (AOPs).

INTRODUZIONE

Sono necessarie nuove soluzioni e strategie innovative per consentire un'efficiente catena di trattamento dell'acqua volta a ridurre la carica batterica dell'acqua e meno sprechi.

International Journal of *Environmental Research and Public Health*

MDPI

Review

Recreational Use of Spa Thermal Waters: Criticisms and Perspectives for Innovative Treatments

Federica Valeriani, Lory Marika Margarucci and Vincenzo Romano Spica *

Public Health Unit, University of Rome "Foro Italico", Rome 00135, Italy; federica.valeriani@uniroma4.it (F.V.); lory.margarucci@tiscali.it (L.M.M.)

* Correspondence: vincenzo.romanospica@uniroma4.it

Received: 26 October 2018; Accepted: 23 November 2018; Published: 27 November 2018

check for updates

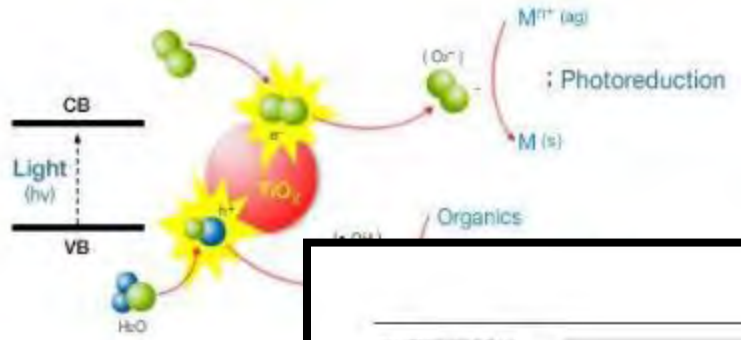
Abstract: Natural spa springs are diffused all over the world and their use in pools is known since ancient times. This review underlines the cultural and social spa context focusing on hygiene issues, public health guidelines and emerging concerns regarding water management in wellness or recreational settings. The question of the "untouchability" of therapeutic natural waters and their incompatibility with traditional disinfection processes is addressed considering the demand for effective treatments that would respect the natural properties. Available strategies and innovative treatments are reviewed, highlighting potentials and limits for a sustainable management. Alternative approaches comprise nanotechnologies, photocatalysis systems, advanced filtration. State of the art and promising perspectives are reported considering the chemical-physical component and the biological natural complexity of the spa water microbiota.

Keywords: recreational water; spa; thermal water; innovative treatment

Table 3. Current and potential applications of antimicrobial nanomaterials.

Nanomaterials	CAS NUMBER	Nature of Disinfection Type		Antimicrobial Mechanism	Current Applications	Potential Future Applications in SPA Pools	References
		Physical	*Chemical*				
Silver nanoparticles (AgNPs)	7440-22-4		☑	AgNPs can disrupt the outer membrane of target cells.	Portable water filters, clothing, medical devices, coatings for washing machines, refrigerators, and food containers	An alternative to traditional chemical disinfectants that are prone to generate harmful disinfection by-products	[101,108–111]
Chitosan	9012-76-4		☑	Membrane damage, chelation of trace metals. Nanoscale chitosan and derivatives exhibit antimicrobial effects towards bacteria, viruses, fungi.	Personal care products, microbicide in agriculture and biomedical products, food wraps, biomedical, flocculants in water and wastewater treatment	They are promising for low-cost and low-tech disinfection applications. In water filtration, chitosan combined with sand filtration removes up to 99% of turbidity	[101–106]
Graphene oxide	1034343-98-0	☑	☑	DNA damages and cytotoxic effects towards prokaryotic cells and detrimentally change the microbial diversity and community structures	Graphene oxide (GO) and silver-graphene oxide (Ag-GO) are used in various fields, such as biotechnology and environmental engineering, due to their unique material properties, including hydrophilicity, high surface area, mechanical strength, and antibacterial activity	In aquatic ecosystems, the stability of nanomaterials is affected by the water chemistry parameters of the receiving aquatic environments such as ionic strength, natural organic matters and pH	[114–119]
H_2S	7783-06-4		☑	H_2S killed microorganisms through inducing oxidative stress by inhibiting antioxidant enzymes.	None	Restore the normal bacteriostatic nature of the thermal water	[24]
Nano TiO_2	13463-67-7	☑	☑	Production of Reactive Oxygen Species (ROS), cell membrane and cell wall damage	Air purifiers, water treatment systems for organic contaminant degradation.	The applicability is in evaluation. The presence of some inorganic ions can be problem, because reduce the performance of TiO_2 in water treatment.	[108,109]
Ultrafiltration	-	☑		Ultrafiltration allowed the removal of suspended matter, as well as a part of the organic matter	Water treatment, swimming pool	Ultrafiltration can be selected as an alternative treatment process because of its ability to remove bacteria and viruses.	[97–102]
ZnO	1314-13-2	☑	☑	Intracellular accumulation of nanoparticles, cell membrane damage, H_2O_2 production, release of Zn^{2+} ions	Antibacterial creams, lotions and ointment, deodorant, self-cleaning glass and ceramics	Surface coating	[108,109]

- Una nuova soluzione può essere rappresentata dalle tecnologie basate su materiali fotocatalitici.
- Queste metodologie possono aumentare le proprietà antimicrobiche native delle acque termali senza modificarne la composizione.



Available online at www.sciencedirect.com
ScienceDirect
journal homepage: www.elsevier.com/locate/watres
WATER RESEARCH

A new silver based composite material for SPA

...randa [b],

Environment International 133 (2019) 105095
Contents lists available at ScienceDirect
Environment International
journal homepage: www.elsevier.com/locate/envint

Untouchability of natural spa waters: Perspectives for treatments within a personalized water safety plan

Lory Marika Margarucci, Vincenzo Romano Spica, Gianluca Gianfranceschi, Federica Valeriani*

ACS APPLIED BIO MATERIALS
www.acsabm.org

Ag/ZnO/PMMA Nanocomposites for Efficient Water Reuse

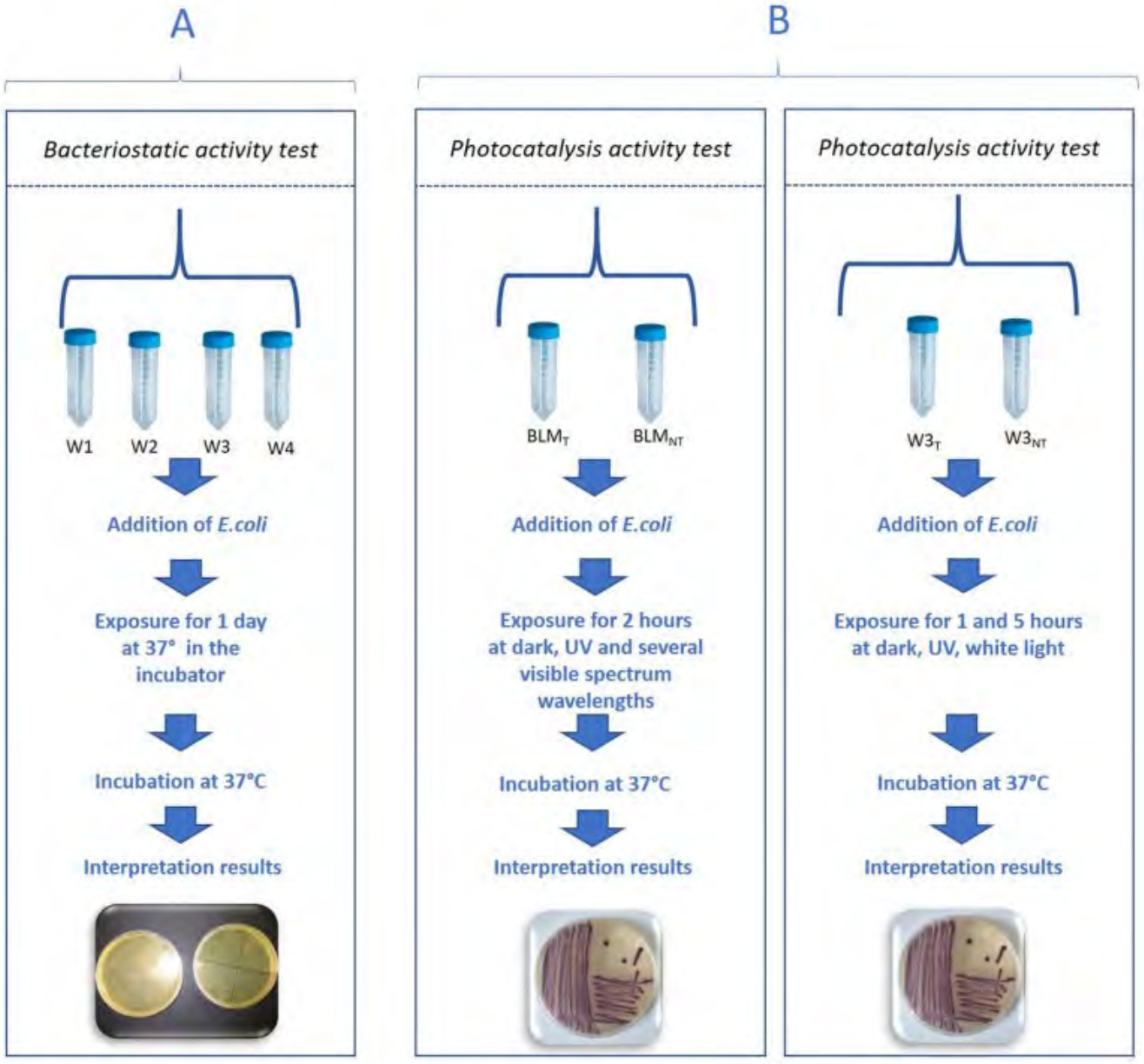
Alessandro Di Mauro, Clayton Farrugia, Stephen Abela, Paul Refalo, Maurice Grech, Luciano Falqui, Giuseppe Nicotra, Gianfranco Sfuncia, Antonio Mio, Maria Antonietta Buccheri, Giancarlo Rappazzo, Maria Violetta Brundo, Elena Maria Scalisi, Roberta Pecoraro, Carmelo Iaria, Vittorio Privitera, and Giuliana Impellizzeri*

Cite This: ACS Appl. Bio Mater. 2020, 3, 4417−4426
Read Online

ELSEVIER
journal homepage: www.elsevier.com/locate/envint
Untouchability of natural spa waters: Perspectives for treatments within a personalized water safety plan
Lory Marika Margarucci, Vincenzo Romano Spica, Gianluca Gianfranceschi, Federica Valeriani*

METODI

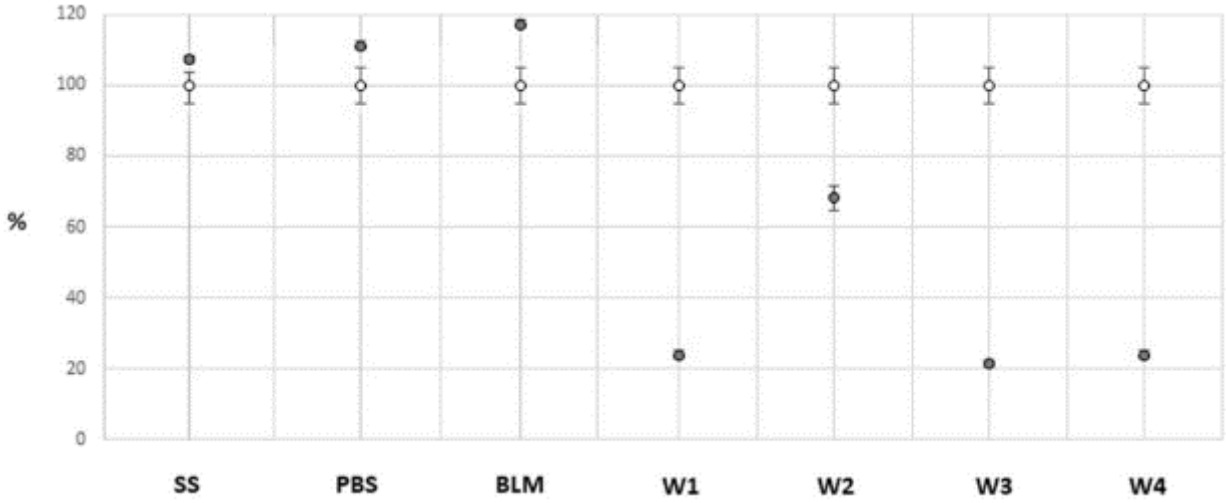
Sono state studiate le proprietà antimicrobiche di diverse acque termali e l'attività battericida dei nanomateriali di biossido di titanio (TiO_2) e/o l'esposizione alla luce a diverse lunghezze d'onda (200-635 nm).

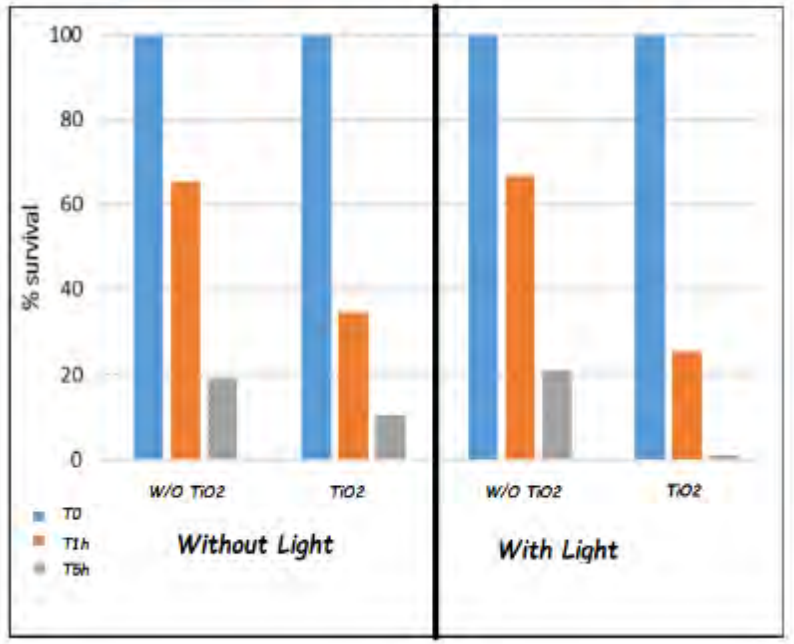


Margarucci, L. M., Romano Spica, V., Gianfranceschi, G., & Valeriani, F. (2019). Untouchability of natural spa waters: Perspectives for treatments within a personalized water safety plan. *Environment international*, *133*(Pt A), 105095. https://doi.org/10.1016/j.envint.2019.105095

RISULTATI

Un'attività antibatterica nativa è stata osservata in tutte le acque ad alto contenuto di minerali, con una riduzione di CFU del 75-80% degli indicatori specifici. L'azione battericida del TiO2 ha mostrato un ulteriore effetto incrementale, con una riduzione di oltre il 99% entro 2-5 ore di questi biomarcatori. Questi risultati hanno aperto diverse strategie innovative di ricerca come la combinazione di sistemi fotocatalitici con metalli nobili.





Margarucci, L. M., Romano Spica, V., Gianfranceschi, G., & Valeriani, F. (2019). Untouchability of natural spa waters: Perspectives for treatments within a personalized water safety plan. *Environment international*, *133*(Pt A), 105095. https://doi.org/10.1016/j.envint.2019.105095

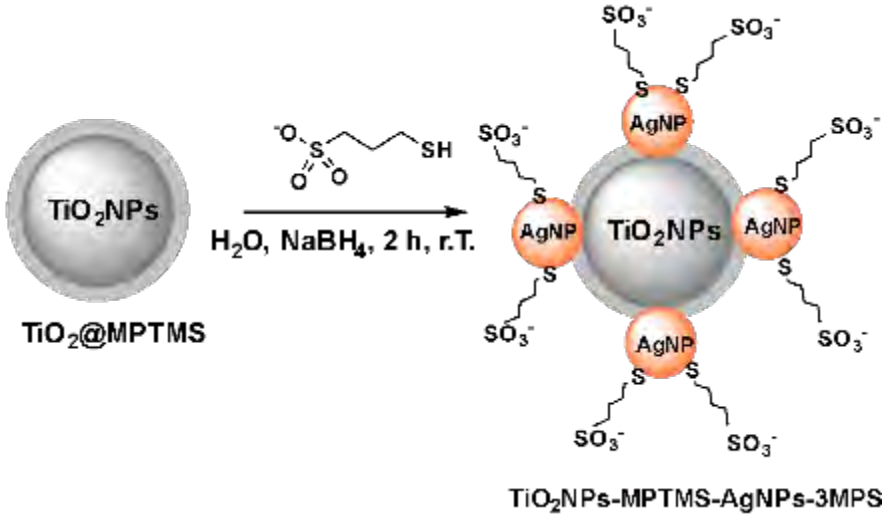
NUOVI PUNTI PER OTTIMIZZARE:

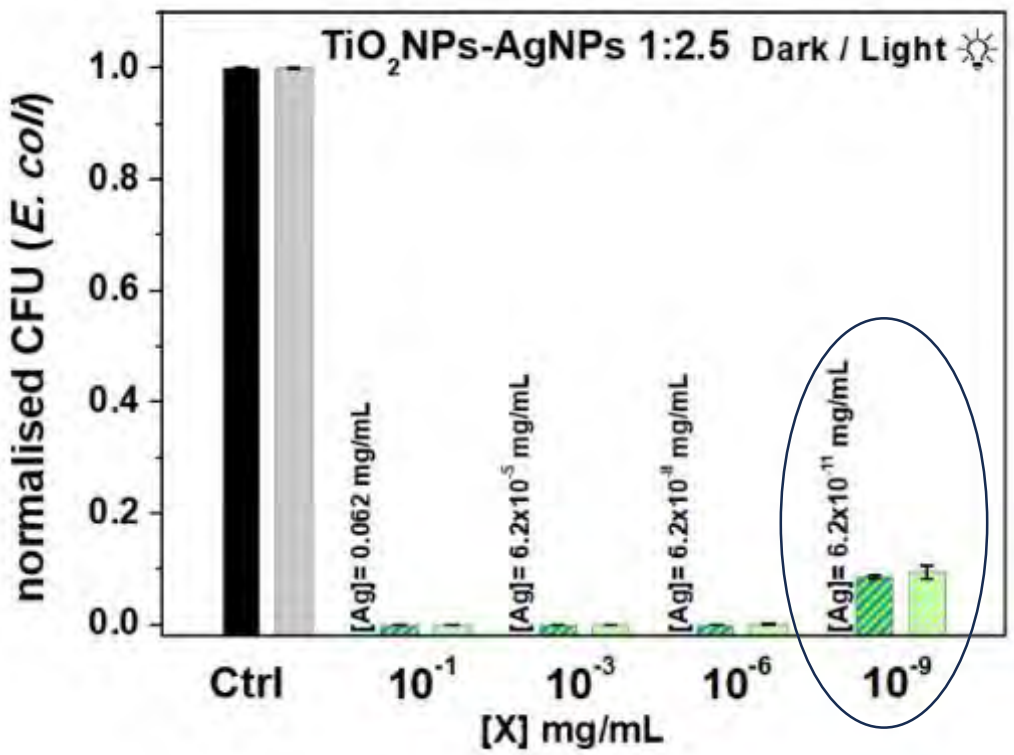
- Tossicità
- Luce visibile
- Concentrazioni

RISULTATI

Questi risultati hanno aperto diverse strategie innovative di ricerca come la combinazione di sistemi fotocatalitici con metalli nobili.

- Riduzione Tossicità
- Possibilità di utilizzo con Luce visibile
- Possibilità di utilizzo anche a basse concentrazioni





CONCLUSIONI

I risultati preliminari ottenuti utilizzando la combinazione di biossido di titanio e nanoparticelle di argento sono promettenti e rendono auspicabili ulteriori studi per valutare e ottimizzare la cinetica e l'efficienza di rimozione anche a basse concentrazioni, suggerendo anche la possibile applicazione in acque termali naturali o altre acque ricreative e il loro riciclo.

UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

SItI

il Gruppo di Lavoro Salute e Ambiente
presenta
Convegno Nazionale
Climate Change & Public Health

Thermal water and climate change: innovative treatments and water recycling chain

Federica Valeriani & Vincenzo Romano Spica

Università degli Studi di Roma "Foro Italico"

federica.valeriani@uniroma4.it