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EXECUTIVE SUMMARY OF THE THESIS

From Recognition to Remediation: Cellulose Nanosponges for Smart Water Purification

TESI MAGISTRALE IN CHEMICAL ENGINEERING – INGEGNERIA CHIMICA

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1. Introduction

Environmental pollution is one of the major challenges of 21st century. In particular, the cleaning up of water resources has gained particular attention, with the introduction of 2030 Agenda for Sustainable Development by the United Nations [1]. Despite global efforts, water resources are still contaminated by persistent and toxic pollutants. Among all heavy metals, mercury is one of the most toxic [2]. Anthropogenic activities have increased the mercury emissions in the atmosphere, making human exposure easier. Once mercury is in the atmosphere, it travels through air, water and sediments, depositing on land, water. In aquatic system, mercury is particularly dangerous because it can convert into methylmercury, penetrating by bioaccumulation and biomagnification in the food chain, contaminating fish and seafood. Fish consumption represents the primary route of human exposure [3].
Similarly, per- and poly- fluoroalkyl substances (PFAS) are major toxic contaminants [4]. PFAS are an emerging class of chemicals, which are frequently used in everyday objects. PFAS, referred to as "forever chemicals", have a highly stable molecular structure due to the carbon-fluorine bond which makes the degradation very difficult. Moreover, PFAS can migrate through the atmosphere on a global scale, depositing on land and water. PFAS bioaccumulate in living organisms due to their hydrophobic, heat-resistant, and non-biodegradable properties [5].
Effective actions are needed to find effective, sustainable remediation material.
Current remediation technologies are often limited to pollutant removal without providing real-time detection capabilities.
A xerogel, composed of TEMPO-oxidized cellulose nanofibers (TOCNF) and branched polyethyleneimine (bPEI), has shown effective adsorption capacity. Nanocellulose is a renewable and sustainable material, having high surface area and versatility [6].

This study aims to combine simultaneous adsorption and detection properties in cellulose-based highly porous materials. To simultaneously include a detection property, nanocellulose is combined with porphyrins molecules, which have

demonstrated colorimetric variation in presence of contaminants [7]. The research was conducted through a collaboration between *Organic Synthesis, Catalysis and Materials Laboratory (OSCM Lab)* at Politecnico di Milano and the *Sensor Group* at the University of Rome "Tor Vergata".

2. Materials and Methods

Cellulose was subjected to TEMPO-mediated oxidation using a catalytic system composed of TEMPO/KBr/NaClO [8]. The resulting suspension was sonicated to obtain TOCNF. The oxidation performance was verified by conductometric titration.
Cellulose nanosponges (CNS) were synthesized using TOCNF and different cross-linkers, bPEI of 25kDa and 1.8 kDa and polyethylene glycol (PEG) 8-arms.
The CNS production process consisted of four steps: (1) mixing the components and casting them into molds, (2) freeze-drying to preserve the three-dimensional structure, (3) thermal treatment to promote crosslinking, (4) washing to remove unreacted reagents. Several formulations of CNS were formulated. The porphyrins sensors were incorporated during the mixing phase through different strategies: direct mixing, cross-linker functionalization or cellulose functionalization. Three porphyrin-based optical chemical sensors, supplied by *Sensor Group*, were employed: 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin ($TPPCH_2$), tetra(4-sulfonatophenyl)porphyrin ($TPPS_4$), and (hydroxy)[5,10,15-tritolylcorrolato]silicon (SiTTC). These sensors exhibited selective responses toward Hg^{2+} ($TPPCH_2$ and $TPPS_4$) and PFOA (SiTTC).
Two cellulose functionalization procedures were analyzed: an amidation reaction using 1,8-diaminooctane and a three different silytation reactions using (3-Aminopropyl)triethoxysilane (APTES). The sensor undergoes an amidation to bind with the 1,8-diaminooctane-TOCNF.

Preliminary colorimetric tests

Preliminary tests on the color response of the SiTTC-functionalized CNSs were made exposing samples to 20 mL of PFOA containing solutions, under agitation for 24 hours, realized with deionized water and PBS-water solution (9.6 g/L) at different concentrations, from 50 to 1000 ppm. PFOA was selected as a model PFAS compound to assess the sensing capability.

3. Results

Materials' characterization

The functionalization efficiency of 1,8-diaminooctane functionalization reaction was evaluated by an elemental analysis, showing a degree of substitution of anhydroglucose unit with amine groups is 0.31. These results imply 55% conversion of carboxylic groups into ammine groups.

An ICP-OES analysis was performed on the APTES-functionalized TOCNF to evaluate the most effective incorporation reactions. The degree of substitution was calculated, and the higher is 0.18. Additionally, on the most effective procedure an ATR-FTIR analysis was performed, demonstrating the stretching vibration of the Si-O bond.

SEM analysis was performed on CNS synthesized with 1,8-diaminooctane (Figure 1), CNS modified with SiTTC (Figure 2). In both cases, the structure is highly porous and heterogenous. The introduction of the sensor doesn't change the structural integrity of the CNS, which is key point for maximizing adsorption performances.

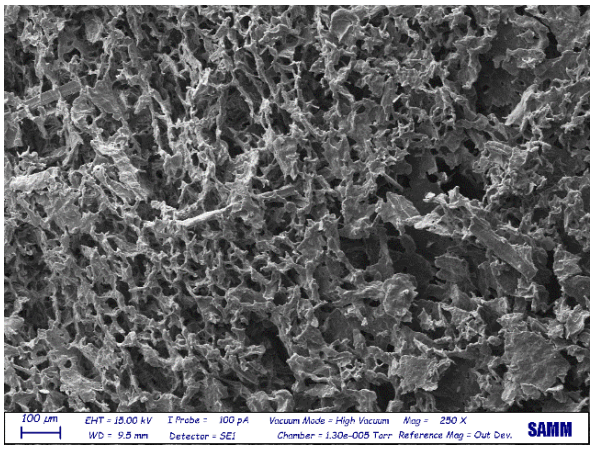

Figure 1: SEM image of 1,8-diaminooctane-$TPPCH_2$ functionalized CNS

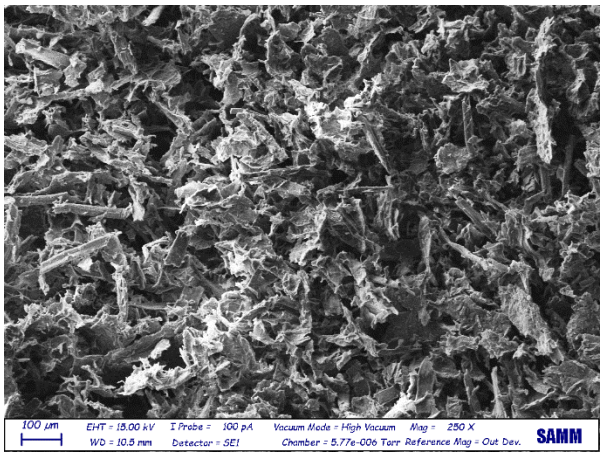

Figure 2: SEM image of SiTTC functionalized CNS

Adsorption tests

Adsorption experiments performed on previously optimized CNS formulations showed equilibrium adsorption capacities for mercury ions ranging from 160 to 200 mg g^{-1}, highlighting the strong remediation potential of the material.

Preliminary colorimetric tests

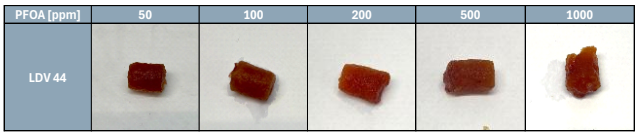

Figure 3: Preliminary colorimetric tests on SiTTC-functionalized CNS

Figure 3 shows the CNS samples after 24 hours in PFOA–PBS solution under shaking conditions. In LDV44, a clear colorimetric response is observed, with a slight but noticeable variation in color as a function of PFOA concentration. Moreover, the three-dimensional structure of the CNS is preserved, with no visible damage.
A yellowing of the solutions was observed, possibly due to bPEI leaching. The functionalized CNS were not washed, as air-drying compromises the three-dimensional structure. A possible solution to prevent bPEI leakage is the introduction of a co-crosslinker, such as citric acid, as previously implemented in the 1:1:18 formulation.

Sediments and scale up

A potential scale-up has been evaluated to solve the large quantities needed to perform sediment remediation applications. A preliminary scale-up was proposed, identifying the reactor as most critical unit operation requiring continuous processing for industrial feasibility.
In-situ sediment capping consists of isolating the contaminated sediment with high porous capping materials, such as CNS.
Particle size analysis was performed to choose the appropriate geotextile fabric.
Further research will be conducted with University of Palermo (UniPA) and the University of Enna "UniKore".

4. Conclusions

This work reports on the successful synthesis of CNS, capable of both adsorbing and detecting water contaminants. CNS exhibited a highly porous three-dimensional structure, as confirmed by scanning electron microscopy.
Compared to conventional adsorbent materials, the developed cellulose nanosponges combine sustainability, high adsorption capacity and integrated sensing capability representing a promising platform for next-generation smart water remediation technologies .
Scale-up studies confirmed the feasibility of large-scale production, supporting practical applications including seawater treatment and sediment remediation

Future improvements will focus on enhancing porphyrin incorporations, improving PFAS detection and adsorption. Further studies on in-situ sediment capping will be carried out.

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