

## Sorption of heavy metals on a chitosan-grafted-polypropylene nonwoven geotextile

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**Abstract.** This work describes the development of an environmental friendly functionalized polypropylene nonwoven geotextile (PP) in order to trap heavy metals in sediments and sludges. Chitosan was chosen as the sorbent because of its ability to trap heavy metals, of its natural origin (from shells), and of its low cost. PP was first functionalized with acrylic acid using a cold plasma process, in order to bring some reactive carboxylic functions onto the surface. Chitosan was then covalently grafted on the acrylic acid modified polypropylene. The functionalized surfaces were characterized by FTIR (Fourier Transform InfraRed) and chitosan was thus proven to be grafted. The ability of the functionalized textile to trap heavy metals was then investigated. Copper was chosen as the model heavy metal, and artificial solutions of CuSO<sub>4</sub> were prepared for the experiments. Sorption studies among the concentration of copper in polluted solutions at 20°C were carried out with PP-g-AA-chitosan (Polypropylene-grafted-Acrylic acid-chitosan) in order to evaluate the maximum of absorption of this surface: the textile can chelate copper increasingly with the initial copper concentration until 800 ppm where it reaches a plateau at about 30 mg/L. The effects of pH and of the ionic strength (absorption in a NaCl containing solution) were finally investigated. The trapping of Cu<sup>2+</sup> decreases slowly when the ionic strength increases. For a seawater-like NaCl concentration of 30g/L, the textile still chelates about 20 mg/L of Cu<sup>2+</sup>. Finally, the optimum pH to trap the maximum amount of copper was determined to be 4.75, which corresponds to the optimum pH for the solubility of the chitosan.

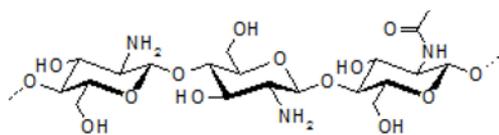
**Key words:** Polypropylene nonwoven, chitosan, cold plasma, heavy metal, depollution, sediment

### Introduction

Massive amounts of sediments are dredged in order to maintain the depth of the navigational waterways, harbors and estuaries worldwide. Land disposal of these dredged materials may affect the surrounding environment due to the presence of harmful components such as organic compounds and heavy metals (Singh et al. 1998). In some harbors, lots of sediments and sludges can be dredged, but nobody can use them further because of their high concentration in heavy metals such as Arsenic, Cadmium, Chromium, Copper, Mercury, Nickel, Lead, Selenium, and Zinc. All these metals can be found in the sediments from seas (Lopez-Sanchez et al. 1996) or from rivers (Louriño-Cabana et al. 2011). To recover sediments and sludges, heavy metals must be removed.

Lots of synthetic molecules however exist, which can trap these heavy metals. For example, poly(DMAEM-CPS) can be used to trap Copper, Cadmium, Mercury or Lead by putting it into the contaminated solution

followed by a filtration step (Mostafa et al. 2011). Natural polymers can also play this role, such as cellulose and alginate (in the form of beads) which can trap heavy metals like Copper, Lead and Zinc (Lai et al. 2010). The most well-known natural molecules are lignin, alginate, cellulose, and chitin, generally put directly into polluted solutions (Misra 2009). They can be activated or modified in order to improve their ability to remove heavy metals. For example, chitosan (Fig. 1) which is the product of deacetylation of chitin, can remove Cadmium, Cobalt, Copper, Chromium, Iron, Lead, Nickel or Zinc (Renault et al. 2009). Its ability to chelate heavy metals is due to the amino and hydroxyl groups (Chen et al. 2011). Indeed, chitosan can be up to three times more efficient than chitin to adsorb heavy metals, evidencing the importance of the amino group.

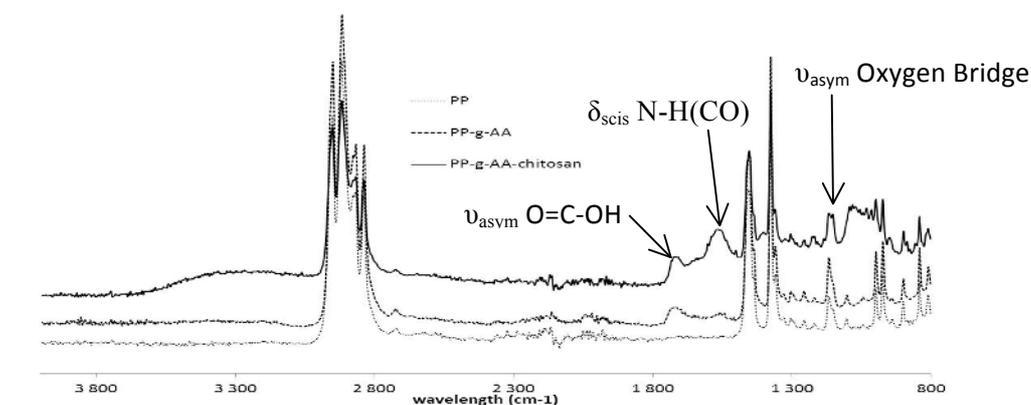


**Fig. 1: Representation of chitosan**

The aim of this study is to functionalize a material with chitosan in order to decontaminate fluvial or marine wastewater. Geotextiles can be used in this field because they are permeable structures that possess filtration and draining capacities. Polypropylene (PP) nonwovens are often used as geotextiles because of its chemical stability. The selected biopolymer, i.e. chitosan, must be then grafted onto the PP nonwoven, without altering its ability to trap heavy metals. However, PP is a hydrophobic inert material and it is necessary to create active functional groups on its surface before immobilizing any molecule. For this purpose, irradiation techniques, especially cold plasma treatments, are used to create radicals upon the surface of polypropylene that improve surface wettability. But plasma treatment effectiveness decreases more or less rapidly, and furthermore does not generate a sufficient density of functional groups on the fibres surface to allow the direct modification with molecules such as chitosan. Therefore, our approach consists in the graft polymerization of a functional monomer, namely acrylic acid (AA) (Saxena et al. 2010) onto the plasma activated surface. This strategy leads to a coating rich in functional groups available for further chemical modifications. In most cases, this grafting is carried out by immersing the activated samples in a bath of monomer at different time and temperature conditions. This approach presents several drawbacks including slow reaction kinetics, risks of homopolymerization, etc. Thus, another grafting pathway, rapid and repeatable, has been developed in the lab to avoid these disadvantages (Degoutin et al. 2012), consisting in activating the sample under low pressure cold plasma, impregnate it in the reactive solution and then graft-polymerize it under cold plasma.

## Materials and Methods

In this study, acrylic acid (Acros organics, purity 99.5%) has been chosen to be grafted onto PP nonwoven (INTN50, 50 g/m<sup>2</sup>, provided by PGI nonwovens, France) by low pressure cold plasma (Europlasma apparatus CD1200-400 COMBI MC, Radio Frequency generator Dressler, 13.56 MHz). First the geotextile was activated (in pure argon flow, at 100 W, for 180 s), then it was immersed in the acrylic acid solution (AA), whose excess was removed using a roll padder and the acrylic acid was graft-polymerized using cold plasma (in pure argon flow, at 100 W for 200 s). The carboxylic functions brought on the textile (PP-g-AA) were then used to covalently graft chitosan (chitosan 342, 85% deacetylated, provided by France Chitin) by formation of an amide group using an intermediate molecule which is a carbodiimide (N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) provided by Sigma-Aldrich). PP-g-AA was immersed for 30 minutes in a bath containing EDC, and then immersed for 24 hours in a solution containing chitosan. FTIR (Thermo Scientific Nicolet 380 FT-IR Spectrometer in the range of 700 – 4000 cm<sup>-1</sup>) analyses were carried out in order to confirm the grafting of these molecules on the textile. The capacity of this new chitosan-grafted PP nonwoven (PP-g-AA-chitosan) to trap heavy metals was determined using an artificial solution of CuSO<sub>4</sub> (Copper (II) sulfate standard solution, 0.1 M, provided by Sigma-Aldrich) prepared with a model heavy metal: copper. Functionalized textiles were immersed in artificial copper solution at 20°C, and the amount of copper trapped on the textile was determined by atomic absorption (Thermo Solar S4 AA Spectrometer, Thermo S Series). Kinetics of copper adsorption at different temperatures were carried out to evaluate the influence of the temperature on the copper chelation. Then, the effect of pH on copper sorption was studied (Standard pH meter, PHM 210, Radiometer analytical), as well as the effect of NaCl concentration, which allows evaluating the effect of the ionic strength.



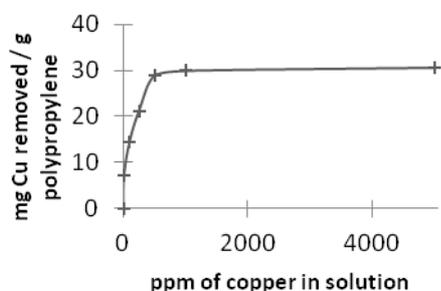
**Fig. 2: FTIR-ATR analysis of the virgin-polypropylene (PP), acrylic-acid-grafted polypropylene (PP-g-AA), and chitosan-acrylic-acid-grafted-polypropylene (PP-g-AA-chitosan)**

**Results and discussion**

Grafting of acrylic acid and chitosan was checked using FTIR. The presence of acrylic acid was proven by FTIR measurements thanks to the peak of asymmetric elongation of the C=O links at 1715.81 cm<sup>-1</sup>. Evidence of the grafting of chitosan is given by the scissoring deformation of the N-H of the amide group at 1563.54 cm<sup>-1</sup>, the asymmetric elongation of the oxygen bridge between monosaccharides at 1153.16 cm<sup>-1</sup> and the saccharide structure characterized by a large peak between 1050 and 1100 cm<sup>-1</sup> (Fig. 2).

Sorption studies giving the evolution of the amount of copper trapped by the textile as a function of the initial metal concentration in the solution were carried out with PP-g-AA-chitosan in order to evaluate the maximum absorption that can be reached (Fig. 3). At 20°C, the grafted-textile can chelate copper increasingly with the initial concentration of the solution until 800 ppm where it reaches a plateau with a maximum absorption of 30 mg of copper per gram of textile. We showed that the sorption of Cu<sup>2+</sup> is a first-order reaction.

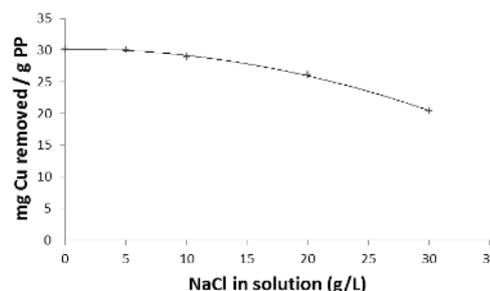
The effects of ionic strength and pH were also investigated to evaluate the effectiveness of the grafted material in seawater, or in sediments enriched in salt. The pH of the solution has been confirmed to reach a value less than 4.85, which is the limit pH of the precipitation of the hydroxyl copper. The textile is then saturated with copper, and it is thus possible to determine the mathematical model describing the sorption of copper at the textile surface: the model of Langmuir, known as Langmuir Isotherm. It consists in plotting the copper concentration in solution against concentration-sorption capacity ratio. We obtain this relation:  $y = 0.0322x + 9E-6$  with  $R^2 = 0.9996$ . This Langmuir Isotherm ( $C/q = 1/(b \cdot q_m) + C/q_m$  with C the concentration of copper (mol/L), q the sorption capacity (mg/g PP), b the Langmuir constant, and q<sub>m</sub> the maximum sorption capacity (mg/g PP)) allows determining the theoretical maximum capacity of sorption at 20°C: 31.06 mg Cu<sup>2+</sup> per gram of textile which is thus close to the experimental value (30mg/g of textile).



**Fig. 3: Variation of the copper concentration in the contaminated water**

The effects of ionic strength and pH were also investigated to evaluate the effectiveness of the grafted material in seawater, or in sediments enriched in salt. We

show on Fig.4 that the higher the ionic strength, the lower the amount of trapped copper. However, this absorption decrease is slow: for a NaCl concentration of 30g/L, the textile still chelates about 20 mg/L of Cu<sup>2+</sup>, which is encouraging for a potential use in seawater.



**Fig. 4: Effect of the ionic strength on the trapping of copper**

The same study was carried out varying the pH: the results show that there is an optimum pH for the trapping of copper which corresponds to the optimum pH for the solubility of the chitosan, namely pH=4.75. This pH is lower than the seawater pH (8.2), but at pH=4.85 the precipitation of Cu<sup>2+</sup> decreases the concentration, and less Cu<sup>2+</sup> can be trapped.

**Conclusion**

The developed Chitosan / Acrylic acid-grafted-PP nonwoven geotextiles were proven to be able to trap copper in a large amount (30 mg/L). The ionic strength has small influence in solutions containing up to 10g/L of NaCl. For high NaCl concentrations (30g/L), the copper absorption still reaches 20 mg/L, which is encouraging for the use of these textiles in seawater. The optimum pH (4.75) for absorption is lower than the seawater pH (8.2) which is explained by the fact that Cu<sup>2+</sup> begins to precipitate at pH=4.85, thus decreasing its concentration in solution.

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