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Résumé de l'article

L'objectif de cette étude était d'élaborer des textiles d'échange ionique (TEI) en greffant des fonctions carboxyliques à la surface de non-tissés en polyéthylène téréphtalate (PET), capables de capter des métaux dans des lixiviats issus de sédiments de dragage, prélevés dans le port de Dunkerque. Un revêtement de surface des fibres, appliqué via la polymérisation in situ d'un mélange maltodextrine/polyacide carboxylique directement sur le textile, a été développé en utilisant l'acide citrique (CTR) ou l'acide 1,2,3,4-butanetétracarboxylique (BTCA). Dans un premier temps, la quantité de fonctions échangeuses d'ions sur les textiles fonctionnalisés a été mesurée puis leur capacité d'adsorption de métaux a été évaluée. Le premier test a été réalisé sur des solutions artificielles de plomb, seul ou en présence de NaCl afin d'imiter l'eau de mer. L'ajout de sel conduit à une réduction modérée du taux d'abattement de 25 % pour le plomb. Le second test a été réalisé sur un lixiviat extrait d'un sédiment prélevé dans le port de Dunkerque. Ce lixiviat étant faiblement contaminé, il a été artificiellement dopé en cadmium, cuivre, plomb et zinc afin d'évaluer son potentiel de revalorisation grâce au traitement via les géotextiles. Plus de 60 % du plomb et du zinc ont été adsorbés, tandis que la totalité du cuivre a été captée par les textiles fonctionnalisés par le CTR. En revanche, de faibles capacités d'adsorption du cadmium ont été obtenues pour ce mélange.

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METALLIC POLLUTANT REMOVAL IN LEACHATES EXTRACTED FROM SEDIMENT BY GEOTEXTILES BASED ON CROSSLINKED BIO-SOURCED POLYMERS

Décontamination métallique de lixiviats issus de sédiments par des géotextiles à base de polymères bio-sourcés réticulés

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ABSTRACT

The aim of this study was to prepare ion exchange textiles (IET) by grafting carboxylic functions onto the surface of polyethylene terephthalate (PET) nonwoven fabrics in order to capture metals in leachates extracted from dredged sediment samples, taken from Dunkerque seaport. A pad/dry/cure coating process, based on the *in situ* polymerization of a mixture consisting of maltodextrin and a polycarboxylic acid on the textile structure, was applied. We used either citric acid (CTR) or 1,2,3,4-butanetetracarboxylic acid (BTCA) as polycarboxylic acids. The amount of ion exchange functions on the geotextiles was first measured and we evaluated their adsorption capacities towards metal cations. To reach that purpose, a first test was carried out on solutions prepared with lead (Pb) in the absence or presence of NaCl, to mimic seawater saline conditions. The presence of NaCl led to a moderate reduction of 25% in lead removal by the IET. The second test was carried out on a sediment leachate. This leachate being weakly contaminated, we artificially doped it with cadmium, copper, lead and zinc in order to evaluate the potential utility of the geotextile treatment. The functionalized textiles adsorbed more than 60% of the lead and zinc. A

complete removal of copper was reached for CTR-based IET and the textiles showed less efficiency towards cadmium in the considered mixture.

Key words: *Leachate, sediments, metals, ion-exchange textile, geotextiles, depollution.*

RÉSUMÉ

L'objectif de cette étude était d'élaborer des textiles d'échange ionique (TEI) en greffant des fonctions carboxyliques à la surface de non-tissés en polyéthylène téréphtalate (PET), capables de capter des métaux dans des lixiviats issus de sédiments de dragage, prélevés dans le port de Dunkerque. Un revêtement de surface des fibres, appliqué via la polymérisation *in situ* d'un mélange maltodextrine/polyacide carboxylique directement sur le textile, a été développé en utilisant l'acide citrique (CTR) ou l'acide 1,2,3,4-butanetétracarboxylique (BTCA). Dans un premier temps, la quantité de fonctions échangeuses d'ions sur les textiles fonctionnalisés a été mesurée puis leur capacité d'adsorption de métaux a été évaluée. Le

premier test a été réalisé sur des solutions artificielles de plomb, seul ou en présence de NaCl afin d'imiter l'eau de mer. L'ajout de sel conduit à une réduction modérée du taux d'abattement de 25 % pour le plomb. Le second test a été réalisé sur un lixiviat extrait d'un sédiment prélevé dans le port de Dunkerque. Ce lixiviat étant faiblement contaminé, il a été artificiellement dopé en cadmium, cuivre, plomb et zinc afin d'évaluer son potentiel de revalorisation grâce au traitement via les géotextiles. Plus de 60 % du plomb et du zinc ont été adsorbés, tandis que la totalité du cuivre a été captée par les textiles fonctionnalisés par le CTR. En revanche, de faibles capacités d'adsorption du cadmium ont été obtenues pour ce mélange.

Mots-clés: *Lixiviat, sédiments, métaux, textiles d'échange ionique, géotextiles, remédiation.*

1. INTRODUCTION

Seaports and waterways are regularly maintained to ensure shipping traffic, including removing sediments that impede boat traffic. These sediments are removed by dredging, which annually generates millions cube meters of material. However, these sediments contain many pollutants such as heavy metals that may be released and spread into the environment, either by surface flow, or by diffusion towards the ground water. The treatment of sediments refers to French and international more and more stringent regulations. Contaminated extracted sediments should be valued after a possible treatment for reuse, for instance as backfill material for road construction. Since sediments are waterlogged at 15 - 20%, a first step is to separate them from water. Though, the heavy metals concentration in the liquid phase may remain too high to reuse it (Décision n° 2003/33/CE). Nowadays, sediments are stored into disposal compartments isolated from underground by geomembranes.

In this context, the goal of this study is to improve the properties of geotextiles in order to lower the metallic content of the sediments and the aqueous supernatant. Ion-exchange textiles is one of the solutions, consisting of the physical or chemical modification of the fibre surface. In this study, the proposed solution consists in applying a green chemistry process developed in our laboratory: the *in situ* crosslinking of maltodextrin (MX) with a polycarboxylic acid, either citric acid (CTR) or 1,2,3,4-butanetetracarboxylic acid (BTCA). This results in the coating of the fibres by a polymeric crosslinked network possessing ion exchange properties (DUCOROY *et al.*, 2008). The main interest of ion-exchange textiles is due to their high specific area. We present here some results concerning their adsorption capacities towards lead in presence of NaCl and the treatment of a leachate that was extracted from dredged sediments.

2. MATERIALS AND METHODS

2.1 Materials

Nonwoven polyester fabrics (INTNI 150) with surfacic weight of $150 \text{ g}\cdot\text{m}^{-2}$, supplied by PGI-Nordlys group (Bailleul, France) were used throughout the study. Maltodextrin (Glucidex® D19) was kindly obtained from Roquette (Lestrem, France). Citric acid (CTR), 1,2,3,4-butanetetracarboxylic acid (BTCA), sodium hydrogencarbonate (NaHCO_3), lead nitrate, copper nitrate trihydrate, cadmium nitrate tetrahydrate, zinc nitrate hexahydrate were purchased from Aldrich Chemicals (Saint Quentin Fallavier, France). Dredged sediments were removed from Dunkerque seaport.

2.2 PET textiles functionalization

The textile finishing process was developed by MARTEL *et al.* (2003) using maltodextrin and polycarboxylic acid (CTR or BTCA) as crosslinking agent (MARTEL *et al.*, 2003; DUCOROY *et al.*, 2008). The reaction consisted of the *in situ* polyesterification between the carboxylic functions of the polyacid and hydroxyl functions of maltodextrin, resulting in the formation of a three-dimensional network coating the fibres, as depicted on [figure 1](#). The amount of -COOH groups available for heavy metal complexation was measured at $1.08\pm 0.02 \text{ mmol/g}$ and $0.69\pm 0.02 \text{ mmol/g}$ for PET-BTCA/MX and PET-CTR/MX textiles, respectively. Before further decontamination tests, samples were treated by a saturated sodium hydrogencarbonate aqueous solution in order to generate carboxylate groups known to present a better complexation ability towards heavy metal cations than carboxylic groups.

2.3 Heavy metal adsorption

Water decontamination assays were carried out by immersing a known mass of textile into 100 ppm lead nitrate synthetic solutions (batch system) for 24 h with or without 30 g/L NaCl. For the second test, we used a sediment leachate taken from Dunkerque seaport. Due to low metal amounts in the leachate, we artificially doped the concentrations in Cu, Pb, Cd and Zn in order to reach class II values (Décision n° 2003/33/CE) and to determine the potential of our geotextiles. Classification of the leachates depending on metal concentrations is given in [table 1](#). Typically, a 5 x 5 cm sample was immersed in 100 mL of doped leachate for 2 h at pH 8.4. Heavy metal cations titrations were carried out by atomic adsorption (ICP-AES Vista-Pro VARIAN). Calibration curves were obtained from external standards purchased from Analytika, Ltd. (Czech Republic).

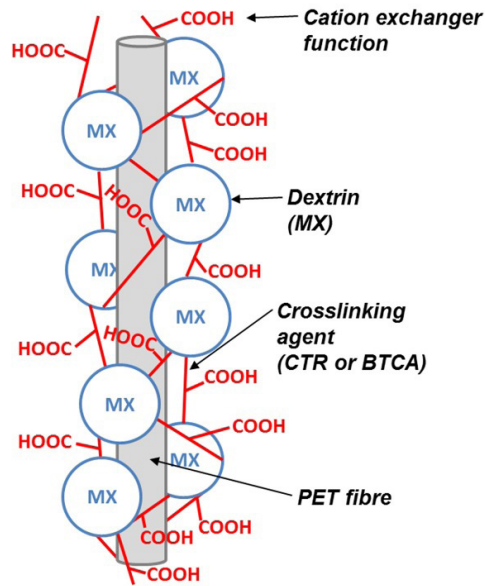


Figure 1. Coating of the fibres with maltodextrin/polycarboxylic acid polymer.
Enrobage des fibres par le polymère de maltodextrine/acide polycarboxylique.

Table 1. Geotextiles efficacy towards four metals in doped sediment leachate and concentration ranges for leachate classification.
Efficacité des géotextiles vis-à-vis de quatre métaux d'un lixiviat dopé et gammes de concentrations pour classification du lixiviat

Metal	Initial concentration (ppm)	Doped concentration (ppm)	Final concentration (ppm)			Class II (<i>non dangerous</i>)	Class III (<i>inert</i>)
			Virgin PET	PET-BTCA/MX	PET-CTR/MX		
Pb ²⁺	0.003	9.430	9.430	3.630	3.580	3 to 15	0.15 to 3
Cu ²⁺	0.010	9.130	9.130	6.440	0.140	30 to 60	0.6 to 30
Cd ²⁺	0.010	1.650	1.610	0.820	1.400	0.3 to 1.7	0.02 to 0.3
Zn ²⁺	0.0075	24.570	24.570	8.790	7.790	15 to 60	1.2 to 15

3. RESULTS AND DISCUSSION

3.1 Influence of salt presence

The adsorption kinetics and isotherms for lead, copper, cadmium and zinc showed the efficiency of the IET for each metal separately (results not presented here). Ionic interactions between two -COO^- groups for one metallic cation are expected. The functionalized textiles were submitted to lead adsorption tests on artificial solutions in presence of

NaCl (30 g/L) in order to mimic saline seawater. As seen on [figure 2](#), the adsorption rate for BTCA crosslinked textile without NaCl is twice that of the CTR crosslinked one, due to the higher amount of free -COO^- groups on this textile. Though, lead removal was reduced by 17% and by 25% for PET-BTCA/MX and PET-CTR/MX respectively in presence of NaCl, because of noticeable Na^+ interactions with COO^- groups at the expense of Pb^{2+} . Moreover, this reduction of lead removal may also be due to the formation of stable and soluble lead-chloro complexes.

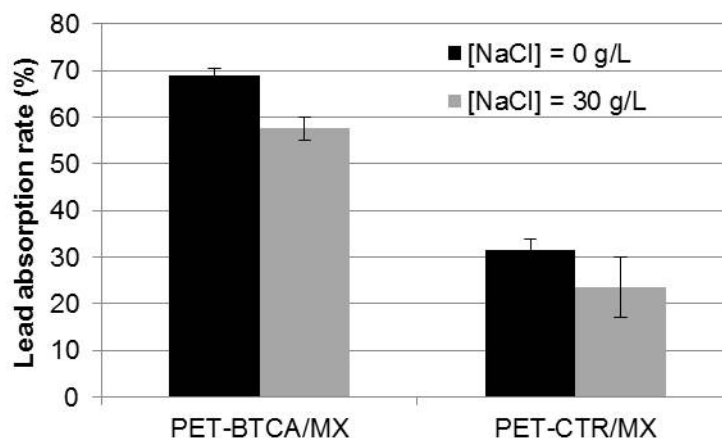


Figure 2. Effect of salt concentration on lead adsorption by functionalized textiles
Effet de la présence de sel sur l'adsorption du plomb par les textiles fonctionnalisés

3.2 Removal of metallic cations from a doped sediment leachate

Before evaluating the adsorption capacity of our functionalized textiles on a real solution, we studied the competition of metal adsorption in artificial solutions containing each heavy metal alone (25 ppm) or a mixture of the four metals studied (25 ppm for each metal in the mixture). The results obtained for PET-BTCA/MX samples are given on [figure 3](#). The adsorption capacity towards lead and copper is slightly affected by the presence of the other metals. On the contrary, a significant reduction of the adsorption of cadmium and zinc is observed, which highlights the affinity of the textile towards lead and copper, in a simple solution and in the absence of salt. Then, the filtrated contaminated leachate from sediment was titrated in order to evaluate Pb^{2+} , Cu^{2+} , Cd^{2+} and Zn^{2+} concentrations. Surprisingly, those concentrations were found lower than for class II wastewater. Therefore, it was decided to artificially dope the solution with nitrate metal salts. The obtained concentrations are given in table 1 as well as the final concentrations after the treatment with textiles. The obtained concentrations after doping of Cd^{2+} , Pb^{2+} and Zn^{2+} are well above class II lower limits, whereas Cu^{2+} concentration is still in class III range. [Figure 4](#) shows that Virgin PET did not adsorb any of the metals, while PET-CTR/MX textiles showed low efficiency towards cadmium on the contrary to single artificial cadmium solution, probably due to a competition between the metals and the presence of salt as previously observed. However, PET-BTCA/MX was found more efficient than PET-CTR/MX. A complete removal of copper was reached for PET-CTR/MX textile, whereas only 29% were adsorbed for PET-BTCA/MX. No significant difference was observed for lead and zinc regarding the functionalized textiles, which adsorbed more

than 60% of those cations. The adsorption phenomena and the affinity towards metals are less obvious than in artificial solutions, due to the complexity of the mixture.

Concerning the targeted valorization of the supernatant down to class III, it was achieved for Zn content. Although copper concentration was still in class III after doping, the concentration is clearly reduced. For lead, the remaining concentrations are reduced but remain slightly above the upper limit of class III wastewater. For cadmium, the final concentrations are still high and in class II range. Finally, a reduction of the concentration was observed for each metal, which shows the potential of our functionalized textiles towards real and complex solutions.

CONCLUSION

In this study, we functionalized a PET textile support with a crosslinked polymer based on maltodextrin, a starch derivate, and a polycarboxylic acid. The obtained textiles possess ion-exchange capacity thanks to the carboxylic groups on their surface and can be used for heavy metal removal in aqueous solutions. In decontamination tests, the presence of NaCl led to a reduction of lead adsorption rate from artificial solutions. In single metal solutions, textiles crosslinked with BTCA were more efficient than with CTR. In doped sediment leachates, the difference between BTCA and CTR crosslinked coatings was not so obvious, due to the complexity of the mixture. However, those textiles remain promising for additional tests on both contaminated leachates and dredged sediments from seaports, for example in dynamic conditions close to real process.

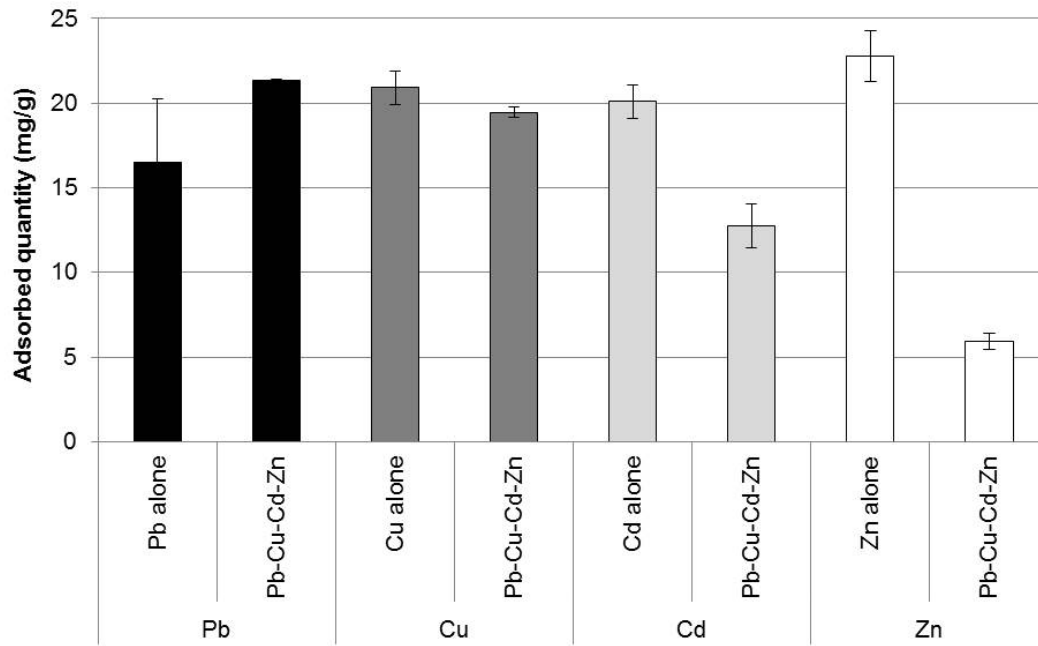


Figure 3. Adsorption capacity of PET-BTCA/MX textile towards lead, copper, cadmium and zinc from single solutions of each metal (25 ppm) or mixtures of the four metals studied (25 ppm of each metal).
Capacité d'adsorption du textile PET-BTCA/MX vis-à-vis du plomb, du cuivre, du cadmium et du zinc à partir de solutions contenant un métal ou le mélange des quatre métaux étudiés, pour des concentrations de 25 ppm pour chaque métal.

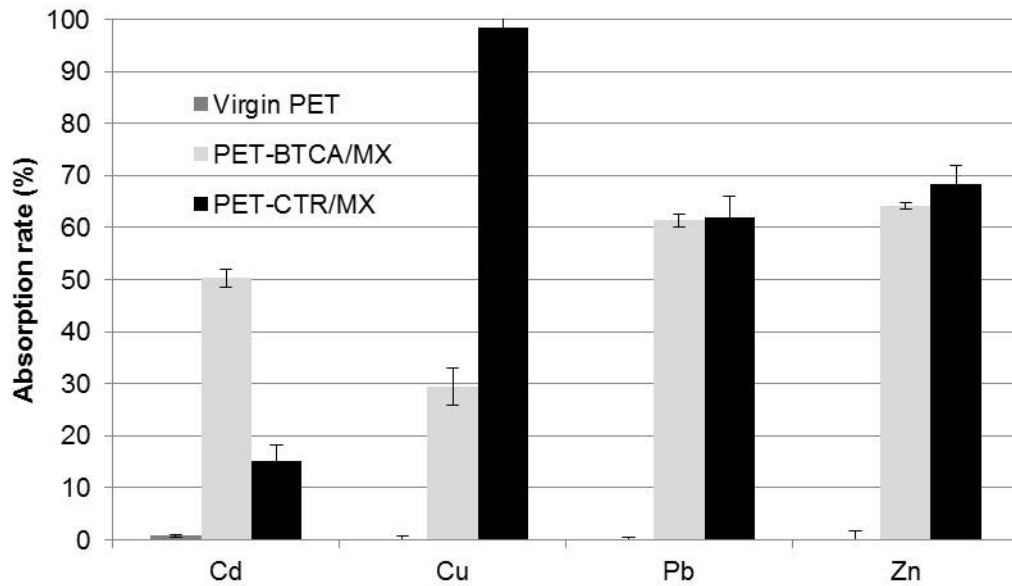


Figure 4. Removal of four metallic cations from a doped sediment leachate by functionalized textiles.
Taux d'abattement de quatre cations métalliques d'un lixiviat dopé par les textiles fonctionnalisés

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