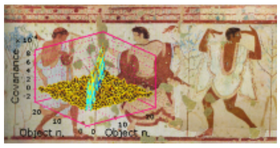

Heavy Metals Removal from Wastewater Using a Versatile Branched Polymer: Carboxylated Polyethylenimine (PEI-COOH)

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Abstract

The presence in the environment of large quantities of toxic heavy metals (i.e. cobalt, cromium, lead, cadmium, zinc, etc.), poses serious health risks to individuals, hence the development of novel methods to eliminate toxic contaminants from wastewaters in efficient and economically viable ways is highly desirable.

In this work we assayed the ability of a polyamine polymer, polyethylenimine (PEI) and its carboxylated derivative PEI-COOH to complex a selection of twenty two heavy metals and remove them from a contaminated water by an ultra-filtration technique. We found that PEI is able to complex efficiently and reduce the concentration of eleven heavy metals (Ag, Al, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn and Zn) to almost a third. In some cases, PEI is very efficient to remove also Cr and Sn to a concentration less than 0.1 ppm. Interestingly, PEI-COOH derivative is able to remove eight heavy metals (Ag, Al, Cd, Co, Cu, Ni, Pb, and Zn) to a concentration less than 0.4 ppm hence increasing the efficiency of polyamine polymers used so far.

In conclusion, the use of carboxylated-PEI in conjunction with the ultrafiltration technique is a valuable tool that may be used for industrial applications to remove a large number of heavy metals.

Introduction

Membrane processes play today an important role in the field of wastewater purification and reuse. This well consolidated technology presents low operative costs, conceptual simplicity, modularity, and optimal quality of treated water. The complexation-ultrafiltration process, also called “polymer assisted ultra-filtration” or PAUF, has been applied for the removal of metal cations from aqueous streams, once complexed these metals with water-soluble polymers [1]. The unbound metals pass through the membrane, whereas the polymers and their complexes are retained. In a recent work, the selective separation of Ni(II) ion from Cu(II) ion, both contained in a same solution, has been studied using polyethylenimine (PEI) as the water soluble polymer [2]. The application of PEUF for the removal of chromium species with pectin and polyethylenimine has been reported [3]. In our work, we report the use of polyethylenimine (PEI) and its carboxylated derivative (PEI-COOH) to complex and remove heavy metals after the ultrafiltration process.

We found that both polymers are able to complex and remove in a great extent a large selection of heavy metals, but PEI-COOH is more efficient and may be potentially used for the industrial wastewater treatment.

Materials & Methods

Synthesis of PEI-COOH. A solution of bromoacetic acid (9.90 g, 71.4 mmol) in water (400 cm3), was added over a period of 3h to a solution of PEI (5g, 0.2 mmol) in water (600 cm3). The resulting mixture was stirred at RT for 1 day, then ultrafiltered through a 10 kDa filter to remove the unreacted acid. The mixture was lyophilized affording PEI-COOH as a white solid. Yield 8.5 g (92%). The substituted polymer may be represented by the stoichiometric formula $(C_2H_4N)_m(C_2H_3O_2)_{0.60m}$, m=595.

Chemical Analysis and Data Elaboration. Heavy metals concentrations were determined by means of an ICP-AES spectrophotometer (Varian, Vista MPX CCD. Simultaneous ICP–OES) equipped with a U5000 AT+ nebulizer (Cetac Technologies, NE, USA). In order to maximize the element sensitivity and to avoid interferences, selected wavelengths were accurately chosen and two spectral regions were investigated. At least one duplicate and one standard sample were run for every 10 samples to calibrate the instrument. Standards were prepared taking into account a preliminary quantification of the sample metal amount. Concentrations were reported as mean values (four replicates) and are all subjected by 5% error. T-test P-Values were calculated and reported (*=P-value<0.005, **=P-value<0.001) for each analyzed species.

Results

Figure 1 shows the residual heavy metals concentration of selected heavy metals treated with PEI and PEI-COOH once recovered after the PAUF process.
Figure 2 shows the residual heavy metals concentration of selected heavy metals treated with PEI-COOH once recovered after the PAUF process.

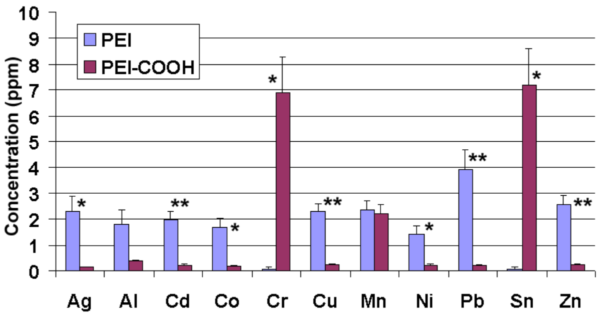

Fig. 1. Residual heavy metals concentration (ppm) of selected heavy metals treated with PEI and PEI-COOH once recovered after the PAUF process.(*=P-value<0.005, **=P-value<0.001)

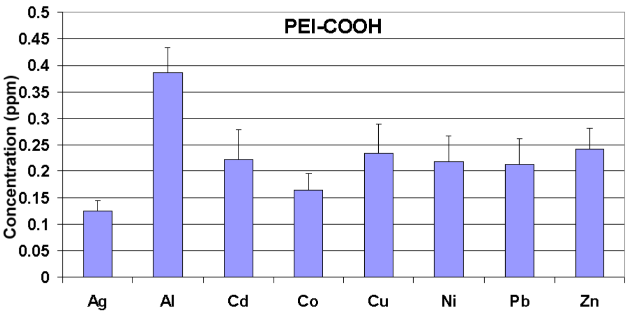

Figure 2. Residual heavy metals concentration (ppm) of selected heavy metals treated with PEI-COOH once recovered after the PAUF process.

Our results are in agreement with reported literature data and clearly indicate that PEI is able to remove a large number or metal with a good efficiency. The best results have been obtained for Cr (0.07±0.07 ppm) and Sn (0.08±0.07 ppm). On the contrary, these two metals are poorly retained by PEI-COOH (Fig. 1). Interestingly, PEI-COOH is able to complex and retain a large number of heavy metal species (Fig. 2) with a metal concentration well above 0.5 ppm for each metals. The best result has been obtained for Ag (0.12±0.02 ppm).

Conclusions

Our work demonstrate the feasibility of using polymers for polymer-assisted ultrafiltration (PAUF) water treatment and suggest the use of PEI-COOH as an efficient candidate for heavy metals removal in industrial wastewater treatment applications.

References

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