

THESIS DEFENSE

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Functionalized track-etched PVDF membrane-electrodes for toxic metal determination in water

Present work reports on radiation grafting of poly(acrylic acid) (PAA), poly(4-vinyl pyridine)(P4VP) and bis[2-(methacryloyloxy)ethyl] phosphate(B2MP) functional polymers inside nanoporous structure of track-etched poly(vinylidene fluoride) (PVDF) membranes for selective pre-concentration of Pb(II), Hg(II) and U(VI) from aqueous solutions. Track-etched PVDF membranes were made by means of swift heavy ion (SHI) irradiation followed by ion track revealing. The resulting nanoporous PVDF membranes were then functionalized through remained radicals at the nanopore walls. EPR spectroscopy was used to examine the amount and reactivity of the trapped radicals, notably towards a novel functionality inside the etched tracks, namely B2MP. It was found that these radicals, alkyl and peroxy ones, were sufficient to initiate free-radical polymerization in presence of the three studied vinyl monomers. FESEM, FTIR and a less conventional zeta-potential measurements were utilized for examination of functional group presence. In case of P4VP grafting, the measured nanopore surface charge *versus* pH demonstrated uniform and relatively dense grafting all along the nanopore channels. As the objective of this work is to develop innovative electrochemical sensors for toxic metal determination in water, adsorption experiments were performed confirming that efficient uptakes of the grafted track-etched PVDF membranes are due to the presence of functional groups that facilitate coordination reactions from pure inherent to PAA electrostatic interaction to chelating complexation with P4VP and B2MP complexation in between. The moderate interaction effect in case of U(VI) adsorption by B2MP is due to the co-existence of ion-exchange and chelating groups in B2MP. For electrochemical sensing, membranes functionalized with abovementioned chelate polymers were converted into electrodes. The pre-concentration of toxic metal adsorbed inside the nanoporosity permit to below stripping voltammetry sensitivity limits to sub-ppb ($\mu\text{g/L}$) level. Time-resolved photoluminescence (TRPL) measurements accompanied with XPS were performed on uranyl adsorbed B2MP-g-PVDF membranes in order to understand deeper the U(VI)-B2MP coordination mechanism.

Keywords: PVDF; irradiation ; track etching ; radiation grafting ; selective adsorption ; toxic metals