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Etched Ion-track grafting for water pollution detection

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The fabrication of nanoporous PAA-g-PVDF membranes is based on the selective chemical etching of Swift Heavy Ions (SHI) tracks in a polymer thin film followed by AA radiografting inside the etched ion-tracks. PAA functionalized nanopores have demonstrated to efficiently trap and preconcentrate metal ions presents in water at open circuit. This passive metal adsorption at solid-liquid interface at the nanopore walls generally follows a Langmuir law. A Square-Wave Anodic Stripping Voltammetry (SW-ASV) protocol for accurate metal analysis at ppb level is established. After the presorption step, the prototyped probe connecting the nanoporous membrane-electrode is immersed in an appropriate buffer electrolyte for analysis. An accumulation potential (-1.2V / -0.8V for a maximum of 120s without stirring) is then performed to electrodeposit presorbed metal ions trapped inside the polymer porosity. The following stripping step reveals the redox potential of each electrodeposited metals (Ag/AgCl pseudo-reference). Multiple measurements in synthetic waters close to the composition of contaminated natural waters exhibited a decreasing precision with the number of readings R (1.65% (R=2) and 6.56% (R=3)) due to the diminution of trapped metal content in the porosity after each measurement. These membrane-electrodes should be used as disposable (one measurement per membrane). The intra-batch mean precision was 14% (n=3) while inter-batches precision was 20% (n=15). Linear and linear-log calibrations allow exploitation of metal concentrations in industrial wastes ranging from 10 to 500 µg.L-1 and 100 to 1000 µg.L-1 respectively. The LOD depends of the metal ion complexation ability with the functionalized entities grafted inside the nanoporosity. For example, it was found equal to 0.1 µg.L-1 for Hg (II) [1] and 4.2 µg.L-1 (3S/N) for Zn(II) [2].

[1] U. Pinaeva, D. Lairez, O. Oral, A. Faber, M-C. Clochard, T.L. Wade, P. Moreau, J-P. Ghestemc, M. Vivier, S. Ammor, R. Nocua, A. Soulé "Early warning sensors for monitoring mercury in water"Journal of Hazardous Materials 376 (2019) 37–47
[2] M-C. Clochard, O. Oral, O. Cavani, M. Castellino, L. Medina Legiero, T. Elan "Zinc detection in oil-polluted marine environment by stripping voltammetry with mercury-free nanoporous gold electrodes"Scientific Reports (2022) 12:15721 https://doi.org/10.1038/s41598-022-20067-0

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