SUMMARY

MODIFIED CARBON NANOMATERIALS IN ADSORPTION AND DETERMINATION OF TRACE METALS USING TOTAL REFLECTION X-RAY FLUORESCENCE

Toxic elements are commonly present in the environment, and due to their easy bioaccumulation in living organisms, their determination at trace and ultra-trace levels is crucial. Modern analytical techniques used for elemental analysis are based on spectroscopy measurements. However, many techniques are characterized by insufficient detection limits to perform trace and ultra-trace analysis, especially in the case of complex matrix samples. Therefore, implementing separation and preconcentration of analytes in the analytical procedures is essential. The solid-phase extraction and dispersive micro-solid phase extraction (DMSPE) are particularly interesting in the scope of the abovementioned issue. Thus, the developing new adsorbents characterized by high adsorption capacities, selectivity, and suitable dispersibility are indispensable in this field.

Within the Ph.D. thesis, several carbon nanomaterials have been developed: graphene oxide/carbon nanotubes membranes (GO/CNT), graphene oxide modified with hydroxyfullerene (GO-$C_{60}(OH)_{22}$), also carbon nanotubes and graphene oxide modified with thiosemicarbazide (CNT-TSC and GO-TSC). The structures and chemical compositions of the synthesized nanomaterials were studied using infrared and Raman spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, X-ray diffraction, and X-ray fluorescence spectrometry. In the next step, their adsorption properties were studied (pH, kinetics, adsorption capacities, also, the influence of ionic strength, and co-existing ions). The GO/CNTs membranes show the effective adsorption of divalent metal ions (Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II)) under the flow condition. GO-$C_{60}(OH)_{22}$ demonstrates high selectivity toward Pb(II) ions, whereas GO-TSC and CNT-TSC toward Hg(II) ions. The adsorption mechanism for each developed material was thoroughly studied.

The GO/CNT membranes were successfully applied for separation/preconcentration of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) ions, and their determination by total-reflection X-ray fluorescence (TXRF). The detection limits of these elements were in the range of 80-210 pg mL^{-1} and 1,0-110 pg mL^{-1} using W and Mo target X-ray tubes, respectively. GO-$C_{60}(OH)_{22}$, GO-TSC, and CNT-TSC, due to their high adsorption capacity and excellent dispersibility in aqueous solutions, were applied in DMSPE. GO-$C_{60}(OH)_{22}$ used in DMSPE allowed determining Pb(II) at ultra-trace levels in water samples using TXRF with the detection limit of 2,3 pg mL^{-1}. GO-TSC and CNT-TSC, as highly selective adsorbents toward Hg(II) ions, were applied in the separation/preconcentration and TXRF determination of these ions in water, beverages, plants, food, and animal tissues. Consequently, the TXRF detection limits were lowered to 2,1-2,6 pg mL^{-1} for the liquid samples and 1,8 ng g^{-1} for solid samples.