

Abstract

Iron oxide nanoparticles are promising materials for many technological and environmental applications due to their versatile functionalization and magnetic properties that allow a facile remote control, separation and analyte recovery. In addition, getting insights into the nature of the physical and chemical interactions that govern the adsorption process is a critical task to achieve a better control of the properties and conditions related with nanometric system. In this contribution we have designed two thiolated nano-platforms based in magnetite as the magnetic material and capped with either *m*-2,3-dimercapto succinic acid (**Fe₃O₄@DMSA**) or a disulfide-containing copolymer of poly[acrylic acid] (**Fe₃O₄@PAA-HED**), in order to study by XPS the character of the interactions between the nanoparticle surface and several heavy metal cations. Both systems were thoroughly characterized by spectroscopic, thermal, XRD, microscopic and magnetic techniques. It was confirmed the presence of the organic ligand, which binds in both cases through iron carboxylate complexes. In **Fe₃O₄@DMSA** sample, thiol groups are oxidized to disulfide bridges, but in **Fe₃O₄@PAA-HED** a proper concentration of free –SH groups is achieved after phosphine reduction (**Fe₃O₄@PAA-HEDred**). Moreover, polythiolated platform is larger than the disulfide-containing one, and also displays strong magnetic interactions that preclude the onset of superparamagnetism. XPS was used for the study of the interactions during the adsorption of Au(III), Pb(II) and Cd(II) ions. The principal route for Au(III) adsorption onto **Fe₃O₄@DMSA** comprises the heterogeneous deposition of subnanometer Au⁰ aggregates caused by the reduction of Au(III); the source of electrons is provided mainly by disulfide groups, although bare magnetite surface can also participate due to surface Fe(II) oxidation. On the contrary, Pb(II) is only adsorbed in minority amounts by forming metal carboxylates with DMSA ligand. When both Pb(II) and Cd(II) were tested with **Fe₃O₄@PAA-HEDred** as sorbent, simultaneous formation of carboxylates and metal thiolates were evidenced. The last kind of complex is the predominant specie. Besides, Pb²⁺ presents a higher deviation from ideal adsorption likely as a result of a lesser selectivity toward the binding sites.