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Abstract

Metal–Phenolic Network-Coated Nanoparticles for Reducing the Toxicity of Metal Nanomaterials †

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The growing use of metal nanomaterials (including Ag-, Cu- and Zn-based nanoparticles (NPs)) in medical applications but also in various green technologies is expected to result in an elevated environmental burden of toxic metals and NPs [1]. Since soluble metal-based NPs cause toxicity via released toxic metal ions [2,3], the safe use of NPs requires strategies for mitigating their toxicity via the removal of these metal ions. Here, a novel class of nano-sized specific adsorbent materials, metal–phenolic networks, are proposed as suitable materials for this purpose due to their biocompatibility, high specific surface area and the presence of functional groups specific for metal-ion binding. Iron–tannic-acid-network-coated Au nanoparticles (Fe-TA@Au NPs) were synthesized and characterized for their physicochemical properties and metal adsorption profile, using Cu ions as model toxicants. The morphology, size, composition and stability in water of the synthesized adsorbent materials were characterized using electron microscopy, Fourier-transform infrared spectroscopy (FTIR), dynamic light scattering, ultraviolet–visible spectrophotometry (UV-Vis) and TXRF spectrometry (S2 PICOFOX, Bruker, Billerica, Massachusetts, USA). The metal ion adsorption capacity, kinetics and specificity of the synthesized Fe-TA@Au NPs were determined in aqueous solutions containing Cu^{2+} ions. A facile two-step synthesis in an aqueous medium at room temperature yielded TA-stabilized Au NPs with a primary size of 25 ± 7 nm which were coated with an Fe-TA amorphous layer (thickness: 7.6 ± 3 nm). The hydrodynamic diameter of the Fe-TA@Au NPs was ~60 nm, and the surface charge was highly negative in both MilliQ water (pH 6.0) and in HEPES buffer (pH of 7.4; zeta potential of −45 and −60 mV, respectively). Aqueous suspensions of Fe-TA@Au NPs were stable over several days. An FTIR analysis indicated the presence of metal coordination bonds between TA and Fe atoms in the metal–phenolic network which were essential for the formation of the network structure. The Fe-TA@Au NPs effectively adsorbed Cu^{2+} in aqueous media, as determined via TXRF spectrometry. When unicellular freshwater protozoa *Tetrahymena thermophila* [4–6] were co-incubated with Fe-TA@Au NPs and $CuSO_4$, the Fe-TA@Au NPs completely rescued protozoa from the toxicity of $CuSO_4$, suggesting efficient adsorption of the Cu ions by the synthesized metal–phenolic networks. The results indicate that NPs coated with metal–phenolic networks have promising applications in environmental remediation.

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