Green mecanochemical process for carbon nanotubes coating with humic acid: application and ecotoxicity evaluation

Francine Coa[1,2], Zaira Clemente[3], Josias Rogerio Lopes[4,1], Laís Luz Rodrigues Neto[4,1], Osvaldo L Alves[4], Vera Lúcia Scherholz Salgado Castro[3], Edison Barbieri[2], Diego Stefani Teodoro Martinez[1]

[1]Centro Nacional de Pesquisa em Energia e Materiais, [2]Instituto de Pesca, [3]Empresa Brasileira de Pesquisa Agropecuária, [4]Universidade Estadual de Campinas

e-mail: francinecoa@gmail.com

Nanomaterials (NM) are promising for environmental remediation due to their unreleased properties such as high surface area and reactivity. Chemical oxidations (H_2SO_4/HNO_3) have been applied to carbon NM in order to favor their application, but these are expensive and hazardous. In this work, industrial grade multiwalled carbon nanotubes (raw-MWCNT) were coated with humic acid (HA) by a ball milling processing (solid state). The aim was to apply a green mechanochemical process to improve the colloidal stability of MWCNTs and their removal capacity of metals. The HA-MWCNT complex was studied by atomic force microscope (AFM), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), dynamic light scattering (DLS), electrophoretic light scattering (ELS) and ultraviolet-visible spectroscopy (UV-Vis). Cu^{2+} sorption from water by HA-MWCNT, MWCNT-COOH and milled-MWCNT were compared. Acute bioassays (96h) were performed with *Daphnia magna* exposed to 0.0; 0.1; 1.0; 5.0 and 10.0 mg/L of HA-MWCNT. Our results showed that the coating process enhanced the zeta potential of raw-MWCNT of -25.4±0.2 mV to -37.4±0.7 mV and reduced their hydrodynamic diameter of 393.2±27.3 nm to 212.5±5.6 nm in ultrapure water. AFM images of HA-MWCNT showed that it has an irregular surface, due to the humic acid coating. The complex was 4 times (84±1.8%) more efficient to remove Cu^{2+} than MWCNT-COOH (20.0±1.4%) and 11 times compared to milled-MWCNT (7.6±3.1%). The increases in Oxygen and the reductions in Carbon on surface of HA-MWCNT relative to raw-MWCNT and milled-MWCNT indicated the introduction of functional oxygenated groups on MWCNT. The HA-MWCNT did not show acute toxicity against *D. magna*. These results suggest that the coating changes the MWCNT surface, resulting in a material with potential to metal remediation,

prepared without oxidizing acids and that did not show toxicity on *D. magna*.

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