Gold (III) and gold nanoparticles interactions with humic acids

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The natural organic matter (NOM) is important in the transport, persistence, mobility, and bioavailability of inorganic and/or organic compounds in the environment. As a consequence, the aggregation behavior and surface properties of mineral particles and nanomaterials (e.g. engineered nanoparticles) in the environment is influenced by the adsorption of NOM to their surfaces and/or by their reactivity. Therefore, the understanding of nanoparticles behavior (fate, transport, and toxicity in natural environments) requires better knowledge of nanoparticles and also of their interactions with NOM in nature.

Humic acids (HA) are the most important part of NOM and represent a complex mixture of partially *"decomposed"* and otherwise transformed organic material from different sources. Some of the components of HA do fluorescence. Fluorescence spectroscopy is fast, relatively easy and powerful method to follow such fluorescence structures but also method for providing knowledge about the chemistry and nature of the interactions between gold (III) or nano-gold and HA. The reduction of Au (III) by HA may be due to functional groups such as e.g. amino, hydroquinone's and phenolic groups present in HA, the functional groups which are recognized to be efficient reducing agents for gold cations [1, 2]. Properties of humic acids, separation and applications were recently reviewed [3] and supramolecular complexation of HA with various xenobiotics demonstrated [4].The aim of the work is to study the interaction between i) Au (III) and soil HA and ii) gold nanoparticles and soil HA, applying spectrophotometry, fluorescence spectroscopy, mass spectrometry, etc. methods.

The HA soil IHSS standard stock solution (200 mg.l^{-1}) was prepared by dissolving the corresponding weight in 36 mM NaOH. Auric acid, $HAuCl_4 \cdot 3H_2O$, was purchased from Sigma-Aldrich (Steinheim, Germany). Sodium hydroxide was from Merck (Darmstadt, Germany). All other reagents were of analytical grade purity. All aqueous solutions were made using ultrahigh purity water obtained using a Mill-Q Plus system (Millipore Co). Perkin-Elmer (Beaconsfield, Buckinghamshire, UK) spectrofluorimeter equipped with a xenon lamp and quartz cuvetteof 1 cm path length and 4 ml inner volume. Diode Array Detector spectrophotometer Hewlett Packard was used, as well. Mass spectra were acquired using a Bruker Autoflex mass spectrometer (Bruker Daltonics, Bremen, Germany). The mass spectrometer was equipped with a time of flight analyzer (TOF) and nitrogen laser (337 nm). Crison (Barcelona, Spain) digital pH-meter furnished with a combined glass–saturated calomel double electrode. Lauda (Königshofen, Germany) MS6 thermostat. Ultrasonic cleaner (Selecta, Seville, Spain) was also used. Mass spectrometric measurements was performed on Axima fromKratos (Manchester, UK).

Via spectrophotometry and fluorescence spectroscopy it was proved that Au (III) reacts with HA in several steps and in the final stage metallic nano-gold is formed. The kinetics depends on pH, HA concentration and temperature. We propose that in the first stage Au (III) is bound to HA, and then reduced to Au (0) generating gold nano-particles (GNP) of various size. The redox reaction is pH dependent (Fig. 1).

The gold nanoparticles were characterized by scanning electron microscopy (SEM), mass spectrometry and spectrophotometry. Because the fluorescence of GNP was found to be influenced by HA, the interaction GNP-HA was suggested (Fig. 2). Homogeneous in size gold nanoparticles can be prepared and at different conditions GNP of various size are formed. The results are important to understand gold mobility in the environment.

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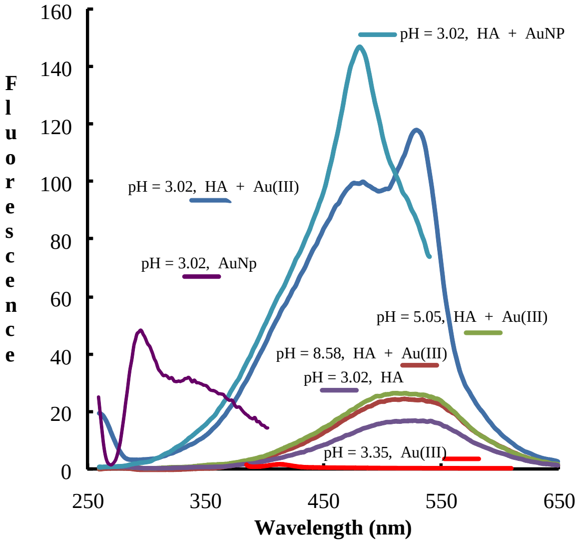

$$m\,\mathrm{Au(III)} + \mathrm{HA} = m\,[\mathrm{Au^{III}}, \mathrm{HA}] = \mathrm{Au_m}$$

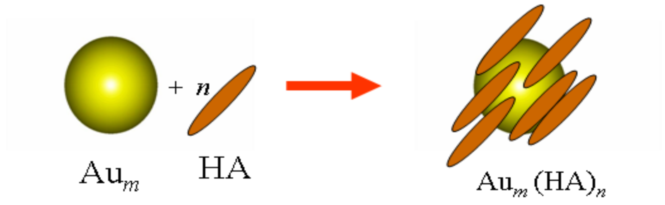

Figure 1. Fluorescence spectra concerning Au (III) and interaction between HA and GNP.

Figure 2. Scheme of redox reaction with HA and complexation of HA with GNP.