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LETTER OF INTENT

to the ISOLDE and Neutron Time-of-Flight Committee

Radioactive probe studies of coordination mechanisms of heavy metal ions from natural waters to functionalized magnetic nanoparticles

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1 Introduction and Motivation

The removal of trace amounts of heavy metals for the treatment of natural waters is of great importance, since their ions are very toxic and accumulate in living organisms. Surface functionalized nanoparticles with organic chelates provide a promising alternative to the more common methods which use flocculation, filtration and precipitation procedures. Nanoparticles have high surface/volume ratios resulting in effective and low-cost water purification powders. The chemical functionalization of the nanoparticles surfaces can improve the efficiency of these materials, since metal ions can be selectively coordinated by functional groups (e.g. carboxylates or thiolates) attached to the nanoparticles surfaces. Of particular interest is the use of magnetic nanoparticles (e.g. iron oxides) since they can later be removed from the solution using magnetic separation methods [1].

Nano-sized magnetite Fe_3O_4 is commonly used for removal of heavy metals in magnetically assisted chemical separation methods, due to its magnetic properties, high surface area, easy synthesis and low toxicity [2]. Usually its surface is modified by attaching very large range of inorganic or organic molecules thus stabilizing the particles, preventing their oxidation or providing them a specific functionality.

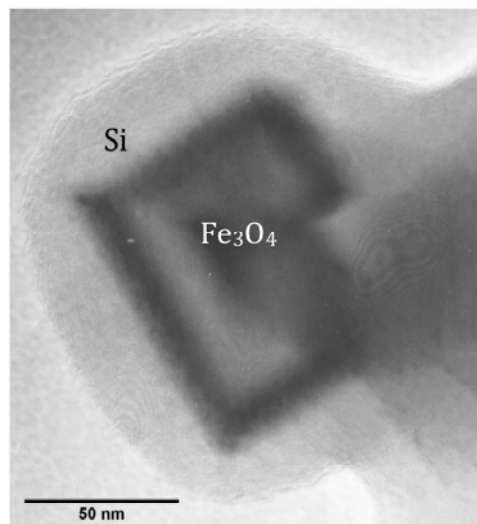
We have been investigating the synthesis, surface modification (with amorphous SiO_2) and functionalization of magnetic Fe_3O_4 particles, namely by grafting dithiocarbamate (DTC)



groups to the particles surface [3,4]. This surface functionalization process introduced dithiocarbamate groups without destroying the morphological characteristics of the magnetite nanoparticles. Figure 1 shows an electron microscopy picture of a silica-coated Fe_3O_4 nanoparticle.

The sorption of Hg^{2+} , Pb^{2+} and Cd^{2+} ions from aqueous solutions has been investigated using natural waters as experimental samples and by monitoring the bulk solution concentration of the cation using vapour atomic fluorescence spectrometry.

The results obtained so far suggest that these nanomaterials are quite effective in heavy metal uptake from aqueous solutions, but there is little understanding on how the nature of the nanoparticles surface influences the overall process. The most obvious possibility is that each metal ion became coordinated by the functional group of the organic ligand located at the nanoparticles surface. However this is an oversimplified picture of this nanodispersed system, because surfaces of inorganic particles are rather complex and the chemical functionalization of those particles is not necessarily uniform. The possibility that one ion binds to more than one molecule (if they are dense enough at the surface) or that two or more ions are loosely bound to one molecule can change dramatically the efficiency and stability of the process. Also, non-passivated regions of the SiO_2 surface can participate in the cations up-take process leading to a distinct behaviour as compared to the chelating sites. Additionally, hydrolysed cationic species can also compete in the coordination to chemical sites. In fact, our preliminary studies of the time dependence of Hg^{2+} uptake has shown non-monotonous effects that may be related to these local effects. By acquiring a deeper knowledge of the nanoparticles surfaces and their local coordination sites to heavy metals, it would make possible not only to increase the efficiency of these particles but also would form the basis for the development of new nanodispersed systems for environmental remediation processes.



Silica-coated Fe_3O_4 nanoparticle

2 Summary

We propose here to use PAC, Perturbed Angular Correlations, to study the local environment of radioactive coordinated ionic species (Hg^{2+} , Cd^{2+} and Pb^{2+}) in the several steps of the cations uptake by functionalized magnetic nanoparticles. Also, we would like to monitor the time dependence of the coordination of those cations at the nanoparticles surfaces. These results might allow us to conclude about the kinetics of the adsorption and desorption processes of the metal cations at the nanoparticles surfaces.

The sample preparation technique here proposed is a simple adaptation of the method actually used at ISOLDE for biophysics experiments [5,6,7]. It consists of the ISOLDE beam implantation in solidified water, which already contains or, to which nanoparticles will be added.

The hyperfine parameters (EFG) at the radioactive probe site will be used to understand the diversity of the local environment and the factors that may affect it (separation, distribution of the functional molecules). A second part of the study is the calculation of the parameters using first principles or semi-empirical molecular modelling to as precisely as possible characterize the environments. The study of different nanoparticle sizes, that can be made to

range from ~300 to ~10 nm, is also of interest, since it modifies the concentration/dispersion of functional species.

Before a full proposal is presented we would like to perform few indicative tests. We propose to study the uptake of Hg and Cd ions in two concepts:

- 1) 3 concentrations of adsorbed ions (clean and previously prepared samples already with some stable ions coordinated, representing the initial and two times after the beginning of sorption in a water cleaning process)
- 2) Study the case of two particle sizes.

3 Beam time request

We estimate a total of 4 shifts of beam time for this LOI, since the work for a full proposal will need around 20 shifts for a 2 years period, due to the diversity of situations to study.

REQUIRED ISOTOPE	ISOLDE BEAM	INTENSITY [AT/ μ C]	TARGET	ION SOURCE	NUMBER OF SHIFTS
^{111m}Cd	^{111m}Cd	$\sim 5.0\text{E}8$	Molten Sn	plasma	2
^{199m}Hg	^{199m}Hg	$\sim 2.0\text{E}8$	Molten Pb	plasma	2

Due to the nature of the sample preparation for PAC measurements, i.e., time collections of 15... 30 min per sample for ^{111m}Cd and ^{199m}Hg , each 4h, the beam time should be shared with other users.

References

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