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ScienceDirect
Physics Procedia 9 (2010) 45–48
Physics Procedia
www.elsevier.com/locate/procedia

12th International Conference on Magnetic Fluids

Synthesis and design of functionalized magnetic nanocolloids for water pollution remediation

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Abstract

This work focus on the potential applications of magnetic nanoparticles on pollution remediation. We draw attention to the chemical design of functionalized magnetic colloids based on tartrate ligands to be used in magnetic separation of heavy metals from wastewater. Coupling the speciation diagrams of nanoferrites particles surface with that of the tartaric acid, it was possible to provide a theoretical prediction of the optimal pH for particle surface – ligand complexation. Finally, from an electrochemical approach based on simultaneous potentiometric and conductimetric titrations it was possible to determine the saturation value of the surface charge density of the functionalized nanoparticles and its pH dependence.

Keywords: magnetic nanoparticles; environmental applications; surface charge density

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1. Introduction

Currently, nanotechnologies have been played a very important role in recent efforts for pollution remediation in systems contaminated with hazardous substances [1]. In the case of magnetic nanosized particles, the procedure of magnetic filtration has been used as an interesting tool concerning the process of heavy metal removal from water [2]. However, since most of these pollutants are not magnetic, it is necessary to develop nanostructured filtration aids to adsorb them allowing their magnetic separation. These magnetic nanosorbents have been prepared through nanoparticle functionalization with polyelectrolyte ligands for example humic acids and dimercaptosuccinic acid (DMSA) which present chemical affinity with the nanoparticle surface as well as with the toxic contaminants [3].

Our group has been working with magnetic colloids based on ferrite nanoparticles dispersed in aqueous medium, known as Electric Double Layered Magnetic Fluids (EDL-MF) [4]. Recently [5], we used electrochemical measurements to point out that the EDL-MF system behaves as a mixture of acids: a strong one related to the bulk

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1875-3892
doi:10.1016/j.phpro.2010.11.012

dispersion and a weak diprotic acid associated to the particle surface which can be functionalized with several chemical groups. Moreover, in the framework of the Two-pK Model, it has been possible to determine both the molar ratio of the nanoparticle surface sites as a function of the pH and the saturation value of the surface charge density. In this way, the intrinsic magnetic behavior of the EDL-MF nanoparticles and their reactive surface make them particularly attractive as precursors for synthesis and design of magnetic nanosorbents for environmental applications. Among the numerous types of chemical ligands of potential interest, the tartrate form remarkably stable chelates with many heavy metal ions in solution [6] and provides a colloidal stability domain in pH region characteristic of the wastewater samples [7].

The main goal of this work is to explore the particle surface-ligand complexation in order to propose an experimental procedure to develop and characterize a new type of magnetic nanosorbent for potential environmental applications composed by EDL-MF nanoparticles functionalized with tartrate. By using our experimental electrochemical approach, we first obtain the pH dependence of the surface charge density for an EDL-MF based on cobalt ferrite nanoparticles. Then, the speciation diagram for the surface sites is coupled with that of tartrate ions to analyze the mechanism of surface complexation. Finally, we determine the pH-dependence of the charged surface sites concentration for the functionalized nanoparticles to investigate their surface charging process.

2. Experimental

2.1. Sample preparation and characterization

The magnetic colloid precursor sample is synthesized by following the procedures described elsewhere [8]. In a first step, it is performed a hydrothermal coprecipitation of aqueous solutions of $CoCl_2$-$FeCl_3$, in alkaline medium. Next, the precipitated is washed and hydrothermally treated with a solution of $Fe(NO_3)_3$ in order to avoid the particle dissolution in acid medium. Then the particles are conveniently peptized in acidic medium by adjustment of the ionic strength. The synthesis of tartrate-functional nanoparticles is carried out by stirring the diluted nanocolloid sample with aqueous tartaric acid solution with controlled pH.

The size determination and the structural characterization were investigated by room temperature X-rays powder diffraction (XRD) performed at the Brazilian Synchrotron source (Laboratório Nacional de Luz Síncrotron - LNLS). The mean crystal size d_{XR} was deduced by means of the Scherrer formula which provided d_{XR} = 14.3 nm.

2.2. Determination of the structural surface charge density

In order to determine the structural surface charge of the EDL-MF nanoparticles we have performed simultaneously potentiometric-conductimetric titrations [5] of 40 mL of a magnetic colloid sample (volume fraction $\phi = 1.5$ %), under CO_2-free atmosphere and using sodium hydroxide as titrant. The same procedure was applied to determine the structural surface charge density of the tartrate-functional nanoparticles.

3. Results and discussion

We plotted in Fig. 1 the coupled speciation diagrams of particle surface and tartaric acid to explore the surface complexation process. According to the Two-pK Model, the charge density of the EDL-MF is provided by a proton transfer mechanism between the bulk dispersion and the particle surface [5]. The concentration of the charged surface sites ($\equiv MOH_2^+$, $\equiv MOH$ and $\equiv MO^-$, where M is the metal of the spinel type nanoparticles) is pH-dependent as well as the concentration of the tartaric acid (H_2L) and its ionized species (abbreviated as HL^- and L^{2-}).