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Measuring and modeling the magnetic settling of superparamagnetic nanoparticle dispersions

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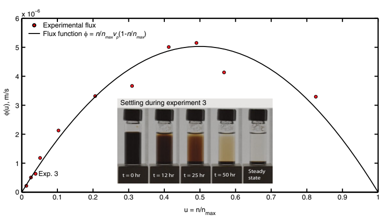
GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we present settling experiments and mathematical modeling to study the magnetic separation of superparamagnetic iron-oxide nanoparticles (SPIONs) from a brine. The experiments were performed using SPIONs suspensions of concentration between 3 and 202 g/L dispersed in water and separated from the liquid under the effect of a permanent magnet. A 1D model was developed in the framework of the sedimentation theory with a conservation law for SPIONs and a mass flux function based on the Newton's law for motion in a magnetic field. The model describes both the hindering effect of suspension concentration (n) during settling due to particle collisions and the increase in settling rate due to the attraction of the SPIONs towards the magnet. The flux function was derived from the settling experiments and the numerical model validated against the analytical solution and the experimental data. Suspensions of SPIONs were of 2.8 cm initial height, placed on a magnet, and monitored continuously with a digital camera. Applying a magnetic field of 0.5 T of polarization, the SPION's velocity was of approximately $3 \cdot 10^{-5}$ m/s close to the magnet and decreases of two orders of magnitude across the domain. The process was characterized initially by a classical sedimentation behavior, i.e., an upper interface between the clear water and the suspension slowly moving towards the magnet and a lower interface between the sediment layer and the suspension moving away from the magnet. Subsequently, a rapid separation of nanoparticle occured suggesting a non-classical settling phenomenon induced by magnetic forces which favor particle aggregation and therefore faster settling. The rate of settling decreased with n and an optimal condition for fast separation was found for an initial n of 120 g/L. The model agrees well with the measurements in the early stage of the settling, but it fails to describe the upper interface movement during the later stage, probably because of particle aggregation induced by magnetization which is not accounted for in the model.

1. Introduction

Superparamagnetic iron-oxide nanoparticles (SPIONs) are used as ferro-fluids in a wide variety of science and engineering applica-

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tions such as electronics, medicine, and subsurface exploration [1]. Generally, ferro-fluids are classified on the basis of their magnetic properties. Diamagnetic materials have repulsion from an external magnetic field. Paramagnetic materials and ferromagnetic materials are instead attracted towards a magnetic field, with the latter maintaining their magnetization even when the magnetic field is removed. Paramagnetic particles with size <20 nm are identified as superparamagnetic nanoparticles as they have a negligible relaxation time to reach zero magnetization making them particularly interesting in applications where fast response and material regeneration is required [2]. Because of their large surface area per mass and magnetic properties, SPIONs allow selective removal and separation of certain chemicals and dispersions from liquids, in addition to the possibility for their regeneration and reuse. Moreover, when their surface is modified in a prescribed manner, the combination of nanosize, magnetic core, and reactive surface make them particularly useful in chemical and biomedical applications such as softening of high salinity water, (e.g., seawater and brines) [3–6], removal of oil droplets from water [7], imaging, and drug delivery [8,9,1]. In these fields of application, attempts have been made to create suspension of magnetite (Fe_3O_4) functionalized (i.e., surface coated) with polymers to allow certain chemical reactions, i.e., adsorption of aqueous ions, oxidation/reduction reactions, and dissolution/crystallization, to occur. Upon reaction, in some cases phase separation is necessary and gravitational settling has been proposed as a cost-effective option. However, it is challenging because of the long time required by the nanoparticles to settle. Using the magnetic properties of the particles the sedimentation process could be therefore speed up, considerably.

Settling (or sedimentation) is a fundamental process which occurs in both natural and industrial systems, such as lakes, rivers, water treatment plants, and mining. First comprehensive physical description of the phenomenon was performed by Coe and Clevenger [10], while the theory was initially formulated by Kynch [11] and then extended by several authors [12–14] to include the effect of flocculation and compression. Bergström [15] studied the settling of colloidal alumina suspension adsorbing various organic compounds on their interface. Based on the adsorbed molecule, the flocculating behavior of the particles changed and consequently their settling rate. Recently, several investigations have been performed on the settling of nanoparticle suspensions, e.g., [16–20]; however, few attempts have been made on the modeling of the process when a high-gradient magnetic field is present.

In this paper, we present experiments and a mathematical model for the quantitative description of the dynamics of the settling of SPIONs from dispersing water. Experiments were carried out using suspensions of known concentrations settling under the effect of a magnetic field and continuously monitored. A 1D model was developed in the framework of the sedimentation theory with a conservation law for SPIONs and a mass flux function accounting for not only gravity force but also magnetic force and Brownian interaction. The model describes both the well-established behavior of colloidal particles during settling and the enhancing effects of the magnetic field due to attraction of SPIONs towards a magnet.

The article is divided in five sections. In Section 2, we report the characterization of the nanoparticles and the method used for the experiments. In Section 3, we present the conservation and the constitutive equations that describe the settling of magnetic nanoparticles under the influence of a magnetic field. In Section 4, we derive the mass flux function from the settling experiments and validate the model with the analytical solution and the experimental data. Finally, in Section 5, we draw the conclusions.

2. Materials and methods

2.1. Characterization of the nanoparticles

Superparamagnetic nanoparticles (EMG 605, Ferrotec, U.S.A.) suspended in water at a concentration of 202 g/L and pH of 9 were employed in this study. The nanoparticles, coated with a cationic surfactant, were used for settling experiments in the presence of a magnetic field generated by a cubic permanent magnet (Ultra-High-Pull Neodymium Rectangular Magnet, McMaster-Carr, U.S.A.) of 2.54 cm length and of 0.5 T polarization. The magnetic field generated by a permanent magnet was measured by means of a hand-held DC gaussmeter (GM1-ST, Alphalab Inc., U.S.A.). All measurements were carried out at 25 °C and the results are shown in Fig. 2. The nominal particle diameter and particle saturation magnetization were 10 nm and 20 mT, respectively.

Before and after the experiments, the nanoparticle suspensions were analyzed to determine the morphology, the particle size distribution (PSD), and the Polydispersity Index (PDI), which is the width of the PSD [21]. PDI is generally used as a qualitative index for the determination of particle aggregation being zero for a monodisperse suspension and increasing with the degree of aggregation. An image of the nanoparticles made by transmission electron microscopy (TEM, Tecnal, U.S.A.) is shown in Fig. 1b. The picture clearly shows a flocculated suspension with flocs of average size as large as 140 nm. A more detailed characterization of the particle size and agglomeration was performed using Dynamic Light Scattering (DLS, Malvern DLS nano ZS, U.S.A.). The PSD and the PDI measured for untreated and settled suspensions upon homogenization are shown in Fig. 1a. The averaged diameter of the untreated and tested suspensions was 120 nm and 126 ± 3.5 nm, respectively. Correspondingly, the PDI was 0.12 and 0.13 ± 0.01. These measurements clearly show that the suspensions contained flocs of nanoparticles, but their size does not change after the experiments indicating that no permanent flocculation occurs during the settling tests.

2.2. Settling experiments

Settling experiments were performed in a 3.7 mL glass vial of height 4.5 cm and internal diameter 1.5 cm. Nanoparticle suspensions of height 2.8 cm, i.e., total volume 3.2 mL, and concentration between 3.15 and 202 g/L were prepared using distilled water. The pH of the resulting suspension varied between 8.1 and 8.6. They were vigorously shaken for about 1 min and then placed on the permanent magnet with a magnetic field in the direction of the gravitational field. The time when the magnetic field was applied defined the beginning of the settling test.

The experiments were monitored continuously with an automatic camera (Nikon digital SLS D7100, Nikon, U.S.A.) and images were taken every 30 min until steady state, i.e., the level of the interface between the clear water and the settled solids was stationary. A ruler was placed next to the vial to measure the height of the interface over time and a LED light panel (Light Beam Industries, U.S.A.) was installed behind the suspension to enhance visibility. The images were analyzed to determine the settling rate for the calculation of the flux function.

3. Mathematical model for the settling of magnetic nanoparticles

3.1. Settling model

Following the theory of batch sedimentation formulated by Kynch [11] and then extended by Bustos et al.[14], we considered