CONTINUOUS SYNTHESIS OF IRON OXIDE NANOPARTICLE DISPERSIONS IN NEAR- AND SUPERCRITICAL WATER AND THEIR CHARACTERIZATION

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The preparation of stable suspensions of electrostatically stabilized, discrete iron oxide nanoparticles in supercritical water is demonstrated. Nanoparticle suspensions were prepared using iron(III) nitrate and an acidified mixture of iron(III) nitrate and iron(II) acetate, leading to different dispersion properties. The dispersions were characterised in detail by differential sedimentation using a disc centrifuge as well as through electrophoretic light scattering. A strong influence of the reaction conditions on the particle/agglomerate size distribution was observed. Powder X-ray diffraction and Raman spectroscopy were used in an attempt to determine the crystalline structure of the iron oxide nanoparticles as a wet paste and in concentrated aqueous dispersion.

INTRODUCTION

Iron oxide nanoparticles play an important role in natural and technical processes. Applications are found in areas such as drinking and waste water treatment, electronics, optoelectronics, diagnostics, therapeutics, and bioseparation [1, 2]. The wide diversity in natural appearance as well as the manifold technical applications of iron oxide (nano)particles are based on their special physical, chemical, and structural properties with the possibility of continuous or abrupt changes of these properties [1].

Iron oxide nanoparticles have been obtained via different routes for a long time (e.g. sol-gel and microemulsion processes, coprecipitation). However, up to now the synthesis – especially in the industrial scale – still faces challenges related to long operation times and/or the use of large amounts of organic solvents and/or additives [3]. The use of supercritical water as an alternative reaction medium and solvent at the same time is an attractive alternative because of its non-toxicity as well as physical and chemical properties. Very promising results, especially of in situ functionalized iron oxide particles, have been obtained with a continuous process based on the mixing of a cold metal salt stream with a hot compressed water stream [4, 5].

In the work presented here, this method was used to prepare iron oxide nanoparticle dispersions without the addition of organic solvents, strong bases or surfactants. Of the many forms of iron oxide, hematite, magnetite and ferrihydrite nanoparticles have been synthesized successfully in hot compressed water [3]. However, both structure and properties of iron oxide nanoparticles strongly depend on their particle size, their history of formation and the surrounding medium [1]. Thus, the goals of this study were twofold:

1. to investigate the influence of mixing ratio, fluid velocity and identity of the starting material on the size distribution of both primary particles and particle agglomerates, as well as on the colloidal stability of the dispersions, and
2. to identify the structure of the particles directly in the aqueous dispersion by means of Raman spectroscopy. This second goal is important because the properties of the iron oxides can be changed during preparation steps for characterization as a powder.

MATERIALS AND METHODS

Appropriate amounts of iron(III) nitrate nonahydrate (purity 99.99%, Sigma-Aldrich, Steinheim, Germany) and iron(II) acetate (Fe 29.5% min., Alfa Aesar, Karlsruhe, Germany) were dissolved in water of HPLC quality (LiChrosolv, Merck, Darmstadt, Germany). Nitric acid (65%, Roth, Karlsruhe) was added in some cases to control the pH-value of the solution. Sucrose (Merck, Darmstadt, Germany) and hydrochloric acid (≥ 32%, p.a., Roth, Karlsruhe, Germany) were used to prepare the density gradient for the characterisation of the particle suspensions with a disc centrifuge. A PVC particle standard with a mode of 377 nm (CPS Instruments, Florida, USA) was used for calibration in the sedimentation analysis.

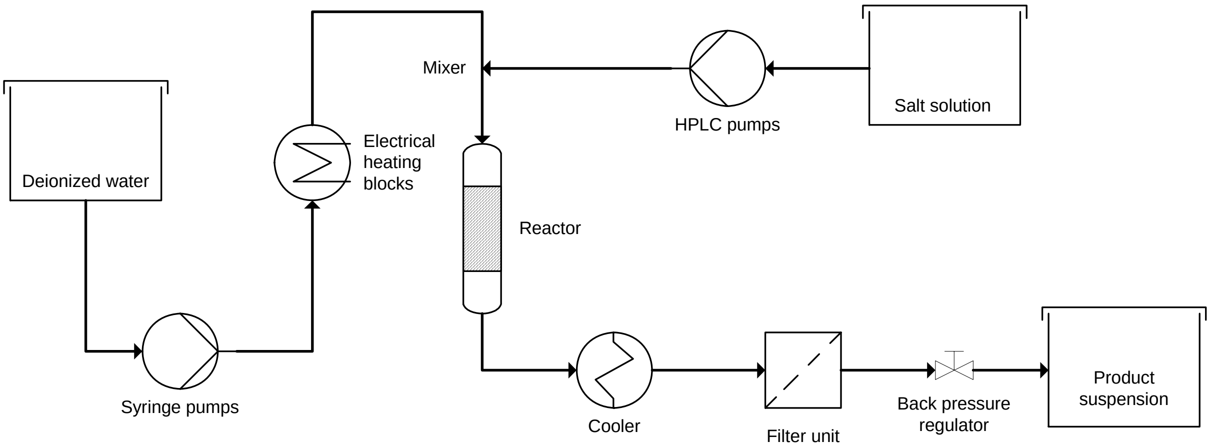

Figure 1 : Simplified flow diagram of pilot plant

The supercritical hydrothermal synthesis was carried out with a high pressure pilot plant (Figure 1). Deionised water with a reduced oxygen content (sparged with nitrogen prior to use) was delivered into the plant with different flow rates using two coupled syringe pumps (model 500D, Teledyne Isco, Inc., NE, U.S.A.) and heated appropriately in order to obtain the same mixing temperature upon mixing with the cold metal salt stream. The cold metal salt stream was delivered using HPLC pumps (2080, Jasco, Gross-Umstadt, Germany). A T-piece (720.1633, Sitec-Sieber, Maur, Switzerland) was used as mixer. The inner diameter of this piece and the adjacent tubing was 1.6 mm. The experimental conditions are summarized in table next to Figure 1. After passing the reactor the stream was cooled with an external water jacket and passed through a filter unit (pore size approx. 10 µm, Swagelok) and a back pressure regulator (Tescom Europe, Selmsdorf) to be recovered as a particle suspension.

Table 1 : Summary of the process parameters

Parameter	**Set value**
Pressure	30 MPa
Mixing and reactor temperature	673 K
Density of the media (assumption: pure water)	357 kg/m^3
Relative dielectric constant	5.9
Total mass flow rate	3.04 – 9.11 kg/h
Mixing ratio (salt stream/total mass flow)	0,05; 0,1; 0,15; 0,2; 0,3
Residence time	200-600 ms
Product concentration of iron	0.001-0.01 mol/L

Powder X-ray diffraction (PXRD) measurements of highly concentrated particle dispersions (paste-like) were performed with a Bragg-Brentano-Goniometer D8 (Bruker AXS) using monochromatic CuKα_1 radiation. The volume weighted crystallite sizes were determined – when possible – using the Scherrer equation. Correction for the instrument broadening was performed using the standard reference material 660a (LaB_6) of the National Institutes of Standards & Technology (NIST). Investigations on the colloidal stability of the product suspensions was carried out via the determination of the electrophoretic mobility and the zeta potential was derived applying the models of Smoluchowski and of Hückel using a Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK). The size distributions of the particles and agglomerates in the suspensions were determined using a disc centrifuge (CPS Instruments, Florida, USA). The density gradient was established with aqueous sucrose solutions (8% – 24% in nine steps) adjusted to pH 3 using hydrochloric acid. A calibration standard (PVC- particles with a mode of 377 nm) was used prior to each measurement. To obtain a size distribution based on volume, the knowledge of certain material properties is required. Because of the difficulty of identifying the exact structure of the particles, as well as variable optical properties of iron oxide nanoparticles, the calculations for obtaining a volume based particle distribution are non-trivial. Parameter studies revealed that the imaginary part of the refractive index plays a major role on the weighting of different size fractions in the calculated size distribution. Therefore, optical and material parameters were chosen conservatively so that the fraction containing larger particles and the size of the particles is more likely to be over than underestimated. Trends and the order of magnitude are not influenced by the choice of parameters.

RESULTS AND DISCUSSION

Particle suspensions synthesized from iron(III) nitrate solutions appeared with an intense – mostly red – colour. However, the colour as well as the degree of transparency was dependant on the process conditions. In Figure 2, a selection of the obtained dispersions is presented. It could be noticed that an increase in transparency – an indicator for the presence of smaller particles – was accompanied with a shift in colour to more intense reddish colours with a touch of purple in comparison to orange-red coloured suspensions (e.g., Figure 2c) which is the characteristic colour of suspensions containing hematite particles < 0,1 µm. Suspensions of hematite particles change their colour to red up to purple upon increasing particle sizes [2]. Therefore, the observed colour change has to be explained. A possible explanation could be that the colour change to darker red is introduced due to oriented aggregates of nanocrystallites. This has been already observed for hematite particles synthesized via a different route [1,2]. Another explanation could be a size dependant change in the structure of the particles.

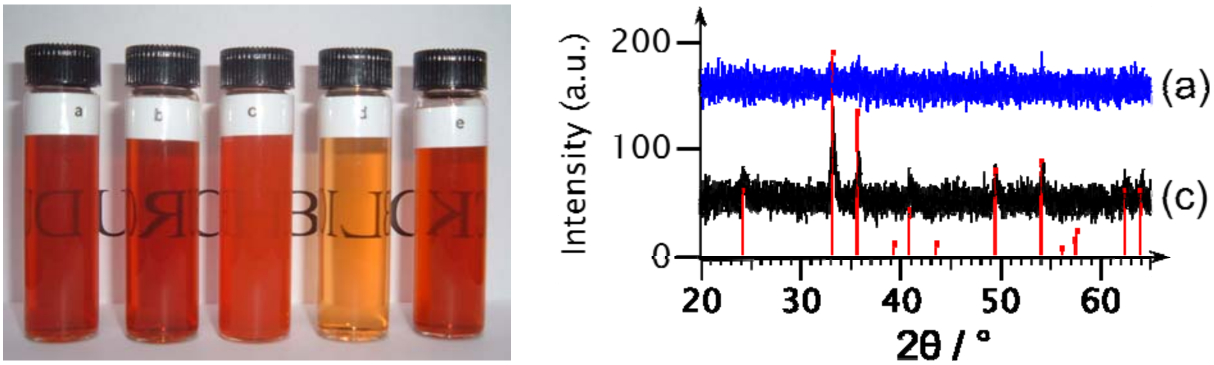

Figure 2 : (left) Selection of particle suspensions: Samples (a) – (c) were synthesized under the same process conditions except for the flow conditions. Sample (d) was synthesized from iron(II) acetate acidified with nitric acid. Sample (e) is a concentrated suspension prepared from sample (d) and has approximately the same solid content as samples (a) to (c). (right) Powder X-ray diffraction patterns of paste-like concentrates of samples (a) and (c). The vertical bars correspond to the diffraction angles of hematite.

To answer this question, PXRD measurements were carried out. The data for the samples (a) and (b) of Figure 2 (left) are given in Figure 2 (right). For the latter one, the structure of the synthesized particles could be identified as $\alpha-Fe_2O_3$ (hematite) with a volume mean crystallite size of 35 nm. However, for samples with a high degree of transparency (e.g. Figure 2 (left), vials a and b), no or very weak diffraction reflexes were present. Therefore, the crystalline structure could not be identified for many samples. Very weak reflexes appeared at the same diffraction angles as the ones of hematite. The small size of the particles, defects and/or structural changes could have caused the disappearance of diffraction reflexes which made it impossible to identify the structure with conventional PXRD for most of the synthesized particles.

To overcome this problem, Raman spectroscopic measurements have been carried out on concentrated samples. First results indicate that hematite is the dominant structure of the particles. However, bands of other structures are also present (data not shown). Systematic studies to allow a more detailed interpretation of the spectra are underway.

Differential sedimentation analysis using a disc centrifuge was used to determine the size distribution of the particles and agglomerates under different process conditions with a high resolution. Figure 3 shows the particle size distribution of dispersions synthesized at two different mixing ratios and two different total mass flow rates keeping the other process conditions constant. The mode of the peak containing the particles with smaller diameter was in all cases around 25 nm in comparison to 60-80 nm for the peak containing the bigger particles. However, the proportion of these two particle fractions varied to a very large extent depending on the conditions investigated. For small total flow rates, the fraction of the bigger particles was dominant. An increase of the total mass flow rate and the mixing ratio led to a decrease of that fraction.

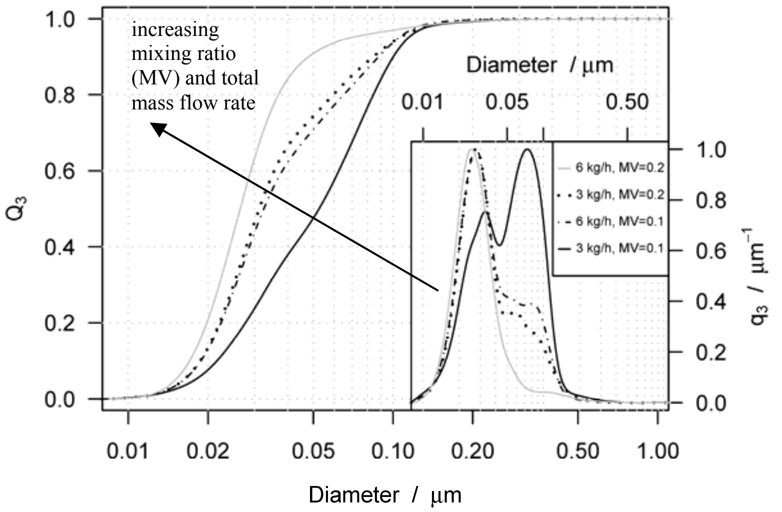

Figure 3 : Particle size distributions (Q_3 and q_3) of dispersions synthesized from iron(III) nitrate solutions with an iron product concentration of 0.0055 mol/L with different total mass flow rates and mixing ratios

It has to be considered that the material properties of the particles are not exactly known (see **MATERIALS AND METHODS**). Therefore, systematic errors concerning the weighting of the two fractions are likely. However, the existence of two particle fractions of different sizes indicates that the nuclei of the two size fractions formed at different locations or that the formation followed a different nucleation and/or growth mechanisms. A reason for that could be inhomogeneous equilibrium conditions during the heating phase of the cold metal salt stream entering the mixer, resulting in the formation of particles of different sizes or different composition. The possibility of particle formation already in the tubing adjacent to the mixer through which the metal salt stream was delivered were noticed in investigations of a different research group – however at much lower flow rates [6].

Furthermore, the electrophoretic mobility of several samples obtained under different process conditions was measured as $3.75 \pm 0.14 \times 10^{-8}$ m^2/Vs. The zeta potential derived by applying the models of Smoluchowski and of Hückel were 47.8 ± 1.8 mV and 71.7 ± 2.7 mV, respectively. No significant differences could be noticed between the samples. Values of the zeta potential well above 30 mV are a strong indication that the particles were electrostatically stabilized in suspension. This was also supported by measuring the size distributions of the course of a few weeks, where no significant changes could be observed (data not shown).

Particle dispersions were also synthesized form mixtures of iron(III) nitrate and iron(II) acetate with the addition of nitric acid. The influence of the ratio between iron(III) and iron(II) as well as the addition of nitric acid and acetic acid has been investigated. For certain compositions and mixing conditions, highly transparent particle dispersions could be obtained (see Figure 2d and 2e) in comparison to other quite turbid dispersions. In Figure 4, two representative particle size distributions of a highly transparent and a turbid dispersion are shown. The first has a very narrow size distribution with a mode at around 15 nm. A particle fraction less than 5% is bigger than 20 nm in diameter. Deviations from the conditions leading to those very narrow size distributions can cause a tailing of the mean peak and the increase of a particle fraction of sizes around 100 nm, as shown in Figure 4. Preliminary results from Raman spectroscopy indicate that the structure of these particles, in contrast to the results discussed above, is not hematite.

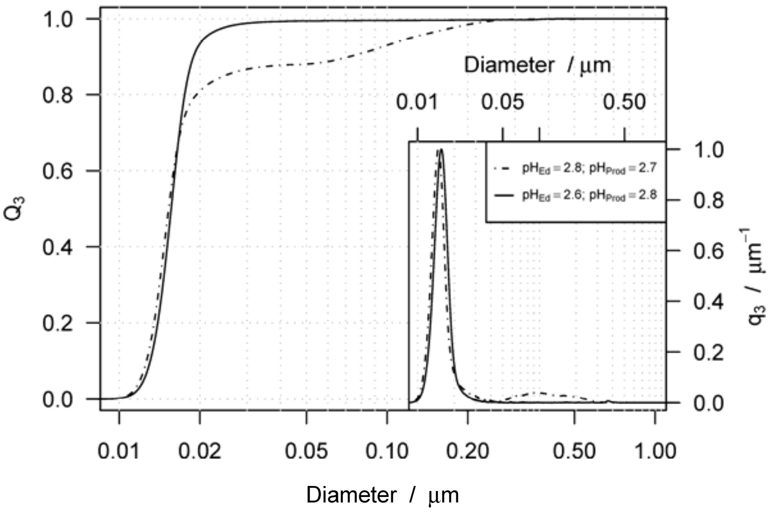

Figure 4 : Two representative particle size distributions (Q_3 and q_3) of dispersions synthesized from acidified mixtures of iron(III) nitrate and iron(II) acetate solutions with an iron product concentration of 0.001 mol/L, a total mass flow rate of 6 kg/h and a mixing ratio of 0.2

CONCLUSION

It is possible to prepare electrostatically stabilized suspensions of discrete iron oxide nanoparticles using supercritical water as a reaction medium. It was revealed by using differential sedimentation analysis, that the reaction and mixing conditions strongly influence the particle/agglomerate size distributions.

Dispersions synthesized form pure aqueous iron(III) nitrate solutions were bimodal. However, the increase of the total mass flow rate and the mixing ratio decreases significantly the fraction of bigger particles (~ 70 nm) in favour of the smaller ones (~ 25 nm). The (partial) substitution of the iron(III) nitrate with iron(II) acetate combined with the acidification using nitric acid can lead to dispersions with average sizes < 20 nm and very narrow size distributions. A definitive determination of the crystalline modification of the iron oxide particles is not possible yet.

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