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Preparation of magnetic nanoparticles by one step synthesis with morphology of particles changed based on time of reaction and temperature treatment

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ABSTRACT
In present study, nanosized iron oxides particles are synthetised by easy one step precipitation from Mohr's salt (\(\text{NH}_4\))\textsubscript{2}Fe(SO\textsubscript{4})\textsubscript{2}\cdot6H\textsubscript{2}O reacting with sodium hydroxide solution in temperature up to 60\textdegree C. When changing the time of reaction, the iron oxide particles of different shape are prepared and when drying wet extracted particles at elevated temperature of 60\textdegree C the change of 2D shaped morphology is observed. Depending on the time of reaction different ratios of FeOOH and Fe\textsubscript{3}O\textsubscript{4} are obtained in this study. DTA – TGA, XRD, FTIR and SEM are used for the characterisation of particles in this study.

1. Introduction
Synthetic routes of nanosized iron oxides particles (ionp) are of great importance due to multiple applications of these particles including biomolecular separation, magnetic resonance imagining, special coating applications, drug delivery, gravity sensors, catalysis and many others [1–3]. Ionp properties include magnetic behaviour, uniform size distribution and high surface volume. Among ionps with magnetic properties we can include a range of iron oxides (maghemite \(\gamma\)-Fe\textsubscript{2}O\textsubscript{3}, hematite \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}, magnetite Fe\textsubscript{3}O\textsubscript{4}), oxide – hydroxides (goethite \(\alpha\)-FeOOH, feroxyhyte \(\delta\)-FeOOH) and the combination of ferrous and ferric oxides.

Many synthetising techniques have been developed to prepare iron oxide nanoparticles with unique magnetic properties, tunable size and shape morphology. These include coprecipitation, microemulsion, laser pyrolysis and hydrothermal synthesis [4–6]. Very common method of their preparation is the coprecipitation where ferrous and ferric salts in water solutions have been reported to produce quite uniformed particles with particles size ranging between 10 nm to 150–200 nm [7–9]. In current approach, the modification of one step precipitation of particles exhibiting magnetic properties is performed using
the solution of Mohric salt \((\text{NH}_4)_2\text{Fe(SO}_4)_2\cdot6\text{H}_2\text{O}\) reacting with the solution of sodium hydroxide in the temperature up to 60 °C as described earlier by Author [10]. Synthesised particles are multiple times magnetically separated and washed in distilled water and the analysers are carried out upon their behaviour during the temperature annealing. XRD is employed in order to recognise the particles formed and their morphology is studied by SEM.

2. Experimental section

2.1. Materials

For the synthesis of particles, following chemicals were used, purchased from Sigma Aldrich: \((\text{NH}_4)_2\text{Fe(SO}_4)_2\cdot6\text{H}_2\text{O}\) pure, NaOH p.a. Furthermore, distilled water and few droplets of sulphuric acid were used. For all syntheses performed during the research, the same stock solutions of chemicals were prepared. The solution of \((\text{NH}_4)_2\text{Fe(SO}_4)_2\cdot6\text{H}_2\text{O}\) with the concentration of 0.03 mol dm\(^{-3}\) was stabilised in acidic area by adding a few droplets of sulphuric acid until the pH of solution reached 3. The solution of NaOH was prepared with the concentration of 0.1 mol dm\(^{-3}\).

2.2. Synthesis of iron oxide nanoparticles

For the preparation of the magnetic particles, the method described previously was used [10]. The reaction apparatus consisted of two-necked round flask with the capacity of 500 ml with mechanical agitator using glass stirrer. The flask was placed to the heated water bath to control the temperature of reaction.

In each reaction, 150 ml of stock solution of Mohric salt were used. The amount of stock solution of sodium hydroxide was empirically verified to reach pH = 11.5, 11.0, 10.5 in order to verify the impact of different pH during the reaction. This was done by mixing 15 ml of stock solution of Mohric salt with different amount of stock solution of sodium hydroxide.

For each reaction, the solution of Mohric salt was placed into the reaction flask placed to heated water bath and stirring of solution was started at medium speed 300 rpm. Calculated amount of stock solution of sodium hydroxide in beaker was then placed to the heated bath as well. When heated solutions reached the temperature of 60 °C, the sodium hydroxide solution was added through a funnel to the round flask during intensive stirring of reacting compounds at the speed of 600–900 rpm. The vigorous stirring was maintained approximately for further 3 min after the addition of whole heated solution of sodium hydroxide. Then, the stirrer speed was set back to 300 rpm and the temperature of reaction was maintained for further 150 min.

The collection of samples was done in each synthesis by pipetting approximately 30 millilitres of reacting solution directly from the flask during stirring. The reaction in heated solution was stopped by the dilution of 30 ml of sample in 150 ml of cold distilled water with the temperature of 15 °C. The particles presented in such diluted sample were magnetically separated, and the solution was mixed with 150 ml distilled water and properly washed and again magnetically separated. This procedure was done multiple times, typically 5–6 times. After this cleaning process, the particles were either dry heated for further 3 h at 40 °C to be analysed by XRD, SEM and DTA or the samples containing these washed particles dispersed in distilled water were stored in well closed plastic vials with the volume of 1.0 ml at laboratory temperature for further comparative analysis.
Such collection of samples was done at 15, 30, 50, 70, 90, 110, 130 and 150 min of a reaction. A sample of reacting solution was also withdrawn at the beginning of the synthesis to be cooled down and to measure the pH of reaction in order to verify the proper dosage of the solution of sodium hydroxide.

2.3. Characterisation

XRD were recorded using EMPYREAN Malvern Panalytical Diffractometer system using CuK-α radiation (λ = 1.5406 Å) operated at 40 KV and 100 mA on powdered samples. The size and morphology of the nanoparticles were determined by JSM-7600F Schottky Field Emission Scanning Electron Microscope operating at 1–5 kV of accelerating voltage with working distance 4–5 mm. The particles were applied either in a solution to metallic holders and left to evaporate for at least 6 h in heated chamber at 40°C or stuck on the carbon coated conductive tape. For the measurement of FTIR, Nicolet IS 10 FTIR spectrometer was used to measure the absorbance spectra in the range of 400–4000 cm⁻¹ using diamond Attenuated Total Reflectance (ATR) sampling accessory. The particles were applied in powder previously dry heated at 40°C for 3 h. TG-DTA-EGA – TA INSTRUMENTS Q600 was used for the determination of nanoparticles behaviour during heating in dry atmosphere.

2.4. Results and discussion

Depending on the time of reaction and pH of reaction, the differences in composition of formed nanoparticles and in their ratio were observed.

2.4.1. XRD and SEM analyses

Figures 1–6 represent XRD and SEM analyses results of particles precipitated at different pH. At the beginning of reaction, the goethite phase (ICSD collection code: 033615) and Magnetite phase (N. Tombs –acta crystallogr. 11) are present. With increasing time, the goethite phase disappears and the crystallinity of magnetite increases.

During the precipitation, the reactions [1–3] are expected to take place in the system of ferrous salt in excess of oxygen from atmosphere and in excess of base solution NaOH [11].

\[
\begin{align*}
\text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4 + \text{NaOH} & \rightarrow \text{Fe(OH)}_3 + 2\text{Na}_2\text{SO}_4 + 2\text{NH}_3 + 8\text{H}_2\text{O} \\
4 \text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{Fe(OH)}_3 \\
2\text{Fe(OH)}_3 + \text{Fe(OH)}_2 & \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}
\end{align*}
\]

The explanation of the goethite formation could be the presence of oxygen in the reaction solution. Goethite was formed by oxidation of Fe(OH)₂ according to the reaction [4, 12].

\[
4 \text{Fe(OH)}_2 + \text{O}_2 \rightarrow 4\text{FeOOH} + 2\text{H}_2\text{O}
\]

Formed platelet particles correspond to the goethite occurrence in anisotropic-shaped crystals. These particles are very thin with the width around 10–20 nm according to SEM. That is also the reason why the particles appear transparent during SEM analysis. Their disappearance later during the precipitation can be explained by the reaction of goethite phase with Fe(OH)₂ according to the reaction [5, 13].

\[
\text{Fe(OH)}_2 + 2\text{FeOOH} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O}
\]
Even though goethite is present according to XRD in the sample withdrawn after 10 min of reaction (see Figure 2), there is only an occurrence of rounded particles observed by SEM analysis in the sample withdrawn after 10 min of reaction. It only takes further 5 min for the platelet particles to be detectable and their highest amount according to semi-quantitative analysis using XRD spectra is detected after 30–50 min with the pH of reaction of 11.5. At 90 min of reaction at the pH 11.5, there are no further 2D structures detected and only the presence of magnetite particles is observed. This observation further confirms the reaction [5] taking place on the surface of the platelet goethite phase.

From the SEM analysis, it could be further confirmed, that the size distribution spectra of produced particles of magnetite phase is broad comprising the particles with the diameter of 10–200 nm. The diameter of platelet structured goethite phase reaches several hundreds of nanometres. During the magnetic separation, it was not expected that the goethite phase would be present in such amount thanks to its very low magnetic
properties. However, the samples with significantly high content of goethite phase can be observed. The diffraction patterns of goethite phase are of low quality which can be assigned to further confirmation of the reaction [5] proceeding on the surface of the platelets of goethite and therefore enhancing its magnetic properties thanks to the region with magnetite – like structure on the surface.

With changing the pH of reaction and shifting the pH of precipitation down to pH = 11.0, the amount of the goethite particles significantly arises with elapsing time of reaction between 50 and 70 min. This is observed in Figures 3 and 4 where XRD and SEM results are presented.

Finally, at the pH of 10.5 the occurrence of particles at highest level can be observed between 70 and 90 min. There are also defects observed on the platelets of goethite particles. This observation confirms that their reaction according to reaction [5] results in the formation of magnetite.

Figure 3. The XRD spectra of specimen withdrawn at different times of reaction; pH = 11.0.

Figure 4. The SEM of particles formed at (D) 30 min, (E) 70 min, (F) 110 min at synthesis; pH = 11.0.
To further confirm this theory, the particles separated after 70 min of precipitation proceeding at the pH of 11.0 were withdrawn and dry heated at 60°C in regular atmosphere resulting in the change of the shape of particles observed in Figure 7. There was no result recorded in XRD spectra for this change of the morphology shape.

2.4.2. DTA/TGA analysis

DTA/TGA analysis with the temperature ramp of 20°C per minute rising up to 1400°C was performed with the samples with the highest occurrence of platelet goethite phase at the pH of 11.0 and the time of 50 min and with the magnetite particles from the same reaction batch collected after 150 min of precipitation. Results are shown in Figures 8 and 9.

The first endothermic peak corresponds to the loss of water up to 100°C and is followed by the first exothermic reaction (peak at 216°C) which is believed to be caused by the oxidation of Fe²⁺ on the surface of very ultrafine magnetite particles resulting in the
formation of a thin protective film of hematite around the core of unaltered magnetite [14]. This peak is broken apart by the endothermic peak connected with significant weight loss of 2% in the region of 220–300 °C. This could be assigned to the dehydroxylation of goethite and its transformation to hematite [15]. The second broad exothermic peak at 620 °C can be attributed to the full oxidation of magnetite due to the process described by Schmidt and Vermaas [14]. Oxygen diffuses into the lattice forming Fe₂O₃ immediately. The oxidation, therefore, progresses from the surface of the grains towards the core of magnetite [14].

The major difference between the sample collected after 150 min of reaction and the sample collected after 50 min of reaction is the weight gain at 200 °C connected with the broad exothermic peak at DTA with the maximum of 175 °C. The TGA data are in accordance with presented study of Kikuchi [16] probably attributed to the quick oxidation of nanoscale
Fe₃O₄ to γ-Fe₂O₃. Further exothermic broad peak with the maximum at 500 °C could be related to the transformation of γ-Fe₂O₃ to α-Fe₂O₃ [16] and the following exothermic peak at 655 °C is quite shifted oxidation of preoxidised Fe₃O₄ due to the crossing of Currie temperature [14]. The total weight loss values of both samples were different. The weight loss of the sample containing FeOOH was 7.0% whereas the weight loss of the magnetite sample was only 2.5%. This weight loss difference between the samples is in good correlation with the semiquantitative analysis of phases from XRD, estimating the amount of goethite to be from 25 to 55 wt.%. Accordingly, the calculated weight loss to be caused by the dehydroxylation of goethite shows, that the concentration of goethite in the sample collected after 50 min of synthesis at the pH of 11.0 is 40–50 wt.%.  

### 2.4.3. FTIR analysis

For the analysis, the samples from the precipitation at pH = 11.0 were selected, withdrawn after 50 min with the maximum incidence of observed platelet nanoparticles of goethite, after 110 min, when the nanoparticles of magnetite were formed and after 150 min, when the nanoparticles of magnetite with better crystallinity were found (see Figure 3). Results of FTIR analysis are presented in Figure 10.

The characteristic FTIR spectrum of pure magnetite phase after 110 and 150 min can be observed in Figure 7. The Fe – O stretch band is present at 530 cm⁻¹. This is in accordance with the study of Lesiak et al. [17]. Although this stretch band is reported elsewhere at 580 cm⁻¹ [18, 19], reported data result from the measurements in a polar environment of KBr pellet, which may shift the peak position.

The FTIR spectrum after 50 min shows the overlap of goethite spectra: 431, 890, 1129, 1638 [20] together with magnetite presented by the absorbance at 538 region for characteristic Fe – O stretch bands at 530 cm⁻¹ [17].
3. Summary and conclusions

Easy, one step precipitation synthesis of magnetic nanoparticles of iron oxides was examined under different pH of reaction and with different time of reaction. The final products of all reactions after the time of reaction of 150 min are pure magnetite particles. Depending on the time of reaction, differently shaped magnetic particles can be prepared. These are presented by extremely thin platelet particles of goethite with the incidence depending on the pH of precipitation synthesis and time of reaction. With increasing pH, their diameter increases. The stability of platelet goethite particles at higher temperature of drying of 60°C was examined. Higher temperature results in the modification of their shape which further conforms to their very easy oxidation in the air atmosphere. All proposed analysis results confirmed that formed particles were goethite and Magnetite nanoparticles.

Disclosure statement

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