Synthesis and characterization of nanostructured hematite for wastewater treatment

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Abstract: *Removal of heavy metals ions from water sources still represents a challenge and different materials are being developed in order to overcome it. Iron oxide nanomaterials receive a lot of attention because of their small size, high surface area, biocompatibility and low cost. However, most of the reported synthesis methods are multi-step and time-consuming. We investigated the co-precipitation method for the synthesis of nanostructured hematite prepared at different temperatures and different calcination times. The obtained materials were characterized by X-ray powder diffraction, scanning electron microscopy and infrared spectroscopy. The adsorption capacity for Pb(II) ions was found to be about 6–12 mg of adsorbed Pb(II) per gram of adsorbent.*
Keywords*: hematite, nanoparticles, nanocrystals, water treatment, microstructure*

1. Introduction

Nanostructured iron oxides have been found suitable for applications in environmental nanotechnology, particularly in wastewater treatment as catalysts, coagulants in flocculation processes and efficient adsorbents for organic wastes and heavy metal ions [1]. Among the various nanostructured iron oxides, hematite (α-Fe_2O_3) nanoparticles have been used for removal of metal ions [2-5], Cr(VI) [6-8], acid dyes [9] and organic carbon [10]. Nanostructured hematite has also been applied for catalytic degradation of organics wastes [6,11-13] and in coagulation and flocculation processes of surface water [14]. These applications are favored by the low toxicity of hematite and the relatively cheap and easy preparation procedures. However, further studies on the methods for preparation of nanostructured hematite are needed in order to find the optimal conditions for production of materials with high adsorption capacity.

Nanostructured hematite is usually prepared by using various modifications of the so-called co-precipitation method [2,5,13,15]. This approach involves precipitation of Fe(III) by alkaline aqueous solutions, followed by washing of the obtained precipitate and its calcination at high temperatures, up to 400–500 °C. Variations in the preparation conditions can result in significant variations in the quality of the final product. In this article we report on the preparation of nanostructured hematite by a modification of the co-precipitation synthesis [2] and studied the effects of calcination temperature and time on the crystallite size and adsorption capacity for Pb(II) ions.

2. Experimental part

Synthesis of hematite. Solution of ammonia (2 M; ~138 ml) was added dropwise to 250 ml 0.1 M ferric chloride (prepared from 6.75 g $FeCl_3.6H_2O$) up to pH 10 upon magnetic stirring (600 rpm) at room temperature. All reagents were of analytical grade. The obtained dispersion was stirred for 2 hours at room temperature and the precipitate was centrifuged (3000 rpm for 10 min), triplicate washed with distilled water to remove soluble salts and let to air dry. The dried substance was calcined in a furnace at different temperatures (200–500 °C) for different time periods (1–4 hours). The calcinated samples were grinded in a mortar before further use.

Characterization of materials. Scanning electron microscopy was performed with Hitachi TM4000 microscope. Samples for SEM were deposited on. double sided duct tape and coated with gold before observation. X-ray powder diffraction (XRD) data were recorded by using a X-ray diffractometer Empyrean (PANalytical) with CuK_α radiation. Fourier transform infrared (FTIR) spectra were measured by using an infrared spectrometer Nicolet 6700 (Thermo Scientific). Samples for FTIR analyses were prepared as KBr tablets.

Adsorption of Pb(II). The tested adsorbent (50 mg) was mixed for 10 minutes with 10 ml 3 mM solution of lead(II) nitrate. The suspension was then filtered through a syringe filter (0.22 μm). The concentrations of Pb(II) in all samples before and after adsorption were determined by standard complexometric titration with 1 mM Na_2EDTA at pH 6 (acetate buffer) and xylenol orange indicator. The adsorbance capacity was expressed as milligrams of adsorbed Pb(II) per gram of adsorbent.

3. Results and discussion

It is known that ferric ions from aqueous solutions are precipitated in alkaline medium as amorphous ferric hydroxide and/or β-ferric oxyhydroxide [16]. Preliminary studies indicated that in the precipitation step of our experiments ferric oxyhydroxide, Fe(O)OH, was obtained with quite small crystallite size of about 3–4 nm. Heating of the dried precipitate at high temperatures (higher than 200 °C) for few hours resulted in the formation of hematite (α-Fe_2O_3) with crystallite sizes of 15–22 nm. Observation by scanning electron microscopy (SEM) showed a powdered material that contained particles of various sizes, from submicron to few micrometers (Fig. 1).

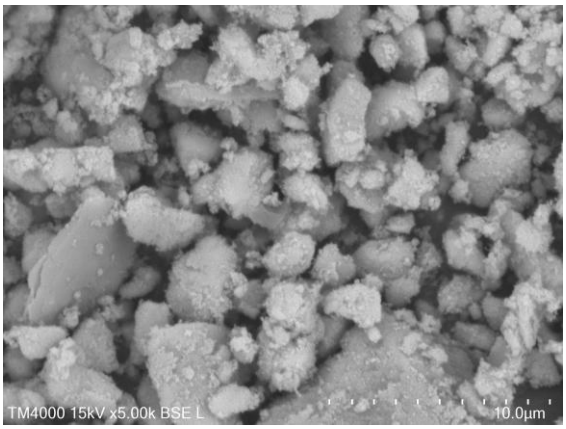

Fig. 1 *SEM image of a hematite sample heated at 400 °C for 2 hours.*

Analysis by infrared (FTIR) spectroscopy showed absorbance peaks for Fe–O bonds at 461 and 536 cm^{-1}, which are characteristic for hematite. Similar FTIR of hematite nanoparticles prepared by the chemical precipitation process were previously obtained, although with a slight different peak positions [17].

XRD diffraction patterns of the samples prepared by heating for 2 hours at different temperatures are shown in Fig. 2. The sample prepared at 200 °C appeared practically amorphous, while those prepared at higher temperatures all contained hematite with average size of crystallites about 15–22 nm. The samples contained also a small amount of amorphous substance. The size of crystallites did not appear to depend significantly on the heating temperature in this particular interval (300–500 °C). Another series of experiments was performed at a constant heating temperature of 400 °C and various heating times. The XRD patterns showed almost identical structure of the obtained hematite phase (Fig. 3).

The experiments on adsorption capacity for Pb(II) ions were performed at relatively high Pb(II) to adsorbent ratio in order to evaluate the maximal adsorption capacity (when the surface of the adsorbent is almost saturated with adsorbed species). The

adsorption capacity of the samples heated for 1–3 hours at 400 °C was about 6–8 mg of Pb(II) per gram adsorbent and did not depend significantly on the heating time (Fig. 4a). The sample heated for 4 hours showed slightly higher adsorption capacity of 12 mg/g. The sample heated for 2 hours at 200 °C showed a similar adsorption capacity of 12 mg/g, while using higher heating temperatures resulted in slightly reduced adsorption capacities of about 8 mg/g (Fig. 4b).

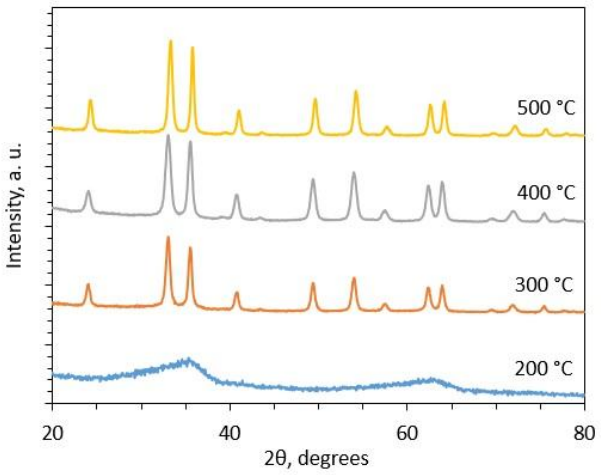

Fig. 2 *XRD patterns of hematite samples prepared by heating at different temperatures for 2 hours.*

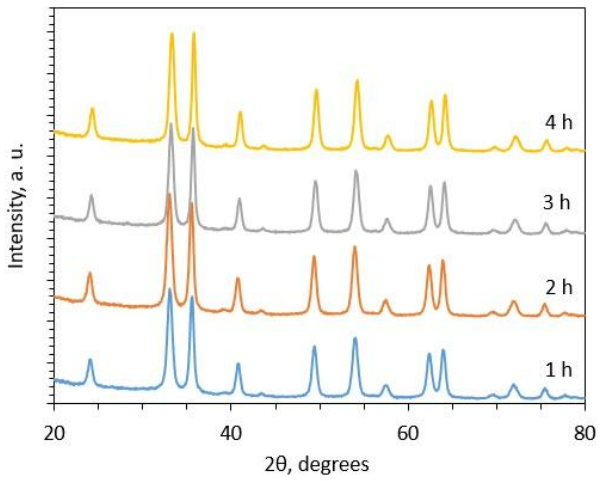

Fig. 3 *XRD patterns of hematite samples prepared by heating at 400 °C for different time.*

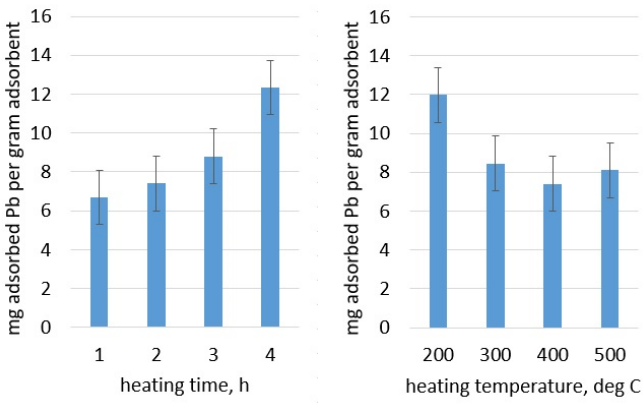

Fig. 4 *Adsorption capacity for Pb(II) of hematite samples prepared by: a) heating at 400 °C for different time; b) heating at different temperatures for 2 hours.*

4. Conclusions

Powder samples of nanostructured hematite were prepared by the co-precipitation, followed by heating at various temperatures (200–500 °C) and time periods (1–4 hours). All samples prepared at temperatures higher than 200 °C contained crystallites of average size about 15–22 nm. The crystallite size and phase composition did not depend significantly on heating time. The obtained materials appeared to be promising candidates for application as adsorbents in wastewater treatment with adsorption capacity for Pb(II) ions within the ranges of 6–12 mg of adsorbed Pb(II) per gram of adsorbent.

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6. References

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