## Supplementary information

To prove the formation of $Fe(OH)_2$ as an intermediate in the synthesis of feroxyhyte nanoparticles a Mossbauer spectroscopy of frozen aqueous solutions (FAS) were used. A set of aliquots was taken from reaction mixture at different stages of synthesis, rapidly frozen by immersion into liquid nitrogen and studied by transmission Mossbauer spectroscopy for identification of intermediates formed. According to spectra obtained, ultradispersed $Fe(OH)_2$ was formed from the $FeCl_2$ solution in alkali medium (pH=8) before oxidation of $H_2O_2$ and stabilized by humic macromolecules.

The Mossbauer spectra of the $Fe(OH)_2$ sample with or without HS are given in Fig.1 and the corresponding fitted parameters are listed in Table. The spectra parameters are close to those of $Fe(OH)_2$ (A. Gehin, J.-M. Greneche, et al. Geochim. Cosmochim. Ac. 2007, 71, 863–876). There are two components in the spectrum of $Fe(OH)_2$ obtained in presence of HS, one of which was ascribed to bulk $Fe(OH)_2$, whereas the second can be described as a new spectral component (($\delta$ = 1,28 mm/s, $\Delta$ = 2,83 mm/s) related to the interaction of HS with the surface of $Fe(OH)_2$.

**Table 1** Hyperfine parameters of the $Fe(OH)_2$

| Sample/ temperature | Component | δ | Δ | Area fraction |
|---|---|---|---|---|
| | | mm/s | | % |
| $Fe(OH)_2$ 78 K | A1 | 1.29 | 3.01 | 100 |
| $Fe(OH)_2$-HS 78 K | B1 | 1.29 | 3.02 | 62 |
| | B2 | 1.28 | 2.83 | 38 |

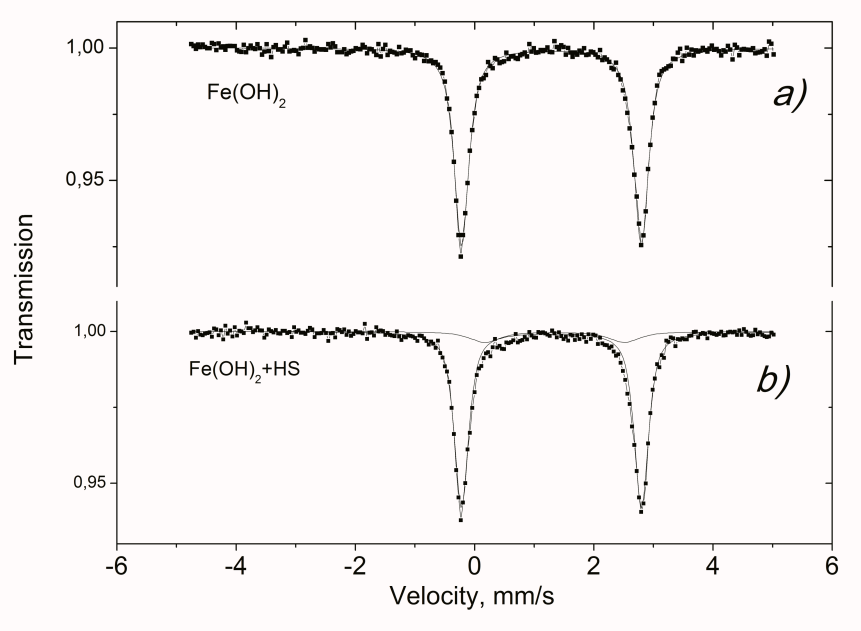



**Fig.1** Mossbauer spectra at 78K of the frozen reaction mixtures (pH 8): a) – $Fe(OH)_2$ and b) – $Fe(OH)_2$ in the medium of HS.

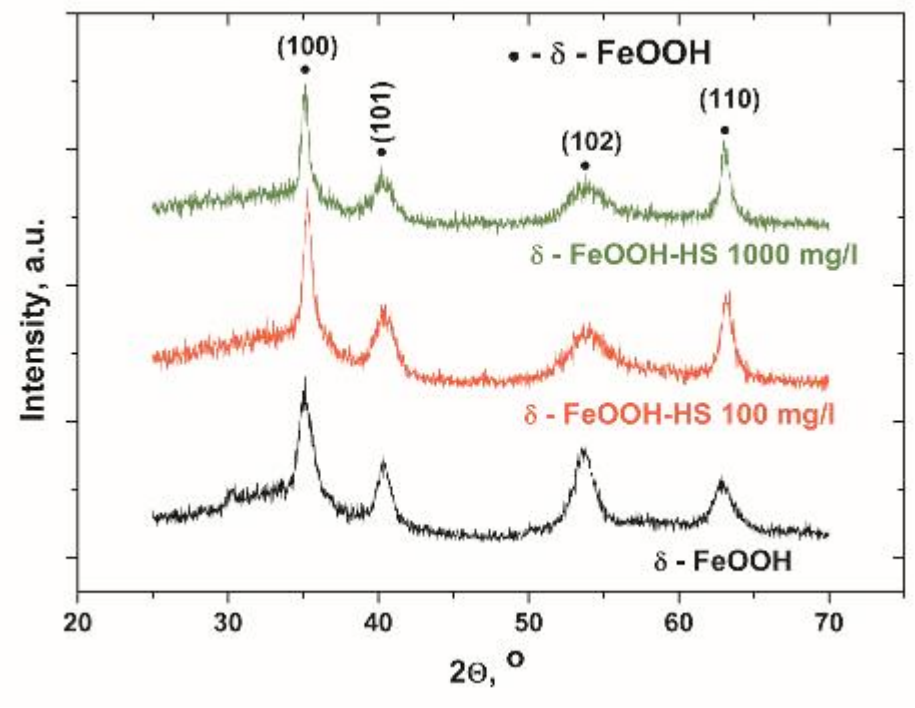
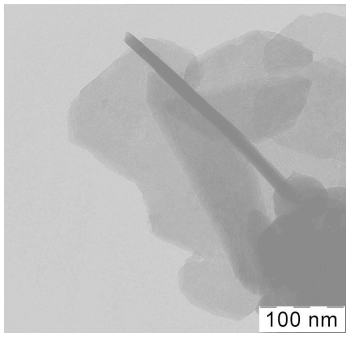


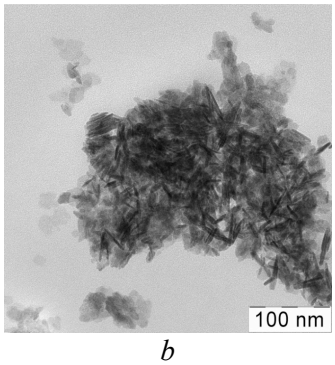

**Fig.2** X-ray diffractograms of δ-FeOOH phases. The lower curve corresponds to pure δ-FeOOH, while middle and upper curves represent δ-FeOOH obtained in 100 mg/ml and 1000 mg/ml HS solutions.

**Table 2** Measurements of FWHM of peaks and unit cell parameters of δ-FeOOH

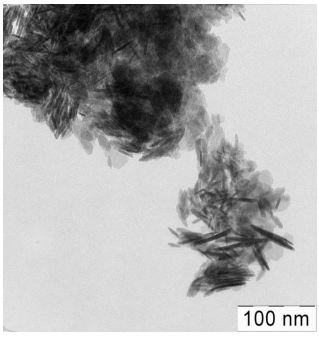
| Sample | Unit cell parameters | | FWHM, deg | | | |
|---|---|---|---|---|---|---|
| | a, Å | c, Å | (100) | (101) | (102) | (110) |
| δ-FeOOH | 2.954(1) | 4.600(2) | 0.96(7) | 1.08(7) | 1.40(9) | 1.66(9) |
| δ-FeOOH -100 mg/ml HS | 2.947(1) | 4.583(6) | 0.59(4) | 1.52(9) | 2.17(9) | 0.82(5) |
| δ-FeOOH -1000 mg/ml HS | 2.943(1) | 4.555(5) | 0.46(3) | 1.49(9) | 2.17(9) | 0.60(4) |



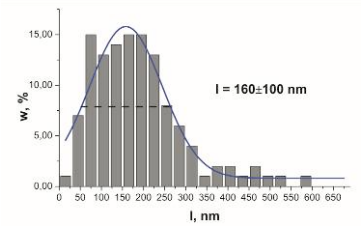

*a*



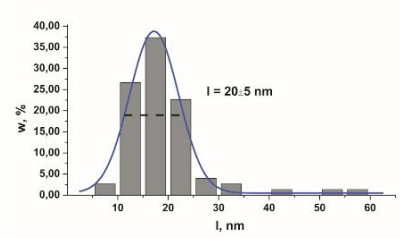

*b*



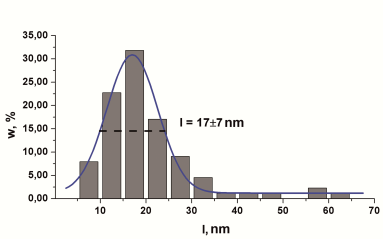

*c*



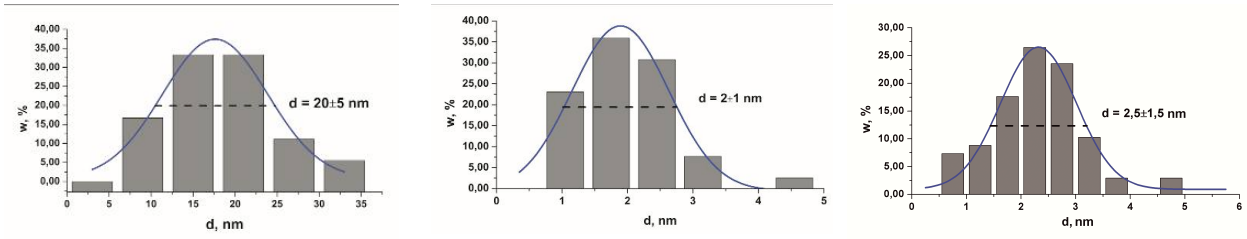

*a-1*




*b-1*




*c-1*




*a-2* *b-2* *c-2*

**Fig.3** TEM micrographs and size distribution (sizes along the largest axis and thickness) for pure δ-FeOOH – *a)* and the composite δ-FeOOH-HS with concentration HS 100 mg/l-*b)* and 1000mg/l-*c)*.

The effects of concentration of humic substance in the composite FeOOH-HS on the size of δ-FeOOH are presented in Figure 3. From these results, it is found that the size of feroxyhyte nanoparticles wasn't significantly increased with an increase of the concentration of HS from 100 mg/l to 1000 mg/l.

Cytotoxicity of prepared anisotropic nanoparticles was analyzed using NCTC clone L929 cells grown in DMEM/F12 (1 : 1) medium with 5 vol% of fetal bovine serum (FBS) and 100 IU/ml penicillin/streptomycin in the atmosphere of 5% $CO_2$. After 1 h, a part of the medium was replaced by suspensions of modified or unmodified feroxyhyte nanoparticles. The final dilution ratio for the suspensions was 10. After 24 h, visual evaluation of the cell culture was carried out using 0.1% solution of trypan blue with a luminescence microscope Axiovert 200 (Zeiss, Germany). In addition, viability of the cells was measured using an MTT assay based on reduction of the MTT reagent (3-(4,5-dimethylthiazolyl-2)-2,5-diphenyltetrazolium bromide, Sigma) by mitochondrial and cytoplasmic dehydrogenases of living metabolically active cells. The cell culture which was incubated in serumless DMEM/F12 (1 : 1) medium was used as a positive control sample. DMEM/F12 (1 : 1) medium with 20% DMSO (Sigma), which provoked mass mortality of cells, was used as negative control.
The cell viability obtained by the MTT assay was expressed as a fraction of viable cells and normalized to that of cells without co-incubation with δ-FeOOH and δ-FeOOH-HS (blank control). The cells with co-cultured δ-FeOOH and δ-FeOOH-HS demonstrated a similar behavior to the blank control. Live / dead staining demonstrated viability about 100 % and 110% for δ-FeOOH and δ-FeOOH-HS, correspondingly. The high viability in the presence of δ-FeOOH-HS can be explained by a stimulating impact of HS on the cell culture. At the same time, the level of MTT reduction in the presence of 20% DMSO was significantly lower than in the control, that demonstrate cell death in the presence of toxic reagent. Thus the results obtained showed no evident cytotoxicity of δ-FeOOH and δ-FeOOH-HS (Fig.4).

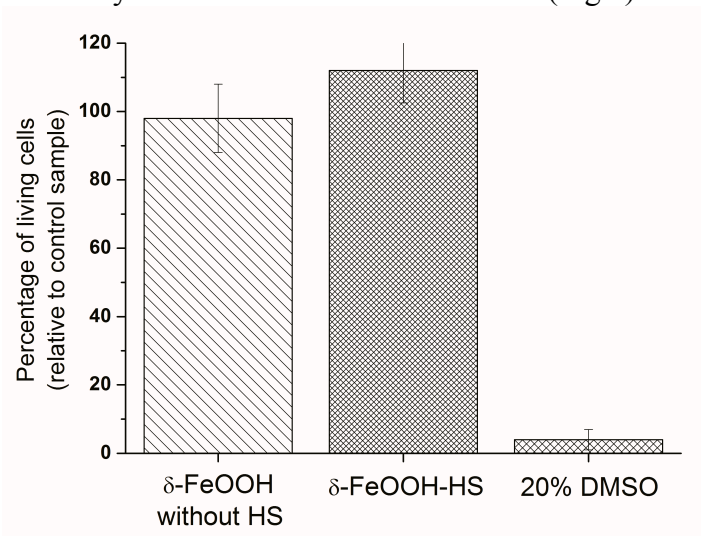



**Fig. 4** MTT reduction by NCTC cells (MTT viability test) in presence of δ′-FeOOH and δ′-FeOOH – HS in the cultural medium of DMEM/F12 supplemented with 5%FBS.

Electronic Supplementary Material (ESI) for CrystEngComm