

# Mechanochemical Formulation of Coating Iron Oxides Magnetic Nanoparticles with Humics

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**Summary:** This paper identifies properties of magnetite nanoparticles when combined with macromolecules of humic substances in a nanocomposite matrix using mechanochemical dispersion technique. This method is described providing an inexpensive production methods for sorbents with the requisite properties for binding heavy metals.

**Keywords:** humic substances; magnetic polymers; metal-polymer complexes; nanocomposites; stabilization

## Introduction

There has been increasing interest in the use of magnetic carriers for separation of various ecotoxins including heavy metals and radionuclides,<sup>[1,2]</sup> because magnetic separation technique possesses the advantages of rapidity, high efficiency towards low levels of pollutants, cost-effectiveness due to using inexpensive natural sorbents, and lack of negative effect on biological activity.<sup>[3]</sup> Magnetic carriers are usually composed of the magnetic cores to ensure a strong magnetic response and a polymeric shell to provide favorable functional groups and features for various applications.<sup>[4,5]</sup> The most commonly used magnetic nanomaterials are  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>, which are formed by either coprecipitation of Fe(II) and Fe(III) or oxidation-precipitation of Fe(II) in a basic environment.<sup>[6,7]</sup> Nano-sized magnetic car-

riers possess quite a good performance due to high specific surface area and the absence of internal diffusion resistance.<sup>[8,9]</sup>

Recently, we reported that magnetic nanocomposites were developed using Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) and humic acids (HA) as NPs stabilizer for use as magnetic sorbents for uranyl ions.<sup>[1]</sup> The sorbents under study were found to reveal a high sorption capacity towards uranyl ions. We have studied the mechanochemical formulation of the nanocomposite at the strict conditions, i.e. only one ratio of organic (humic acids) and inorganic (magnetite) precursors at 30 min of dispersion to prepare the humics-conjugated Fe<sub>3</sub>O<sub>4</sub> particles. This study was aimed to estimate effects of various concentration of humic substances and various dispersion time at the mechanochemical synthesis of magnetic humics-based nanocomposites. This method is described providing an inexpensive production methods for nanocomposites to be used as sorbents with the requisite properties for binding ecotoxins. These nanocomposites were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Mössbauer and Fourier transform infrared (FTIR) spectroscopy, and acoustic spectroscopy.

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## Experimental Part

### Parent Humic Material

Sodium humate used as humic preparation (HP) for humics-bound magnetite NPs formulation were isolated from commercially available HP of brown coal from Sakhalin deposit "Solntsevskoe" (Biomir-2000 Ltd, Russia). For this purpose, a weight of sodium humate was dissolved in distilled water and centrifuged to discard the insoluble mineral part present and evaporated to dryness at 60 °C. Elemental and functional group composition of HP, mass, %; C - 32.6; H-2.6; N -1.4; ash -26; total acidity - ~4.8 mmol/g.

### Preparation and Characterization of Magnetic Particles

The bare  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles were synthesized at pH 10 with stirring under pH control as described previously.<sup>[1]</sup> The magnetic humics-based nanocomposites were synthesized by mechanochemical dispersion technique. In a typical procedure, magnetite concentration embedded in each composite ranged from 20 to 80 wt. %, i.e. a weight of 1 to 4 g of magnetite prepared and a weight of 4 to 1 g of HP accordingly were placed into an wolfram carbide mortar with wolfram carbide balls (21,5 g) and milled in a SPEX SamplePrep high-energy grinder at the rate of 1425 rpm during 1–30 min accordingly.

All magnetic preparations obtained are listed in Table 1

Acoustic spectrometry was carried out using Dispersion Technology – Acousto-Phor ZetaSize 1200, Dispersion Technology Inc. The phase composition analysis of the nanocomposites obtained was performed using X-ray diffractometry on a DRON-UM-2 diffractometer using  $\text{Cu}(\text{K}_\alpha)$

radiation. Fourier transform infrared (FTIR) spectra were obtained by pressing the HP sample into KBr pellet and analyzing with a FTIR spectrometer IR-200 (ThermoNicolet, USA) on spectral range of 400–4000  $\text{cm}^{-1}$  (4  $\text{cm}^{-1}$  resolution, 64 scans per spectrum). Mössbauer spectra were recorded on a spectrometer (MS-1101-E, Mostec) with a  $\text{Co}^{57}(\text{Rh})$  source in the constant acceleration regime. The calibration by rates was performed relative to the spectrum of metallic  $\alpha$ -Fe. Characterization of samples by scanning electron microscopy (SEM) was carried out by using a SUPRA 55VP-32-49 microscope.

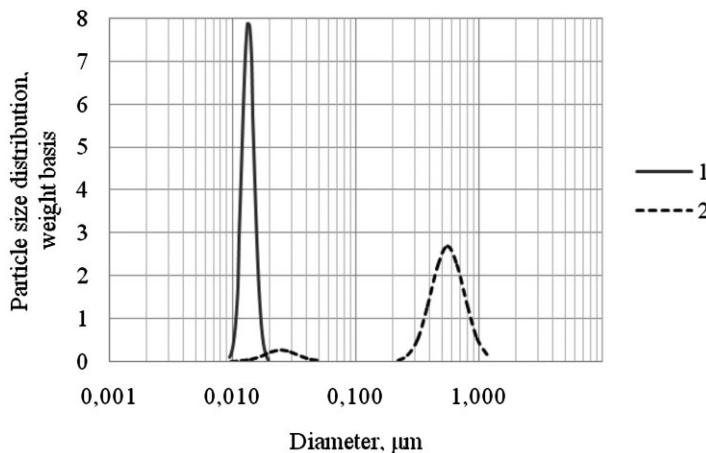
## Results and Discussion

Acoustic spectrometry methods have been found to be useful tools for the analysis of a near process characterization for particles. Particle size distribution analysis of nanocomposites suspensions (pH ~8) showed (Figure 1) an average size of ~14 nm for the as-prepared bare  $\text{Fe}_3\text{O}_4$  particles, also the aggregation of the prepared material in 2 weeks, that results in ~1  $\mu\text{m}$  in size and wide particle size distribution. These results clearly demonstrated that the bare  $\text{Fe}_3\text{O}_4$  nanoparticles aggregated due to magnetic self-aggregation of the particles. Therefore, mentioned above can be the basic reason for the stabilization of magnetic nanoparticles to avoid aggregation of nanosized particles.

According to ref.<sup>[6,7]</sup>, humic acids have a high affinity to  $\text{Fe}_3\text{O}_4$  nanoparticles, and sorption of HA on the  $\text{Fe}_3\text{O}_4$  nanoparticles enhanced the stability of nanodispersions by preventing their aggregation. The data of acoustic spectrometry for composites produced by mechanochemical dispersion

**Table 1.**  
Magnetic preparations produced.

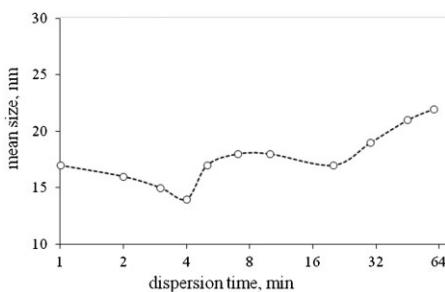
Derivative	Cipher	Description
$\text{Fe}_3\text{O}_4$ -HP20-M10		$\text{Fe}_3\text{O}_4$ -HP at 80:20 wt. % ratio, dispersion time is 10 min
$\text{Fe}_3\text{O}_4$ -HP50-M10		$\text{Fe}_3\text{O}_4$ -HP at 50:50 wt. % ratio, dispersion time is 10 min
$\text{Fe}_3\text{O}_4$ -HP80-M		$\text{Fe}_3\text{O}_4$ -HP at 20:80 wt. % ratio, dispersion time is varied from 1 (M1) till 30 (M30) min

**Figure 1.**

Dynamics of aggregation of the bare  $\text{Fe}_3\text{O}_4$  particles: (1) - as-prepared, (2) - in 2 weeks.

(Figure 2) have shown reduction of mean size for  $\text{Fe}_3\text{O}_4$  nanoparticles in the period to 20 min of dispersion. The most prominent decrease of the mean size for  $\text{Fe}_3\text{O}_4$  (up to  $\sim 14$  nm) occurred at 4 min of dispersion. Up to  $\sim 25$  nm enhanced the mean size in 30 min of dispersion as compared with native  $\text{Fe}_3\text{O}_4$  was found.

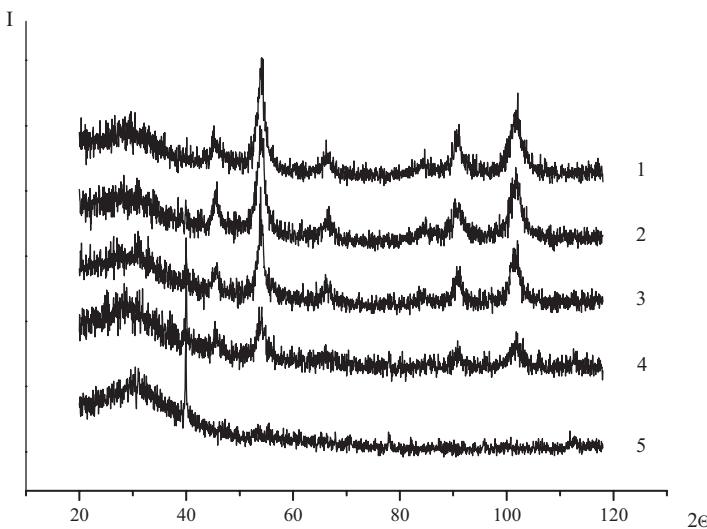
Comparative analysis of the diffractograms of magnetic composite samples has shown that the major phase formed during a mechanochemical dispersion in the presence of humic substances is a magnetite  $\text{Fe}_3\text{O}_4$  (Figure 3). XRD results indicate that the addition of humics to  $\text{Fe}_3\text{O}_4$  nanoparticles have not changed the crystal structure of nanoparticles, the intensity of the peaks is reduced with using of humic substances.

**Figure 2.**

Dynamics of the mean size of  $\text{Fe}_3\text{O}_4$  in the process of dispersion for  $\text{Fe}_3\text{O}_4\text{-HP80-M}$ .

Infrared spectra of the parent humic material and magnetic composite are shown in Figure 4. For all samples of magnetic humics-based composites obtained by mechanochemical dispersion same major bands can be seen as for parent humic materials, nominally: 3300, 2900–2800, 1600, 1400, 1110, 750 and  $850\text{ cm}^{-1}$ . It should be noted that intensity of the band at 3550–3450  $\text{cm}^{-1}$  (H-bonded hydroxyl groups) is the highest in the magnetic composites. The latter shows the successful coating of humate on the  $\text{Fe}_3\text{O}_4$  surface. FTIR spectrum (Figure 4) shows the C=O stretches of  $\text{Fe}_3\text{O}_4\text{-HP}$  at  $\sim 1600\text{ cm}^{-1}$ , indicating the carboxylate anion interacting with the iron oxides surface as the C=O stretches in free carboxylic acid would above  $1700\text{ cm}^{-1}$ .<sup>[3]</sup> Very pronounced alterations across the whole spectral range were observed under 30 min of dispersion for composite. The intensity of all bands for  $\text{Fe}_3\text{O}_4\text{-HP80-M30}$  is decreased with an increase in dispersion time, which is due to the disappearance of bonds in various structural units. This might be attributed to the fact that native composite based on humate macromolecules and magnetite has been destroyed during dispersion.

The Mössbauer spectra of the initial sample of magnetite (zero test) and nanocomposites measured at 295 K are pre-



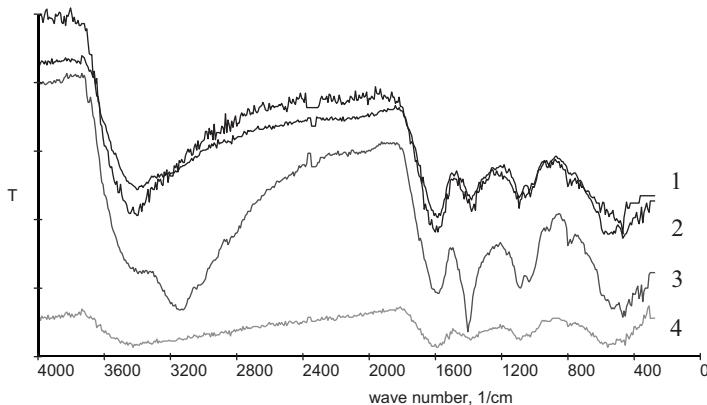
**Figure 3.**

XRD-patterns of composites and their precursors: (1) -  $\text{Fe}_3\text{O}_4$ ; (2) -  $\text{Fe}_3\text{O}_4$ -HP20-M10; (3) -  $\text{Fe}_3\text{O}_4$ -HP50-M10; (4) -  $\text{Fe}_3\text{O}_4$ -HP80-M10, (5) - HP.

sented on Figure 5. The spectra represent a sextet with wide asymmetric lines. The Mössbauer spectra of the investigated samples are characteristic for small particles of magneto-ordered phases. Presence of quadrupole doublet allows to draw a conclusion about presence in the samples of small superparamagnetic particles. The analysis of the obtained spectra and the restored distribution has shown that sextet lines became narrower. Modeling decoding of a spectrum has shown that the synthe-

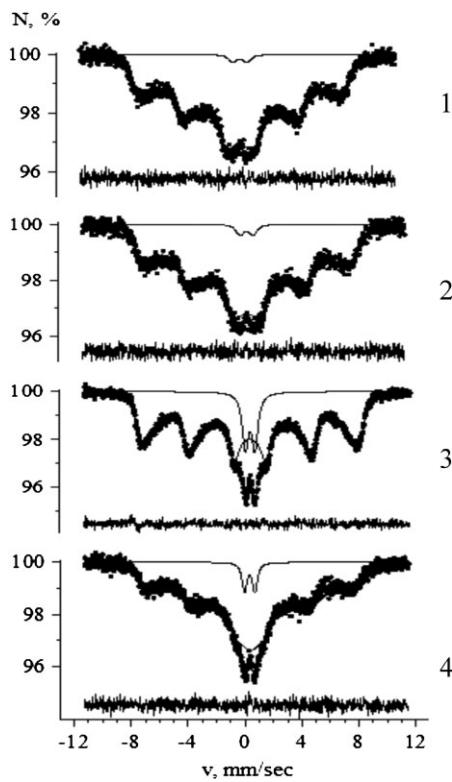
sized substances apparently is maghemite or a mix of maghemite and magnetite.

Clearly, with increasing humate concentration an decrease in the intensity of signals can be detected, that means the decline of particles size. At the same time in composite  $\text{Fe}_3\text{O}_4$ -HP50-M10 there are narrower lines in the sextet. It can be concluded that for this sample there are more homogeneous particle size distribution in comparison with native  $\text{Fe}_3\text{O}_4$  due to introduction of HP in the system.



**Figure 4.**

FTIR spectra for: (1) - HP; (2) -  $\text{Fe}_3\text{O}_4$ -HP80-M1; (3)  $\text{Fe}_3\text{O}_4$ -HP80-M10; (4)  $\text{Fe}_3\text{O}_4$ -HP80-M30.

**Figure 5.**

$^{57}\text{Fe}$  Mössbauer spectra of nanocomposites with different  $\text{Fe}_3\text{O}_4$  concentrations: (1) the bare  $\text{Fe}_3\text{O}_4$ ; (2)  $\text{Fe}_3\text{O}_4$ -HP20-M10; (3)  $\text{Fe}_3\text{O}_4$ -HP50-M10; (4)  $\text{Fe}_3\text{O}_4$ -HP80-M10.

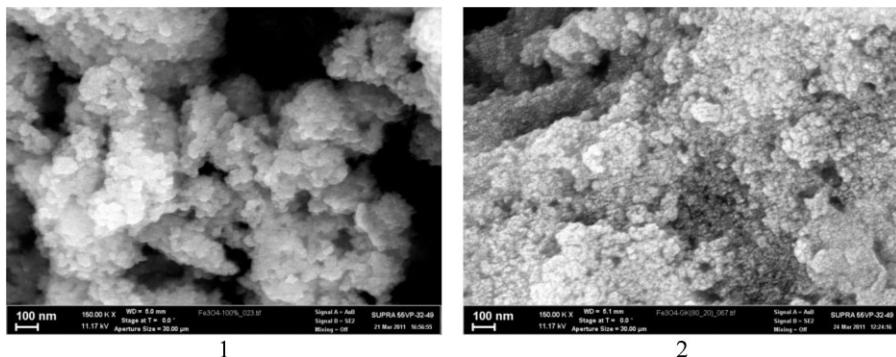
The synthesized iron oxide particles had a mean diameter ranged from 20 to 60 nm as determined by SEM. Figure 6 shows the

SEM images of the as-prepared  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ -HP20-M10.

The entire  $\text{Fe}_3\text{O}_4$ -HP20-M10 particles contained aggregates with uniform size and fractal feature, the core of the  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles conjugated with humate is decreased as compared to the bare  $\text{Fe}_3\text{O}_4$  nanoparticles.

## Conclusion

In the present work a synthesis of magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles was carried out by mechanochemical dispersion directly into matrix of natural polyelectrolytes (humic substances). According to electron microscopy data and acoustic spectrometry, in presence of humic substances spherical magnetite nanoparticles with transversal size 20–100 nm are formed. At the same time absence of humic substances in reaction mixture leads to uncontrolled growing of nanoparticles up to micron sizes. Size effect of stabilization of the magnetite nanoparticles using humic substances were confirmed by XRD and Mössbauer spectroscopy. Apparently such differences in efficiency of stabilization of nanoparticles with different concentration of humic substances are connected with ability of HS to form organo-inorganic compounds with metal ions, oxides due to a set of functional groups. This data open up possibilities for development of new tech-

**Figure 6.**

SEM images: (1) for the humics-free  $\text{Fe}_3\text{O}_4$  particles and (2) humics-conjugated magnetite particles  $\text{Fe}_3\text{O}_4$ -HP20-M10.

niques of stabilization of iron oxide nanoparticles using natural polyelectrolytes.

**Acknowledgements:** This work supported by Federal Program of the Russian Science and Education Ministry (GK 02.740.11.0693, GK 14.740.11.0415).

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