

NANOCOMPOSITES BASED ON MAGNETITE AND ACTIVATED CARBON: SYNTHESIS, SORPTION PROPERTIES, BIOAVAILABILITY

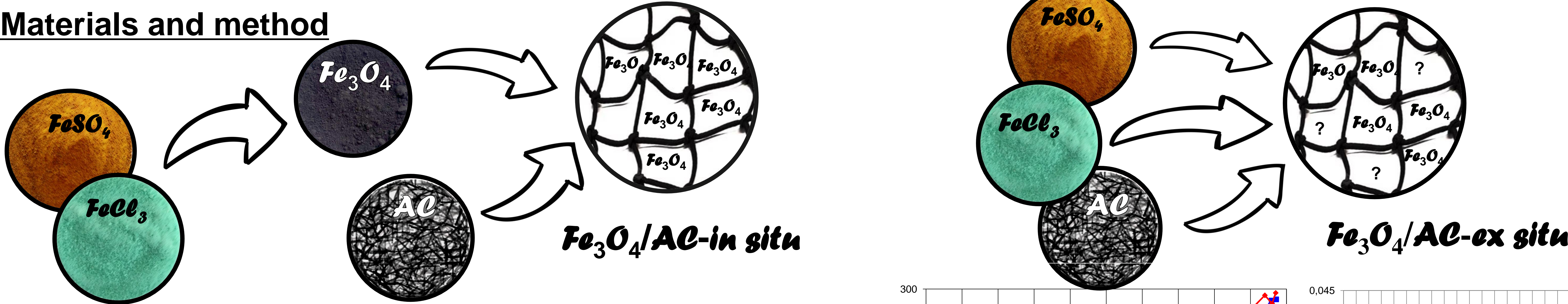


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Hybrid organo-inorganic sorbents based on activated carbon (AC) filled with magnetically active nanoparticles provide the efficiency of purification of technogenic environment by combining the sorption properties of AC and magnetic properties of nanoparticles in order to further use the magnetic separation technique. This study was aimed to search for an effective method for the synthesis of magnetic nanocomposites based on AC and magnetite nanoparticles by chemical coprecipitation using two approaches: by preliminary synthesis of magnetite nanoparticles by chemical coprecipitation from solutions of ferrous and ferrous salts and the subsequent introduction of nanoparticles into AC matrix (Fe_3O_4 -AC-*ex situ*) and by synthesis of magnetite nanoparticles into AC matrix (Fe_3O_4 -AC-*in situ*).

Materials and method



Microstructure

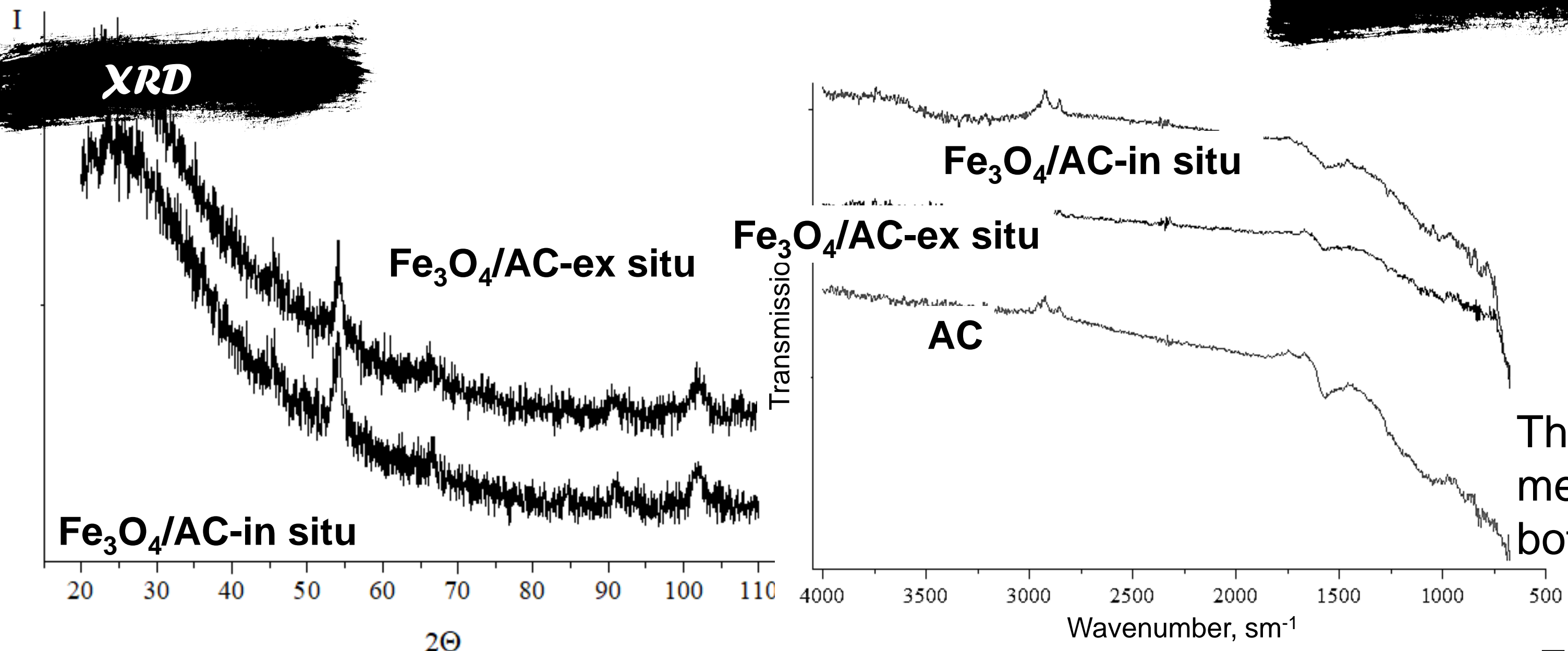


Fig. 1 XRD and Mossbauer spectra for NPs (DRON-UM-2, Cu(K α), 1 θ /min; MS-1101-E, Mostec, helium cryostat SHI-850-5 (4.5 \div 500 K), ^{57}Co in matrix of Rh, etalon is α -Fe)

According to XRD: major phase is a magnetite Fe_3O_4 . The average particle size is 6.4 and 9.2 nm for Fe_3O_4 /AC-*in situ* and Fe_3O_4 /AC-*ex situ* samples, respectively. A weakening of the characteristic vibrational band of the carbonyl group (Fe_3O_4 /AC-*ex situ*) is observed. Simultaneously, bands corresponding to symmetric and asymmetric vibrations of carboxylate ions appear in the spectra.

Texture characteristics

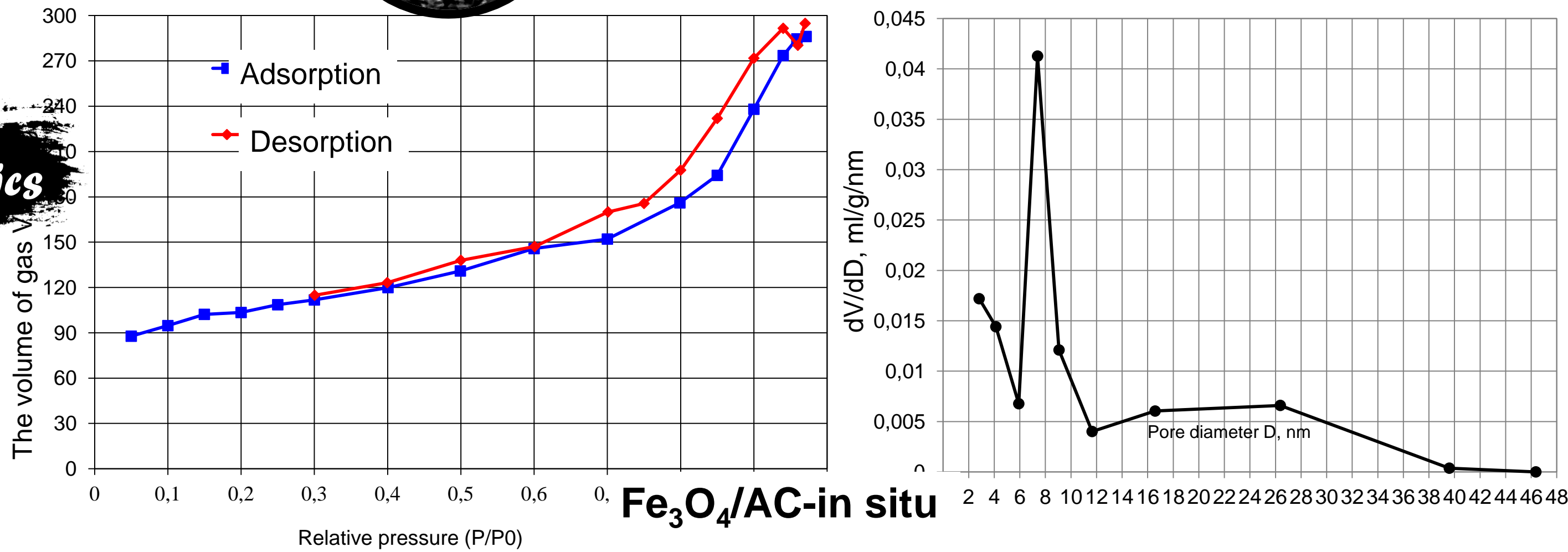


Fig. 2 Isotherms of nitrogen adsorption and desorption of samples and pore size distribution diagrams

The structure of Fe_3O_4 /AC-*in situ* and Fe_3O_4 /AC-*ex situ* samples is dominated by mesopores with a diameter of 3–9. The nucleation and growth of nanoparticles in both synthesis methods occur on the surface of AC, not into AC pores.

Table 1. Textural characteristics of the samples

| Sample name | BET specific surface area, m ² /g | Average pore diameter according to BJH method, nm | Specific pore volume, cm ³ /g | Specific micropore volume, cm ³ /g |
|---|--|---|--|---|
| Fe_3O_4 | 63.8 \pm 3.8 | 15.8 \pm 0.9 | 0.2 \pm 0.01 | - |
| AC | 699.3 \pm 41.9 | 3.8 \pm 0.2 | 0.6 \pm 0.04 | 0.21 \pm 0.01 |
| Fe_3O_4 -AC- <i>in situ</i> | 312.8 \pm 18.7 | 4.2 \pm 0.2 | 0.3 \pm 0.02 | 0.09 \pm 0.005 |
| Fe_3O_4 -AC- <i>ex situ</i> | 259.4 \pm 15.5 | 4.8 \pm 0.3 | 0.3 \pm 0.02 | 0.05 \pm 0.002 |

Sorption capacity

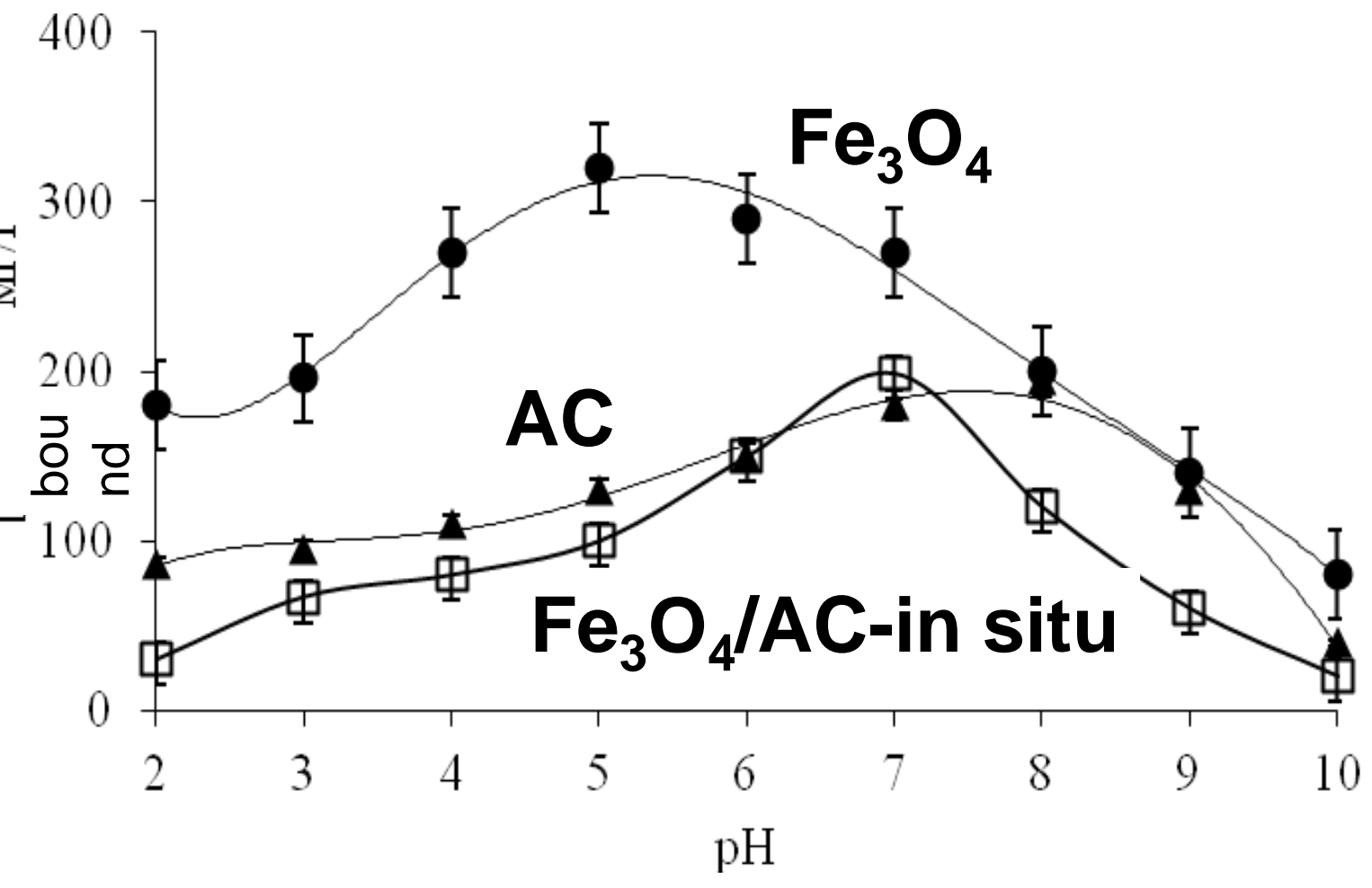


Fig. 3 pH Sorption capacity of Pb²⁺ preparations

The sorption activity of Fe_3O_4 /AC-*in situ* reached its maximum values even at pH 5.0. The highest sorption capacity upon binding of Pb²⁺ to Fe_3O_4 nanoparticles was 320 mg/g, to AC (pH 7.5) and Fe_3O_4 /AC (pH 7) - 230 and 192 mg/g, respectively.

Bioactivity



The toxicity indices for the initial preparations of AC and magnetite Fe_3O_4 with respect to *infusorians* turned out to be similar and rather high IC₅₀-0.078% and 0.075%, respectively. Fe_3O_4 /AC-*in situ* showed an order of magnitude lower toxicity of IC₅₀ - 0.17%.

A sharp decrease in the bioavailability of the synthesized nanocomposites is most likely due to the microstructural characteristics of the nanocomposite.

Table 2. NOEC and EC₅₀ (%) for *Paramecium caudatum* and *Scenedesmus quadricauda* test cultures

| Test function | Fe_3O_4 | | AC | | Fe_3O_4 /AC- <i>in situ</i> | |
|---|-------------------------|------------------|--------------------|------------------|---|------------------|
| Mortality <i>Paramecium caudatum</i> | NOEC ₁₀ | EC ₅₀ | NOEC ₁₀ | EC ₅₀ | NOEC ₁₀ | EC ₅₀ |
| | 0.0003 | 0.075 | 0.0005 | 0.078 | 0.0014 | 0.17 |
| Chlorophyll fluorescence <i>Scenedesmus quadricauda</i> | NOEC ₂₀ | EC ₅₀ | NOEC ₂₀ | EC ₅₀ | NOEC ₂₀ | EC ₅₀ |
| | 0.1 | 0.44 | 0.064 | 0.74 | 0.011 | 0.1 |

Conclusions

- Comparison of two methods for nanocomposites formulation in terms of elemental and texture characteristics of nanoparticles indicates benefits of *in situ* synthesis method.
- The results of biotesting of composites towards *S. quadricauda* indicate the absence of a high toxic effect on microalgae cells compared to *P. caudatum* (IC₅₀ in the range 0.44% - 0.10%). Based on IC₅₀, the toxicity of preparations for microalgae decreases in the order Fe_3O_4 /AC-*in situ* > Fe_3O_4 > AC.
- Even if the sorbent is not completely removed from the medium after the magnetic separation procedure, the toxicity of the aqueous phase will not pose a danger to living systems.

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