

MAGNETIC Fe₃O₄ NANOPARTICLES, SYNTHESIS, SURFACE MODIFICATION AND PHYSICOCHEMICAL CHARACTERIZATION

¹Ondřej SOLNIČKA, ¹Leona KUBÍKOVÁ, ²Jaromír BAČOVSKÝ, ¹Šárka SOVOVÁ,
¹Petr SEDLÁČEK, ¹Martina KLUČÁKOVÁ, ¹Miloslav PEKAŘ, ^{1,†}Vojtěch ENEV

¹Faculty of Chemistry, Brno University of Technology, Brno, Czech Republic, EU, [†]enev@fch.vut.cz

²Delong Instruments a.s., Brno, Czech Republic, EU

<https://doi.org/10.37904/nanocon.2022.4597>

Abstract

Surfactants coated magnetic nanoparticles have shown greater application potentials in freshwater source treatment processes for their antibacterial properties.

In this work, we prepared magnetic nanoparticles Fe₃O₄ which surface were modified with Cethyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB) and Carbaethopendecine bromide (Septonex), respectively. Their physicochemical properties and morphology were investigated using thermal analysis (i.e. elemental and thermogravimetric analysis), infrared spectroscopy with Attenuated Total Reflectance (ATR-FTIR), dynamic light scattering (DLS) and transmission electron microscopy (TEM).

The highest surfactant content was obtained for Fe₃O₄ nanoparticles coated with Cethyltrimethylammonium bromide. The presence of –CH₂–, –CH₃ and ammonium salt functional groups in infrared spectra implied that all surfactants had been successfully anchored onto the surface of native Fe₃O₄ nanoparticles. All modified nanoparticles were surface charged and they not tended to agglomerate in deionize water. The highest value of zeta-potential (approximately 40 mV) was obtained for Fe₃O₄-TTAB. Another characteristic coefficient is polydispersity index (PDI) its relative value was comparable for all modified nanoparticles. The transmission electron microscopy (TEM) analysis showed all modified nanoparticles were approximately spherical morphology with the core size in the range 5–15 nm.

Keywords: Magnetic nanoparticles, modification, surfactants, FTIR, DLS

1. INTRODUCTION

Magnetic nanoparticles such as magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃), consisting of superparamagnetic core which can be conveniently separated with magnetic field, have been widely used to remove pollutants from water environment [1–3].

With successful and proper functionalization, magnetite and/or maghemite, which are environmentally risk-free and nontoxic inorganic nanomaterials with paramagnetic properties, could be employed to remove pathogenic bacteria (i.e. *Escherichia coli*, *Klebsiella*, *Salmonella*, *Citrobacter*) from freshwater and water environment [4–6]. The unique combination of superparamagnetic nanoparticles and different bioactive substances of natural and anthropogenic origin such as D-mannose, antibiotics and surfactants prompts us to embark on a research work in this scientific field.

CTAB, TTAB and Septonex, cationic surfactants with relative small and long-chain molecules, could be very easily anchored onto the surface of magnetite nanoparticles by a facile and simple two-step their preparation process. These surfactants have been used to specific modification of adsorbent surface to remove negatively

charged pollutants from water environment. The positive charged surfactant+ could be interacting with negative charged of pathogenic Gram-negative bacteria.

In this work, we applied modified procedure of preparation magnetic nanoparticles with surfactants using CTAB, TTAB and Septonex as a cationic surfactants and obtained nanomaterials to a complex physicochemical and morphology characterization utilizing methods of spectroscopic, DLS and optic analysis.

2. MATERIALS AND METHODS

2.1. Materials

Cethyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), Carbaethopendecine bromide (Septonex), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NH_4OH were purchased from Sigma-Aldrich (Sigma-Aldrich, Praha, Czech Republic). All the reagents were analytical grade.

2.2. Preparation Fe_3O_4 nanoparticles

The unedited and surfactants coated Fe_3O_4 magnetic nanoparticles were synthesized with methods modified from literature [7] and [8].

Briefly, 40 mL 1 M FeCl_2 and 80 mL 1 M FeCl_3 were mixed with a stirring blade in a 300 mL beaker containing 40 mL of degas deionized water (oxygen free Mili-Q water). N_2 gas was used to create an oxygen-free solution during the synthesis process. The solution was heated to 85 °C in software controlled heating circulating water bath. Then NH_4OH (~ 30%) was dropped into the mixture until the pH reached around 11, and black precipitate was formed. The suspension was then stirred at 85 °C for another 30 min. After cooled to room temperature, the black precipitate was collected with magnet and repeatedly washed with Mili-Q water until the pH of suspension was about 7. Then surfactants were anchored onto the Fe_3O_4 nanoparticles surface by explosion the black solid proportion 200 mL of 0.06 M surfactant solution i.e. CTAB, TTAB, Septonex for 30 min under sonication conditions. After that, the black precipitates were collected with magnetic decantation and washed with deionized water five times to wash away the unreacted CTAB, TTAB and Septonex with controlled using ATR-FTIR spectroscopy. The unedited and modified nanoparticles were freeze-drying for 48 h.

2.3. Methods

Elemental and thermogravimetric analysis

The relative content of organic elements in the modified Fe_3O_4 nanoparticles was determined using EA 3000 CHNS/O analyzer (Euro Vector, Pavia, Italy). Approximately 1.0–1.5 mg of the sample was weighted in a tin capsule, the capsule packed and combusted at 980 °C in the analyzer using oxygen as the combustion gas. Calibration of the determination of relative contents of organic elements from the obtained gas chromatograms was provided using sulfanilamide as a reference standard sample.

Thermogravimetry of the nanoparticles was performed using a 5500 Discovery TG analyzer (TA Instruments, New Castel, DE, USA). Approximately 10 mg of sample was weighed into a platinum pan. After inserting the pan into the TG analyzer, the sample was incinerated at a heating rate of 10 °C min⁻¹ from laboratory temperature to 1000 °C under nitrogen atmosphere. The weight loss occurring at 100–120 °C was measured and taken as the moisture content. The final residue, after heating to 1000 °C, was measured and taken as the Fe_3O_4 content. During the TG analyses, the relative sample weight was recorded continuously with ± 0.1% mass accuracy.

ATR-FTIR spectrometry

Fourier transform infrared (FTIR) spectra of the modified Fe_3O_4 nanoparticles were recorded on Nicolet iS50 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) using the Attenuated Total Reflectance (ATR)

measuring technique (single reflection built-in diamond ATR crystal and external germanium ATR crystal). MID measurements were taken at 25 °C in the spectral range 4000–400 cm⁻¹ at 4 cm⁻¹ resolutions as an average of 128 scans. On the other hand, FAR spectra of nanoparticles were measured in the spectral range 1800–200 cm⁻¹ at 8 cm⁻¹ resolutions as an average of 256 scans. A background spectrum was collected from the clean dry surface of the ATR crystal (diamond and/or Ge) in an ambient atmosphere. Raw absorption infrared spectra with no artificial processing (such as baseline or ATR corrections, atmospheric suppression) are presented and evaluated.

Dynamic light scattering (DLS) and zeta potential measurement

Zeta potentials and average scattered light intensity of modified Fe₃O₄ nanoparticles were measured using Zetasizer Nano ZS (Malvern Panalytical Ltd., UK). All modified Fe₃O₄ dispersions were investigated by the method of electrophoretic light scattering using universal DIP cell (Malvern Panalytical Ltd., UK). The obtained experimental data from DLS and ELS analysis were processed by the Zetasizer software (version 7.11).

TEM analysis

Nanoparticles were sonicated and drop of solution was placed on hexagonal grid with ultrathin carbon supporting layer. Imaging was done by low-voltage transmission electron microscopes LVEM5 and LVEM25 produced by DeLong Instruments. These instruments operate with accelerating energy 5kV (LVEM5) and 25kV (LVEM25), which brings a very high image contrast. Micrographs were captured in TEM and also STEM mode.

3. RESULTS AND DISCUSSION

3.1. Elemental and thermogravimetric analysis

The elemental composition, moisture and surfactants content of native and modified Fe₃O₄ nanoparticles are presented in **Table 1**.

Table 1 Surfactant content, moisture content and elemental composition of unedited and modified Fe₃O₄ nanoparticles

sample	surfactant	moisture	C	H	N
	(wt.%)				
Fe ₃ O ₄	–	1.97	0.004	0.002	–
Fe ₃ O ₄ -CTAB	3.01	1.21	0.110	0.020	0.070
Fe ₃ O ₄ -TTAB	3.89	1.53	0.167	0.032	0.012
Fe ₃ O ₄ -Septonex	2.92	1.33	0.082	0.014	0.005

The surfactants content of modified Fe₃O₄ samples ranged from 2.92 % to 3.89 % (relative to the type of surfactant used) varying with the affinity of surfactants to the unedited Fe₃O₄ surface. The highest surfactant content was obtained for Fe₃O₄ nanoparticles modified with TTAB. In contrast, the lowest content of surfactant (2.92 %) was obtained in the case of the sample Fe₃O₄-Septonex modified using Carbaethopendecine bromide. The content of moisture of unedited and modified Fe₃O₄ nanoparticles ranged from 1.21 % to 1.97 %. The lower content of moisture for modified Fe₃O₄ samples is not surprising with respect to surfactants high content of hydrophobic structural constituents such as –CH₃ and –CH₂– functional groups.

The organic elements of all modified nanoparticles are presented in **Table 1**. Despite their modification using different surfactants, the elemental compositions of the nanoparticles are comparable: carbon (C), 0.08–0.17 wt. %; hydrogen (H), 0.01–0.03 wt. % and nitrogen (N), ~ 0.01 wt. %. Nitrogen represents a minor component of all modified Fe₃O₄ nanoparticles and its content ranged from 0.005–0.012 wt. %. The highest elemental compositions were found for Fe₃O₄ nanoparticles modified using TTAB surfactant. The presence of

organic elements such as carbon, hydrogen and nitrogen implied that surfactants had been successfully anchored onto the surface of Fe_3O_4 nanoparticles.

3.2. ATR-FTIR spectrometry

The ATR-FTIR spectra of unedited and modified Fe_3O_4 nanoparticles are presented in **Figures 1a, b**. Interpretation of their absorption bands has been carried out according to the literature data [4,9].

The broad and intensive absorption band centered at about 3300 cm^{-1} corresponds to O–H stretching of water molecules (moisture), which are connected with an intermolecular hydrogen-bond. This absorption band is well pronounced in FTIR spectrum of unedited magnetic nanoparticles. Presence of the water molecules are usually also manifested by the broad band centered at about 1635 cm^{-1} resulting from the O–H stretching functional groups. The fingerprint zone is characterized by two bands at 1435 cm^{-1} and 1257 cm^{-1} corresponding to the O–H \cdots O stretching in water molecules (i.e. overtone bands of water molecule). The FAR spectrum (marked red in **Figure 1a**) is characterized by a sharp and intensive Fe–O stretching band at 544 cm^{-1} (magnetite).

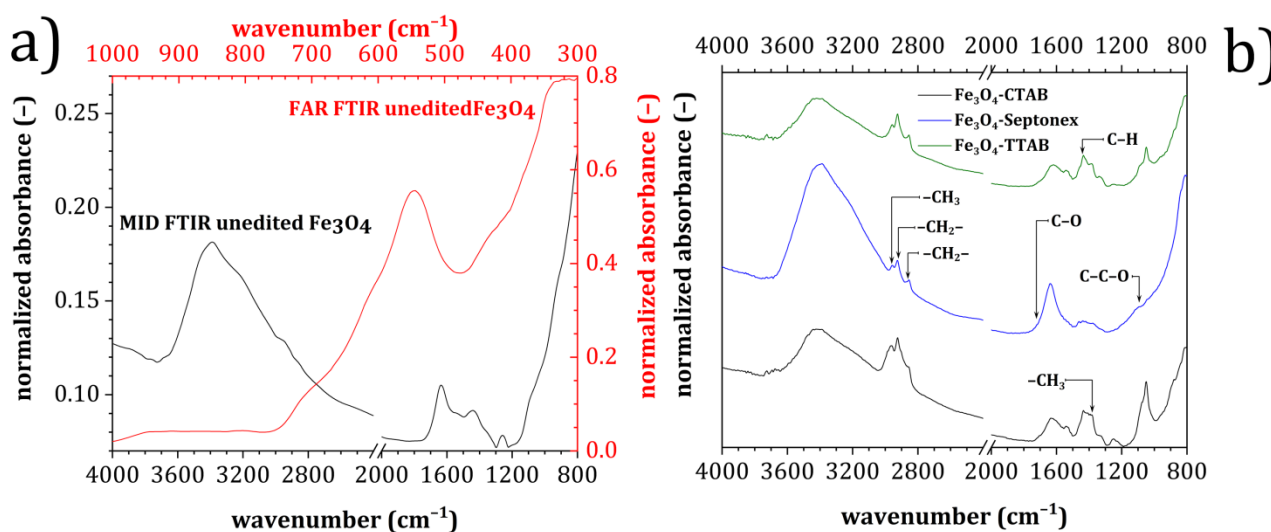


Figure 1a, b ATR-FTIR spectra of unedited and modified Fe_3O_4 nanoparticles

The second set of spectral features that are in common for all the modified Fe_3O_4 samples refer to their content of surfactants such as aliphatic and N-containing molecular moieties. The relative content of aliphatic chains of used surfactants is evaluated primarily in the $3000\text{--}2800\text{ cm}^{-1}$ spectral range (see **Figure 1b**). The presence of aliphatic groups is revealed by the bands at 2927 cm^{-1} and 2854 cm^{-1} which are attributed to asymmetric and symmetric C–H stretching in $-\text{CH}_2-$ functional groups, respectively. The band at 2962 cm^{-1} is the most intensive in the spectrum of $\text{Fe}_3\text{O}_4\text{-TTAB}$ which is attributed to asymmetric vibration mode of $-\text{CH}_3$ groups. The deformation vibrations of the $-\text{CH}_2-$ and $-\text{CH}_3$ groups at 1431 cm^{-1} and 1384 cm^{-1} respectively occur in the all modified nanoparticles. A band with variable intensity located at around 1253 cm^{-1} is attributed to C–N stretching in ammonium salts. A weak band at 1080 cm^{-1} can be ascribed to C–C–O stretching in alkyl-ester of Septonex.

3.3. Dynamic light scattering (DLS) and zeta-potential

Dynamic light scattering (DLS) is concerned with measurement of particles suspended within in liquid. The size distribution curves of the studied magnetic nanoparticles are shown in presented poster. For the modified Fe_3O_4 nanoparticles, the average size of surfactant-coated Fe_3O_4 nanoparticles ranged from 86 nm to 247 nm. The average sizes of modified particles were found as 85.9 nm $\text{Fe}_3\text{O}_4\text{-CTAB}$, 108.3 nm $\text{Fe}_3\text{O}_4\text{-TTAB}$, and

246.6 nm Fe₃O₄-Septonex in dynamic light scattering measurements. For all modified nanoparticles, a polydispersity index (PDI) ranged from 0.12 to 0.23, approaches 1.0 for low PDI values (monodisperse systems), and increases with the system polydispersity. The lowest PDI of samples (0.12) was obtained in the case of the magnetic nanoparticles Fe₃O₄ coated using Septonex.

To verify the effect of surfactant modification on the zeta potential (ζ) and water dispersibility of Fe₃O₄ nanoparticles, samples were diluted to the same concentration and assessed using a Zetasizer Nano ZS particle size analyzer. The zeta potential of modified Fe₃O₄ nanoparticles was found to range between 23.3 ± 1.2 mV and 39.4 ± 4.0 mV, which was in agreement with the findings of previous studies [4,10]. The zeta potential value of unedited Fe₃O₄ was smaller than the three modified nanoparticles, indicating that Fe₃O₄-CTAB, Fe₃O₄-TTAB and Fe₃O₄-Septonex were stable in aqueous suspension.

Table 2 Average size, zeta potential and polydispersity index of modified Fe₃O₄

sample	average size (nm)	zeta potential (mV)	PDI
Fe ₃ O ₄ -CTAB	85.9	37.0 ± 0.9	0.23
Fe ₃ O ₄ -TTAB	108.3	39.4 ± 4.0	0.13
Fe ₃ O ₄ -Septonex	246.6	23.3 ± 1.2	0.12

3.4. TEM images

Figures 2(a, b, c) shows the typical TEM image of modified Fe₃O₄ nanoparticles, from which we can see that the sizes of all samples are practically uniform and considerable part of modified nanoparticles are approximately spherical with the diameter in the range 5–15 nm.

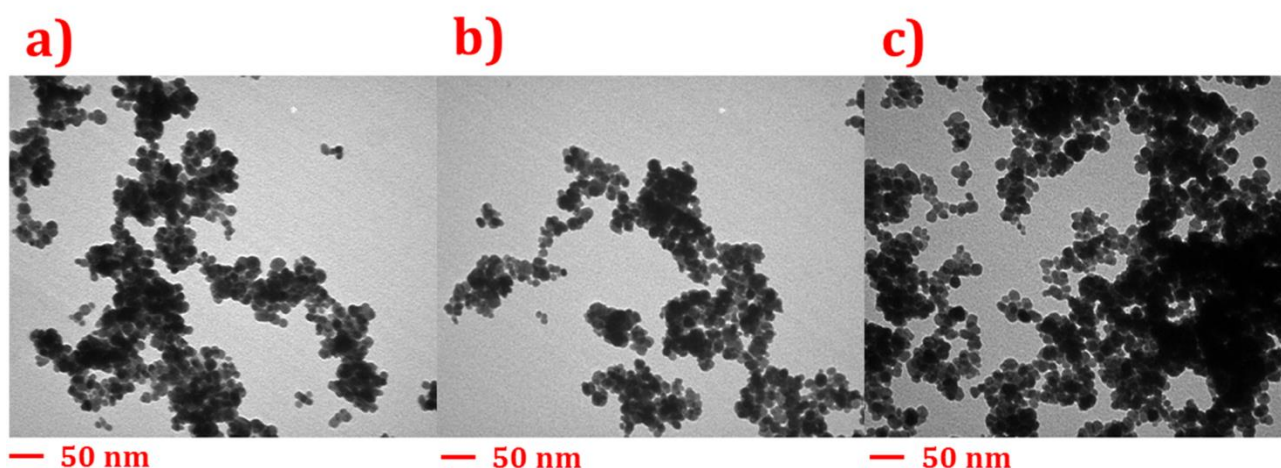


Figure 2 TEM images of modified Fe₃O₄ nanoparticles: **a)** Fe₃O₄-CTAB; **b)** Fe₃O₄-TTAB; **c)** Fe₃O₄-Septonex

4. CONCLUSION

Magnetic nanoparticles Fe₃O₄ were prepared by co-precipitation method. The unedited Fe₃O₄ nanoparticles were modified using selected cationic surfactants. Unedited and modified magnetic nanoparticles were obtained and subjected to a physicochemical characterization utilizing method of morphological analysis. Advanced instrumental techniques such as Attenuated Total Reflectance (ATR-FTIR), dynamic light scattering (DLS), electrophoretic light scattering (ELS), and TEM analysis were supplemented with thermal analysis.

The nanoparticles have been fully characterized using different methods; in particular TEM images reveal good morphological properties which correspond to the particle size in the range 5–15 nm. Further, it was noticed that there were interactions between the cationic surfactants and the surface of the native nanoparticles as

confirmed by thermal analysis and FTIR spectroscopy. The determined zeta potential values and polydispersity index (PDI) of modified nanoparticles show the positive charge of particles (in the range 23–39 mV) and very good PDI values, which supports the expectations that the selected surfactants to stabilize of nanoparticles in water environment.

ACKNOWLEDGEMENTS

The authors would like to thank Delong Instruments a.s. for realization of TEM measurements.

REFERENCES

- [1] AKBARZADEH, A., SAMIEI, M., DAVARAN, S. Magnetic nanoparticles: preparation, physical properties, and applications in biomedicine. *Nanoscale Research Letters*. 2012, vol. 7, pp. 1-13. Available from: <https://doi.org/10.1186/1556-276X-7-144>.
- [2] SICILIANO, G., MONTEDURO, A.G., TURCO, A., PRIMICERI, E., RIZZATO, S., DEPALO, N., CURRI, M.L., MARUCCIO, G. Polydopamine-Coated Magnetic Iron Oxide Nanoparticles: From Design to Applications. *Nanomaterials*. 2022, vol. 12, pp. 1-17. Available from: <https://doi.org/10.3390/nano12071145>.
- [3] JIN, Y., LIU, F., TONG, M., HOU, Y. Removal of arsenate by cetyltrimethylammonium bromide modified magnetic nanoparticles. *Journal of hazardous materials*. 2012, vol. 227-228, pp. 461-468. Available from: <https://doi.org/10.1016/j.jhazmat.2012.05.004>.
- [4] JIN, Y., DENG, J., LIANG, J., SHAN, C., TONG, M. Efficient bacteria capture and inactivation by cetyltrimethylammonium bromide modified magnetic nanoparticles. *Colloids and Surfaces B: Biointerfaces*. 2015, 136, pp. 659-665. Available from: <https://doi.org/10.1016/j.colsurfb.2015.10.009>.
- [5] PRABHU, Y.T., RAO, K.V., KUMARI, B.S., KUMAR, V.S.S., PAVANI, T. Synthesis of Fe₃O₄ nanoparticles and its antibacterial application. *International Nano Letters*. 2015, vol. 5, pp. 85-92. Available from: <https://doi.org/10.1007/s40089-015-0141-z>.
- [6] EL-GENDY, N.S., NASSAR, H.N. Biosynthesized magnetite nanoparticles as an environmental opulence and sustainable wastewater treatment. *Science of The Total Environment*. 2021, vol. 774, pp. 145610. Available from: <https://doi.org/10.1016/j.scitotenv.2021.145610>.
- [7] LIU, J.F., ZHAO, Z.S., JIANG, G.B. Coating Fe₃O₄ magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water. *Environmental science & technology*. 2008, vol. 42, pp. 6949-6954. Available from: <https://doi.org/10.1021/es800924c>.
- [8] MAITY, D., AGRAWAL, D.C. Synthesis of iron oxide nanoparticles under oxidizing environment and their stabilization in aqueous and non-aqueous media. *Journal of Magnetism and Magnetic Materials*. 2007, vol. 308, pp. 46-55. Available from: <https://doi.org/10.1016/j.jmmm.2006.05.001>.
- [9] ENEV, V., SEDLÁČEK, P., ŘIHÁK, M., KALINA, M., PEKAŘ, M. IR-Supported Thermogravimetric Analysis of Water in Hydrogels. *Frontiers in Materials*. 2022, vol. 9, pp. 1-8. Available from: <https://doi.org/10.3389/fmats.2022.931303>.
- [10] LI, W., HINTON, C.H., LEE, S.S., WU, J., FORTNER, J.D. Surface engineering superparamagnetic nanoparticles for aqueous applications: design and characterization of tailored organic bilayers. *Environmental Science: Nano*, 2016, vol. 3, pp. 85-93. Available from: <https://doi.org/10.1039/C5EN00089K>.