ELECTROCHEMICAL SYNTHESIS OF NANOMAGNETITE MODIFIED WITH BIOCOMPATIBLE SURFACTANTS

N. Makhaldiani[1], M. Donadze[1,2*], G. Tatishvili[2], N. Gergauli[1], L. Targamadze[1], G. Maghradze[1,2], E. Burduladze[1]

[1]Georgian Technical University, 0160, Tbilisi, Georgia, Kostava 77,
[2]Rafael Agladze Institute of Inorganic Chemistry and Electrochemistry, Ivane Javakhishvili Tbilisi State University, 11 Mindeli St., Tbilisi, 0186, Georgia
**e-mail: makhaldianinino@gmail.com; mob.: +995598235587*

Received 26.05.2025
Accepted 22.06.2026

Abstract: *Magnetic nanoparticles are currently gaining significant attraction in various fields, including modern engineering and ecology, particularly in biomedical, therapeutic, and diagnostic technologies. An environmentally friendly electrochemical synthesis method was used to produce magnetic nanoparticles. Iron sulfate was dissolved in a mixture of water-ethanol, while polyvinylpyrrolidone (PVP) was used to enhance the biocompatibility of the magnetite nanoparticles. Particle size in a sol obtained with 1 vol% PVP, at a current density of 20-60 A/dm^2, and at varying water and ethanol ratios, was measured using the dynamic light scattering (DLS) method transmission electron microscopy (TEM). Zeta potential was measured to determine the stability of the magnetite sol. In the presence of PVP, the best results (12-18 nm) were obtained with water/ethanol ratios of 50/50 and 60/40 vol.%. Magnetite nanoparticles were characterized using a Zetasizer Malvern instrument, scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FT-IR), and thermogravimetric analysis.*
Keywords: *Electrosynthesis, Polyvinylpyrrolidone, Water/ethanol, Magnetite, Zeta potential*
DOI: 10.65382/2221-8688-2027-1-141-148

Introduction

Nanotechnology, as a rapidly developing field, has opened unprecedented avenues for innovation in various scientific disciplines. Among many nanomaterials, iron oxide nanoparticles, especially magnetite Fe_3O_4, have garnered considerable interest owing to their distinctive superparamagnetic behavior, low toxicity, and high surface area. These properties make magnetite nanoparticles very attractive for a variety of applications [1-2]. After being accepted as a safe contrast agent through the Food and Drug Administration, the demand for magnetic nanoparticles in magnetic resonance imaging has increased [2].

A critical aspect for the successful integration of magnetite nanoparticles into biomedical applications is their biocompatibility and colloidal stability in physiological environments. Bare magnetite nanoparticles tend to aggregate because of strong magnetic interactions and elevated surface energy, which leads to the loss of the desired superparamagnetic properties and hinders their biological efficacy. To overcome these limitations, it is necessary to modify the surface with biocompatible surfactants, which, by adsorbing on the surface of the nanoparticles, prevent agglomeration, enhance dispersibility in aqueous solution, and reduce nonspecific interactions with biological components, thereby improving their *in vivo* circulation time and targeting efficiency. Various biocompatible surfactants were successfully used for this purpose, including polymers such as polyethylene glycol (PEG), dextran, and chitosan, along with citric, acid and oleic acid. In addition, the surface of nanoparticles can be modified with various functional groups to impart different properties [1-4].

In ecology, nanomagnetite is employed to purify water and soil from heavy metal ions and organic pollutants. It is an active adsorbent and oxidizer, due to the presence of Fe^{2+} and Fe^{3+} ions. It participates in Fenton-type reactions and completely decomposes organic matter and its

derivatives [5-7]. Traditional methods for the synthesis of magnetite nanoparticles often involve coprecipitation, hydrothermal, or sole-gel techniques. Although these methods offer control over size and morphology, they can have drawbacks such as high reaction temperatures, the use of toxic solvents, and the difficulty of achieving precise control over the surface chemistry. Electrochemical synthesis represents a promising alternative that offers a more ecological, economical and highly controllable approach to the production of nanomaterials. The method allows precise control of the reaction parameters (potential, current density and electrolyte composition) making it possible to synthesize nanoparticles with tailored, required properties and reduced negative environmental impact. Electrochemical synthesis is primarily carried out in potentiostatic, galvanostatic, or pulsed modes, using a two-electrode or three-electrode electrolyzer. Alternative modes, including cyclic voltammetry, pulsed potential, and pulsed current, are commonly employed in research [7-17].

The scope of application of magnetic particles obtained by the electrochemical method of synthesis is wide. The method is simple, environmentally friendly and does not require large economic costs. As an anode, which is also a source of iron ions, a low-carbon steel or pure iron electrode is used. The cathode can be either iron or other metals, for example, platinum. Without using other oxidizing and reducing agents, with the help of a universal reducing agent – electron – and finding optimal parameters (current density, temperature, potential), it is achievable to effectively tune the size and shape of magnetite nanoparticles.

An innovative method of electrochemical synthesis (in a two-layer bath on a rotating cathode) makes it possible to obtain magnetic nanoparticles with specified properties by varying the content of electrolyte, organic solvent, surfactant, cathode-arc area, cathode rotation speed, and other electrosynthesis parameters. An iron anode and an aluminum cathode arc are used as electrodes. After oxidation of the iron anode, divalent iron is obtained, which, under the influence of the anode surface, dissolved oxygen, current density, and potential, is partially oxidized to trivalent iron. Under the pressure of hydrogen released at the cathode, the acidity of the medium increases, which promotes the formation of magnetite. In our previous studies, in a two-layer bath on a rotating cathode, magnetite obtained impregnated in an aluminosilicate substrate gave good results in the purification of contaminated model water with manganese ions and phenol [7].

Our aim was the electrochemical synthesis of PVP-modified biocompatible nanomagnetite in a water/ethanol medium. The comparative analysis with a previous study of oleic acid-modified nanomagnetite is also presented [8].

Experimental Part

For the obtained nanomagnetite, a single-layer electrochemical bath was used, and as reagents $FeSO_4 \times 7H_2O$ (Sigma-Aldrich, chemical grade), PVP 25K (Sigma Aldrich, purity 99%) deionized water, and ethanol (chemical grade, 99%). In the electrochemical process, the anode (99.19% Fe, 0.75% Mn, 0.053% Cu) and the aluminum ring cathode (surface area 0.015 dm^2) were used.

In previous studies, during the synthesis of nanoparticles (silver, zinc and magnetite) in a two-layer bath, hexane (or toluene) was used as an organic solvent, evaporated at 40–45°C and particle aggregation occurred [7, 15, 16]. In this study, the organic solvent was replaced with a water/ethanol media, which made the approach economically justified, and environmentally friendly. Iron sulfate in different concentrations (0.05–1.00 M) was used as an electrolyte in the synthesis of nanomagnetite; the best concentration was 0.08 M [8].

The optimal concentration of iron sulfate was dissolved in a mixed water-ethanol solution, to which polyvinylpyrrolidone (1 mass%) was added. The rotating cathode-arc provides the formation of iron-containing nanoparticles, however, due to the rotation of the cathode, the processes of coating formation and crystal growth on the surface are limited. Before electrolysis, the electrodes are cleaned with emery paper. For fat removal, the surface was cleaned with ethanol, washed with distilled

water, dried at 100°C, and weighed for determination of current efficiency. After 30 min of electrosynthesis, the sol is centrifuged (10 min, 8000 rpm), and the particle size and (ξ) zeta potential was determined by the DLS method (DLS Malvern, ZEN 3600).

PVP is a well-dispersible in water and ethanol, biocompatible amphiphilic polymer with a hydrophobic backbone and hydrophilic side chains. PVP is linked to the nanoparticle by C=O and C–N groups; CH_2 provides flexibility and stability, prevents aggregation, and is ideal for functionalizing magnetic nanoparticles (Fig. 1).

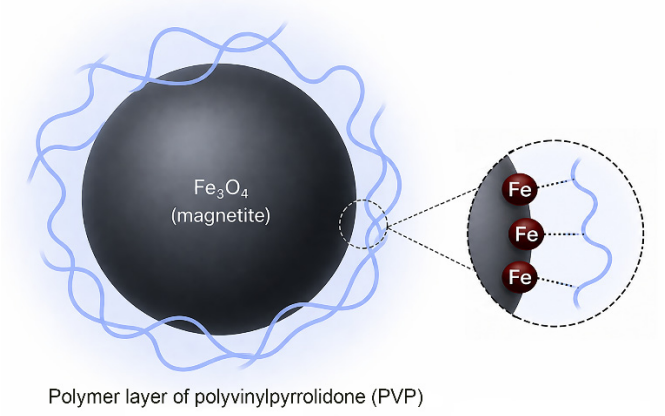

Fig. 1. Schematic representation of PVP-coated magnetite nanoparticles

PVP at a concentration of 1.0 wt% was added to a solution of iron sulfate in a water-ethanol medium. PVP 25K with a molecular weight of 25 kDa (10 g in total) was dissolved in 200 mL of deionized water at 80°C under magnetic stirring to obtain a homogeneous mixture. Then, the PVP solution was added to a mixture (800 mL) of different water/ethanol ratios (50/50, 40/60, 30/70, 20/80 or 10/90) under vigorous stirring. After 5–7 min of the electrolysis the transparent colorless solution begins to change color and a straw-colored, reddish, and finally (after 25–30 min) black sol is obtained, which indicates the formation of goethite, hematite, and magnetite, respectively. For each sample obtained at a temperature of 45°C (different water/ethanol ratios and current density), the particle size was determined by the DLS method. After measurement in a cuvette, the sample was diluted 1:4 in ethanol. The elemental analysis of the calcined at 300°C sample showed the composition of iron and oxygen around 60 and 40%, respectively.

The samples of PVP-modified nanomagnetite, obtained by electrochemical synthesis, were characterized by thermogravimetry analysis (TGA-DSC, NETZSCH, STA-2500 Regulus), FT-IR spectra (TENSOR II FTIR spectrometer, Bruker), X-ray diffraction analysis (Diffractometer DRON-4 with Cu-Kα radiation), TEM (TEM microscope Tesla BS 500), and SEM (SEM microscope JSM, 6510 LV) analysis.

Results and Discussion

The synthesis optimisation was performed by changing of electrochemical parameters, such as the water/ethanol ratio, to achieve sol stability and narrow dispersion of nanoparticle sizes. PVP possesses great solubility in water and ethanol; it allows modification of PVP solutions with water/ethanol at different ratios. Thus, the best results are obtained with a water/ethanol ratio of 50/50 and 40/60 (Fig. 2a). If we continue to increase ethanol volume in the water/ethanol mixture, as a result, an unstable sol is formed, which over time precipitates in 2-3 h. Magnetite nanoparticles are stable when dispersed in PVP in 100% water due to the orientation of the hydrophilic end groups relative to water and, in the case of 100% ethanol, due to the orientation of the hydrophobic end groups relative to ethanol. However, if water or ethanol in an amount of 5–20 vol.% is added to one of the media, the orientation of PVP molecules is disrupted, the bond with magnetite weakens, and aggregation and, consequently, sedimentation increase [18]. The change in current density

within the range of 20–40 A/dm^2 does not significantly affect the particle size, as can be seen from Fig. 2.

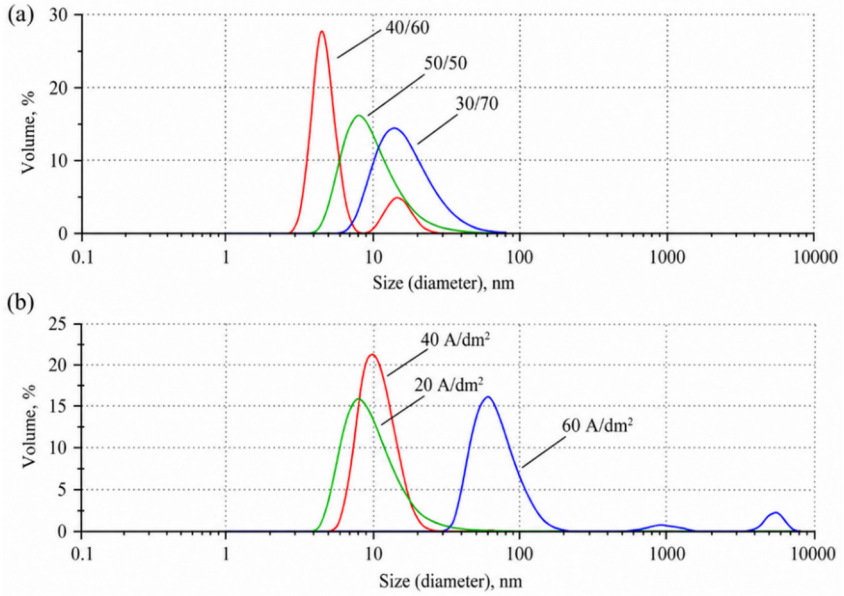

Fig. 2. Dependence of PVP (1 vol.%) coated particles' sizes in (a) different water/ethanol ratios at 20 A/dm^2, and (b) current density at water/ethanol ratio 50/50

At the 20 A/dm^2 current density, the sol obtained is much more monodisperse, and the particles' sizes are 8–15 nm, while at 40 A/dm^2, the particle sizes are 5–25 nm. At a high current density of 60 A/dm^2, the obtained sol is polydisperse and the particles' sizes range from 100 to 1000 nm (Fig. 2b).

The stability of the magnetite band is also determined by the zeta potential (ζ). The zeta potential is the potential between the surface of a particle and the surrounding diffusion layer and determines the stability of the particle in a colloidal solution. Typically, when the absolute value of the zeta potential of the particle is high, the attractive force between the particles is large, the sol is stable, and the particles do not precipitate. Magnetic nanoparticles were synthesized in a water-ethanol solution and maintained stability at pH 8–10. In case of a single-layer bath, in the band obtained under our experimental conditions at neutral acidity pH 6–7, zeta potential is in the range from -20 to -23 mV, which is a normal characteristic for PVP 25K (Fig. 3). As described by Feda Alzoubi et al. [17], the zeta potential of a magnetite particles without modification with a surfactant is 9.2 mV. They also studied PVP 10K, PVP 25K, and PVP 40K with various molecular weights. The best outcomes were obtained using PVP 40K, where ζ is -42.5 mV.

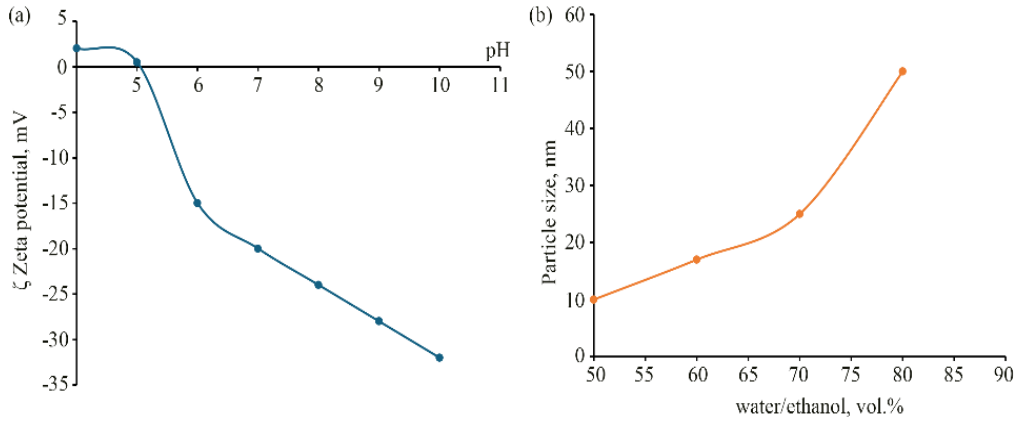

Fig. 3. Dependence of (a) Zeta potential on pH and (b) nanoparticles' sizes on water/ethanol ratio (20 A/dm^2, PVP 1 mas.%)

The obtained nanomagnetite sol under optimal conditions was dried at 120°C, and identified using FT-IR spectroscopy; see Fig. 4. The FT-IR spectrum of PVP modified nanomagnetite shows vibration peak 614 cm^{-1} corresponding to the Fe–O bond and the related C–C ring stretching. The line at 880 cm^{-1} refers to the PVP-coated magnetite, the line at 1045 cm^{-1} corresponds to the C–N bond vibration, 1325 cm^{-1} and 1422 cm^{-1} to the CH_2 bending, and scissor stretching. The vibration 1662 cm^{-1} refers to the PVP-coated nanomagnetite. The peak at 2927 cm^{-1} corresponds to the asymmetric vibration of C–H bond and the 3316 cm^{-1} to the coresponding vibration of the OH groups. The FT-IR fully reflects the bond between PVP and nanomagnetite, which ensures its ultradispersity.

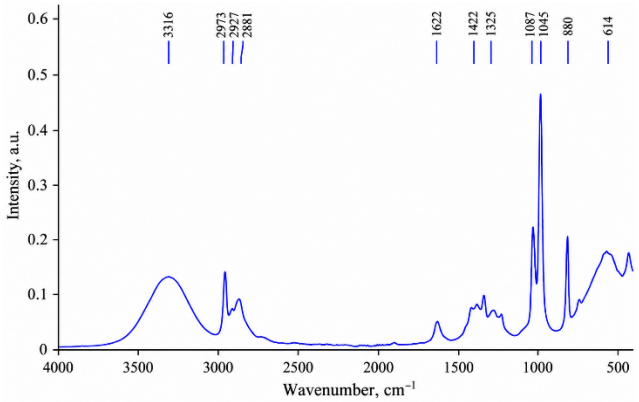

Fig. 4. FT-IR spectrum of PVP-coated nanomagnetite

The identification of PVP-coated nanomagnetite was performed using XRD analysis. The sample after electrolysis was dried at 120°C for 5 h and then calcined at 300°C for 3 h. The diffractograms showed the sharp peaks, especially for the calcinated sample, at 30.14° (220), 35.47°(311), 43.10° (400), 53.69° (422), 57.16° (511), and 62.77° (440), which matches well with the characteristic peaks of Fe_3O_4 magnetite [5,18-20]. Thus, the XRD analysis shows that the peaks correspond to magnetite, and the main phase is magnetite only (Fig. 5).

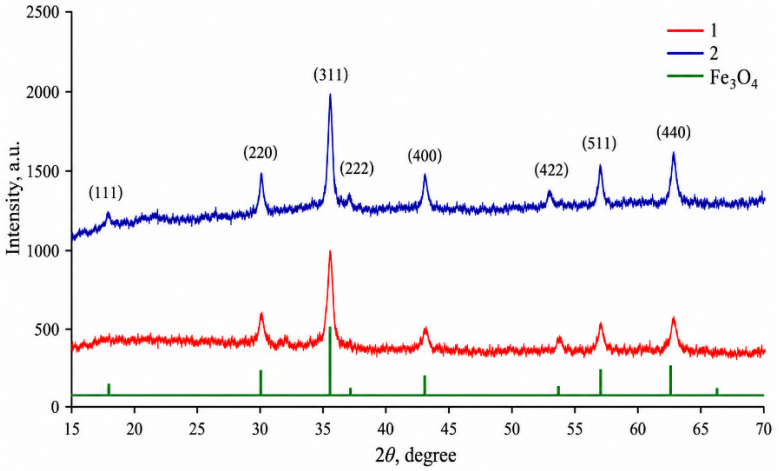

Fig. 5. XRD patterns of the PVP-coated magnetite particles (1) dried at 100°C and (2) calcined at 300°C

Morphological analysis of these obtained sols was performed using SEM; see Fig. 6. The sample was prepared for study by multiple washings in ethanol and deionized water and roasting at 300°C for 5 h. The sample particles are partially aggregated due to the effect of temperature and partial degradation of the PVP shield.

The TEM image of the obtained sample, after evaporation of a strip droplet on a copper grid under optimal conditions (current density 20 A/dm^2, water/ethanol ratio 50/50 vol.%), shows electron-dense particles of predominantly spherical shape, which are spatially separated from each other by space. The nanoparticles' sizes from the TEM image are consistent with the

results obtained using DLS method, the nanomagnetite sizes range from 10 to 18 nm (Fig. 7).

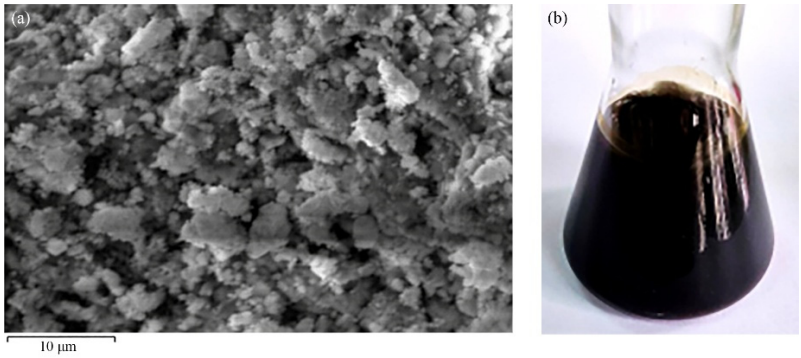

Fig. 6. The images of (a) the SEM micrograph image of the PVP-coated magnetite nanoparticles and (b) the obtained original magnetic sol

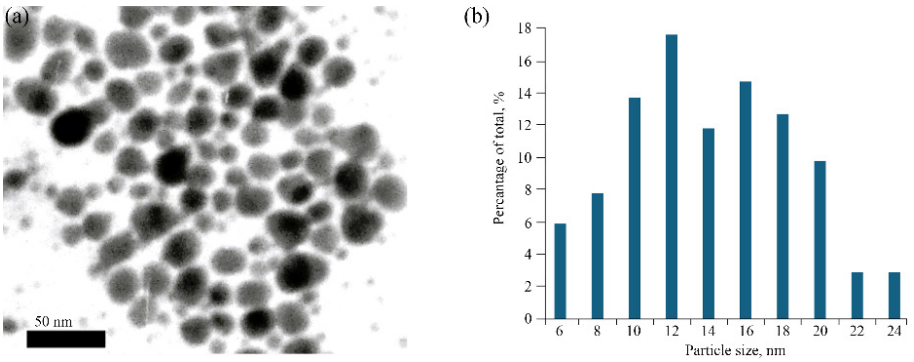

Fig. 7. TEM micrograph and a histogram of particles' size distribution of PVP-coated nanomagnetite

During the thermal analysis, a weighed sample was heated from 20 to 1000°C at a rate of 10°C per minute. Enthalpy-related processes were observed, with peaks corresponding to thermal transformations and mass changes (Fig. 8). The thermal curves show a three-step mass decrease. First, water remaining after drying is removed (hygroscopicity), the mass decreases by 15% (in the region up to 200°C), the subsequent mass decrease is associated with the degradation of PVP and, accordingly, the mass decreases by another 21.5% at 500°C, which may be due to the formation of monomers (vinylpyrrolidone), and small oligomers [21]. The further mass decrease (about 8%) at 500–820°C may be the result of the recovery of magnetite with gases obtained during the burning of PVP. The residual mass of the PVP-coated sample is about 55%.

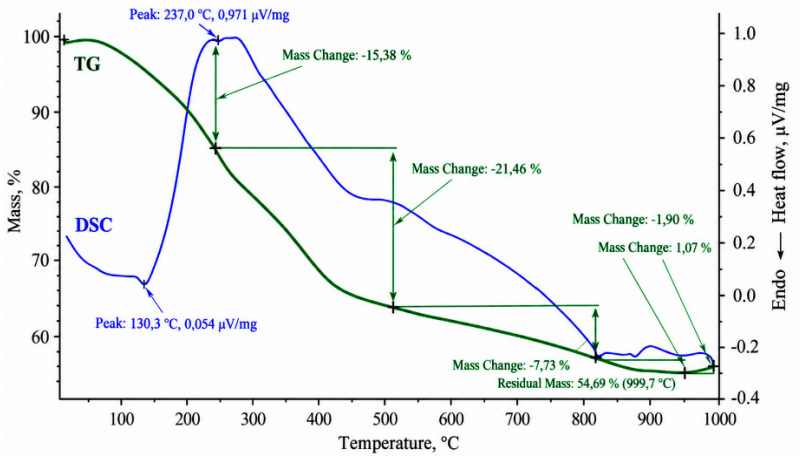

Fig. 8. Thermoanalytical curves of TG (green) and DSC (blue) of the PVP-modified nanomagnetite

The developed electrochemical approach enables the controlled synthesis of PVP-modified nanomagnetite with high colloidal stability and tunable particle size in an environmentally friendly water-ethanol medium. The obtained nanoparticles demonstrate promising physicochemical characteristics, making them suitable for applications in biomedicine.

Conclusion

Magnetic nanoparticles modified with biocompatible PVP were obtained by a simple, environmentally friendly electrolysis process. An iron sulfate diluted at different water/ethanol media solution, an iron anode, and an aluminum cathode-arc was used as the electrolyte and the mixture of ethanol and water, making the process economically viable and environmentally friendly. The optimal PVP-modified nanomagnetite sols are obtained at a current density of 20 A/dm^2, 1 mass.% PVP, and the water/ethanol ratio is 50/50 and 60/40 vol.%. The size of the PVP-coated nanomagnetite nanoparticles (12-18 nm) characterized by DLS method is consistent with TEM images and its identity confirmed by FT-IR and XRD analysis.

Acknowledgements. *This study was financially funded by Shota Rustaveli National Science Foundation of Georgia (SRNSFG) Grant YS-23-511. All authors are highly thankful to R. Agladze Institute of Inorganic Chemistry and Electrochemistry, TSU (Tbilisi, Georgia)) for physicochemical analysis.*

Conflicts of Interest

The authors announced that there are no conflicts of interest regarding this current work.

References

1. Ling W., Wang M., Xiong Ch., Xie D., Chen Q., Chu X., Qiu X., Li Y., Xiao X. Synthesis, surface modification, and applications of magnetic iron oxide nanoparticles. *J. of Materials Research*. 2019, **Vol. 34(11)**, p. 1828–1844. DOI: 10.1557/jmr.2019.129.
2. Jeon M., Halbert M.V., Stephen Z.R., Zhang M. Iron oxide nanoparticles as T1 contrast agents for magnetic resonance imaging: Fundamentals, challenges, applications, and prospectives. *J. Adv. Mater.* 2021, **Vol. 33(23)**, p. 1–18. DOI: 10.1002/adma.201906539
3. Nguyen M.D., Tran H., Xu Sh. and Lee T.R. Fe_3O_4 nanoparticles: Structures, synthesis, magnetic properties, surface functionalization, and emerging applications. *J. Appl. Sci.* 2021, **Vol. 11**, 11301. DOI: 10.3390/app112311301
4. Zhang L., Tong S., Zhang Q., Bao G. Lipid-encapsulated Fe_3O_4 nanoparticles for multimodal magnetic resonance/fluorescence imaging. *J. ACS Appl. Nano Mater.* 2020, **Vol. 3**, p. 6785–6797. DOI: 10.1021/acsanm.0c01193
5. Humbatova S.F., Tapdyqov Sh.Z., Guliyeva J.E., Gulamirov A.M., Malikov E.Y., Mammadova S.M., Fariz A.A., Kazimova S.Sh. Investigation of mass gradient of concrete filled with polyacrylamide/Fe3O4 magnetite nanoparticles in Caspian sea and formation water medium. *Chemical Problems* 2024, **Vol. 1(22)**, p. 95–102. DOI: 10.32737/2221-8688-2024-1-95-102
6. Orimolade B.O., Adekola F.A., Adebayo G.B. Adsorptive removal of bisphenol A using synthesized magnetite nanoparticles. *J. Applied Water Science*. 2018, **Vol. 8(46)**, p. 1–8. DOI: 10.1007/s13201-018-0685-y
7. Donadze M., Makhaldiani N. Electrosynthesis of nanomagnetite and application for purification phenol previously contaminated water. *Advanced Polymer Structures Chemistry for Engineering Applications*. Pub. Location New York. Apple Academic Press. 2023. 25. ISBN 9781774913017. 544 p.
8. Makhaldiani N., Donadze M., Targamadze L., Gergauli N, Khutsishvili S. "Green" electrochemical synthesis of oleic acid modified magnetite nanoparticles. *Digest*

Journal of Nanomater. and Biostr. 2025, **Vol. 20(3)**, p. 859–868. DOI: 10.15251/DJNB.2025.203.859

9. Fajaroh F., Setyawan H., Widiyastuti W., Winardi S. Synthesis of magnetite nanoparticles by surfactant-free electrochemical method in an aqueous system. *J. Advanced Powder Technology*. 2012, **Vol. 23**, p. 328–333. DOI: 10.1016/j.apt.2011.04.007
10. Cabrera L., Gutierrez S., Menendez N., Morales M.P., Herrasti P. Magnetite nanoparticles: Electrochemical synthesis and characterization. *J. Electrochim. Acta*. 2008, **Vol. 53**, p. 3436−3441. DOI: 10.1016/j.electacta.2007.12.006
11. Lozano I., Casillas N., de León C.P., Walsh F.C., Herrasti P. New insights into the electrochemical formation of magnetite nanoparticles. *J. Electrochemist. Soc.* 2017, **Vol. 164**, p. 184−191. DOI: 10.1149/2.1091704jes
12. Montoya P., Marín T., Mejía, S., Arnache O., Calderón J.A. Elucidation of the mechanism of electrochemical formation of magnetite nanoparticles by in situ Raman spectroscopy. *J. Electrochem. Soc.* 2017, **Vol. 164**, p. 1056−1065. DOI: 10.1149/2.0181802jes
13. Starowicz M., Starowicz P., Zukrowski J. Przewoznik J., Lemanski A. Czesław A., Kapusta C., Bana J. Electrochemical synthesis of magnetic iron oxide nanoparticles with controlled size, *J. Nanopart Res.* 2011, **Vol. 13**, p. 7167–7176. DOI: 10.1007/s11051-011-0631-5
14. Rahimdad N., Khalaj A., Azarian Gh., Nematollahi D. Electrochemical device for the synthesis of Fe_3O_4 magnetic nanoparticles. *J. Electrochemical Society.* 2019, **Vol. 166(2)**, p. E1-E6. DOI: 10.1149/2.0231902jes
15. Agladze T., Donadze M., Gabrichidze M., Toidze P., Shengelia J., Boshkov N., Tsvetkova N. Synthesis and size tuning of metal nanoparticles. *J. Zeitschrift für Physikalische Chemie.* 2013, **Vol. 227**, p. 1187-1198. DOI: 10.1524/zpch.2013.0362
16. Khutsishvili S.S., Toidze P., Donadze M., Gabrichidze M., Makhaldiani N., Agladze T. Structural surface features of paramagnetic multifunctional nanohybrids based on silver oleic acid. *J. Cluster Science.* 2021, **Vol. 32**, p. 1351–1359. DOI: 10.1007/s10876-020-01904-6
17. Alzoubi F.Y., Noqta O.A., Zoubi T. A., Al-Khateeb H.M., Alqadi M.K., Abuelsamen A., Makhadmeh Gh.N. A novel one-pot synthesis of PVP-coated iron oxide nanoparticles as biocompatible contrast agents for enhanced T2-weighted MRI. *J. Compos. Sci.* 2023, **Vol. 7(131)**, p. 1–12. DOI: 10.3390/jcs7030131
18. Leng Y., Sato K., Li J.G., Ishigaki T., Iijima M., Kamiya H., Yoshida T. Iron nanoparticles dispersible in both ethanol and water for direct silica coating. *J. Powder Technology*. 2009, **Vol. 196**, p. 80–84. DOI: 10.1016/j.powtec.2009.07.012
19. Sung-Jei H., Ajin J., Sang H.H., Byeong J.K., Young S.K., Suwon Y., Jae-Yong L. Effect of polyvinylpolypyrrolidone surfactant on characteristics of iron-oxide nanoparticles synthesized by using recycled waste permanent magnets. *J. Micromach.* 2022, **Vol. 13**, 2020. DOI: 10.3390/mi13112020
20. Khutsishvili S.S., Aleksandrova G.P., Vakul'skaya T.I., Sukhov B.G. Structural and magnetic properties of biocompatible coated magnetite nanoparticles for treating antianemia. I*EEE Trans. Magn*. 2021, **Vol. 57(10)**, 5200309. DOI: 10.1109/TMAG.2021.3101904
21. Kumar M., Devi P., Shivling V.D. Thermal stability and electrochemical properties of PVP-protected Ru nanoparticles synthesized at room temperature. *J. Mater. Res. Expres.* 2017, **Vol. 4**, 085006. DOI: 10.1088/2053-1591/aa7b42