ISSN 1027-5495. Functional Materials, 33, No.1 (2026), p. 46-53
doi:http://dx.doi.org/10.15407/fm33.01.46

Novel Na^+,Mg^{2+}(Cu^{2+}),CO_3^{2-}/(BO_3^{3-},BO_2^-)-substituted hydroxyapatites/$CuFe_2O_4$ composites: synthesis and investigation

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Received November 7, 2025, accepted January 15, 2026

Calcium phosphates modified with complexes of ions Na^+,Mg^{2+},Cu^{2+},CO_3^{2-}/ ($BO_3^{3-}BO_2^-$) or Na^+,Mg^{2+},Cu^{2+},Fe^{3+},CO_3^{2-}/(BO_3^{3-},BO_2^-), as well as composites based on calcium phosphate containing Na^+,Mg^{2+},CO_3^{2-}/(BO_3^{3-},BO_2^-) and (10 or 25 wt%) $CuFe_2O_4$ have been obtained from the aqueous solution and further heated to 600°C. It was found that borate-ions in the initial solutions allowed stabilization of the apatite-type phase, whereas in the case of a carbonate-containing system a biphasic calcium phosphate was obtained in composite with 25 wt% $CuFe_2O_4$. Systems containing carbonates produced larger particles (28-34 nm) than borate-containing systems (range 19-23 nm). The presence of different types of anions (PO_4^{3-}, CO_3^{2-}, BO_3^{3-}, BO_2, OH^-) was confirmed by FTIR spectroscopy. Composites based on biphasic calcium phosphate with 25 wt% $CuFe_2O_4$ demonstrated higher activity with respect to partial dissolution in the model solution compared to modified calcium phosphates and composites based on them with $CuFe_2O_4$. The highest antibacterial properties against *S. aureus* or *P. aeruginosa* strains were found for borate-containing apatite. Obtained results can be important in the creation of materials with special bioactivity and antibacterial properties for medical application.

Keywords: hydroxyapatite; ferrite; magnesium; copper; sodium; borate; carbonate; biphasic calcium phosphate.

Нові Na^+,Mg^{2+}(Cu^{2+}),CO_3^{2-}/(BO_3^{3-},BO_2^-)-заміщені гідроксиапатити/$CuFe_2O_4$ композити: синтез та дослідження. *Н.Ю. Струтинська, Є.О. Комащенко, І.І. Гринюк, О.В. Лівіцька, О.М. Василюк*

Кальцій фосфати, модифіковані комплексом іонів Na^+,Mg^{2+},Cu^{2+},CO_3^{2-}/(BO_3^{3-},BO_2^-) чи Na^+, Mg^{2+},Cu^{2+},Fe^{3+}, CO_3^{2-}/(BO_3^{3-},BO_2^-), та композити на основі Na^+, Mg^{2+},CO_3^{2-}/(BO_3^{3-},BO_2^-)-вмісних кальцій фосфатів з (10 чи 25 мас%) $CuFe_2O_4$ були синтезовані з водних розчинів та нагріті до 600°C. Встановлено, що борат-іони у вихідному розчині дозволяють стабілізувати структуру кальцій фосфату апатитового типу, в той час, як у карбонат-вмісній системі одержано біфазні кальцій фосфати у складі композиту з 25 мас% $CuFe_2O_4$. В карбонатвмісних системах одержано частинки більших розмірів (28-34 нм), ніж відповідні у боратвмісних системах (19-23 нм). Наявність різних типів аніонів PO_4^{3-}, CO_3^{2-}, BO_3^{3-}, BO_2, OH^-) була підтверджена за допомогою методу ІЧ-спектроскопії. Композит на основі біфазного фосфату кальцію з 25 мас.% $CuFe_2O_4$ характеризувався вищою активністю до часткового розчинення в модельному розчині, ніж модифіковані фосфати кальцію та композити на їх основі з $CuFe_2O_4$. Найвищі антибактеріальні властивості проти штамів *S. aureus* або *P. aeruginosa* були виявлені для боратвмісного гідроксиапатиту. Отримані результати можуть бути важливими при розробці матеріалів зі спеціальною біоактивністю та антибактеріальними властивостями для медичного застосування.

1. Introduction

Magnetic materials are being extensively studied due to their unique properties, such as a high adsorption, optical and magnetic properties, which provide a wide range of applications from industrial to biomedical fields [1-3]. Considerable attention has been given to ferrites of transition metals, such as copper ferrite, which exhibit a high saturation magnetization, making them promising candidates for use in magnetically controlled drug delivery systems. Moreover, $CuFe_2O_4$ demonstrates antibacterial properties and biocompatibility, making it an attractive subject for research and for the development of composites based on this material for medical application [4-7]. For example, composites of ferrite with apatite-type calcium phosphate ($Ca_{10}(PO_4)_6(OH)_2$) attract a great attention. Synthetic calcium phosphates are considered as bone tissue substitutes or as coatings for implants due to their bioactivity, osteoconductivity, non-toxicity; in addition, they have a structure similar to that of biological materials. Their porous surface can enhance the potential of ferrite for drug delivery applications [8-10].

The properties of calcium phosphate can be further modified through substitutions in the cationic and anionic crystal sublattices due to their structural flexibility. In particular, Mg^{2+} cations play an important role in the early stages of osteogenesis and in the processes of bone and dentin mineralization. Similarly, Na^+ cations are involved in bone metabolism and can regulate cell adhesion activity. Thus, the incorporation of Mg^{2+} and Na^+ into the hydroxyapatite structure improves its biological characteristics and increases its biodegradation rate [11-12].

Anionic substitutions in apatite can occur at the PO_4^{3-} tetrahedral sites (B-type substitution) and at the OH^- group sites (A-type substitution). The most common among these involves CO_3^{2-} ions, which enhance the biological activity of the synthetic material. Carbonate is also present in natural bone mineral, predominantly at B-sites; its presence can be further increased by the inclusion of monovalent cations in the apatite structure [13-16]. The inclusion of boron exerts a regulatory effect on osteoblastic cell activity and positively influences apatite formation during synthesis. At B-sites, boron is incorporated into the lattice as BO_3^{3-} anions, while at A-sites, it is present in the form of BO_2^- [17-18].

The aim of present work was preparation of calcium phosphates modified with complex ions Na^+, Mg^{2+},Cu^{2+},(CO_3^{2-}/BO_3^{3-}), BO_2^- or Na^+, Mg^{2+},Cu^{2+},Fe^{3+},(CO_3^{2-}/BO_3^{3-}), BO_2^-, as well as composites based on calcium phosphate containing Na^+, Mg^{2+}, (CO_3^{2-}/BO_3^{3-}), BO_2^- -ions and $CuFe_2O_4$ in one step and their characterization including *in vitro* testing in model solution and thermal stability for some samples. The influence of calcium phosphates modification with complex of Na^+,Mg^{2+},Cu^{2+},CO_3^{2-}- or Na^+,Mg^{2+},Cu^{2+},BO_3^{3-},BO_2^--ions against *S. aureus* or *P. aeruginosa* strains were also determined.

2. Experimental procedure

Preparation of samples. Calcium phosphates modified with complexes of ions Na^+,Mg^{2+},Cu^{2+},(CO_3^{2-}/BO_3^{3-}),BO_2^- or Na^+, Mg^{2+},Cu^{2+},Fe^{3+},(CO_3^{2-}/BO_3^{3-}), BO_2^-, as well as composites based on calcium phosphate containing Na^+, Mg^{2+},(CO_3^{2-}/BO_3^{3-}),BO_2^- and $CuFe_2O_4$ were obtained in aqueous solutions at different molar ratio of components (Table 1). The following initial components (analytical grade) were used: $Ca(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $NaNO_3$, $(NH_4)_2HPO_4$, NH_4HCO_3 and H_3BO_3. Calculated amounts of nitrates were dissolved in 25 ml of deionized water, and the solution containing a mixture of (PO_4^{3-} + CO_3^{2-}) or (PO_4^{3-} + BO_3^{3-}) anions was added with stirring. After this, 3 ml of NH_3*H_2O (25%) was added. The water was evaporated and powders were heated to a temperature of 600 °C. A muffle furnace SNOL-7.2/900 with a TermoPro-601 temperature controller was used.

Methods of characterization. X-ray powder diffraction was used to characterize the composition of samples. Shimadzu XRD-6000 diffractometer (in the range of 2θ from 5 to 60°, at a rate of 1.2°/min) was used for recording XRD patterns. The apatite- and ferrite-type phases were identified using references (PDF2 #01-

Table 1. Samples of composites with different molar ratios of components in the initial solution

Sample	Molar ratios in an initial solution						
	Ca^{2+}	Na^+	Cu^{2+}	Mg^{2+}	Fe^{3+}	PO_4^{3-}	An^-
	Ca^{2+}-Na^+-Cu^{2+}-Mg^{2+}-Fe^{3+}-PO_4^{3-} -CO_3^{2-}						
Sample 1	36.5	1	1	1	-	22	2
Sample 2	36.0	1	1	1	1		
Sample 3	37.5	1	1.8	1	3.6		
Sample 4	37.1	1	5.2	1	10.4		
	Ca^{2+}- Na^+-Cu^{2+}-Mg^{2+}-Fe^{3+}-PO_4^{3-}-BO_3^{3-}						
Sample 5	37.5	1	1	1	-	22	8
Sample 6	37.5	1	1	1	1		
Sample 7	38.5	1	1.8	1	3.6		
Sample 8	38.5	1	5.2	1	10.4		

089-6495) and (PDF2 #01-077-0010), respectively, from the ICDD (International Center for Diffraction Data) database. The crystallite sizes for the apatite-type phase were calculated using the Debye-Scherrer equation.

Fourier transform infrared spectroscopy was used to confirm the presence of different type anions. A PerkinElmer Spectrum BX spectrometer was used (frequency range 400-4000 cm^{-1}) to record spectra of samples in KBr pellets.

The thermal stability of the prepared composite was investigated using a Shimadzu DTG-60H synchronous thermogravimetric and differential thermal analyzer. The powders were placed in a platinum crucible and heated in air at a rate of 10 °C/min from 25 °C to 900°C. α-Al_2O_3 was chosen as the standard sample.

The influence of the synthesized composites on the pH of a model solution (phosphate-buffered saline) was studied *in vitro* at pH = 7.45 and 37 °C. The pH value of the sample solution was measured over 4 days (in 24 hour increments) using an OHAUS Started 2100pH meter.

The antibacterial activity of the modified calcium phosphates against microorganisms *Staphylococcus aureus* ATCC 25923 and *Pseudomonas aeruginosa* ATCC 9027 was investigated as described in [19] with some modifications. The microbial strains used were cultured for 24 hours in tryptone soya broth at 37° C in duplicate. Before studying the antibacterial activity, the samples were sterilized in an autoclave at a pressure of 0.75 atm and a temperature of 112°C for 30 minutes. After this, different amounts of samples (5 mM, 10 mM or 20 mM) were added to sterile bottles with nutrient medium and 2% the overnight culture (10^5 CFU/ml) – *S. aureus* or *P. aeruginosa strains*. Cultivation of the culture without powder was used as a control. The bottles were incubated at 37±1°C for 24 hours, after which suspensions of the 24-hour bacterial culture with samples were plated on Petri dishes containing tryptone soya agar. The amount of bacterial colonies of tested strains on the surface of the agar medium was counted the next day. Statistical analysis of data was performed using the program «Statistica 7.0». To assess the reliability of quantitative indicators of differences in different strains, a post hoc test using the LSD criterion was used. Differences were considered statistically significant at P≤0.05.

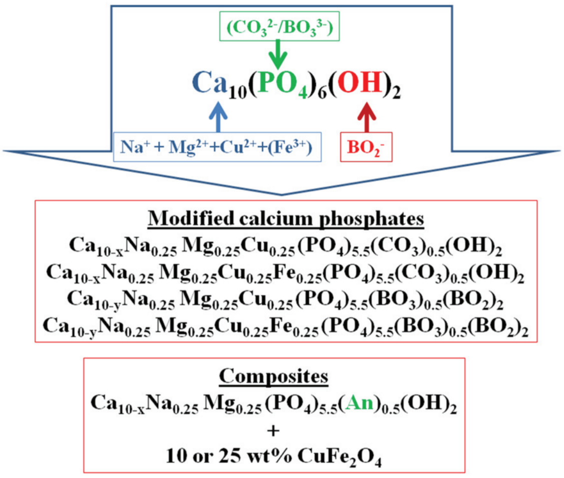

Fig. 1. The principles of substitution in hydroxyapatite structure determining compositions of modified calcium phosphates and composites based on them with $CuFe_2O_4$

3. Results and discussion

At the first step, the formation of calcium phosphates was studied in the presence of complex microelements (Na^+, Cu^{2+}, Mg^{2+}) various types of anions (CO_3^{2-} or BO_3^{3-} and BO_2^-) in the molar ratios presented in the Table 1

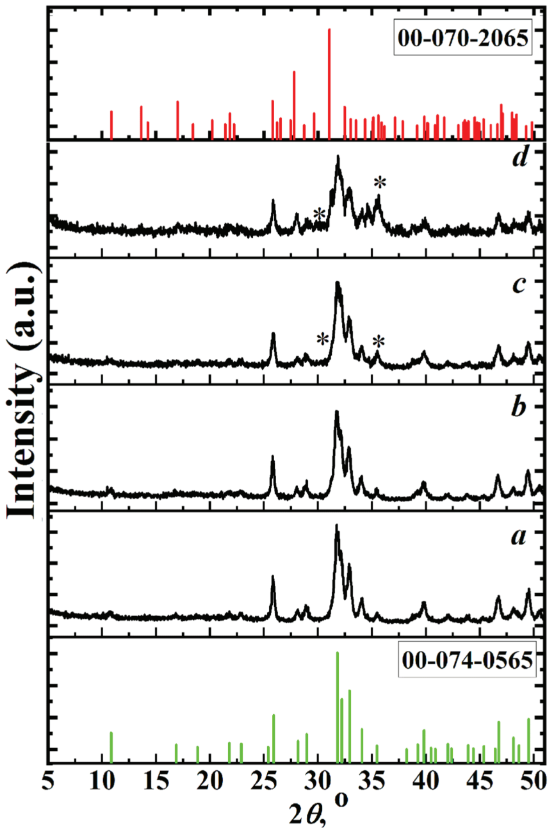

Fig. 2. XRD patterns for samples obtained in the system Ca^{2+}-Na^+-Cu^{2+}-Mg^{2+}-Fe^{3+}-PO_4^{3-}-CO_3^{2-}: Sample 1 (a), Sample 2 (b) Sample 3 (c), Sample 4 (d) heated at 600°C for 2 hours. Reference patterns for $Ca_{10}(PO_4)_6(OH)_2$ (#00-074-0565), ß-$Ca_3(PO_4)_2$ (#00-070-2065) and * shows ferrite-type phase.

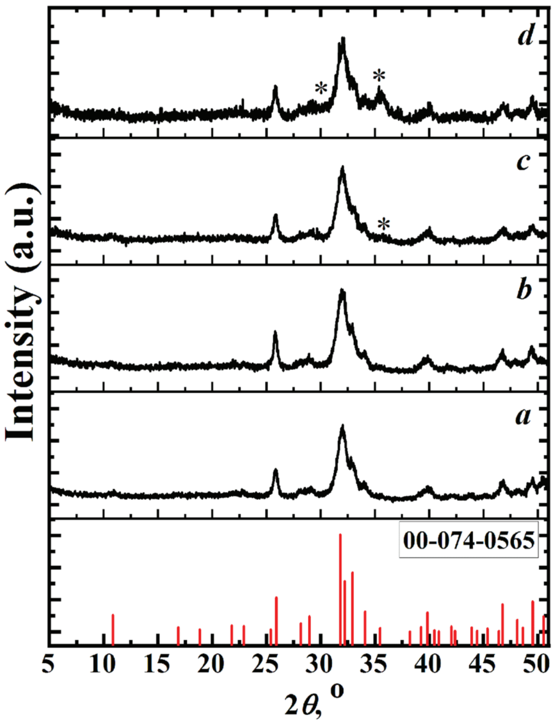

Fig. 3. XRD patterns for samples obtained in the system Ca^{2+}-Na^+-Cu^{2+}-Mg^{2+}-Fe^{3+}-PO_4^{3-}-BO_3^{3-}: Sample 5 (a), Sample 6 (b) Sample 7 (c), Sample 8 (d) heated at 600°C for 2 hours. Reference patterns for $Ca_{10}(PO_4)_6(OH)_2$ (#00-074-0565) and * - shows ferrite-type phase.

(Sample 1 and Sample 5). After this, the addition of a small amount of Fe^{3+} to the initial solution was studied to achieve partial substitution of calcium atoms in the structure of calcium phosphate with simultaneous modification by complex trace elements in order to establish the influence of Fe^{3+} in the initial solution on the phase formation of calcium phosphates (Table 1 and Fig.1). According to XRD results, single-phase modified calcium phosphates associated with apatite, which belong to the hexagonal system (space group (space group $P6_3/m$) were obtained in all systems (Fig. 2 a, b – Sample 1-2 and Fig. 3 a, b – Sample). In the next step, attempts were made to obtain composites based on modified calcium phosphate with 10 or 25 wt.% $CuFe_2O_4$ using a one-step synthesis method. The effect of increasing the amount of Cu^{2+}+Fe^{3+} in the initial carbonate-containing solution with the formation of biphasic calcium phosphate (a mixture of phases based on $Ca_{10}(PO_4)_6(OH)_2$ – hexagonal system, space group $P6_3/m$ and ß-$Ca_3(PO_4)_2$ – trigonal system, space group *R-3c*) was established (Fig. 2 d – Sample 4). At the same time, in the case of a borate-containing system with the same molar ratio of components in the initial solution, a single-phase apatite-type calcium phosphate was obtained (Fig. 3 d – Sample 8). These results indicate the important role of borate-anion in the formation of calcium apatite phosphate in a multicomponent aqueous solution during the preparation of ferrite composites by a one-step method.

The sizes of modified apatite-related calcium phosphate particles were calculated using the Debye-Scherrer formula. It was found that the nature of the cations in the initial multicomponent solutions did not affect the size of particles, whereas the nature of the doping anion did. In the case of carbonate-containing systems, larger particles of 28-34 nm were formed than particles in systems containing borates (19-23 nm).

The FTIR spectra of the synthesized modified calcium phosphates and composites based on them with $CuFe_2O_4$ are shown in Figure 4. Characteristic vibrations of phosphate tetrahedra were observed in the frequency ranges of

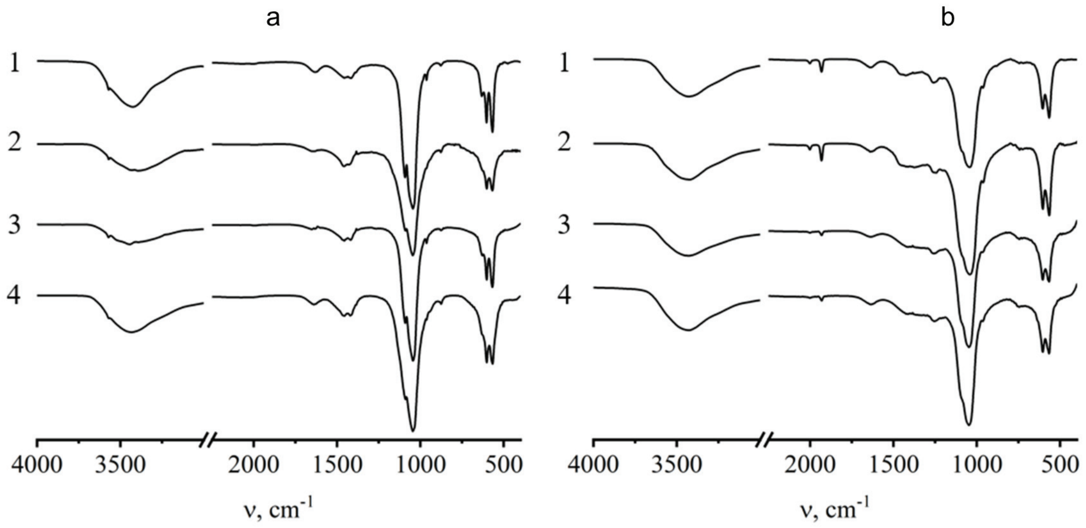

Fig. 4. FTIR spectra of samples obtained in the system Ca^{2+}-Na^+-Cu^{2+}-Mg^{2+}-Fe^{3+}-PO_4^{3-}-An: An – CO_3^{2-} (a) and BO_3^{3-} (b): Samples 1 and 5 (curves 1), $^-$Samples 2 and 6 (curves 2), $^-$Samples 3 and 7 (curves 3), $^-$Samples 4 and 8 (curves 4) heated at 600°C for 2 hours.

550-640 cm^{-1} (v_4) and 980-1150 cm^{-1} (v_1 and v_3), a broad band in the range 3200-3600 cm^{-1} and 1590-1700 cm^{-1} corresponds to vibrations of sorbed water. In the spectra of carbonate-containing samples (Fig. 4a), vibrations of the OH^- groups were noted at 3570 cm^{-1}, while vibrations of the carbonate groups were detected in the frequency ranges of 1380-1530 cm^{-1} (v_3) and 874 cm^{-1} (v_2). The positions of these bands confirm the implementation of partial substitution of the phosphate anion by the carbonate anion (B-type) in the hydroxyapatite structure. The characteristic vibrations of the borate groups were observed in the frequency regions of 1205-1294 cm^{-1} (v_3) and 760 cm^{-1} (v_2), their positions confirm the implementation of partial substitution of phosphate by borate in the calcium phosphate structure (Fig. 4b). The presence of an additional pair of peaks at 1930-2005 cm^{-1} indicates the substitution of the OH^- group by linear BO_2^- - anions (Fig. 4b).

The results of thermogravimetric analysis of the obtained samples are similar regardless of their phase composition, but depend on the modification of the anion sublattice of the calcium phosphate structure with carbonate or borate-anions. For illustration, the obtained results for Sample 3 and Sample 7 are presented in Fig. 5 which shows 6.6 and 1.4 wt % mass loss during their heating to 800 °C, respectively. In the case of Sample 3, containing carbonate, the more significant and continuous decrease in mass is due to the removal of sorbed water and partial loss of carbonate, whereas for sample 7, containing borate, the most noticeable change in mass (up to 1.2% by mass) was recorded upon heating to 100 °C. This mass loss is mainly due to the removal of adsorbed water. A further increase in temperature for Sample 7 results in a mass change of only 0.2% mass (Fig. 5 b).

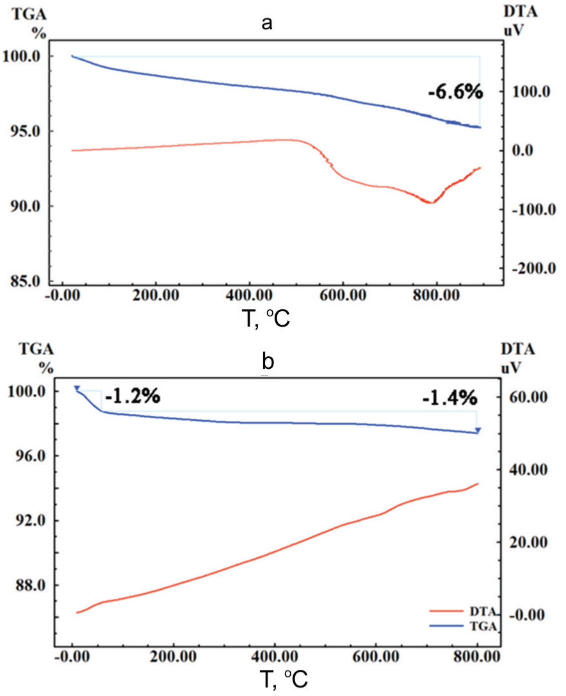

Fig. 5. TG-DTA for obtained samples: Sample 3 (a) and Sample 7 (b).

In vitro testing of synthesized calcium phosphates modified with complex Na^+,Mg^{2+},Cu^{2+},CO_3^{2-}/(BO_3^{3-},BO_2^-)-ions, as well as composites based on calcium phosphates

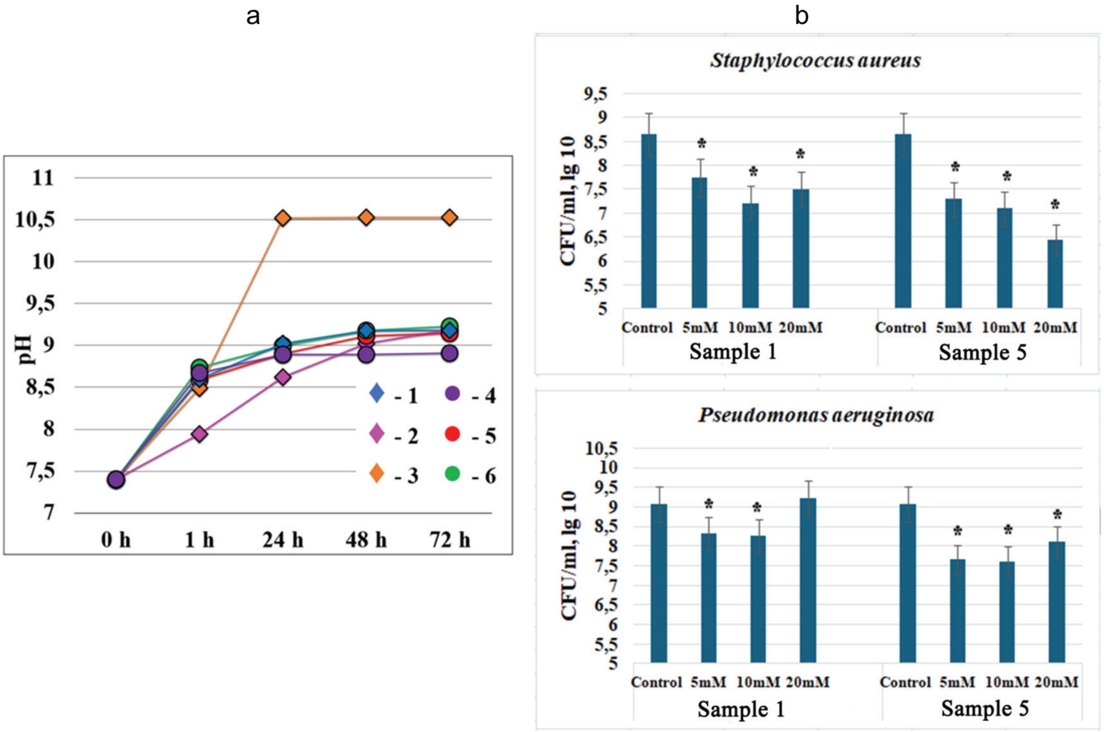

Fig. 6. Changing of the pH value of model solution (with pH = 7.45 at temperature 37 °C) in the presence of obtained samples: (a); the antibacterial activity against *Staphylococcus aureus* ATCC 25923 and *Pseudomonas aeruginosa* ATCC 9027 for different amounts (5, 10 and 20 mM) of Sample 1 and Sample 5 (M ±m, n = 4,* – $p < 0.05$ compared to control) (b).

containing Na^+,Mg^{2+},CO_3^{2-}/(BO_3^{3-},BO_2^-) with (10 or 25 wt%) $CuFe_2O_4$ was performed in the model solution (pH = 7.45 and temperature 37 °C). The results are shown in Figure 6*a* as the change in the pH values of the model solution at a temperature of 37° over 72 hours of study.

The obtained results indicate an increase in the pH values for all samples already after the first hour of testing. For carbonate-containing samples, the highest activity was observed during the first 24 hours, while the increase in pH compared to the initial value ranged from 16 to 42%. The most significant increase in pH was observed for Sample 4, that is a composite based on biphasic calcium phosphate with $CuFe_2O_4$ (25 wt.%) (Fig. 6a, curve 3). For other carbonate-containing apatite-type calcium phosphates, the activity was lower over 72 hours of research, independently of the presence of ferrite. For borate-containing samples, the activity was highest only during the first hour of the experiment, resulting in a pH increase in the range of 16-18%, without a significant change in the subsequent hours of the investigation.

The increase in the pH values of the model solution is associated with the partial dissolution of the calcium phosphate component, while the increase in ferrite content practically does not affect the dissolution process, which is observed for all studied samples. The exception was biphasic calcium phosphate: its activity turned out to be higher (Fig.6a, curve 3), which indicates the leading influence of the phase composition. In this study, anionic modifications demonstrated similar results, except for the effect of borate on the formation of the calcium phosphate phase.

The effect of modification of apatite-related calcium phosphate with complexes of microelements and carbonate or borate anions (Sample 1 and Sample 5) on *S. aureus* and *P. aeruginosa* was also investigated (Fig. 6). Borate-containing hydroxyapatite (Sample 5) demonstrated higher antibacterial activity against both *S. aureus* and *P. aeruginosa* strains compared to carbonate-containing hydroxyapatite (Sample 1) (Fig. 6). When 5 or 10 mM of Sample 1 were added, only 8.0 or 27.0 times inhibition of the S. *aureus* strain growth was observed, whereas in the presence of 5, 10 or 20 mM borate-containing hydroxyapatite (Sample 5), significantly greater inhibition was found – 22.6, 35.7 or 157.0 times – compared to the control (Fig. 6b). When Sample 5 was added at 5, 10, or 20 mM, the growth inhibition of *P. aeruginosa* was 25.7, 28.5, or 9.0 times, respectively (Fig. 6). At the same time, a 5.6- or 6.4-fold decrease in the number of *P. aeruginosa* was detected with the addition of only 5 or 10 mM of Sample 1 containing carbonate (Fig. 6b). Obtained results showed that prepared hydroxyapatites modified with complexes of Na^+, Mg^{2+},Cu^{2+},(CO_3^{2-} or (BO_3^{3-}, BO_2^-) ions have an effect on *S. aureus* and *P. aeruginosa* strains, and the presence of borate-anion can significantly improve this characteristic..

4. Conclusions

The hydroxyapatites modified with complexes of Na^+,Mg^{2+},Cu^{2+},(CO_3^{2-}/BO_3^{3-},BO_2^-) or Na^+, Mg^{2+},Cu^{2+},Fe^{3+},(CO_3^{2-}/BO_3^{3-}, BO_2^-) ions were obtained from aqueous solutions, and the powders were annealed at 600°C for 2 hours. It was found that the presence of borate-anions in the initial solution leads to the formation of hydroxyapatite modified with complexes of ions with 25 wt% $CuFe_2O_4$, whereas in the carbonate-containing system, the composite based on biphasic calcium phosphate with 25 wt% of $CuFe_2O_4$ is formed. The presence of CO_3^{2-}, BO_3^{3-} and BO_2^- anions was confirmed using the FTIR spectroscopy method. Thermogravimetric analysis data showed the stability of the borate-containing calcium phosphate, while carbonate loss was observed when heated to 800 °C. A study of the effect of prepared hydroxyapatites containing Na^+,Mg^{2+},Cu^{2+},CO_3^{2-} or Na^+,Mg^{2+},Cu^{2+},BO_3^{3-},BO_2^- complexes against *S. aureus* and *P. aeruginosa* strains showed that modification of calcium phosphate with borate-ions can improve its antibacterial properties. In the future, the magnetic properties of the obtained composites will be studied in order to assess the prospects for their use as materials with special magnetic characteristics in orthopedics.

Acknowledgements

This research was supported by National Research Foundation of Ukraine (Grant №2023.03/0109). Strutynska Nataliia is grateful to the II European Chemistry School for Ukrainians for providing a comprehensive overview of current trends in European chemical science. https://acmin.agh.edu.pl/en/detail/s/ii-european-chemistry-school-for-ukrainians.

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