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Historical Perspective

Composites of hydroxyapatite and their application in adsorption, medicine and as catalysts

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ABSTRACT

Composites of hydroxyapatite, recognized by its peculiar crystal architecture and distinctive attributes showcased the potential in adsorbing heavy metal ions and radioactive elements as well as selected organic substances. In this paper, the intrinsic mechanism of adsorption by composites hydroxyapatite was proved for the first time. Subsequently, selectivity and competitiveness of composites of hydroxyapatite for a variety of environments containing various interferences from cations, anions, and organic molecules are elucidated. Next, composites of hydroxyapatite were further categorized according to their morphological dimensions. Adsorption properties and intrinsic mechanisms were investigated based on different morphologies. It was shown that although composites of hydroxyapatite were characterized by excellent adsorption capacity and cost-effectiveness, their application is often challenging due to inherent fragility and agglomeration, technical problems required for their handling as well as difficulty in recycling. Finally, to address these issues, the paper discusses the tendency of hydroxyapatite composites to adsorb heavy metal ions and radioactive elements as well as the limitations of their applications. Summarizing the limitations and future directions of modification of HAP in the field of heavy metal ions and different substances contamination abatement, the paper provides insightful perspectives for its gradual improvement and rational application.

1. Introduction

Hydroxyapatite (HAP) is a commonly known calcium phosphate mineral. It belongs to the apatites and is expressed in the formula $Ca_{10}(PO_4)_6(OH)_2$. HAP is a part of human bones, including teeth giving them mechanical strength and proper durability. In general, there are a few prevailing compounds among calcium phosphates minerals, i. e. tricalcium phosphates, biphasic calcium phosphates or tetracalcium phosphates. However, each material exhibits different properties and there are some differences in their action. The studies showed that hydroxyapatite is more common considering its properties, i.e. stability, reactivity, large adsorption capacity, large surface area, inexpensiveness. Moreover, it is biodegradable, friendly for the environment and can be synthesized by various methods which do not demand aggressive substances. Furthermore, its biocompatibility is of great importance. Due to its characteristics hydroxyapatite is used in numerous branches of industry and human life. In medicine it finds application as a drug and gene delivery system, coating material, bone implant. Moreover, HAP can be used in bioimaging, magnetic resonance, tissue engineering, cell separation or hyperthermia method [1–4]. What is more, due to its sorption capacity HAP can be utilized as an adsorbent. In the literature, adsorption of metal ions, i.e. chromium, lead, cadmium, nickel, zinc, aluminum, copper, cobalt, iron, manganese, or bar ions is extensively described [5–24]. Additionally, hydroxyapatite proved to be an effective adsorbent in the removal of radionuclides, e. g. uranium, cesium, strontium, iodine [25–31]. Moreover, sorption capacity of organic compounds [32–38] as well as inorganic ones i.e. fluoride and selenium [39–42] was studied by many scientists.

Hydroxyapatite appears to be an ideal material. However, it possesses some drawbacks. The most significant are weak toughness and tensile strength. Moreover, there are some difficulties in its separation from a solution. Therefore, numerous modifications of hydroxyapatite were developed to improve its properties and expand its application horizon [2,3].

Adsorption of cations on the surface of hydroxyapatite can occur through ion exchange with calcium ions from the crystal lattice. In this reaction, calcium (Ca^{2+}) in the hydroxyapatite structure is partially replaced by other cations (Me^{2+}), leading to the formation of a new

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compound with an altered number of calcium atoms and guest metal ions (Me). Instead of remaining only on the surface of the material (as would happen in surface adsorption), the Me^{2+} metal ions enter deep into the crystal structure of the hydroxyapatite and replace the calcium cations at the nodes of the crystal lattice. The reaction taking place is not surface adsorption, but rather an ion exchange reaction in which Me^{2+} cations are permanently incorporated into the crystal lattice through exchange with Ca^{2+} ions.

$$Ca_{10}(PO_4)_3(OH)_2 + xMe^{2+} \rightarrow Me_xCa_{(10-x)}(PO_4)_3(OH)_2 + xCa^{2+} \quad (1)$$

The second mechanism of adsorption of cations on the surface of hydroxyapatite is adsorption of metal cations on surface groups:

Adsorption of cations on the hydrogen phosphate group

$$HAp - POH + Me^{2+} \leftrightarrow HAp - PO - Me^{+} + H^{+} \quad (2)$$

$$2HAP - POH + Me^{2+} \rightarrow (HAp - PO^{-})_2Me^{2+} + 2H^{+} \quad (3)$$

Adsorption of cations on hydroxyl groups of hydroxyapatite:

$$HAp - OH + Me^{2+} \leftrightarrow HAp - O - Me^{+} + H^{+} \quad (4)$$

$$2HAP - OH + Me^{2+} \rightarrow (HAp - O^{-})_2Me^{2+} + 2H^{+} \quad (5)$$

The concentration of Ca^{2+} ions on the HAp surface determined by radioisotope method and calculated from crystallographic data was 4.5 Ca^{2+} ions/nm^2. The concentration of PO_4^{3-} ions on the HAp surface determined by radioisotope method and calculated from crystallographic data was 3.02 PO_4^{3-} ions/nm^2. The concentration of -OH groups calculated from crystallographic data was 2.5 -OH groups/nm^2, while, on the basis of IR spectra analysis, the concentration of these groups was determined to be 1 ± 0.4 groups -OH/nm^2.

In the process of exchange of metal cations with calcium on the surface of hydroxyapatite, two properties of the ions are considered: ionic radius and electronegativity. The following two conditions have been formulated in the literature to characterize calcium-exchanging cations in the hydroxyapatite crystal lattice [42]:

– The radius of the exchanged cation should not differ from that of Ca^{2+} by more than 15 %, so its replacement in the HAp lattice structure will not cause significant deformation of the crystal lattice. Suzuki and co-workers determined the range of radius of exchanged ions from 0.09 to 0.13 nm.
- High electro-negativity, up to 2.4, promotes ion substitution.

In addition to the ion exchange of metal cations with calcium ions from HAp and the adsorption of ions on HAp's surface functional groups, a third process is described in the literature, which results in the uptake of metal cations from solution by hydroxyapatite. This process involves the dissolution of hydroxyapatite, followed by the precipitation of a new solid phase. It occurs at a high initial concentration of divalent metal cation>0.001 mol/dm^3 and an acidic pH of the solution according to the following reactions:

$$xMe^{2+} + (5-x)Ca^{2+} + 3H_2PO_4^{-} \leftrightarrow (Me_xCa_{5-x})(PO_4)_3OH + 7H^{+} \quad (6)$$

$$xMe^{2+} + (5-x)Ca^{2+} + 3HPO_4^{2-} + 2H_2O \leftrightarrow (Me_xCa_{5-x})(PO_4)_3OH + 4H^{+} \quad (7)$$

Fig. 1. shows the solubility diagram of hydroxyapatite, which was constructed taking into account the following values: the solubility product of hydroxyapatite $pKs0(Ca_5(PO_4)_3OH) = 57.43$, phosphoric acid dissociation constants: pKa1 = 2.16, pKa2 = 7.21, pKa3 = 12.32,

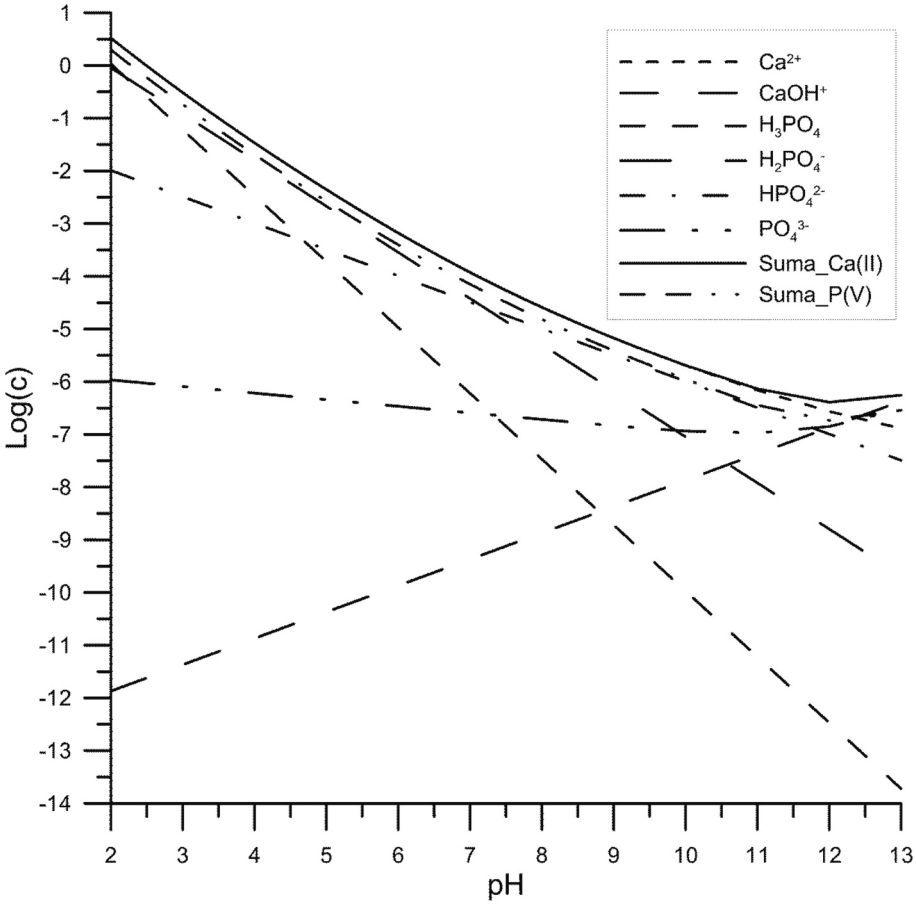

Fig. 1. Hydroxyapatite solubility diagram.

and stability constants of calcium phosphate complexes $pK(CaH_2PO_4^+) = -0.84$, $pK(CaHPO_4) = -2.55$, and $pK(CaPO_4^-) = 5.54$ [42]. The solubility diagram of hydroxyapatite as a function of pH indicates that the minimum solubility of hydroxyapatite occurs at pH ~ 12. The studied range of metal ion adsorption as a function of pH is limited due to the solubility of hydroxyapatite to pH from ~6 to pH ~ 11. In this pH range, the solubility of hydroxyapatite changes significantly, the concentration of calcium and phosphate ions decreases about nine hundred times. (See Figs. 2–4.)

High solubility of hydroxyapatite at high concentrations of adsorbed cation, above 0.001 mol/dm^3, may cause precipitation of a new phase due to reaction of metal cations with phosphate ions.

1.1. The magnetic properties and characteristics of Fe_2O_3 depend on its phase type

Adsorption is considered to be the most effective method of various removal processes from solutions. Of the other methods, i.e. ion exchange, precipitation, membrane filtration, complexation, reverse osmosis, oxidation, irradiation, or electrochemistry, it is characterized by easy procedures, low cost, efficiency, universality. Nowadays, it is of vital importance due to the growing amount of impurities in the environment. Many substances or metal ions get from industry, medicine or accidently into the ecosystem. Some of the compound can be poisonous and can cause diseases. Hence, it is significant to develop processes of effective purification utilizing proper adsorbents [43,44].

Combination of hydroxyapatite and iron oxide (Fe_2O_3 or Fe_3O_4) allows to obtain a multifunctional core-shell material, where the iron oxide is a core, and hydroxyapatite is an outer layer. Moreover, the addition of Fe_2O_3 or Fe_3O_4 gives magnetic properties to the material, which is important in separation processes due to the possibility of applying an external magnet to remove the adsorbent from the solution [1,45].

One of the most toxic ions in the ecosystem is cadmium. The sources of contamination are, e. g. metallurgical industry, mines, battery manufacturing, electroplating engineering, or pigments production. Cd is extremely harmful even at a low level of concentration due to its accumulation in human body. The studies on cadmium adsorption on the surface of HAP/ Fe_2O_3 composite were carried by Shen et al. [46]. The material was obtained by the chemical co-precipitation method described in the paper. The adsorption experiments included effects of pH, adsorbent mass, contact time, temperature and the addition of other substances. The data proved that the synthesis process was successful and the obtained composite exhibited appropriate surface properties. The highest adsorption value reported in the study was 277.78 mg/g. Moreover, with pH increase, adsorption was becoming more effective. A similar tendency was observed in the study of the effect of adsorbent mass, where adsorption improved with the increasing amount, which can be related to a greater number of sites capable of binding such a metal. Additional elements present in the system are also important - Na^{2+} and Pb^{2+} ions in the solution. Due to the competition between elements, the binding efficiency of Cd ions decreased. In real systems, organic components are often present, so studying their influence is of great practical importance. Shen et al. showed that the presence of humic acid as a representative of a substance with organic nature resulted in the enrichment of the composite surface, which was associated with a direct improvement in adsorption processes. The studies of kinetics of cadmium ion binding showed that this it is a pseudo second-order process, described with good accuracy by the Langmuir isotherm. The research on thermodynamics revealed that the process was spontaneous and endothermic. Shen et al. also tried to analyze the mechanism of cadmium ion binding on the HAP/Fe_2O_3 surface, but the results were inconclusive. Adsorption was found to involve electrostatics, complexation, and ion exchange [46]. Similar research was carried by Xiao et al. [47] and Feng et al. who additionally studied adsorption of Zn on the composite surface [48]. In the first paper, the highest adsorption value was 258 mg/g. In turn, in the Feng et al. studies the adsorption was 196,4 mg/g for cadmium ions and 215,1 mg/g for zinc ones. Interestingly, Xiao et al. experiment showed that the cadmium ion binding process followed the Freundlich isotherm., which is different from the previous studies.

Lead (Pb) as a representative of heavy metals has also a harmful impact on all living organisms when its excessive quantities are in the environment. Moreover, cadmium originally from mines and battery industries, as well as pharmacy, oil and gas, motor vehicles was a negative effect. Due to the toxic effects of lead there is a need to develop a proper adsorbent to remove the impurities. Vahdat et al. [49] synthesized the HAP/ Fe_3O_4 composite utilizing the chemical deposition method. FTIR, SEM and EDS techniques were employed to characterize the surface and its properties. The results proved that the synthesis process was successful. The research on the influence of pH showed that when its value was increasing from 2 to 6, the adsorption was also increasing. However, when pH = 6 lead ions removal efficiency was decreasing. Another vital dependency is the temperature influence. Vahdat et al. reported that adsorption was less effective with the temperature increase. In turn, the longer the adsorbent was in contact with Pb from solution, the more effective adsorption was recorded. A similar tendency was reported during the studies concerning the composite mass. The researchers came to the conclusion that removal of lead ions is more effective when the sorbent mass is larger, which is caused by a greater amount of active sites on the composite surface. Moreover, the experiments proved that the adsorption processes were in agreement with both the Freundlich and Langmuir approaches, which indicates homogeneous and heterogeneous characteristics. Vahdat et al. reported the maximum value of lead adsorption equal 109.89 mg/g. Furthermore, the scientists took into account the pseudo second order kinetic model. Moreover, the process seemed to be exothermic and spontaneous. Unfortunately, the paper did not present a possible mechanism of adsorption [49]. A different approach concerning Pb removal is shown in the research carried by Zhuang et al. [50]. In this study HAP/ Fe_3O_4 microspheres were obtained. Furthermore, the material was characterized by common methods, i. e. SEM, XRD, XPS, ASAP, which proved that the composite was composed of iron oxide and hydroxyapatite phase. Moreover, the most effective pH range for Pb removal was from 2 to 3. At this point adsorption value was equal to 440 mg/g. Zhuang et al. obtained data similar to those presented in the previous paper. The adsorption process was described as the pseudo second order kinetic model. However, the results based on the isotherm corresponded better with Langmuir model. The author distinguished two possible mechanisms of lead ions removal, namely the ion exchange (pH = 3–6) and dissolution-precipitation (pH = 2) [50]. Dong et al. [51] studied also possible Pb adsorption on the HAP/ Fe_3O_4 composite, which was obtained using the co-precipitation method. The approach was similar to the previous approaches. However, there were some differences among the results. Dong et al. reported the maximum adsorption capacity equal 598.8 mg/g. The paper proved dissolution-precipitation mechanism, but it presented also possibility of surface complexation. Moreover, the experiments showed that the presence of additional ions, e.g. sodium, potassium, calcium or magnesium, did not influence the removal process. In turn, humic acid was employed as a representative of organic compound. Its presence in the solution made the adsorption decrease [51].

As it is well known, heavy metals are harmful to all living organisms and constitute a serious problem in the environment. Copper and nickel belong also to this group. These elements are common in the metal industry. Their adsorption problem was studied by Thanh et al. [52]. The adsorbent structure was composed of Fe_3O_4 nanoparticles, which were covered by hydroxyapatite nanorods. The composite was characterized by common methods (TEM, XRD, ASAP) which confirmed formation of a predicted structure. What is more, the data exhibits heterogeneous character of the surface. The author reported that the ion binding process is consistent with the pseudo second order model. Moreover, the

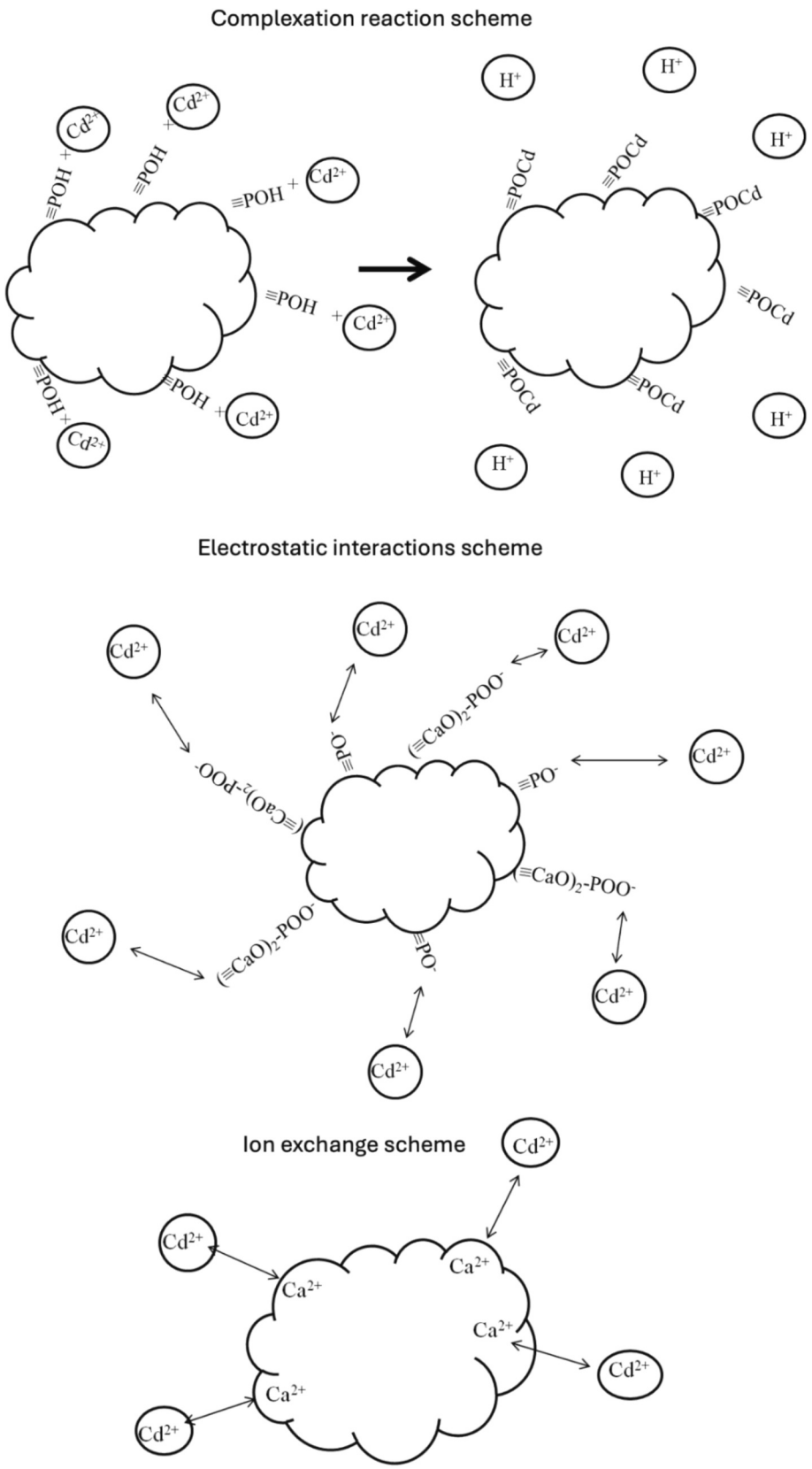

Fig. 2. Various reaction schemes.

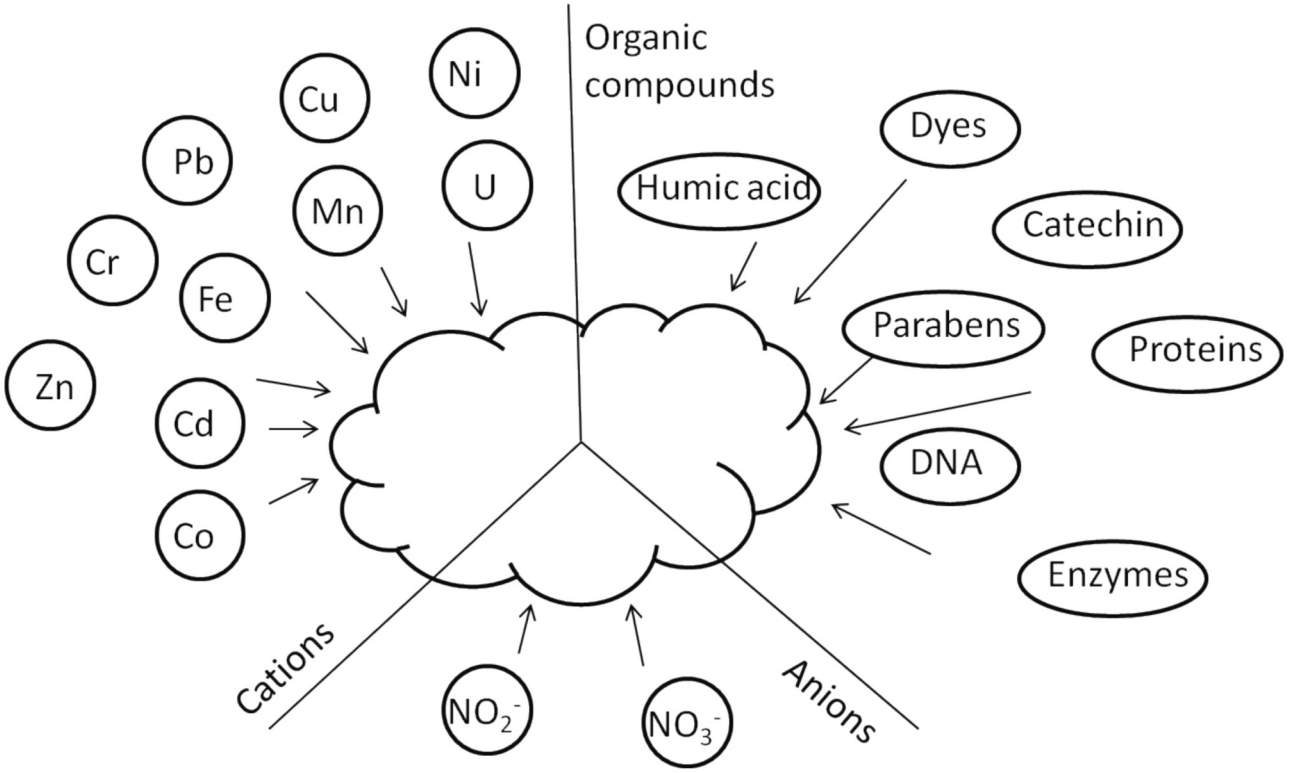

Fig. 3. Different possibilities of adsorption.

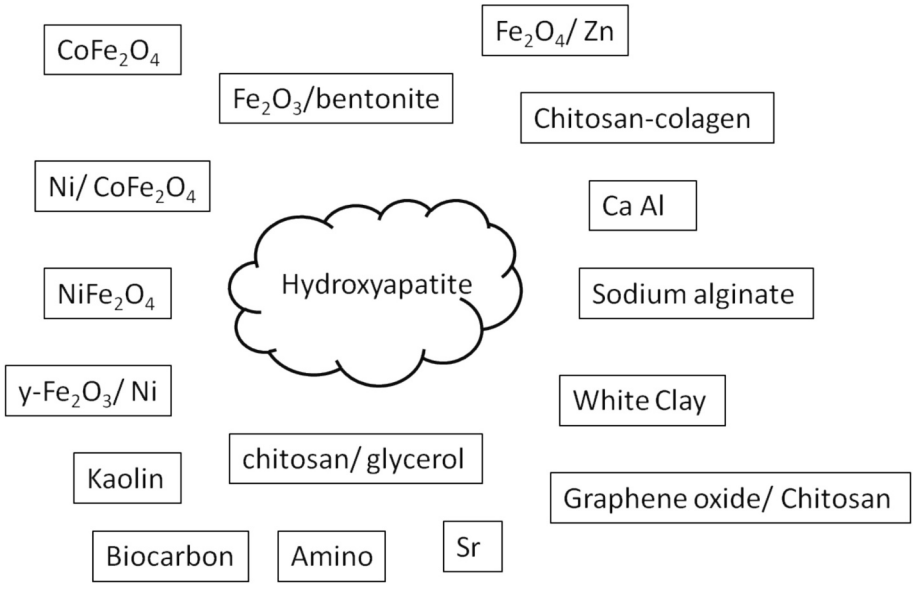

Fig. 4. Types of hydroxyapatite modifications.

results are better correlated with the Freundlich isotherm. The largest adsorption capacities for copper and nickel ions were 5.86 mg/g and 29.07 mg/g. It can be noticed that these values are significantly lower than for other ions. The research on the potential adsorption mechanism revealed that it was a mixed process of ion exchange and complexation reactions. Moreover, Thanh et al. proved that modification with magnetic iron oxide facilitates the separation process from the solution [52]. Furthermore, Mercado et al. studied the Cu^{2+} adsorption efficiency employing hydroxyapatite nanoparticles doped with iron obtained in the co-precipitation synthesis method [53]. The author revealed some differences in the synthesized structure in comparison with the original one utilizing following methods: XRD, XPS, IR, ASAP, TGA, HRTEM, ICP-AES. Hydroxyapatite modified by iron exhibited smaller crystalline phase as well as the amount of calcium ions decreased. Moreover, the surface was enriched with oxygen, iron oxide and phosphated iron. The VSM method also confirmed that the composite had magnetic properties due to the presence of iron. The maximum adsorption of 265 mg/g was successfully achieved. Furthermore, the process followed the Langmuir model [53].

Elkady et al. [54] carried out the studies concerning the problem of

iron and manganese presence in the environment. The harmful role of these metals as well as the vital need to reduce their amount were pointed out to. As follows from the studies a larger quantity of adsorbent made the removing process more effective. In turn, an increase in pH resulted in the increased adsorption. Moreover, similarly to the previous studies, the temperature affects also the process. According to the kinetic experiments, it can be concluded that the data was well fitted to the pseudo second order model. Among the various approaches, it was the Langmuir model that matched the obtained results best. This indicates the presence of a homogeneous surface with a finite number of adsorption sites, therefore it can be inferred that the ion exchange mechanism dominates in such a case. However, it is not clear which mechanism prevails. It is assumed that also complexation reactions and electrostatic interaction are involved in the adsorption process. The adsorption capacity for Fe(II) was 0.704 mg/g and for Mn(II) was 0.665 mg/g [54]. The same authors facilitated the synthesis process by microwave in the other paper. The research scheme was alike. However, the adsorption capacity for Fe(II) was 4.9 mg/g and for Mn(II) 4.8 mg/g which is significantly better than in the previous studies [55].

It is necessary to emphasize the importance of removing radioactive contaminants. Uranium represents the radionuclide group. It exhibits extremely harmful effects on living organisms. Therefore, the scientists are searching for a best solution to control the uranium concentration in the environment. El-Maghrabi et al. prepared magnetic hydroxyapatite nanocomposite utilizing the facile microwave combustion method [56]. The obtained material was subjected to the following analyses: TEM, XRD, FT-IR, BET and magnetization measurements. The researchers reported that the most efficient process was at pH = 5 at 25 °C whereas the maximum adsorption was 310 mg/g. The isotherm study proved the agreement with the Langmuir model. Moreover, the experimental data was better described by the pseudo second order equation. The paper presents also the thermodynamics results. It can be concluded that the uranium removal process on the composite surface was endothermic, spontaneous and irreversible. The author noted that the uranyl ions were bound utilizing phosphate groups (present in the hydroxyapatite outer layer) in the complexation reactions [56]. Moreover, good adsorption conditions while removing uranium from solution were reported by Zeng et al. [57]. In this research the maximum adsorption was equal to 798.58 mg/g which is a very high value in comparison with the previous studies.

Nuclear industry is a rich source of radioactive elements which can get accidentally into the environment by an accident. The radioactivity problem is of great interest. Nuclear power plants are specific places where radioactivity is present. People working there are exposed to danger every day. One place of particular risk is the reactor coolant tank. During the reactor work, the coolant vessel can corrode, and the products of this process, i.e., Co^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} are also radioactive and pose a danger [58]. Therefore, Venkatesan et al. conducted experiments concerning the utilization of magnetic composite as an adsorbent. The solid was analyzed using the following methods: XRD, TEM, SEM, XPS. Moreover, the zeta potential and magnetic properties were also measured. The experiment proved that the PSO model described better the adsorption process. In addition, the obtained values correspond properly with the Langmuir isotherm, indicating presence of homogeneous monolayer. The largest adsorption value was 68.95 mg/g [58].

The versatile use of magnetic hydroxyapatite is also evidenced by the research carried out by Ghasemi et al. [59], who studied anions, i.e. nitrate and nitrite ions, adsorbed on the composite surface. These ions can have toxic effect on living organisms and environment, thus their level must be monitored. In the experiment, the material was analyzed by means of the following methods: XRD, SEM, FTIR, VSM. The results showed that the adsorption % in tap water, river water, wastewater and soil for nitrite ions was as follows: 101, 99, 95, 95 and for nitrate ions: 97, 93, 96, 97. It can be seen that the studied adsorbent could be a promising material for anions removal from different samples [59].

Not only anions show the likelihood of sorbing on this composite, but also organic compounds, as Shi et al. [60] proved by studying the adsorption of humic acid. This substance is known for its negative effect on water quality. The authors examined the solid using the XRD, FTIR, TEM and VSM methods. The studies proved that the sorption process was chemisorption according to the PSO model. Moreover, the Sips isotherm corresponds better to the obtained data. The maximum adsorption value that was recorded in the study was 601.91 mg/g [60].

The issues related to the removal of synthetic dyes, which have their origin in the ecosystem from the textile industry, are also all important aspect in the research. That is why, Sahoo et al. presented a probable solution to the problem [61]. The authors examined the possibility of utilizing the Hap/Fe_2O_3 composite in the Eriochrome Black T dye removal. The adsorbent was characterized by XRD, FTIR, SEM, VSM. The study showed that adsorption occurs through chemisorption, as indicated by a good fit of the data to the pseudo second order model. Moreover, the Langmuir isotherm described better the process. Thus, the monolayer is formed on the material surface. The maximum value obtained for adsorption was 43.47 mg/g. Moreover, the solid was characterized by antibacterial activity according to the experiment with *Escherichia coli* (*E. coli*) and *Micrococcus luteus* (*M. luteus*) strains [61].

In addition to the applications involving the removal of contaminants from aqueous solutions, Hap/Fe_2O_3 also shows the ability to adsorb substances of a biological nature. Yusoff et al. studied possibility to adsorb catechin [62]. It turned out that the maximum value which can be adsorbed was 110.97 mg/g. Moreover, the substances, e.g. parabens [63], proteins [64,65], plasmid DNA [66] or enzymes [67] can be adsorbed as well.

1.2. Hydroxyapatite composites characterized by adsorption properties

Another option to develop the hydroxyapatite magnetic properties is to obtain its composite in combination with Zn and Fe_2O_4 as shown in a study by El-Maghrabi et al. [68]. In this research the solid was synthesized and analyzed by means of the following methods: FTIR, XRD, HRTEM, SAED, EDX, VSM. The adsorbent was put in fixed-bed columns and the possibility of oil adsorption was studied. The result showed that the best removal process was with the flow rate 3 ml/min and the bed height 178.26 mm. The following conclusion was drawn during the experiment, namely the best flow rate for the material was in the range 1–5 ml/min. Moreover, the short column did not provide adequate activation of the solid and active sites, thus the height of the column had to be increased [68].

The same composite was obtained by Das et al. [69]. However, the study focused on cadmium adsorption. The material was characterized by XRD, FTIR, SEM, EDX, TEM, VSM. The obtained data was better described by the PSO model. As for the adsorption isotherms, the Freundlich isotherm showed better agreement. Moreover, the noted maximum adsorption value was 120.33 mg/g. The authors inferred that the likely mechanism is electrostatic, complexation and ion exchange [69].

Yet another combination was demonstrated by Foroughi et al. [70]. The scientists obtained the composite composed of hydroxyapatite, Fe_2O_4 and Co ($CoFe_2O_4$/ Hap) and used it to adsorb Zn(II) ions. As in the previous studies, the material was examined by means of XRD, VSM, TEM. Kinetic studies showed that the PFO model described better the process. Moreover, the Freundlich isotherm was more fitted to the data than the Langmuir isotherm. Thus, this indicated the presence of heterogeneous surface and multilayer adsorption [70].

Das et al. [71] modified the above mentioned composite additionally by nickel (Ni/Hap/$CoFe_2O_4$). It was also characterized by XRD, FTIR, SEM, TEM, VSM and XPS methods. The research addressed the problem of organic dyes removal from solutions, i.e. methyl orange and methylene blue. Moreover, the solid proved to be catalytically active. The studies were carried out in the presence of H_2O_2. The experiment showed promising data, which indicated that the degradation of methyl

orange was 90 % and for methylene blue 99.1 %. It is worth mentioning that the composite was characterized by high catalytic stability [71].

Another study utilizing nickel was presented by Mohamed et al. [72]. In this experiment the hydroxyapatite/$NiFe_2O_4$ composite was synthesized and analyzed by means of FTIR, XRD, TG-DTA, SEM, VSM methods. The composite was used in a chromatographic separation of Eu (III) and Tb(III). The maximum adsorption value for europium was 137.35 mg/g and for terbium 130.43 mg/g.

A different approach was presented by Phasuk et al. [73]. Instead of nickel, they incorporated nickel oxide into the composite with hydroxyapatite and γ-Fe_2O_3. The material was characterized by the same methods as in the previous studies. The main goal of the research was to examine the possibility to adsorb an organic dye, i.e. methylene blue. The adsorption process proved to be a chemisorption according to the kinetic PSO model, which presented better agreement with the data. The studied concerning isotherms showed that the Langmuir isotherm is more suitable, as indicated by the presence of a monolayer on the homogeneous surface. Moreover, the maximum adsorption was 7.20 mg/g [73].

Ain et al. obtained the composite composed of hydroxyapatite, magnetite and bentonite, which was applied in the adsorption processes of Pb(II), Cd(II) and crystal violet dye [74]. The material was analyzed utilizing the following methods: FTIR, XRD, SEM, VSM, XPS. The results proved that the solid is a promising adsorbent. The process of removing compounds from aqueous solutions proceeded at a high level, i.e. for Pb (II) it was 404.56 mg/g, for Cd(II) 310.36 mg/g and for crystal violet 1201.30 mg/g. Moreover, the adsorption was better described by the Freundlich isotherm model and PSO kinetic model, which indicated a porous and heterogeneous surface [74].

Another interesting adsorbent based on the hydroxyapatite is a material presented in the studies by Li et al. [75]. The authors obtained the composite via in situ grown of nano-hydroxyapatite on magnetic CaAl-layered double hydroxides and followed by calcining. Furthermore, the material was tested for adsorption capabilities, specifically for uranium adsorption. The already known methods were used to characterize the adsorbent, i.e. XRD, FTIR, TEM, VSM. The studies on isotherms showed that the Langmuir isotherm had the best fit. Moreover, it can be concluded that uranium ions formed a monolayer on the composite surface. The maximum adsorption value was noted as 45 °C and yielded 261.1 mg/g. What is more, the obtained data was better described by the PSO model. It can be also assumed that the probable mechanism of uranium binding on the composite surface is through complexation reactions [75].

Due to the fact that uranium is extremely toxic to living organisms and the ecosystem, its concentration should be controlled. Therefore, much research is focused on the topic of its removal and development of new adsorbents. An interesting solution was proposed by Broda et al. [76]. In the research the hydroxyapatite/ white clay composite was synthesized and characterized by XRF, XRD and ASAP. Moreover, the analysis of particle distribution and electrokinetic measurements was conducted. The best fit was shown by the Langmuir-Freundlich isotherm model. According to the obtained data, the maximum adsorption was 670 mg/g. Moreover, the mechanism was based mainly on ion exchange processes between the hydroxyl groups and the uranyl cations [76].

Another study concerning uranium removal was carried out by Feng et al. [77]. In the experiment amino modified hydroxyapatite was obtained and then analyzed by known methods. A distinguishing factor in these studies was the rapid time in which the equilibrium was reached, i.e. 20 min. By analyzing the obtained data, a conclusion was drawn regarding the kinetics of the reaction, namely there was a better fit to the PSO of the model, which indicated chemisorption. Moreover, the Freundlich isotherm model characterized better the process. The adsorption capacity was 96 mg/g [77].

A different combination with hydroxyapatite was presented by Akartasse et al. [78]. Utlilizing the dissolution/ recrystallization method the hydroxyapatite/ chitosan/ glycerol composite was obtained in the film form. Furthermore, it was analyzed using the ATR-FTIR and TGA/ DTA methods. The main aim of the research was studying the possibility of Cd(II) and Zn(II) ions adsorption. The gathered data indicated that the process was in the agreement with the Langmuir isotherm. Moreover, the PSO model fitted the best. The highest adsorption values obtained were 120 mg/g for Cd (II) and 90 mg/g for Zn(II) [78].

A slightly different composite was presented in the studies by Azin et al. [79]. The scientists synthesized chitosan-colagen/ hydroxyapatite from fishery wastes. Moreover, the material was cross-linked with tripolyphosphate. The purpose of the study was to test the sorption capacity of copper ions. The composite was characterized by the FTIR and SEM methods. Similarly to the previous study the PSO model and the Langmuir isotherm described the adsorption process. The maximum sorption values yielded 170 mg/g. Moreover, the main adsorption mechanism was based on electrostatic interactions [79].

Hoa et al. proposed another combination, namely the hydroxyapatite/ graphene oxide/ chitosan composite for methylene blue and Cu(II) adsorption [80]. The material surface was characterized by the FTIR and SEM techniques. Adsorption studies proved the presence of a monolayer according to the Langmuir isotherm. Moreover, the maximum capacity for methylene blue was 99 mg/g and for Cu(II) was 256.41 mg/g. The obtained data indicated better fit for the PSO kinetic model.

The adsorption capabilities of fluorine ions also represent an interesting field for research. This issue was addressed by Laonapakul et al. [81]. In this study, the composite calcined-kaolin/ hydroxyapatite composite was obtained and characterized by the known methods. Moreover, the fluoride adsorption capability was examined. However, the adsorbent was not very effective. The maximum capacity yielded 1.74 mg/g [81].

An interesting composite was presented by Liao et al. [82]. The main goal of this study was preparation of hydroxyapatite/ biocarbon composite and examination of uranium ions adsorption. The obtained material was analyzed using the FTIR, XRD, SEM methods. The gathered data indicates better agreement with the PSO kinetic model, which proved that the process was chemisorption. Moreover, the Langmuir isotherm showed the best fit. The maximum adsorption yielded 834.8 mg/g, which is a distinctive value compared to those of various adsorbents [82].

Excellent uranium adsorption properties are also presented by Ma et al. [83]. The composite used in this study consisted of hydroxyapatite and ordered mesoporous carbon. The adsorption processes were described by the Langmuir isotherm and the PSO kinetic model. Noteworthy is the fact that the highest recorded adsorption capacity was 1072 mg/g [83].

The multifunctionality of hydroxyapatite is evidenced by the fact that it forms numerous composites with many compounds. Another interesting combination is the hydroxyapatite/sodium alginate composite presented by Song et al. [84]. In this research the solid was tested for Cd(II) adsorption. Firstly, it was synthesized and examined by known methods similarly to the previous studies. The removal of cadmium ions proved to be well characterized by the Freundlich isotherm and the PSO model [84].

Still another solution is to place other ions in the hydroxyapatite structure. This approach is presented in the studies by Zhu et al. [85,86]. In both experiments the solid hydroxyapatite/strontium was obtained in the sol-gel method and then analyzed by the XRD, FTIR, EDS, SEM techniques. The first paper presented Pb(II) ions adsorption. The removal of lead from water solutions was characterized by the PSO kinetic model and the Langmuir isotherm. Moreover, the maximum adsorption capacity yielded 651.175 mg/g [85]. The second paper deals with the adsorption of cadmium ions using the same adsorbent. The isotherm and the kinetics of adsorption were the same. However, the maximum adsorption value was 158.30 mg/g [86].

A similar composite was tested by Zhou et al. [87]. However, the scientists doped hydroxyapatite nanorods by Sr and examined the adsorbent with respect to Cr(VI) adsorption. The obtained data proved

that the Langmuir isotherm was in better agreement, indicating monolayer formation. Moreover, the maximum adsorption capacity was 443 mg/g [87].

Table 1 summarizes the information obtained about adsorption using on the listed adsorbents. It is evident that magnetic hydroxyapatite has the most studied applications. Among the similar isotherm models, the Langmuir isotherm dominates. In addition, all studies show agreement with PSO. In contrast, the adsorption mechanisms are very different, and it is not possible to unequivocally pick out the dominant one. It can be unequivocally concluded that not all studies were complete, as some lack information regarding kinetic models, mechanism and isotherms.

Moreover, Fig. 5. presents the possible structure of different composites obtained by the TEM method. As it can be seen they are quite similar. Stick-like shapes are visible. What is more, agglomerates are formed. Moreover, Fig. 6. displays the SEM photographs of other composites. The surfaces are similar to each other. They form a compact whole. Small spindly shapes can be seen.

2. Hydroxyapatite composites and their biological/ medical applications

In the biomedical and medical fields, biocompatible materials play a key role in the development of innovative therapies and technologies. One of the most promising materials used in this area is hydroxyapatite. However, it is characterized by an unsatisfactory mechanical property. Thus, scientists are looking for some improvements and modifications to develop more efficient materials. Some of the modifications are presented in papers [88,89].

2.1. Drug delivery systems

The literature reports a number of hydroxyapatite-based composites tested for drug transport in the human body. One of the proposed material is Fe_3O_4/SiO_2/hydroxyapatite presented in the paper by Orooji et al. [90]. The mesoporous solid was obtained using the sonochemical method. In order to achieve high efficiency the composite was combined with 3-aminopropyl triethoxysilane. The FESEM, XRD, VSM, HRTEM, EDX and FTIR techniques were employed to characterize the structure. The experiment addressed the issue of binding and releasing an anti-inflammatory drug – sulfazaline. The results showed that the substance was bound on the composite surface with an efficiency 59.1 %. However, after 36 h the drug was released completely. The authors pointed out the advantages of obtained composite, i.e. small toxicity, extended release, large substance concentration and the being environmentally friendly [90].

A different approach was presented by Foroughi et al. [91]. In the paper the hydroxyapatite/$MgFe_2O_4$ composite was tested for ibuprofen loading and releasing processes. Interactions between the drug and the adsorbent were mainly based on hydrogen interactions. The first stage of release was the fastest yielding 19.7, 31.6, 42.3 % for the samples with different calcination temperatures of the composite material, respectively. The main conclusion was that the drug release process is strongly influenced by the pore size and surface development of the carrier material [91].

A possible application of magnetic hydroxyapatite/ FexOy composite as a provider of therapeutic substances in the body was presented by Ignatovich et al. [92]. The studied drug was from the 2-arylaminopyrimidine group with a pharmacophore fragment which is acknowledged by the antitumour treatment. During the releasing process, almost 80 % of the substance was unleashed in 2 h. The rest of it was released after next 3 h [92].

A significant issue was studied by Sangeetha et al. [93]. In the research the composite was composed of cobalt ferrite, magnetite and hydroxyapatite. The material was loaded with doxorubicin – a chemical drug for cancer treatment. It was observed that after 10 h 50 % of the drug was released. Furthermore, the process was slowing down. Eventually, after 98 h the rest of it was unleashed [93].

Binding and release of ibuprofen was also studied in the system with the Hap/Si/carbon nanotubes composite [94]. In the studies carried out by Barabas et al. the material with and without Si ions was examined. The obtained results proved that additional presence of Si made the composite more effective as regards adsorption. Moreover, the Hap/Si/carbon nanotubes composite exhibited prolonged release of ibuprofen [94].

Furthermore, Jariya et al. [95] tested the chitosan-alginate/ hydroxyapatite composite doped additionally with fluorine for the release of Ciprofloxacin, which is known for its antibacterial properties. The study was carried out for 11 days. Drug release was slow and controlled

Table 1
Possible adsorbents for different metals or compounds.

Adsorbent	Compound/ metal	Adsorption capacity [mg/g]	Isotherm model	Kinetic model	Possible mechanism	Reference
HAP/ Fe_2O_3 or Fe_3O_4	Cd	277.78	Langmuir	PSO	Complexation, ion exchange, electrostatic interactions	46
	Pb	109.89	Freundlich, Langmuir	PSO	–	49
	Cu, Ni	5.86, 29.07	Freundlich	PSO	Ion exchange, complexation	52
	Fe, Mn	0.704, 0.665	Langmuir,	PSO	Electrostatic interactions, complexation	54
	U	310	Langmuir	PSO	Complexation	56
	Humic acid	601.91	Sips	PSO	–	60
	Eriochrome Black T	43.47	Langmuir	PSO	–	61
Zn/Fe_2O_4/HAP	Cd	120.33	Freundlich	PSO	Complexation, ion exchange, electrostatic interactions	69
$CoFe_2O_4$/HAP	Zn	–	Freundlich	PSO	–	70
NiO/Fe_2O_4/HAP	Methylene blue	7.20	Langmuir	PSO	–	73
HAP/magnetite/ bentonite	Pb, Cd, crystal violet dye	404.56, 310.36, 1201.30	Freundlich	PSO	–	74
CaAl layered HAP	U	261.1	Langmuir	PSO	Complexation	75
HAP/white clay	U	670	Langmuir-Freundlich	–	Ion exchange	76
HAP/chitosan/glycerol	Cd, Zn	120, 90	Langmuir	PSO	–	78
HAP/chitosan-colagen	Cu	170	Langmuir	PSO	Electrostatic interaction	79
HAP/graphene oxide/ chitosan	Methylene blue, Cu	98, 256.41	Langmuir	PSO	–	80
HAP/biocarbon	U	834.8	Langmuir	PSO	–	82
HAP/ Sr	U, Cd	651.175, 158.30	Langmuir	PSO	–	85, 86
	Cr	443	Langmuir	–	–	87

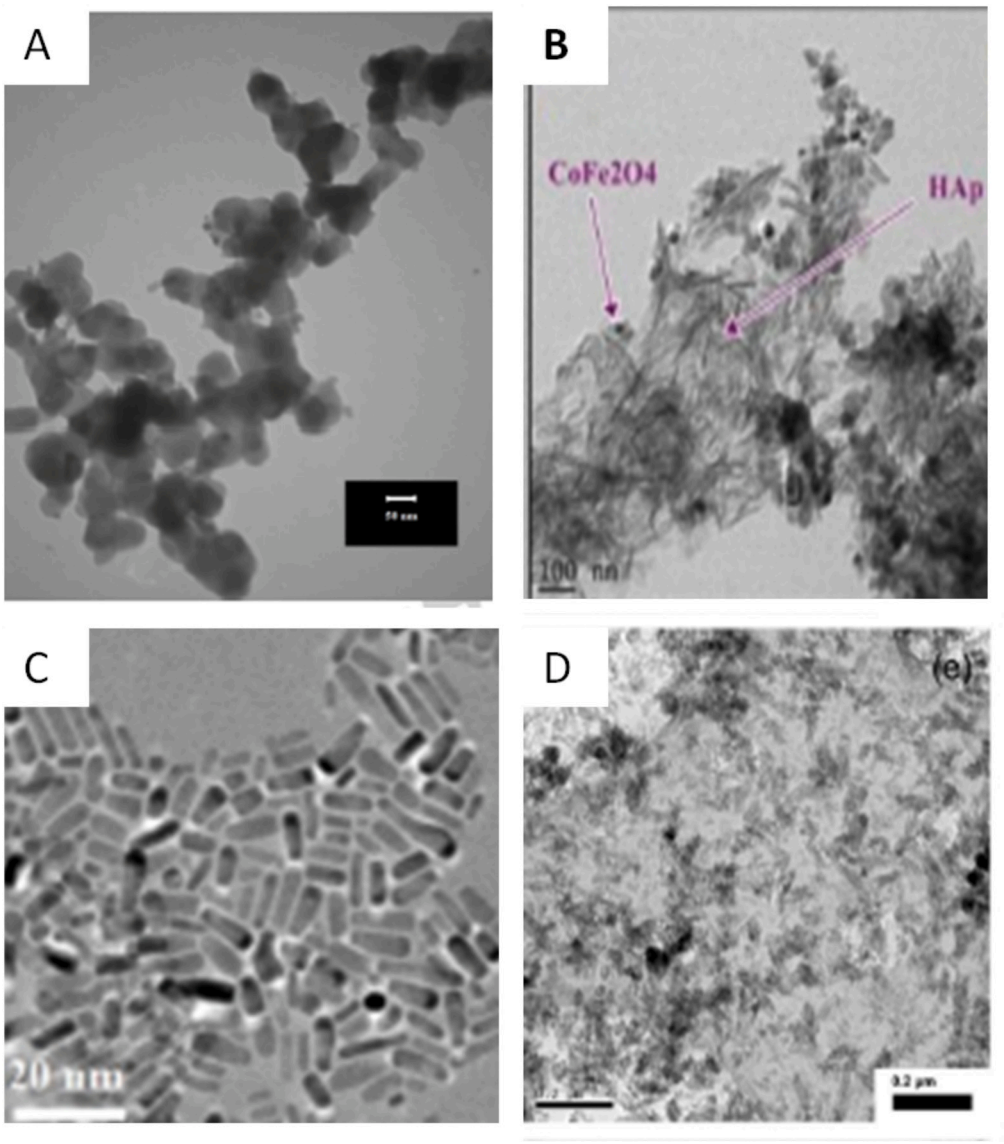

Fig. 5. TEM photos of different composites: A: CoFe2O4– hydroxyapatite [70], B: Ni/HAP/CoFe2O4 [71], C: CaAl-layered nano-hydroxyapatite [75], D: Sr/HAP [87].

with a total release of 60 %. The paper proved that the tested composite is a promising material in regulated drug release processes [95].

It is proved that chitosan has a positive effect on unleashing drugs from the composites based on hydroxyapatite, which is presented in the studies by Wu et al. [96]. The scientists obtained hydroxyapatite/gelatin composite coupled with chitosan. Furthermore, it was examined in the doxorubicin releasing processes. Comparing binding and drug release properties between the composite without chitosan and that containing chitosan, it was found that its addition increases the amount of bound drug significantly due to presence of hydrogen bonds. In addition, the time of its release has also increased, which is extremely important in processes of this type. Doxorubicin did not change its properties during the study [96]. The study without chitosan was presented by Madhumanti et al. [97].

A very common issue in the research is utilizing polymers to modify the hydroxyapatite structure. Forte et al. [98] used polyethylenimine to obtain a new composite and tested it for risedronate adsorption and release. The studies showed that the binding process was based on chemisorption and physisorption. Moreover, the releasing process was fast at first and then it slowed down. This complex mechanism confirms better delivery of the drug [98].

A different polymer was employed in the research by Macha et al. [99,100]. Polylactic acid was loaded into the hydroxyapatite structure. Moreover, the gentamicin drug was tested. The scientists listed the following advantages of the composite: controlled rate of releasing over an extended period of time, stable and prolonged effect, increased ability to maintain its stability, efficacy and biological activity. Moreover, the material was characterized by a potent antimicrobial activity [99].

Furthermore, Minaev et al. [101] proposed a composite composed of polyester and hydroxyapatite. However, it was not tested for drug release processes.

Another combination with hydroxyapatite was presented by Ram Prasad et al. [102]. In this paper the apatite material was combined with poly(vinyl alcohol) and tested for methotrexate and gemcitabine drugs release. The study showed better adsorption efficiency with gemcitabine. The most important conclusion drawn from the experiments is that drug release was a slow process. Complete release could take up even months. Moreover, both therapeutic substances act synergistically, which can increase the efficiency [102].

Furthermore, Babaei et al. [103] presented poly(sodium 4-styrene sulfonate)/hydroxyapatite composite and loaded it with vancomycin

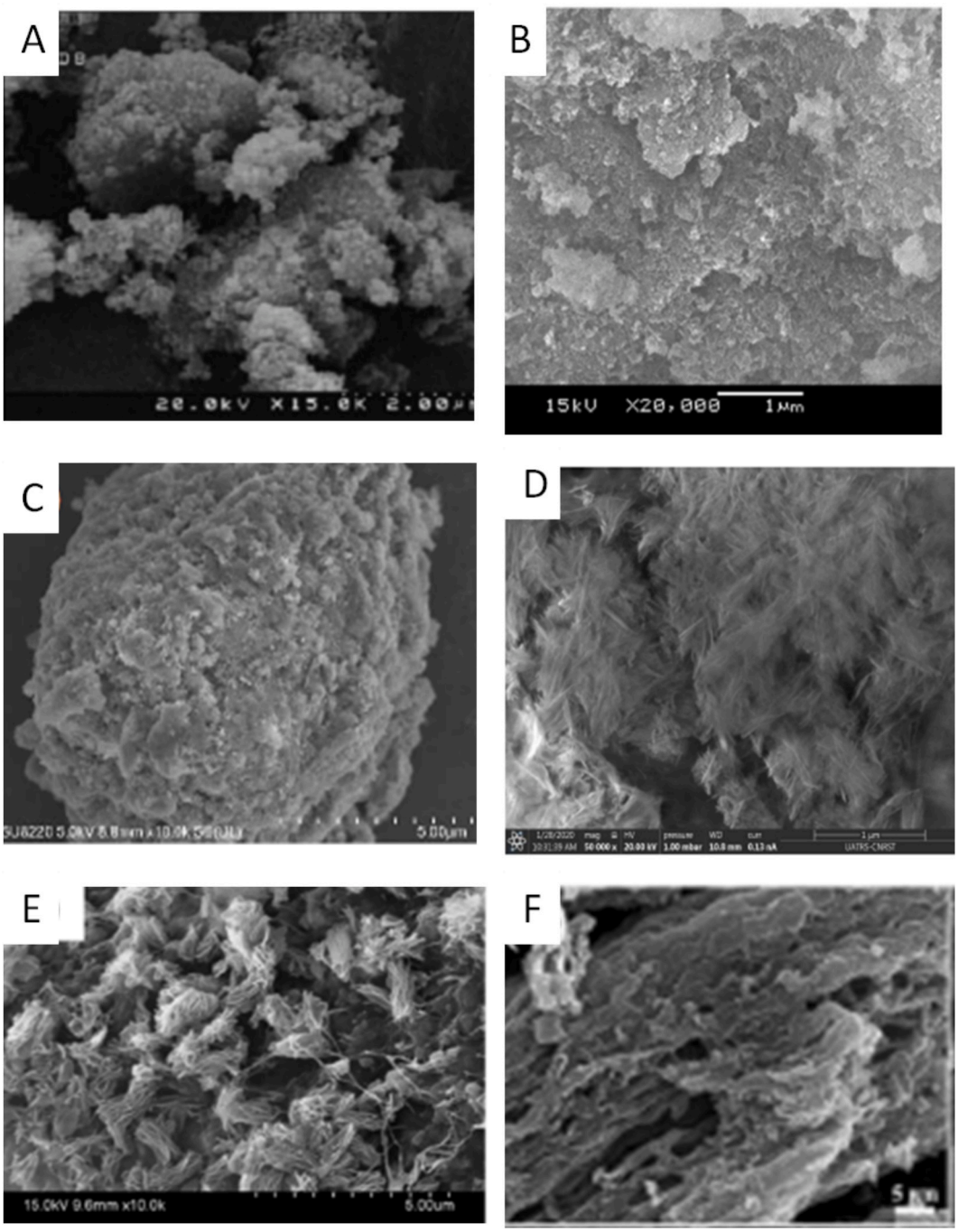

Fig. 6. SEM photos of different hydroxyapatite composites A: zeolite-Hap [54], B: Hap/NiO [73], C: Hap/magnetite/bentonite [74], D: Chitosan/Hap [78], E: Hap/biocarbon [82], F: Hap/CMK-3 [83].

for the release experiment. It is worth mentioning that the presence of polymer slowed down the releasing process. Moreover, the amount of drug released after 2 weeks increased with the increasing hydroxyapatite concentration [103].

Promising results were obtained by Mohammadzadeh et al. [104]. The study involved preparation of lactose hydroxide-hydroxyapatite composite and doxorubicin release examination. The entrapment effectiveness was 88.4 % and the drug capacity was 18.84 %. The releasing process proved to be easy to control. Moreover, it depended on the pH value [104].

The common natural polymer – gelatin was used in the study by Sangeetha [105]. The release process was fast at first, then slowed down after about 6 h. In turn, the release of the therapeutic substance from the hydroxyapatite surface was almost immediate and the entire amount of the drug was released within 5 h. It can be concluded that the addition of polymer has a beneficial effect on this process [105].

Table 2 presents the selected composites and drugs tested as part of a controlled drug delivery system. It can be clearly seen that the Hap/FexOy composite, which one proved to be the most efficient as well as the lactose/ layered double hydroxide-HAP. (See Tables 1 and 2.)

Fig. 7. presents different structure obtained in the studies. They differ from each other. Circular shapes can be noticed in each image. Some of them form a compact solid while others are loosely arranged. One structure is characterized by excellent porosity.

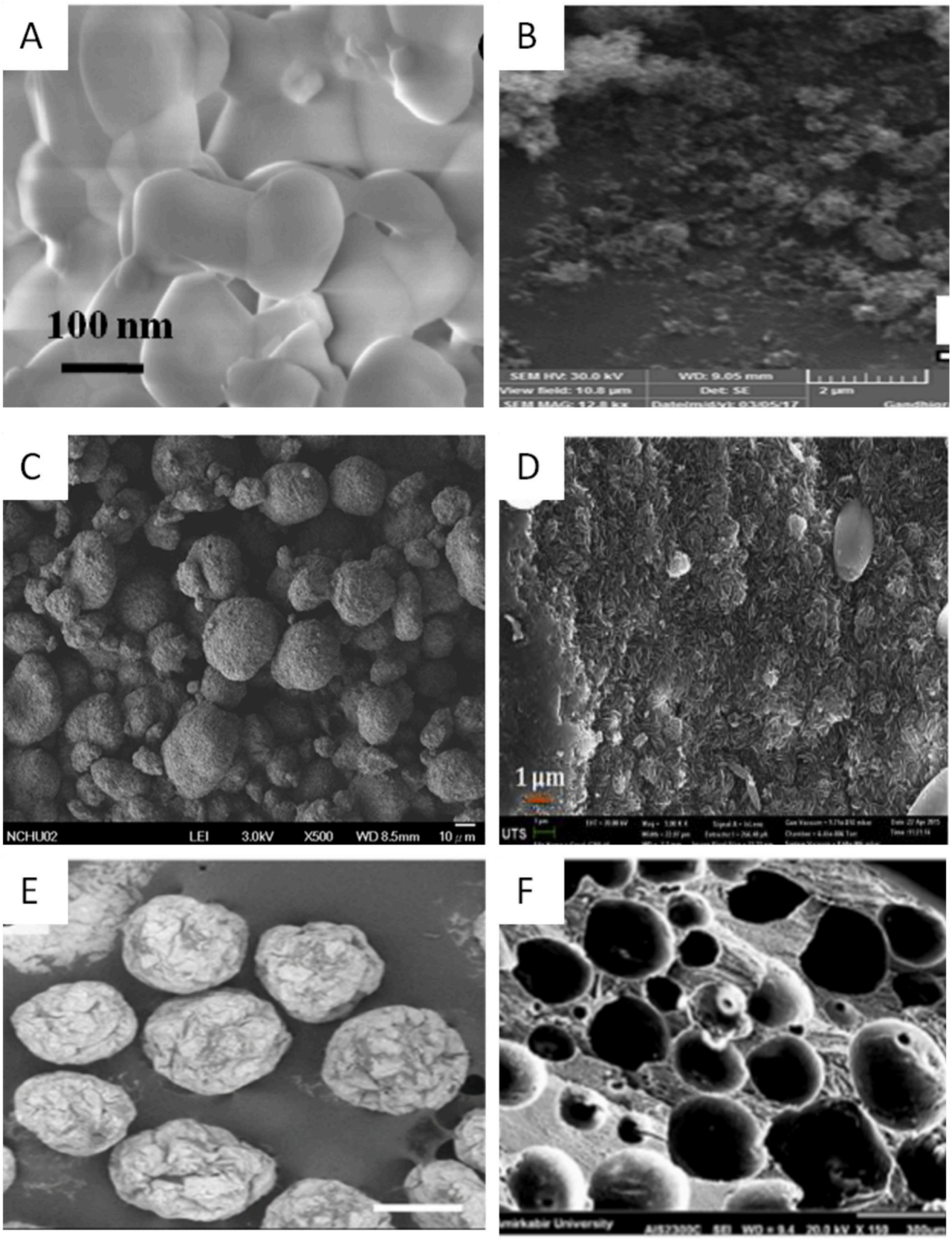

Fig. 7. SEM photographs of different composites A: CoFe/Hap [93], B: chitosan/alginate/Hap [95], C: Chitosan/Hap/gelatin [96], D: poly-ethylenimine/Hap [98], E: Polyester/Hap [100], Poly (sodium 4-styrene sulfonate)/Hap [102].

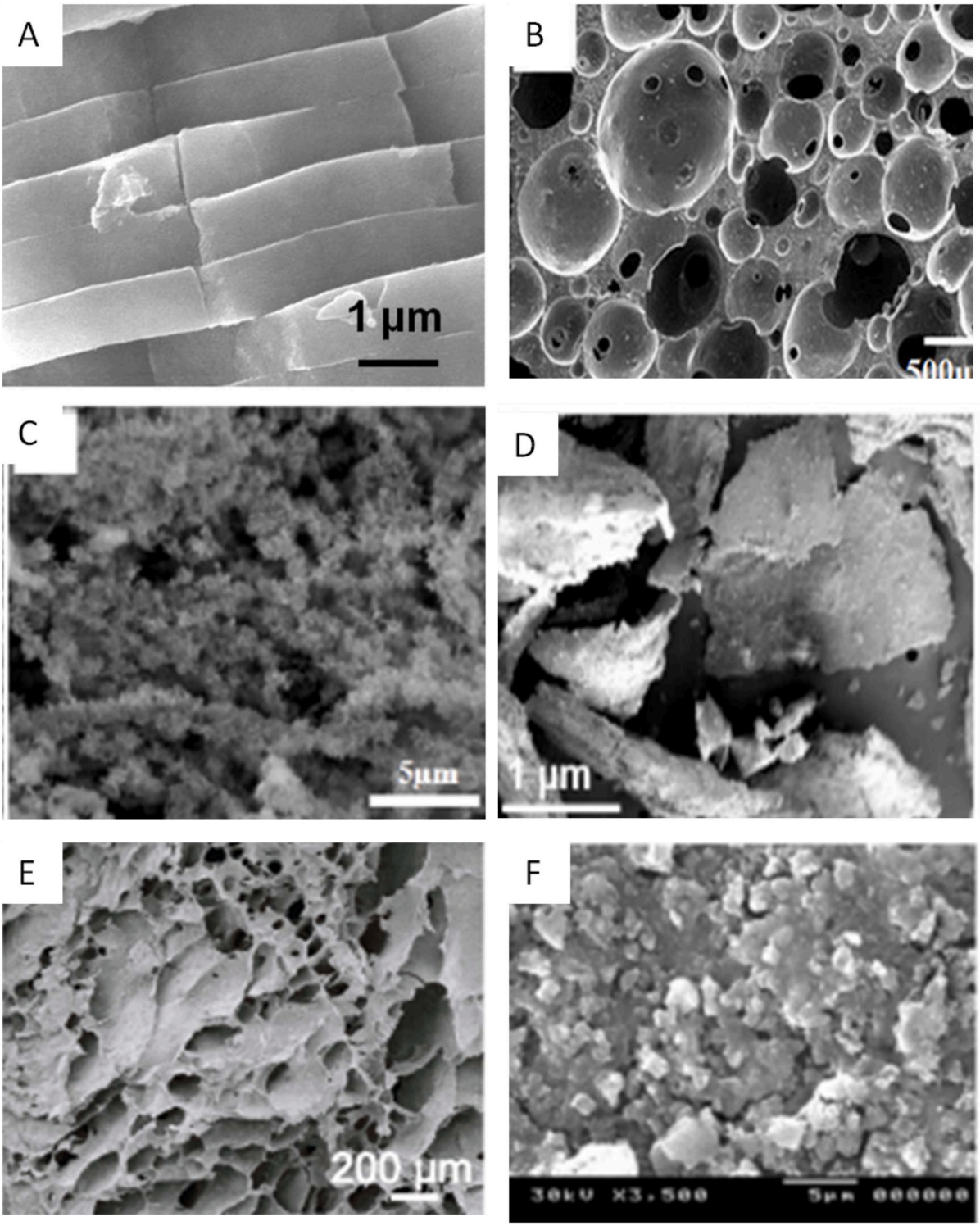

Fig. 8. SEM photographs of different composites A: Hap/ Fe_3O_4 [114], B: Hap/ Fe_3O_4/PU [115], C: Celulose/Hap/ Fe_3O_4 [117], D: MHap/gelatin [118], E: MHap/ La/Chitosan [120], F: Hap/chitosan [125].

2.2. Bone regeneration processes and implants

The demand for materials compatible with the human body is extremely large these days. Hydroxyapatite has a particularly remarkable biocompatibility and is extensively studied for its use in bone regeneration or implants. However, it is not an ideal material and often requires modification for the practical use. There are a lot of papers studying various hydroxyapatite composites that could be potentially applied in orthopedics [106–113]. Moreover, most of them provide preliminary results. This chapter will present the most common hydroxyapatite composites with their potential use in bone regeneration processes and implants.

Magnetic materials are very common these days. One of the magnetic composites was obtained in the study by Agalya et al. [114]. In the paper Hap/ Fe_3O_4 was synthesized by the one-step ultrasonic method and then was analyze applying already known methods. The synthesis was

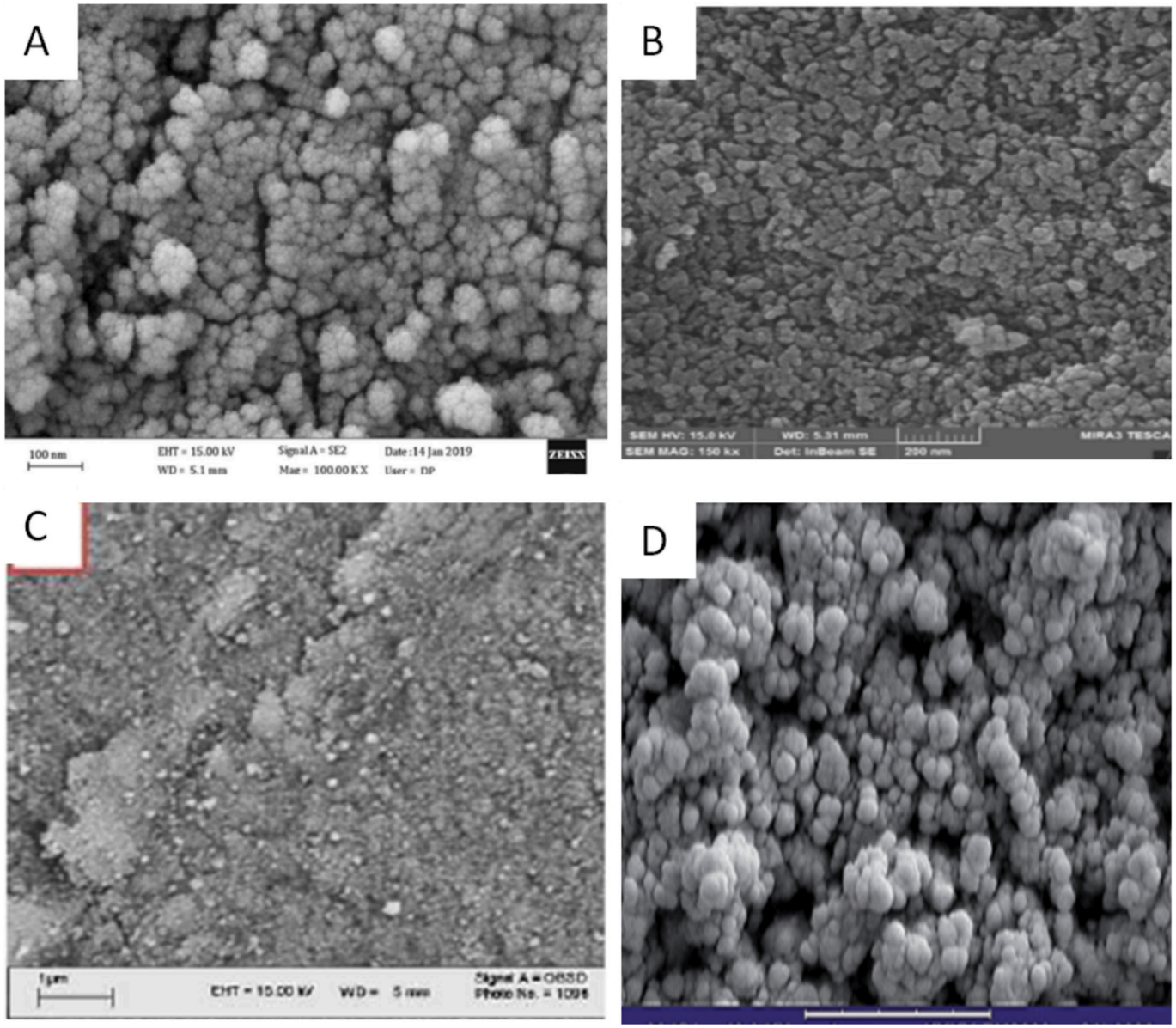

Fig. 9. SEM photographs of different catalysts A: γ-Fe_2O_3/HAp/CPTMS/AT [181], B: β-Cyclodextrin/γ-Fe_2O_3/Hap [185], C: γ-Fe2O3@HAp-SO_3H [187], D: guanidinium chloride/Fe_2O_3/HAp [202].

Table 2
Selected composites and drugs in the drug delivery systems.

Composite	Drug	Binding/ releasing efficiency [%]	Reference
Fe_3O_4/SiO_2/HAP	Sulfazaline	59.1	90
HAP/$MgFe_2O_4$	Ibuprofen	42.3	91
HAP/Fe_xO_y	2-arylaminopyrimidine	80	92
Cobalt ferrite/ magnetite/HAP	Doxorubicin	50	93
HAP/Si/carbon tubes	Ibuprofen	–	94
Chitosan-alginate/ HAP	Ciprofloxacin	60	95
Lactose/layered double hydroxide-HAP	Doxorubicin	88.4	104

successful. The study in Simulated Body Fluid (SBF) was also carried out. Formation of apatite aggregates could be seen in the SEM photos. This phenomenon occurred due to the presence of Ca^{2+}, PO_3^{4-} and OH^- ions. It can be concluded that the material was bioactive and it can find potential applications in bone regeneration treatment [114].

A slightly different approach was presented by Yan et al. [115]. The researchers modified the Hap/Fe_3O_4 composite with polyurethane. This study was carried out more precisely. In addition to the surface characteristics, other properties relevant for medical applications were also studied. It can be observed that specific cells dispersed well along the scaffolding and then multiplied. Multilayered structures also appeared. Endurance was also investigated. The material is able to withstand 4.16 MPa of pressure without cracking [115].

Furthermore, the Hap/ Fe_3O_4/ sodium alginate composite was synthesized in the study by Sukhodub et al. [116]. The results proved biocompatibility of the material. The continuous and stable increase in the number or growth of fibroblast cells was observed during the specified time of the experiment. No negative effects of the magnetic substance on cells were observed [116].

Table 1
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Chitosan-alginate/ HAP	Ciprofloxacin	60	95
Lactose/layered double hydroxide-HAP	Doxorubicin	88.4	104

The versatility of magnetic hydroxyapatite is also evidenced by its ability to be combined with cellulose, as presented in the study [117]. The Hap/Fe_3O_4/bacterial cellulose composite was obtained by means of the ultrasonic irradiation method and then characterized by the commonly applied techniques. This modification improved porosity and mechanical properties of the material. The obtained values were similar to those of human bones. No toxic effects on cells were reported. Moreover, the composite showed significant osteogenic potential [117].

There were also studies on coating a scaffold constructed of magnetic hydroxyapatite with gelatin and ibuprofen. The tested material showed a good potential for bone tissue engineering. However, the strength of the scaffold was greatly influenced by the contribution of magnetic particles [118].

In turn, more detailed studies using mice were in carried out by Liu et al. [119]. In the paper silk fibroin/ hydroxyapatite was tested. Moreover, the scaffold also included iron oxide, which exhibited superparamagnetic properties. The solid was placed into the mice bodies. The researchers found good porosity, strength and thermal stability parameters. In the further study, the bone marrow-derived mesenchymal stem cells were applied into the scaffold, promoting enhanced cell adhesion and proliferation. Such conditions were indicative of effective osteogenesis. These processes were also described using the MRI and CT methods [119].

The studies on rat bone defects of the other composite were submitted by Wang et al. [120]. They described the magnetic lanthanum/ hydroxyapatite/chitosan scaffold. Histological and micro-CT studies proved that this type of material improves significantly the damaged tissue regeneration. The authors emphasized that their research was promising for potential application [120]. It is worth noticing that composites with chitosan are very common in studies [121–124]. Moreover, they can also take form of coatings [125–128].

What is more, studies concerning hydroxyapatite based composites additionally doped with metals, i.e. Sr [129–134], Ti [135–141], Co [142], Zn [143–148], Ge [149,150], Mg [151–153], Ag [154] and Fe [155] are becoming more and more common these days.

Another type of hydroxyapatite-based composites that was extensively studied are the composites combining of different polymers. Promising results were published by Tut et al. [156]. Using 3D printing technology, the researchers obtained a polyvinyl alcohol/whey protein isolate/hydroxyapatite composite. Further, the material was loaded with the Gentamicin drug. The findings from endurance tests fulfilled the mechanical requirements of human bone. A specific cell analysis unveiled that biocompatible forms were present leading to robust cell adhesion [156].

Furthermore, Carette et al. [157] proposed a polylactide/ hydroxyapatite composite. However, in the paper a poly(ethylene glycol)-b-polylactide compolimer was proposed as a compatibilizer. The presence of hydroxyapatite facilitated the mineralization process in Simulated Body Fluid. Moreover, its influence is stronger in the presence of the copolymer. The mechanical and bioactivity improvement is clearly observed [157]. A study concerning the same polymer was presented by Hwangbo et al. [158] and Song et al. [159].

A different polymer was attached to the hydroxyapatite composite in the studies by Sadeghi et al. [160]. The scientists presented the polycaprolactone/ gelatin/ hydroxyapatite material. Thermal stability and mechanical properties were significantly better after the combination of three substances. The tested scaffold exhibited excellent biocompatibility with cells and supported cell proliferation. Furthermore, the cultured cells adhered seamlessly to the scaffolds and infiltrated their porous structure. The resulting research makes the material a promising solution in orthopedics [160]. Polycaprolactone was also utilized in the study by Nawrotek et al. [161].

In turn, Yang et al. [162] presented HAPs/polymer monolithic composites templated from CO_2 in-water high internal phase emulsions. The studied material featured an expanded open-cell macro-porous architecture and better flexibility. Moreover, the composite showed non-toxicity to the cells present in the organism [162].

The composite composed of poly(ethylene glycol) diacrylate and hydroxyapatite was tested by Chen et al. [163]. In this study the material was obtained by the 3D printing technique. The main and most important conclusion that can be drawn from this research is that the composite had good mechanical properties that matched the strength of human bone [163]. Polyethylene glycol was also studied by He et al. [164].

Polyethylene/ hydroxyapatite composite was proposed by Silvio et al. [165]. The results showed that the proliferation rate was significantly better. Moreover, cells formed the cytoskeleton efficiently [165]. Another study concerning polyethylene polymer in the combination with hydroxyapatite was presented by Schappo et al. [166].

An interesting approach was shown by Dos Santos et al. [167] where poly(vinylidene fluoride) was proposed as a matrix into which hydroxyapatite particles were incorporated. The process allowed to obtain a composite membrane. After the immersion in Simulated Body Fluid, the apatite phase started to grow, which confirmed its bioactive nature. The structures showed no harmful cytotoxicity, providing a potential for their future use [167].

Moreover, a complex combination of different constituents was proposed by Sabreeswari et al. [168], whereby the electrospinning method the Ce/Ag-hydroxyapatite/ polyvinyl alcohol/ carboxy methylcellulose composite was obtained. The material was characterized by the utmost tensile strength, exceptional antimicrobial activity and facilitated apatite formation [168].

Some studies also presented other combinations with polymers, namely poly(lactic-*co*-glycolic acid) [169], γ-polyglutamate acid [170], polymethylmethacrylate [171].

Fig. 8. displays different structures for possible composites. One of them is characterized by its layered location. These strips fit tightly to each other. The other structures show considerable porosity. Numerous pores are present.

2.3. Other applications in medicine

Medical applications are numerous. These are not just bone implants and orthopedics but also various healing processes. One example of the use of hydroxyapatite-based composites is enzyme immobilization. Couthino et al. [172] presented the hydroxyapatite/ $CoFe_2O_4$ composite. Owing to its magnetic properties the solid became easy to recover, especially from solutions. The authors described promising results, namely the immobilization rate was 70–100 % and the recovery was 78–100 %. Moreover, this solution is environmentally friendly [172]. The same composite was studied in another paper, confirming its good immobilization properties [173].

Furthermore, protecting wounds and accelerating their healing is also of great importance. Such studies were undertaken by El Halawany et al. [174], who proposed the alginate/ hydroxyapatite composite as a wound protector after tooth extraction. In the research, the material was loaded with tranexamic-acid. It turned out that such a combination stopped bleeding and clots formation. Although the in vivo studies are still needed for complete testing of the feasibility of such a solution, it can be concluded that the results are promising [174]. A different composite with antimicrobial and antifungal activities was presented by Saidi et al. [175], Shaer et al. [176] and Wang et al. [177].

One of the most important issues in current medical trends is the detection and treatment of cancer. To this end, the use of hydroxyapatite-based composites was studied. De Lama-Odria et al. [178] published an extensive and comprehensive paper on potential modifications of hydroxyapatite that could benefit cancer detection and treatment. Moreover, in addition to the solutions mentioned in the above paper, the others proposed composites were: cobalt ferrite/ hydroxyapatite [179], zinc ferrite/ hydroxyapatite [180].

3. Hydroxyapatite-based composites in catalysis processes

Catalysis is an essential part of green chemistry. It aims at development of sustainable and eco-friendly chemical reactions. An appropriate catalyst can facilitate chemical processes remaining unchanged. That is why this area of knowledge is becoming more visible. Taking care of the environment and the surroundings in which we live is an extremely important factor. The literature reports many solutions for the hydroxyapatite-based catalysts. Extremely common in research is the magnetic hydroxyapatite composite. It comes with various combinations, i.e. 3-chloropropyltrimethoxysilane and 3-amino-1,2,4-triazole [181], Ag [182–184], β-cyclodextrin [185,186], -SO_3H [187–193], Cu [194,195], Fe [196,197], Ni [198–201], guanidinium chloride [202], thiourea dioxide [203], melamine [204], Mo [205], Au [206], Pd [207], Ru [208], Polyethylene Glycol-(N-Methylimidazolium) Hydroxide [209], SiO_2 [210]. Furthermore, Chen et al. [211] proposed the hydroxyapatite/MnO_2 catalyst. Another combination was presented by Wang et al. [212] who synthesized the NiC*ex*/hydroxyapatite catalyst. A composite with metal oxide was tested in the paper by Labrag et al. [213].

Fig. 9. presents the structures of different catalysts. The surfaces are similar to each other. They show high granularity and heterogeneity. The particles form larger agglomerates.

The cited papers indicate clearly the great popularity and versatility of magnetic composites. There are a myriad of combinations through which this material gains catalytic capabilities in a variety of reactions. This makes it multifunctional and widespread. On the other hands, there are a few modifications of hydroxyapatite itself. Perhaps there are difficulties in synthesizing such materials and they do not have adequate catalytic properties.

4. Conclusions

In summary, hydroxyapatite modification is a key area of research that has contributed to expanding its application potential. Through continuous development and optimization of modification processes, researchers are striving to eliminate limitations such as poor mechanical strength and difficulties in separation from solutions. As a result, new forms of modified hydroxyapatite are finding applications in many fields, in medicine, as an effective drug delivery system and in bone tissue regeneration, as well as a covering material for implants. In addition, their unique adsorption properties make them valuable tools in removing impurities from solutions and detecting cancerous substances. In the field of catalysis, hydroxyapatite modifications are opening the door to efficient chemical reactions, contributing to the sustainability of industrial processes.

Creating HAP composites with other materials or modifying their surface can promote synergistic effects and increase efficiency in pollutants removal as well as other environmental and medical applications. Methods such as hybrid modification (combining HAP with other materials) can increase specific surface area, mechanical strength, crystallinity and adsorption capacity of HAP. Surface modification leads to the HAP surface to increase which in turn results in increasing capacity of appropriate cations and anions. In summary, hydroxyapatite composites can improve significantly the potential for HAP applications in environmental protection, to become a powerful tool in the fight against global water contamination, and in medical applications. However, while these composites can provide new functionalities for HAP, they can also create new problems such as increased production costs or secondary contamination. In addition, some composites can alter biocompatibility or stability of HAP, which in some cases may confine their medical applications. The future should address current issues, taking into account the new challenges they may bring.

As the research on hydroxyapatite modifications continues to expand, we can expect new innovative approaches that will further broaden their spectrum of applications. Combined with dynamic scientific and technological advances, hydroxyapatite modifications have the potential to contribute to the improvement of human life and health, as well as to the development of new technologies of global significance.

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CRediT authorship contribution statement

Adrianna Biedrzycka: Writing – original draft, Formal analysis, Data curation. **Ewa Skwarek:** Writing – original draft, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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