A Study of Preparing Samples of Hydroxyapatite with Different Densities Using Charcoal Powder

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Abstract. The powder of hydroxyapatite with the chemical formula \( \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 \) was prepared locally from cow bones in the hexagonal crystal phase, and this was confirmed through the X-ray diffraction system. The proportions that formed the prepared hydroxyapatite were confirmed through the X-ray fluorescence system and found the ratio of calcium oxide to phosphorous oxide is 1.718. The hexagonal phase of the prepared hydroxyapatite was also stabilized (fixed) for the samples before and after the heat treatment. Some physical and mechanical properties were also conducted for the prepared samples. It was found that it is possible to prepare samples of different densities by adding different proportions of carbon (charcoal) percentage to the prepared hydroxyapatite.

Keywords: Hydroxyapatite, porous material, carbon, medical applications.

1. Introduction

During recent years, there has been a great revolution in the use of ceramics in order to improve the quality of human life as a result of the development of specially designed and manufactured ceramics called Bio-ceramics in order to repair and rebuild damages and damaged and decaying parts of the body [1]. Ceramics is that field that relates to the treatment of inorganic materials in various ways, including the use of heat to produce and manufacture many materials for general uses such as pottery, ceramics, construction materials such as bricks, polishing materials, glass, cement and others. Ceramic materials have some important properties such as heat resistance, corrosion resistance, heat insulation ability and good electrical properties. The need for ceramics has emerged as a result of the development of technical uses of ceramic materials in important fields such as cutting machines, space technology, electronics and electrical insulators. The importance of ceramics increases with the advancement of science and technology because of the important qualities it carries, and it has become about (7%) of engineering materials as it has an increasing use in the electrical industries, especially porcelain insulators and biomedical materials [2]. The ceramic materials
specially developed for medical use and dental implants are called bio-ceramics. These include alumina, zirconia, bio-glass, ceramic glass and hydroxyapatite [1].

Hydroxyapatite $Ca_{10}(PO_{4})_{6}(OH)_{2}$ is a compound based on calcium phosphate. It has excellent capacity for bone growth and vital activity because its chemical structure resembles a mineral in bones and teeth, but its properties are weak [3]. Due to its biocompatibility and biodegradability, it is widely exploited in the interdisciplinary field of science that includes chemistry, biology and medicine [4].

Hydroxyapatite (HAp) is the most emerging biological biomaterial, which is widely used in various biomedical applications, mainly in orthopedics and dentistry [5].

Calcium apatite, which is hydroxyapatite from its group, is distinguished by a general chemical formula of the form $(Ca_{5}(PO_{4})_{3}X)$, where $(X)$ can be an electronegative or a halogen group or a group $(OH)$ [6].

Hydroxyapatite can be obtained naturally from several sources, including: From coral [7], from fish bones [8], its preparation from egg shells [9], its preparation from human teeth [10,11], its preparation from cow bones [3]. Several methods were used to prepare hydroxyapatite, including; deposition technology, sol-gel technology, aqueous technology, biological simulation deposition technique, electrostatic deposition technique and other methods [12].

Hydroxyapatite is an inorganic biological material as it forms a strong chemical bond with bone tissue, and that bone is composed of organic and inorganic compounds consisting mainly of collagen (9%), calcium phosphate (69%) and water (20%), and other organic materials such as proteins, sugars and fats are present in small amounts, and bones are high in calcium phosphate [3].

Hydroxyapatite (HAp) is considered one of the best materials used in the process of replacing or repairing damaged bones, due to its characteristics, the most important of which are; biocompatible (it has no side effects in the living environment), it has a chemical formula close to the bone formula that makes it integrates quickly and easily into the treatment site and quickly interacting with the biological medium [13].

The color of pure hydroxyapatite powder is white, and it may be found in different colors such as brown, yellow, green and others [14]. The biological behavior of hydroxyapatite depends on several factors such as chemical composition, phase, microstructure, and pore size, as it forms a direct chemical bond with hard tissues, and this behavior is considered one of the biological properties of hydroxyapatite [15]. Among its benefits is its rapid compatibility and interaction with body tissues, and its disadvantages are its weak mechanical properties [16,17].

Hydroxyapatite is a porous, bio-ceramics granular in nature and has wide application in biomedicine, dentistry and orthopedics [18]. It is also brittle [19]. It is also non-toxic and also biologically active, that is, it has the ability to form a direct chemical bond with living tissues. Calcium and phosphate ions are not rejected by the human body, so this property has led to an increase in the use of hydroxyapatite in orthopedic fractures and in osteoporosis operations. It is also used as a coating material to improve the biocompatibility of biomaterials and it has been found that (HAp) forms strong chemical bonds with bone in vivo and remains stable under harsh conditions if used as biomaterials.

The physical and mechanical properties can be calculated through the following relationships:
1.1. Apparent density

It is the ratio between mass and apparent volume, and it is calculated through the following relationship [20,21]:

$$\rho = \frac{w_d}{w_s - w_n}$$  \hspace{1cm} (1)

whereas: \(\rho\): Apparent density \((g / cm^3)\), \(W_d\): dry sample weight \((gm)\), \(W_n\): the submerged weight of the sample \((gm)\) and \(W_s\): wet sample weight \((gm)\).

1.2. Apparent Porosity and Water Absorption

Porosity is defined as the size of open pores to the total volume of the body [22,23]:

$$A.P = \frac{W_s - W_p}{W_s - W_n} \times 100\%$$  \hspace{1cm} (2)

$$W.A = \frac{w_s - w_d}{w_d} \times 100\%$$  \hspace{1cm} (3)

whereas: \((A.P)\) Apparent porosity and \((W.A)\) water absorption ratio.

1.3 Radial Shrinkage

Shrinkage is calculated by diameter using the following relationship [24].

$$\text{Shrinkage} (\%) = \frac{\text{Change in dimension or volume}}{\text{Initial dimension or volume}}$$  \hspace{1cm} (4)

1.4 Vickers Hardness

The hardness property is one of the important surface mechanical properties that can be defined as the material’s resistance to stitches or scratches, which enables it to hold its body together under the influence of external forces. Hardness, like other mechanical properties, depends on the type of surface, its temperature, and the conditions affecting it [25].

$$H_v = \frac{1.854 P}{d^2}$$  \hspace{1cm} (5)

whereas: \(H_v\): Hardness in units \((MPa)\), \(P\): represents weight in units \((kgf)\) and \(d\): represents the length of the long trace in units \((\mu m)\).
1.5 Compressive Strength

It is defined as the tensile force acting perpendicular to the cross-sectional area (A) of the sample, and it can be calculated through the following relationship [25]:

$$\sigma_c = \frac{F}{A}$$  

whereas: $\sigma_c$: compressive strength in units (N/m²), F: the uniaxial tensile force applied perpendicular to the sample cross-section (N) and A: It is the area of the original cross-section (m²).

1.6. The aim of the study

To prepare locally hydroxyapatite and samples of hydroxyapatite with different densities.

2. Experimental procedure

2.1. Hydroxyapatite powder (HAp)

It was prepared from local cow bones according to the following steps; the first step is to clean the bones from fats, protein materials and external deposits, the second step is the process of boiling with water for a period of five hours and the process can be repeated two or three times until ensuring that the largest possible amount of fatty and protein substances is removed from the bones, then the drying was done at a temperature of 100°C for 24 hours, the third step was the calcination process in the electric oven at a temperature of 750°C for three hours, to ensure that the parts of the bones became white and free of black greasy deposits, and fourth step using ceramic ball mill with alumina balls to grind the powders, and then seiving the powder to obtain hydroxyapatite with a particle size equal to or less than 150μm.

2.2. Charcoal powder (Carbon: C)

It was supplied from wood charcoal available in the local markets, and it was ground using a ceramic ball mill, and then seiving into a particle size equal to or less than 150μm.

2.3. The binder material

Polyethylene glycol, which has a molecular weight of 6000 mw, was used and supplied by a German company (SIGMA-ALDRICH - W.G) with a weight of 1%. The solution was prepared by dissolving polyethylene glycol with ethyl alcohol, at 1gm polyethylene glycol versus 100ml of ethyl alcohol at 40°C with the use of a magnetic stirrer, the movement of the magnet moves the solution continuously to obtain a homogeneous solution.

2.4. Sample formation and heat treatment

Samples were formed through the following steps; carbon was added to the hydroxyapatite with different weight ratios as shown in table 1, and the binder was added to the mixture, and the materials were mixed well using a magnetic stirrer device, dry the samples with a dryer at 75°C for 24 hours, samples are pressed under pressure 2.75ton, it was then dried by dryer at 100 °C for 24 hours and heat treatment of the samples
was performed at a temperature of 1350°C for a period of 3 hours, at the rate of rise and fall of the furnace in the amount of 5°C/min.

| Table 1. It shows the weight ratios of mixtures of carbon and hydroxyapatite |
|-----------------------------------------------|
| HAp (wt%) | 100 | 99.9 | 99.8 | 99.7 | 99.6 | 99.5 | 99.4 | 99.3 | 99.2 | 99.1 | 99 |
| C (wt%) | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1 |

3. Results and discussion

The prepared hydroxyapatite powder was examined through the X-ray diffraction system and it was found that the phase is hydroxyapatite in the hexagonal crystal type by comparing it with the attached library with the X-ray diffraction system as shown in Figure 1. After compression of a group of samples and a heat treatment procedure on them and performing the same X-ray diffraction examination also, the phase of the samples was found to be hydroxyapatite with a hexagonal crystalline phase, as shown in figure 2.

For the prepared powder, X-ray fluorescence was used to calculate the proportions of the substances that make up hydroxyapatite, and it was found that the ratio of calcium oxide to phosphorous oxide is 1.718, which is close to what was published in the literature 1.67[26].

Figure 3 shows the change in the apparent density of the prepared hydroxyapatite with the carbon ratios added at a temperature of 1350°C for a period of three hours, and a decrease in the density values appeared by increasing the carbon ratios up to the ratio of 0.7. The reason is that the heat treatment led to the departure of carbon atoms (coal) quickly, causing an increase in the affinity of the hydroxyapatite particles, which led to a higher density.

Figure 4 shows the effect of adding different percentages of carbon to hydroxyapatite on porosity. Figure 5 shows the effect of adding different percentages of carbon to hydroxyapatite on water absorption. We note that the highest value of porosity and water absorption ratio is at the carbon ratio of 0.7%, and the behavior of porosity and water absorption rate is as expected, reversing the behavior of apparent density and this is consistent with the reference [27].

Figure 6 shows the change of radial shrinkage for hydroxyapatite with the change of carbon ratios added at a temperature of 1350°C for a period of three hours. We note that the highest value of the diagonal shrinkage is at 0.7%, and this is consistent with the interpretation of the decrease in apparent density at this ratio.

Figure 7 shows the change in Vickers hardness with the added carbon ratios and represents an almost linear decrease, this decrease in the amount of hardness is due to the increase in the amount of pores in the samples due to the increase in the carbon ratios, where the carbon during the heat treatment leaves the samples and leaves the pores that reflect on the physical and mechanical properties, including the hardness.

Figure 8 illustrates changing the compressive strength of hydroxyapatite by changing the added carbon ratios at a temperature of 1350°C for three hours. We note that the highest strength is at the ratio and the
behavior is almost similar to the behavior of hardness and low due to the voids arising within the structure of the models due to the carbon leaving the samples.

4. Conclusion

Hydroxyapatite powder with the chemical formula Ca10 (PO4)6 (OH)2 was prepared locally from cow bones in the hexagonal crystal phase. The hexagonal phase of the hydroxyapatite was also stabilized (fixed) for the samples before and after the heat treatment.

It is possible to prepare samples of hydroxyapatite with different densities by adding different percentages of carbon (charcoal) percent, and this property is very important when manufacturing parts that may enter the human body according to the required density, and the work of the pores is also important through interlocking and interacting with the tissues of the living body.

Figure 1. X-ray spectrum of the prepared powder and standard
Figure 2. X-ray spectrum of the prepared form after heat treatment of 1350°C for 3 hours and the standard

Figure 3. The change of the apparent density of the hydroxyapatite with carbon ratios at a temperature of 1350°C for three hours.
**Figure 4.** The change of the porosity of the hydroxyapatite with carbon ratios at a temperature of 1350°C for three hours.

**Figure 5.** The change of the water absorption of the hydroxyapatite with carbon ratios at a temperature of 1350°C for three hours.

**Figure 6.** The change of the radial shrinkage of the hydroxyapatite with carbon ratios at a temperature of 1350°C for three hours.
Figure 7. The change of the Vickers hardness of the hydroxyapatite with carbon ratios at a temperature of 1350°C for three hours.

Figure 8. The change of the compressive strength of the hydroxyapatite with carbon ratios at a temperature of 1350°C for three hours.

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