OPTIMISATION OF MILLING PARAMETERS DURING MECHANICAL ACTIVATION FOR DIRECT SYNTHESIS OF HYDROXYAPATITE

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Abstract

Mechanical activation is one of the methods to synthesize a single-phase hydroxyapatite. In this work, hydroxyapatite was directly synthesized by mechanical milling in a planetary ball mill, using calcium phosphate dibasic dihydrate, $CaHPO_4.2H_2O$, and calcium hydroxide, $Ca(OH)_2$, as the precursors or raw materials. The milling parameters investigated included the duration of milling, the milling media, and the ball-to-powder ratio (BPR). The results thus far indicated that the parameters of milling can be optimised down to 2 hours of milling duration, using either stainless steel or agate milling media, and a BPR of 10:1. The optimization was confirmed principally by x-ray diffraction (XRD) which indicated that only single-phase hydroxyapatite was the final product in this milling reaction. Other characterization methods employed were scanning electron microscopy (SEM), transmission electron microscopy (TEM) and particle size analysis. Characterization by SEM and TEM showed that the morphologies of the hydroxyapatite particles are needle-shaped and the sizes are dependent on the changes in the parameters used in the mechanical activation milling process.

Keywords: Hydroxyapatite, Mechanical activation, Milling

Introduction

Scientific investigations by materials scientists have been continuously directed towards improving the properties and performance of materials. Significant improvements in mechanical, chemical and physical properties have been achieved through chemistry modifications and conventional thermal, mechanical and thermomechanical processing methods[1]. Mechanochemical processes (MCP) use mechanical energy to activate chemical reactions and structural changes. A ball mill may be considered to be a chemical reactor in which a wide range of chemical reactions can be mechanically initiated [2].

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ or HA), classified as a biomaterial, is a synthetic material used to replace parts of a living system or to function in intimate contact with living tissues [3]. This substance is present in substantial amounts in the mineralized tissue of vertebrates, i.e. 60–70% of the mineral phase of the human bone [4].

There are several methods to synthesize HA such as the sol-gel synthesis[5,6], hydrothermal methods [7,8], solid-state reactions [9,10], wet precipitation methods [11,12], mechanochemical methods [13,14], etc. Incidentally, pure HA can only be obtained at temperatures above 900°C by solid-state reactions, or at 375°C by hydrothermal methods. However, in mechanochemical processing, reactions that need high temperatures will occur at lower temperatures in a ball mill without any need for external heating [15].

Synthesis of hydroxyapatite using a mechanochemical process was investigated in this research work. Initially, the objective was to synthesize HA directly without the need for a two-stage process where mechanical activation for 60 hours was followed by a heat-treatment process at 1100^{o}C [16,17].The milling parameters were systematically investigated, and these included the milling duration, the types of milling media and the ball-to-powder ratio. The use of milling media, i.e. the balls and the jars, was restricted to the same material as compared to dissimilar materials which had been reported in the literature [18,19] The ultimate objective of the present work was to synthesize a single-phase hydroxyapatite directly within the shortest possible duration, thus contributing to a reduction in time and energy of the process.

Apart from that, many different combinations of precursors had also been reported in the literature [4]. The mechanical activation of calcium pyrophosphate and calcium carbonate precursors had been reported, but in that instance, the milled powder needed to be heated to 1100^{o}C before HA can be crystallized out. In this work, calcium phosphate dibasic dihydrate, $CaHPO_4.2H_2O$, and calcium hydroxide, $Ca(OH)_2$, were chosen as the precursors and were milled in a planetary ball mill so that their chemical reactions could be mechanically activated to produce hydroxyapatite directly without any need for heat-treatment.

Materials and Methods

The precursors used in this work were commercially available hydrated calcium hydrogen phosphate ($CaHPO_4.2H_2O$,Riedel-de Haen, 98%) and calcium hydroxide ($Ca(OH)_2$, Fluka, 96%). The raw materials were mixed in a planetary ball mill (Retsch, PM100) in a stoichiometric proportionality of the oxides as given in reaction 1,

$$4\,Ca(OH)_2 + 6\,CaHPO_4.\,2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18\,H_2O \qquad (1)$$

Milling was performed in a wet condition using a weight ratio of sample to distilled water 1:3 with the initial parameters of milling set of 15 hours milling duration at 400 rpm rotation speed [20]. In order to avoid excessive heat, milling was carried out in 30 minutes milling intervals with 2 minutes pause. The milling media to start off with was stainless steel (ball and jar) and the ball-to-powder ratio (BPR) was fixed at 20:1. The milling parameters were then systematically varied to observe their effects on the reaction, i.e. the duration of milling, media of milling, and BPR used.

Initially, a milling duration of 15 hours was chosen whilst the other parameters were fixed. Subsequently, the duration of milling was almost halved to 8 hours, and then further reduced to 3 hours, 2 hours and 1 hour to determine the lowest possible millling time to produce single-phase HA. Subsequently, when the lowest possible milling duration had been determined using stainless steel milling media, the effects of using other milling media were investigated, viz. agate, alumina and zirconia milling media. Once this was established, another parameter of milling, i.e. the ball-to-powder ratio (BPR), was investigated using stainless steel media and 2 hours of milling duration whilst the other parameters remained thesame. An initial BPR of 20:1 was systematically reduced until the reaction can no longer form single-phase HA.

An x-ray diffractometer (D8 Advance, Bruker AXS) was used as the main analytical tool to determine that HA was produced in all the reactions and to detect other phases that might be present from the reactions. Scanning electron microscopy (Supra, Zeiss) and transmission electron microscopy (CM12, Philips) were used to observe the morphology and shape of the HA particles. The particle sizes of the powder samples were also analysed using a particle sizer (RODOS, SympaTEC).

Results and Discussion

X-ray Diffraction (XRD)

The first parameter of milling investigated was the duration of milling and the result is shown in Figure 1. The duration of milling was initially set at 15 hours, based on a previous work [18] whilst the other parameters were fixed as stainless steel media, BPR 20:1, speed of milling 400 rpm with 30 minutes milling interval and 2 minutes pause. The result shows that after 15 hours of mechanical milling, a single-phase HA can be successfully obtained. Subsequently, as the duration was halved, single-phase HA can still be produced, even as the milling duration was eventually decreased down to 2 hours. However, as the duration was further lowered to 1 hour of milling, an incomplete reaction is evidenced by the presence of $CaHPO_4$, which is one of the precursor materials. Hence, it can be concluded that the lowest milling duration to produce single-phase HA is 2 hours of milling. This can be contrasted to a duration of milling of up to 60 hours [17] and 6 hours [15] even though, admittedly, the other parameters were not exactly similar. Apart from savings in energy during milling, the lowest possible milling duration is expected to result in lower amounts of possible contamination [21].

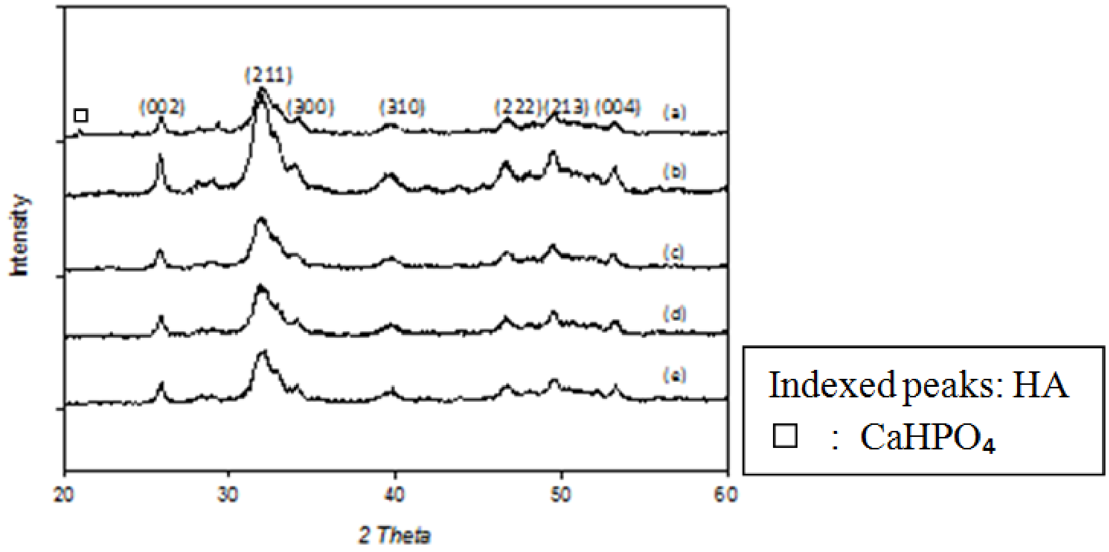

Figure 1. XRD patterns of samples after different duration of milling.(a) 1 hour, (b) 2 hours, (c) 3 hours, (d) 8 hours and (e) 15 hours

The next parameter was the media of milling apart from stainless steel, i.e. either agate, zirconia or alumina. This referred to the balls and jar for milling, even though the use of dissimilar materials for the balls and the jars had also been reported in previous works [22]. Only this parameter was changed, whilst the milling duration was fixed at 2 hours and the other parameters were fixed as in the previous milling. The results in Figure 2 show that single-phase HA is obtained when stainless steel and agate milling media were used, whilst the diffractograms obtained when zirconia and alumina media were used exhibit other phases apart from HA. When an alumina media was used, an Al2O3 phase becomes the dominant phase in the diffractogram, whilst incipient formation of HA can also be observed. This proves that an alumina media is not suitable for this set of milling parameters because it led to heavy wear and tear of the alumina balls and jar upon collisions during the milling process due to the brittle nature of the alumina. On the other hand, the contamination due to wear is much lesser when using a zirconia media and the formation of the HA phase can be seen to be much more significant. Hence, it can be concluded that for this set of fixed milling parameters, only an agate and stainless steel milling media lead to the formation of a single-phase HA.

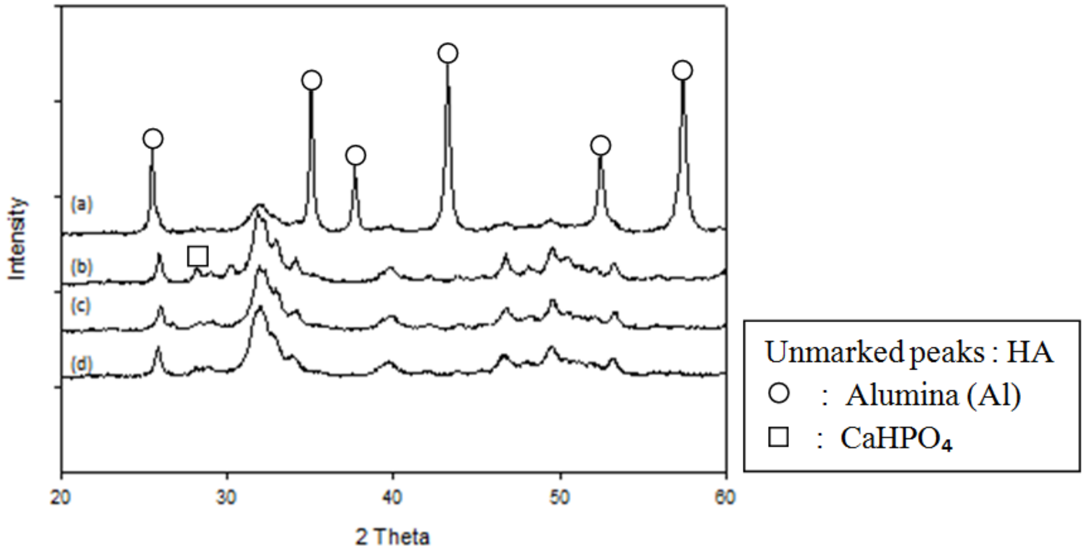

Figure 2. XRD patterns of samples milled in different media after 2 hours of milling: (a) Alumina, (b) Zirconia, (c) Agate and (d) Stainless steel

Subsequent investigation carried out was on the ball to powder ratio. Figure 3. shows the results using BPR 20:1, 15:1, 10:1 and 5:1. For the first three higher BPR ratios, a single-phase HA is obtained whilst a BPR of 5:1 still indicates the presence of the initial raw material due to incomplete reaction. These effects are related to the average frequency of collisions that increases with increasing BPR.

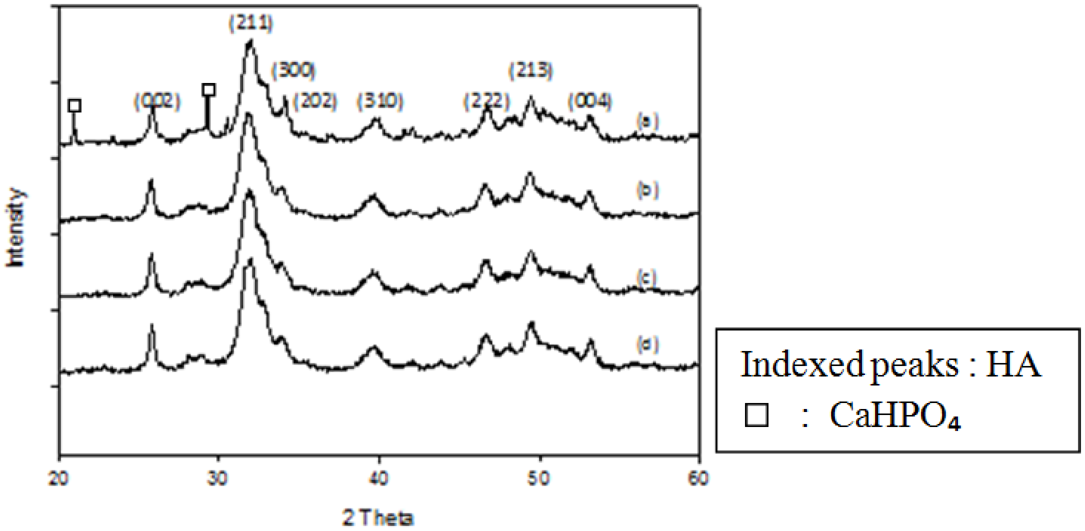

Figure 3. XRD patterns of samples milled using different ball-to-powder ratios: (a) 5:1, (b) 10:1, (c) 15:1 and (d) 20:1

Scanning Electron Microscopy (SEM)

For the SEM analysis, only representative samples were highlighted. The first set of comparison was between samples which had been milled using a stainless steel and an agate media with the following fixed milling parameters, viz. a BPR of 20:1, milling duration of 2 hours and a milling speed of 400 rpm.

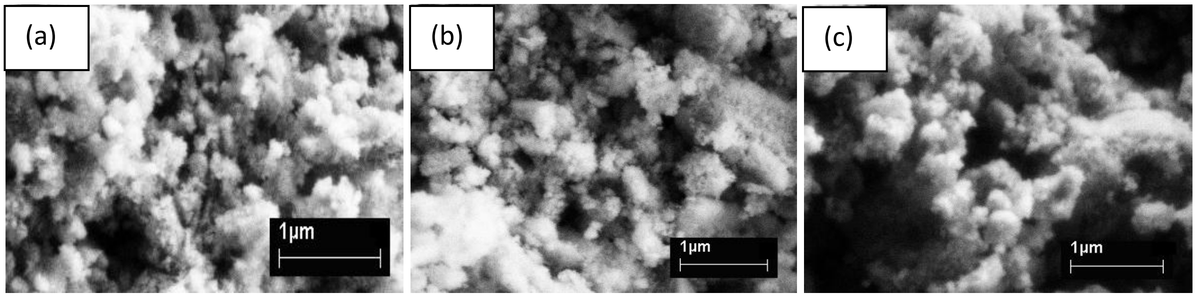

Figure 4. Scanning electron micrographs of sample milled in (a) stainless steel media (BPR 20:1), (b) agate media (BPR 20:1), (c) stainless steel media (BPR 10:1)

It can be observed that upon comparison between the two media, the stainless steel media produces a much finer powder (Figure 4(a)) as compared to that produced using an agate media (Figure 4(b)). This is attributed to the higher-density of stainless steel, and hence, a much higher amount of energy was impacted during the collisions. Subsequently, upon comparison between HA powder produced using a lower BPR, i.e. 10:1 compared to 20:1, the HA powder produced using the lower BPR is finer (for stainless steel). This is attributed to the longer path before collisions in the 10:1 BPR. Upon close scrutiny of the HA powder produced using an agate media at BPR 20:1 (Figure 4(b)) and that using stainless steel at BPR 10:1(Figure 4(c)), it is evident that the latter is finer. This can possibly be taken as suggestive to the higher influence that the ball-to-powder ratio (inevitably, the path before collisions) exerts on the particle size compared to the difference in the density of the media itself. This gradation in particle size wass supported by the results conducted using a powder particle size analyser whereby powder (a) =1.61μm, (b) =1.65 μm, and (c) =1.45 μm.

Transmission Electron Microscopy (TEM)

Figure 5 shows a bright field TEM micrograph of samples with the different parameters of milling as highlighted in Section 3.2. It can be observed that all HA samples consist of particles which exhibit a rod-shape or needle-shape configuration which is in contrast to the findings in another work [15] where the particles were reported to be spherical in shape, i.e. about 20nm in size. It can be observed that upon comparison, the size of the rods is obviously much finer using the stainless steel media (Figure 5(a)) as compared to that using the agate media (Figure 5(b)). As explained for the SEM micrographs, a much higher amount of energy was impacted during the collisions when using a higher-density stainless steel media compared to the agate media. The particle sizes are estimated to be in the range of 40-100 nm in length and 10 nm diameter. Upon subsequent comparison between HA powder produced using a lower BPR, i.e. 10:1 compared to 20:1, the HA powder produced using the lower BPR is finer (for stainless steel), viz. 40 nm compared to 60 nm in length. As above, this is attributed to the longer path before collision for the case with a 10:1 BPR. However, if Figure 5(b)) is compared to Figure 5(c), it is much more evident that milling using stainless steel at a lower BPR of 10:1 produces a finer powder compared to that using an agate media with a of BPR of 20:1. This further reinforces the suggestion offered for the SEM micrographs in Section 3.2.

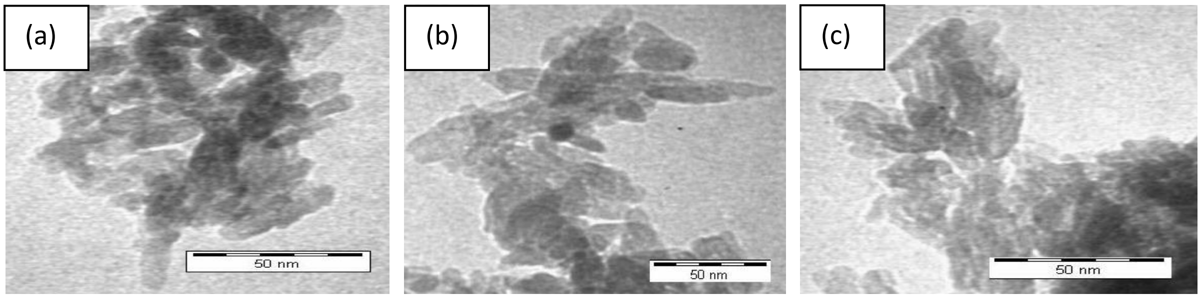

Figure 5. Transmission electron micrograps of samples using: (a) stainless steel media (BPR 20:1), (b) agate media (BPR 20:1), (c) stainless steel media (BPR 10:1)

Conclusions

In conclusion, the results thus far indicate that the parameters of milling can be optimised down to 2 hours of milling duration, using either stainless steel or agate media, and a BPR of 10:1 to synthesize directly a single-phase hydroxyapatite. The optimization was confirmed principally with X-ray diffraction (XRD) which indicated that only a single-phase hydroxyapatite was the final product in this milling reaction. Microscopy results indicate that stainless steel media produces finer powders compared to that of agate due to the higher energy impacted by the higher density media. Likewise a BPR of 10:1 (compared only to 20:1), for stainless steel media, produces a finer powder due to the longer (and possibly the optimum distance) path before collisions, and hence, a higher amount of energy impacted. The use of alumina or zirconia milling media is found to be unsuitable under the set of milling conditions employed in the present work.

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References

[1] C. Suryanarayana, “Mechanical alloying and milling,” *Materials Science,* Vol. 46, No. 1-2, pp. 1-184, 2001.

[2] P.G. McCormick, and F.H. Froes, “The fundamentals of mechanochemical processing,” *The Journal of the Minerals, Metals & Materials Society*, Vol. 50, No. 11, pp. 61-65, 1998.

[3] T. Kokubo, *Bioceramics and Their Clinical Applications,* CRC Press LLC, New York, United States, 2008.

[4] C.C. Silva, A.G. Pinheiro, R.S. de Oliveira, J.C. Go´es, N. Aranha, L.R. de Oliveira, and A.S.B. Sombra, “Properties and in vivo investigation of nanocrystalline hydroxyapatite obtained by mechanical alloying,” *Materials Science & Engineering: C,* Vol. 24, No. 4, pp. 549-554, 2004.

[5] A. Deptula, W. Lada, T.Olczak, A.Borello, C. Alvani, and A.diBartolomeo, “Preparation of spherical powders of hydroxyapatite by sol-gel process,” *Journal of Non-crystalline Solids,* Vol. 147-148, pp. 537-541, 1992.

[6] S. Jadalannagari, S. More and M. Kowshik, “Low temperature synthesis of hydroxyapatite nano-rods by a modified sol–gel technique,” *Materials Science and Engineering: C*, Vol. 31, No. 7, pp. 1534-1538, 2011.

[7] T. Hattori, Y. Iwadate, and K. Kato, “Hydrothermal synthesis of hydroxyapatite from calcium pyrophosphate,” *Journal Material Science Letter*, Vol. 8, pp. 305-306, 1989.

[8] X. Zhang, and K.S. Vecchio, “Hydrothermal synthesis of hydroxyapatite rod,” *Journal of Crystal Growth*, Vol. 308, No. 1, pp. 133–140, 2007.

[9] S. Pramanik, A.K. Agarwal, K.N. Rai, and A. Garg, “Development of high strength hydroxyapatite by solid-state-sintering processs,” Ceramic International, Vol. 33, No. 3, pp. 419-426, 2007.

[10] B. Nasiri-Tabrizi, P. Honarmandi, R. Ebrahimi-Kahrizsangi, and P. Honarmandi, “Synthesis of nanosize single-crystal hydroxyapatite via mechanochemical method,” *Materials Letter*, Vol. 63, No. 5, pp. 543-546, 2009.

[11] L.T. Bang, K. Ishikawa, and R. Othman, “Effect of silicon and heat-treatment temperature on the morphology and mechanical properties of silicon - substituted hydroxyapatite,” *Ceramic International*, Vol. 37, No. 8, pp. 3637-3642, 2011.

[12] I. Mobasherpour, M. Soulati Heshajin, A. Kazemzadeha, and M. Zakeri, “Synthesis of nanocrystalline hydroxyapatite by using precipitation method,” *Journal of Alloys and Compounds,* Vol. 430, No. 1-2, pp. 330-333, 2007.

[13] M. Toriyama, A. Ravaglioli, A. Krajewski, G. Celotti, and A. Piancastelli, “Synthesis of hydroxyapatite-based powders by mechano-chemical method and their sintering,” *Journal of the European Ceramic Society*, Vol. 16, No. 4, pp. 429-436, 1996.

[14] S. Cai, Y.W. Wang, Lv Hong, Z.Z. Peng, and K.D. Yao, “Synthesis of carbonated hydroxyapatite nanofibers by mechanochemical methods,” *Ceramics International*, Vol. 31, No. 1, pp. 135-138, 2005.

[15] A.J. Coreno, A.O. Coreno, R.J.J. Cruz, and C.C. Rodiguez, “Mechanochemical synthesis of nanocrystalline carbonate-substituted hydroxyapatite,” *Optical Materials*, Vol. 27, No. 7, pp. 1281-1285, 2005.

[16] S.H. Rhee, “Synthesis of hydroxyapatite via mechanochemical treatment,” *Biomaterials*, Vol. 23, No. 4, pp. 1147-1152, 2002.

[17] C.C. Silva, A.G. Pinheiro, M.A.R. Miranda, J.C. Go´es, and A.S.B. Sombra, “Structural properties of hydroxyapatite obtained by mechanosynthesis,” *Solid State Sciences*, Vol. 5, No. 4, pp. 553-558, 2003.

[18] K.C.B. Yeong, J.Wang, and S.C. Ng, “Mechanochemical synthesis of nanocrystalline hydroxyapatite from CaO and CaHPO4,” *Biomaterials*, Vol. 22, No. 20, pp. 2705-2712, 2001.

[19] M.H. Fathi, and E. Mohammadi Zahrani, “Mechanical alloying synthesis and bioactivity evaluation of nanocrystalline fluoridated hydroxyapatite,” *Journal of Crystal Growth*, Vol. 13, No. 5, pp. 1392-1403, 2009.

[20] H. El Briak-BenAbdeslam, M.P. Ginebra, M. Vert, and P. Boudeville, “Wet or dry mechanochemical synthesis of calcium phosphates? Influence of the water content on DCPD-CaO reaction kinetics,” *Acta Biomaterialia,* Vol. 4, No. 2, pp. 378-386, 2008.

[21] S. Montinaro, A. Concas, M. Pisu, and G. Cao, “Immobilization of heavy metals in contaminated soils through ball milling with and without additives,” *Chemical Engineering Journal*, Vol. 142, No. 3, pp. 271-284, 2008.

[22] G. Gonzalez, A. Sagarzazu, and R. Villalba, “ Mechanochemical transformation of mixtures of $Ca(OH)_2$ and $(NH_4)_2HPO_4$ or P_2O_5,” *Material Research Bulletin*, Vol. 41, No. 10, pp. 1902-1916, 2006.