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Original Article

Novel bioactive Co-based alloy/FA nanocomposite for dental applications

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ABSTRACT

Background: Dental cobalt base alloys are biocompatible dental materials and have been widely used in dentistry. However, metals are bioinert and may not present bioactivity in human body. Bioactivity is the especial ability to interact with human body and make a bonding to soft and hard tissues.The aim of the present research was fabrication and bioactivity evaluation of novel cobalt alloy/ Fluorapatite nanocomposite (CoA/FaNC) with different amounts of Fluorapatite (FA) nanopowder.
Materials and Methods: Co-Cr-Mo alloy (ASTM F75) powder was prepared and mixed in a planetary ball mill with different amounts of FA nanopowders (10, 15, 20% wt). Prepared composite powders were cold pressed and sintered at 1100°C for 4 h. X-ray diffraction (XRD), scanning electron microscopy and transition electron microscopy techniques were used for phase analysis, crystallite size determination of FA and also for phase analysis and evaluation of particle distribution of composites. Bioactivity behavior of prepared nanocomposites was evaluated in simulated body fluid (SBF) for 1 up to 28 days.
Results: Results showed that nucleus of apatite were formed on the surface of the prepared CoA/ FaNC during 1 up to 28 days immersion in the SBF solution. On the other hand, CoA/FaNC unlike Co-base alloy possessed bone-like apatite-formation ability.
Conclusion: It was concluded that bioinert Co-Cr-Mo alloy could be successfully converted into bioactive nanocomposite by adding 10, 15, 20 wt% of FA nano particles.

Key Words: Bioactivity, Co-Cr-Mo alloy, FA nanopowder, nanocomposite

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INTRODUCTION

Metallic biomaterials have been successfully used for dental and orthopedic applications. However, metallic implants are bioinert and present poor interfacial bond between the tissue and the implant due to bioinert surface. Surface treatment, compositional improvement, structural modification or changing the bioinert property into bioactivity could increase the interfacial bond between living cells and implant materials in order to increase the *in vivo* lifetime of metallic implants.[1-4]

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Since Bioglass was discovered by Hench *et al*. in the early 1970s,[5] the application potential of various bioactive ceramics in the medical field has been investigated.[6] Bonding of these bioactive ceramics to living cells has been achieved through a biologically active bone-like apatite (i.e., carbonate-containing apatite) layer, which is formed on their surface without forming the fibrous tissue around them.[7-10]

It is well known that bioactive materials can integrate well with living bone tissues by spontaneously forming a biologically active bone-like apatite layer on their surfaces.[11] Fluorapatite (FA) $[Ca_{10}(PO_4)_6F_2]$ is one of the bioactive ceramics which has excellent biocompatibility with hard tissue. FA is an attractive material due to its similarity in structure and composition to teeth and bone with the added benefit of fluoride release. *In vitro* studies have shown that FA is biocompatible, has higher stability in comparison with hydroxyapatite and also provides fluoride release at a controlled rate to ensure the formation of a mechanically and functionally strong bone.[12-17]

Dental cobalt base alloys are biocompatible dental materials and have been widely used in dentistry.[18] FA is a bioactive material and has low modulus elasticity in comparison with Co-Cr-Mo alloys.[19] It seems that by producing metal matrix composite materials containing a metallic matrix and a bioactive bioceramic filler, the advantage of bioactivity of bioactive ceramics could be achieved.[20] On the other hand, design and preparing of composites based on Co-Cr-Mo alloy with bioactive ceramic filler might be an approach to the challenge of aseptic loosening of the implants.

The main goal of presented research was to fabricate nanocomposite based on dental Co-Cr-Mo alloy with different amounts of FA nanopowder using the powder metallurgy route and also to evaluate the bioactivity of the prepared nanocomposites and to investigate how various FA content affected on the biological properties of nanocomposites.

MATERIALS AND METHODS

Preparation of nanocomposites

Starting materials used in this experimental research were the small billets of Co-Cr-Mo alloy (ASTM F75) which were produced by Wironit Co. (Germany) and also FA nanopowders which were prepared in Biomaterials and Dental Materials Research Group at Isfahan University of Technology. Chemical composition of Co-Cr-Mo alloy is shown in Table 1.

In order to produce Co-Cr-Mo alloy powder, the billets of cast Co-Cr-Mo alloy were chipped by machining process. The chips of Co-Cr-Mo alloy were crushed to powder by mechanical ball milling under argon atmosphere. The ball-to-mass weight ratio was 20:1 and the time of ball milling was 7 h. The obtained powder was screened. Figure 1 shows SEM micrograph of the Co-Cr-Mo alloy powder. Size distribution of prepared Co-Cr-Mo alloy particles was 55-150 µm.

Fabrication of the FA nanopowder was performed based on our previous work.[21] The FA nanopowder was prepared by mixing calcium hydroxide ($Ca(OH)_2$), phosphorous pentoxide (P_2O_5) and calcium fluoride (CaF_2) in a planetary high energy ball mill using zirconia vial and zirconia balls with ball-to-powder weight ratio of 35:1, rotational speed of 300 rpm, and the time of 6 h.[21,22] Figure 2 shows transition electron microscopy micrograph of the FA powder particles. Size distribution of FA particles was 35-65 nm.

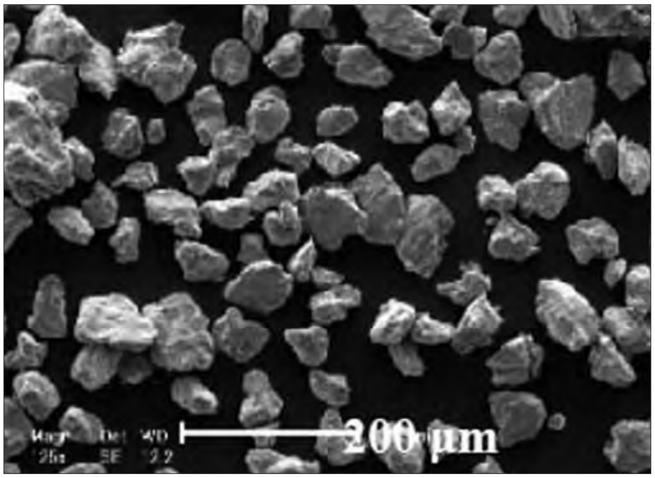

Figure 1: SEM micrograph of Cr-Co-Mo alloy powder

Table 1: Chemical composition (wt%) of Co-Cr-Mo alloy as reported by supplier (Wironit Co., Germany)

Element	Wt%
Co	64
Cr	28
Mo	5
C	Max 0.35
Mn	Max 0.35
Si	Max 0.35

In order to prepare cobalt base alloy/FA nanocomposite (CoA/FaNC), the powder of Co-Cr-Mo alloy was mixed with different amounts of FA nanopowder (10, 15, 20% wt) in a planetary ball mill for 1 h under argon atmosphere. The ball-to-powder weight ratio was 20:1 and rotational speed was 300 rpm. Then, the mixed powders were cold pressed under 750 MPa and the prepared compact samples sintered at 1100°C for 4 h in argon atmosphere. Heating rate of furnace was 10°C/min and the sintered specimens were cooled in the furnace slowly. Water displacement (Archimedes) method was used for density measurement. Measurements were performed on the three polished samples in distilled water. The theoretical density of the composites was calculated using the mixing rule.

The theoretical density of the Co-Cr-Mo alloy is 8.34 g/cm^3 whereas the theoretical density of the FA is 3.19 g/cm^3.

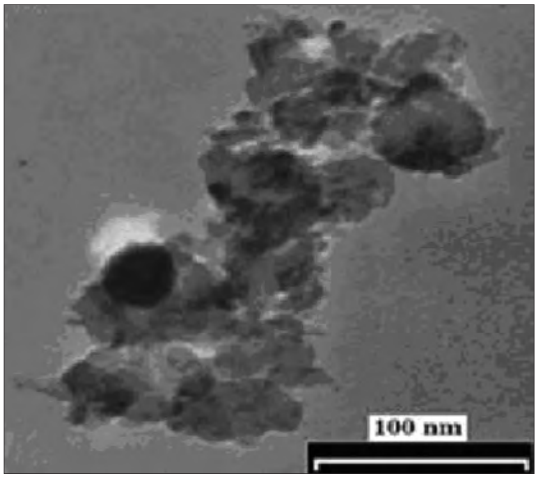

Figure 2: TEM micrograph of prepared FA nanopowder

Microstructural study and phase compositional evaluation

The phase analysis of prepared nanocomposite materials based on Co-Cr-Mo alloy reinforced with 10, 15, 20 wt% FA was carried out by X-ray diffraction (XRD) technique using a Philips X'PERT MPD diffractometer (Cu Kα radiation: λ=0.154056 nm at 40 kV and 30 mA) over the 2θ range of 20–100° at a scan rate of 0.05°/min. The crystallite size of FA of the sintered composites was determined using XRD patterns and Williamson–Hall approach. Scanning electron microscopy (A Philips XL30) technique was used to evaluate the morphology of prepared nanocomposites.

In vitro bioactivity assessment

To assess bioactivity behavior of the nanocomposites, the immersion tests were carried out in a simulated body fluid (SBF) according to ASTM-G31-72,[23] since this procedure has been widely used to prove the similarity between *in vitro* and *in vivo* behavior of certain compositions. SBF was prepared according to the procedure described by Kokubo and Takadama.[9,10,12]

The inorganic ion concentrations in the SBF were nearly equal to those in human blood plasma as shown in Table 2. Appropriate amounts of reagent grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, Na_2SO_4 and tris-hydroxymethylaminomethane (CH_2OH_3-CNH_2) were dissolved into deionized water and buffered to pH 7.25 at 36.5°C with hydrochloric acid (1 M HCl).

Table 2: Nominal ion concentration of SBF solution in comparison to those in human blood plasma

Ion	Ion concentrations (mM)	
	Blood plasma	SBF
Na^+	142.0	142.0
K^+	5.0	5.0
Mg^{2+}	1.5	1.5
Ca^{2+}	2.5	2.5
Cl^-	103.0	147.8
HCO^{3-}	27.0	4.2
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5
pH	7.2-7.4	7.4

Samples were prepared according to the standard metallographic techniques. Each of the sintered nanocomposites was placed in a sterilized bottle containing the SBF solution. The immersion tests were performed in SBF for 1, 14 and, 28 days. The immersion tests were carried out in a shaking bath maintained at 37°C. After the end of soaking time, the samples were rinsed with deionized water to remove SBF solutions, dried and stored.

The apatite formation on the surface of the samples as a consequence of the dissolution and precipitation process of calcium phosphate was investigated by (SEM, A Philips XL30). The apatite formation on the surface is an indication of bioactivity behavior. The concentrations of Ca and P ion in the SBF solutions after soaking were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES: Jobin Yvon, Horiba Group) and the changes in pH of soaking solutions were also measured at pre-determined time intervals (1–28 days) using an electrolyte-type pH meter.

RESULTS

Microstructural and compositional study

Figure 3 shows XRD patterns of Co-Cr-Mo alloy powder and prepared nanocomposites with 10, 15, 20 wt% FA after sintering at 1100°C for 4 h. Phase analysis of the nanocomposites confirmed the existence of FA, cobalt and chromium as the resulting chemical phase.

The crystallite size of FA in the prepared nanocomposites was determined using XRD patterns and Williamson–Hall approach (equation 1):[24]

$$B\cos\theta = \frac{0.89\lambda}{D} + 2\varepsilon\sin\theta \tag{1}$$

where B is the full-width at half maximum intensity, λ is the wavelength of the X-ray used (λ=0.154056 nm), D is the average crystallite size (nm), θ is the Bragg

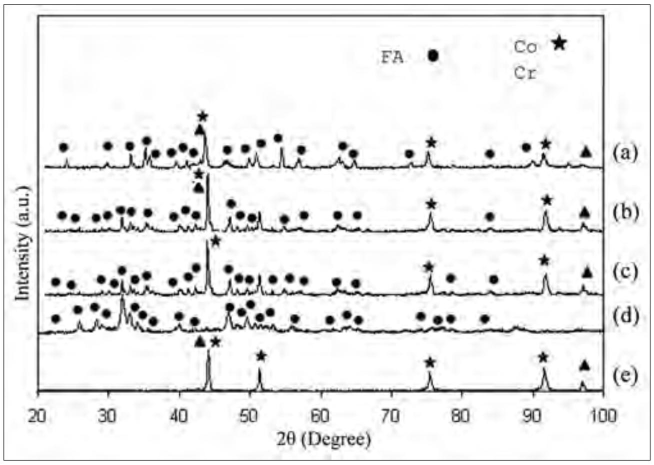

Figure 3: XRD patterns of: (a) cobalt base alloy-20 wt% FA nanocomposite after sintering, (b) cobalt base alloy-15 wt% FA nanocomposite after sintering, (c) cobalt base alloy-10 wt% FA nanocomposite after sintering, (d) FA nanopowder, (e) Co-Cr-Mo alloy powder

angle, and ε is the average strain.

The crystallite size of FA in the prepared nanocomposites with 10, 15, 20 wt% FA, after sintering at 1100°C, could be determined in the range of 78-82 nm.

Physical properties of samples

Relative and theoretical density of the nanocomposites after sintering is given in Table 3. According to these measurements, it was observed that by adding the FA nanoparticles (up to 15 wt %) as reinforcement to the Co-Cr-Mo alloy, relative density of sintered nanocomposites was increased in comparison with pure sintered Co-Cr-Mo alloy. On the other hand, with increasing of the FA content (20 wt% FA) in nanocomposites, density was decreased.

In vitro bioactivity evaluation

The surface morphologies of the nanocomposites after immersion in the SBF solution for 1, 14, 28 days are shown in Figures 4-6. According to the photomicrographs, formation of particles could be observed on the surface of nanocomposites after soaking in SBF solution. Figure 7 shows the changes of the pH of the SBF solution after soaking the specimens in SBF for various times. Figures 8 and 9 illustrate the concentrations of Ca and P in SBF solution after soaking the specimens for various times. These results confirmed the obtained results of SEM study.

DISCUSSIONS

Table 3: Relative and theoretical density of prepared specimens

Sample	Theoretical density (g/cm^3)	Relative density (%)
FA	3.190	-
Co-Cr-Mo alloy	8.340	78.1
Vit-10 wt% FA	7.699	82.5
Vit-15 wt% FA	7.448	80.6
Vit-20 wt% FA	7.198	74.2

As it could be seen in Figure 3, no characteristic peaks of more phases such as TCP, TTCP and CaO were observed in the prepared nanocomposites. It could be observed that the FA particles were stable after sintering at 1100°C and no thermal decomposition of FA was occurred, indicating that the kinetics during sintering is restricted to diffusion between and within particles.

The crystallite size of FA in the prepared nanocomposites was in the range of 78-82 nm. This means that the crystallite size of FA could be remained in the nanometer range during fabrication process. This matter could be explained with the existence of Co-Cr-Mo alloy particles around the FA particles and their ability to prevent the growth of FA particles.

By adding the FA nanoparticles to the Co-Cr-Mo alloy, relative density of sintered nanocomposites was increased in comparison with pure sintered Co-Cr-Mo alloy. This was due to filling of porosities in intersections of grains of matrix by reinforcements. On the other hand, with increasing of the FA content (20 wt% FA) in nanocomposites, density was decreased. With increasing of the FA content in the nanocomposites, the internal friction between the particles increases which prevents suitable mixing of FA and matrix particles and thereby prevents filling the pores.

In vitro tests [Figures 4-6] indicated that nucleus of apatite as a consequence of the dissolution and precipitation process of calcium phosphate was formed on the surface of nanocomposites after 1 day. The size of apatite particles was small after 1 day soaking. With increase in time of soaking, the size and amount of precipitated apatite were increased. Larger quantity of nucleus was observed on the surface of samples with higher FA content after soaking in the SBF. As the immersion time increased up to 14 and 28 days, these tiny precipitated crystals grew in size and increased in number. SEM photomicrographs illustrated that bone-like apatite crystals were agglomerated and the size of agglomerated precipitations on the surface of samples increased as a result of increasing FA content in the samples.

The pH changes of the SBF solution [Figure 7] after soaking the specimens in SBF for various times and also the concentrations of Ca and P in SBF solution [Figures 8 and 9] after soaking the specimens for various times confirmed the obtained results of SEM study. Results showed that with increasing of soaking time of the composites in SBF solution up to 14 days, the Ca concentration was increased. This phenomenon was due to ion exchange between the nanocomposites and SBF solution during soaking time. Change in the Ca concentration was uniformed due to precipitation of calcium phosphate on the surface of the nanocomposites which was due to stable thermodynamic conditions.

Results showed that with increase in soaking time of the nanocomposites in SBF solution, P concentration was decreased due to precipitation of calcium phosphate on the surface of the nanocomposites.

With increase in FA content in CoA/FaNC, Ca concentration was increased and P concentration was decreased. These results showed that the increase in precipitation of hydroxy carbonate apatite (HCA) on the surface of composites might have occurred with increase in content of bioactive phase in the composites. SEM micrographs also confirmed these mentioned results. Results of pH measurements showed an increase in the pH of SBF solution with increase in time of soaking. After that, when the stable thermodynamic conditions were dominated, the pH of SBF solution was uniformed. With the release of Ca ion from the nanocomposites and ion exchange

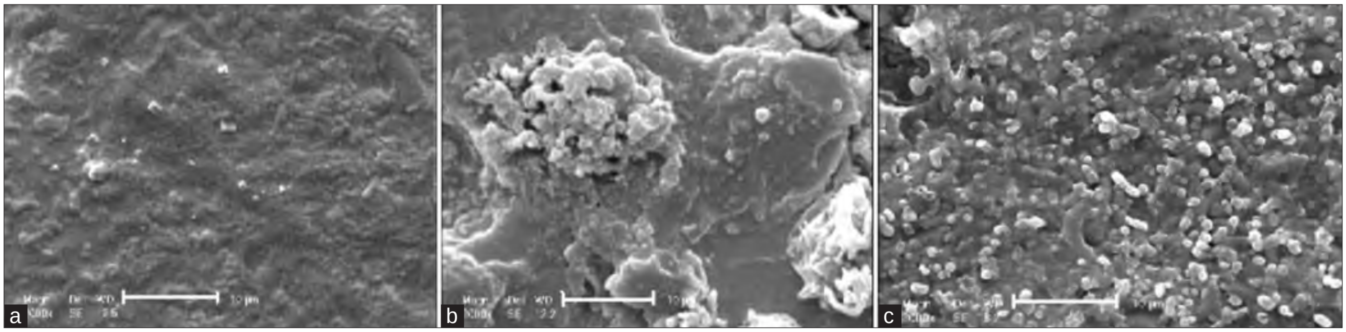

Figure 4: SEM photograph of the Co-base alloy/10 wt% FA after soaking in SBF solution for (a) 1 day, (b) 14 days and (c) 28 days

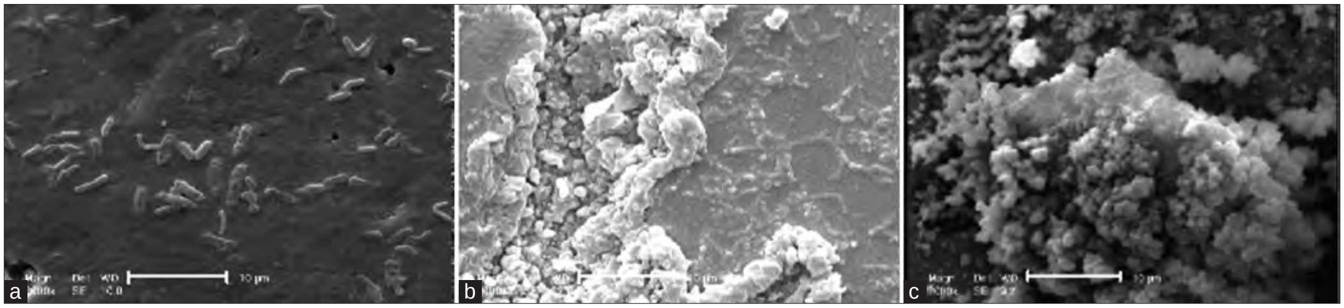

Figure 5: SEM photograph of the Co-base alloy/15 wt% FA after soaking in SBF solution for (a) 1 day, (b) 14 days and (c) 28 days

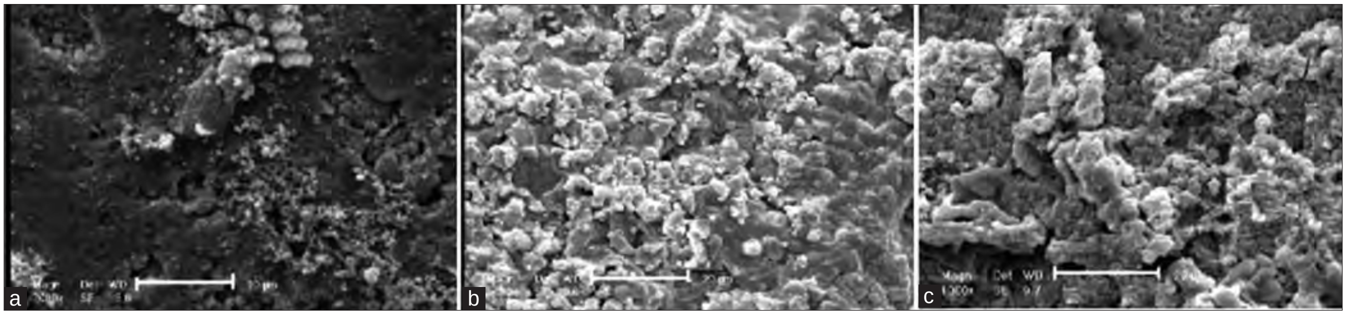

Figure 6: SEM photograph of the Co-base alloy/20 wt% FA after soaking in SBF solution for (a) 1 days, (b) 14 days and (c) 28 days

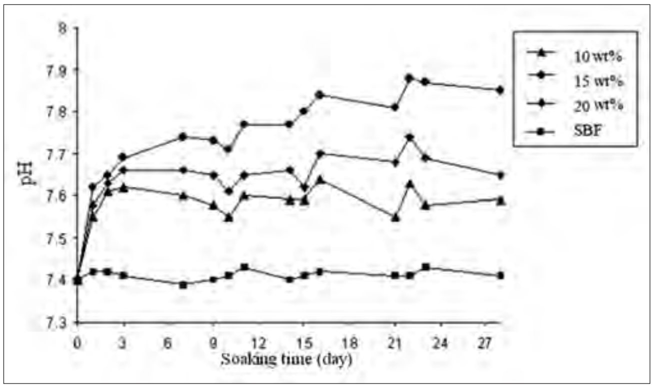

Figure 7: Changes of pH of the SBF solution after soaking the Co-base alloy/FA composites for various times

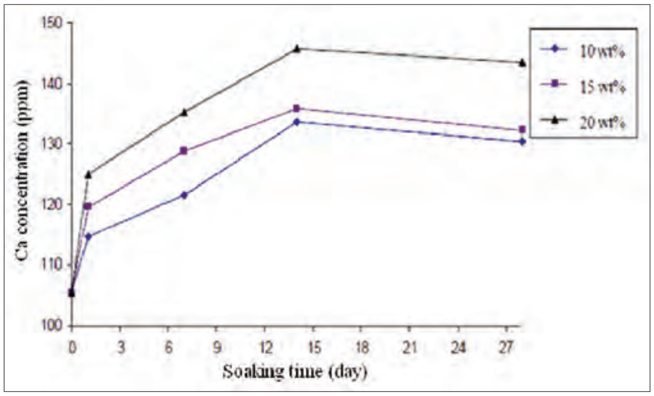

Figure 8: Changes of Ca concentrations in the SBF solution after soaking the Co-base alloy/FA composites for various times

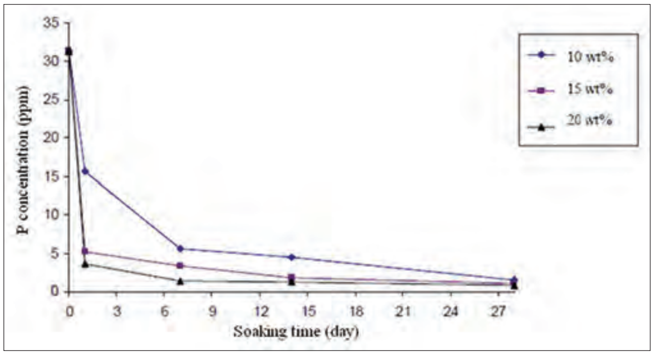

Figure 9: Changes of P concentrations in the SBF solution after soaking the Co-base alloy/FA composites for various times

between Ca^{2+} of the nanocomposites and H^+ of the SBF solution, pH was increased. After consuming Ca^{2+} and OH^- ions for formation of HCA on the surface, change of the pH in SBF solution was uniformed.

Metallic dental materials and biomaterials are classified as bioinert materials since they do not bond with the bone material under clinical conditions. Changing the bioinert property of metallic dental materials and biomaterials into bioactivity character may increase the interfacial bond between living cells and restoration and implant dental materials in order to increase the *in vivo* lifetime of metallic restoration and implant dental materials. It seems that the novel cobalt base alloy/FA nanocomposite with different amounts of FA nanopowder might be a good candidate for the mentioned purpose.

CONCLUSION

Novel cobalt base alloy/FA nanocomposite (CoA/FaNC) with different amounts of FA nanopowder (10, 15, 20% wt) was fabricated via ball milling the starting powders and, then cold pressing and sintering process. Bioactivity evaluation of prepared nanocomposites showed that nucleus of apatite was formed on the surface of specimens after 1, 14, 28 days immersion in SBF. It was concluded that bioinert dental Co-Cr-Mo alloy could be successfully converted to a Co-Cr-Mo bioactive type by adding 10, 15, 20 wt% FA nanopowder.

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