ORIGINAL ARTICLE

Preparation and Characterization of Natural Rice Husk-Derived Silica and Eggshell-Derived Calcium Carbonate Composite as a Coating Material

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ABSTRACT

The world is facing from two emerging problems being scarcity of virgin resources and the excess waste production. Utilization of the excess waste in the main stream production can resolve these problems. The production sector are focusing on utilization of the waste in their products.

Aim: To prepare a natural composite $CaO-SiO_2$ based bioactive material derived from naturally sustained raw materials. $CaO-SiO_2$ based ceramics have been regarded as potential candidates for artificial bone due to their excellent bioactivity and biocompatibility.

Methods: Avian eggshell-derived calcium carbonate and rice husk-derived silica were extracted from natural resources to synthesize the composite material. The synthesized material was characterized using X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR) and particle size analyzer. XRD, XRF and FTIR.

Results: The results revealed that the synthesized powder contained calcium carbonate and silica and further confirmed their mixed formulation as a composite material. The average particle size of silica and calcium carbonate was 500 and 300 nm respectively.

Conclusion: The composite coating material prepared from natural resource waste is suitable to be used as a coating material for ceramic dental implant with promising biological and mechanical properties.

Keywords: Rice husk, Silica, Eggshell, Calcium carbonate, $CaO-SiO_2$-based ceramics.

INTRODUCTION

Attention has been growing towards discovering materials that are sustainable and bioactive which can increase the bone apposition to enhance the osseointegration of bioinert implant substrate[1]. The ceramic biomaterials are used to replace lost tissue or organic structure and function[1,2]. The $CaO-SiO_2$ based ceramics have been regarded as a potential alternate for artificial bone due to their excellent bone bioactivity and biocompatibility.[2] Use of waste or by-products from different industries and the agricultural sector has received increasing attention in the scientific, technology, ecological, and economic spheres in recent years [3]. Rice husk **(**RH) has a high silica content in the amorphous form. The applications of RH in different fields and the uses of RH silica to synthesize some advanced non-oxide ceramics, silicon, and nano SiO_2, has been widely studied[4,5,6]. Rice husk (RH) is a by-product of rice milling and rice husk ash (RHA). RHA contains huge quantity (85–95%) of amorphous silica[6].

Eggshells are rich in calcium carbonate ($CaCO_3$) or limestone. Studies concluded that 96−97% of the eggshell comprises of calcium carbonate with 3−4% organic matter [7,8]. The porous glass-ceramic implants were produced from eggshell-based calcium-silicate glasses provide an abundance of pores for ingrowth of fibrovascular tissue in order to fasten the implants to tissues and provides an adequate blood supply within the implants [9]. Clinical observations revealed no adverse reaction related to the prepared eggshell hydroxyapatite implant at the site of operation such as foreign body reaction or immune rejection [10]. The properties of RHA depend on the ecological circumstances of its origin[11].

In the present study, biological silica was extracted from Iraqi rice husk and calcium carbonate was obtained from eggshells. This study aims to formulate and characterize a novel natural composite based implant-coating material derived from biological excess waste.

MATERIALS AND METHODS

Preparation of biological silica: Following the milling process, the rice husk was filtered by using stainless steel mesh (500 µm pore size). Rice husk was thoroughly washed with deionized water using mechanical stirring for 1 hour and then dried at 70°C using a dry heat oven. The rice husk were then treated with 1 M hydrochloric acid as a leaching agent for 2 hours at 90°C to minimize metallic contamination followed by rinsing with deionized water to achieve neutral pH. The mixture was then placed in a kiln at 700°C for 2 hours for the calcination process as seen in Figure 1(A). After the calcination, around 1000 mg of rice husk ash was placed in a glass beaker containing 20 ml of 1.5 M sodium hydroxide at 90°C for 1 hour Figure 1(B), producing sodium silicate solution[12].

Resultant sodium silicate was then in dissolved (250) mL of pure ethanol, followed by dilution with (1000) mL water for 10 minutes. The solution was gently titrated with 3

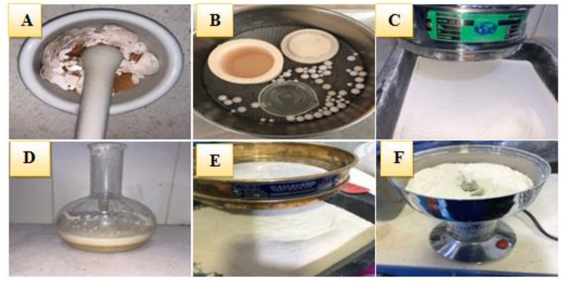
M orthophosphoric acid till yellowish gel formation at neutralized pH Figure 1(C). The gel was then washed with warm distilled water to remove any remnants of sodium phosphate or sodium silicate followed by centrifugation for (15) minutes at (4000 r/min.) speed. The gel was then dried at 90°C for (2) hr followed by calcination in a furnace at 550°C for 30 minutes Figure 1(D) to produce silica powder Figure 1(E)[4].

Figure 1: (A) Preparation of rice husk ash; (B) Rice husk ash in NaOH; (C) Titration with H_3PO_4; (D) Calcination furnace; (E) Resultant silica

Preparation of eggshell-derived $CaCO_3$ powder: Avian eggs (hen origin) were acquired from local poultry market. Fresh eggshells with intact internal membranes were initially crushed by hand in a mortar and pestle to a convenient volume (Figure 2(A)). 100 grams of coarse powder of eggshell was filtered by sieve No. 35. The filtered powder was then milled using ball milling machine with water (Figure 2(B)) resulting slurry mixture. The solution was then dried at 105 °C for 24 hours to achieve fine powder. The powder was again filtered using No. 35 sieve Figure 2(C). 10 grams of the powder was then soaked of 50% concentrated sodium hypochlorite (bleaching agent) for 10 minutes Figure 2(D). The powder was then rinsed with water for 5 times to eliminate any bleach deposits. The powder was dried in hot oven at 105 °C for 24 hours. The powder was further ground using electrical grinding machine and then filtered using No. 230 sieve to achieve $CaCO_3$ according to ASTM [13] (Figure 2(E)).

After the characterization of the silica and calcium carbonate, the two powders were mixed with a mechanical stirrer at an ambient temperature according to the intended ratios Figure 2(F) (70% $CaCO_3$ with 30% SiO_2). The resultant mixture was investigated by powder X-ray diffraction (XRD), X-ray fluorescence (XRF) and Fourier-transform infrared spectroscopy (FTIR) in order to determine the composition and concentration of elements.

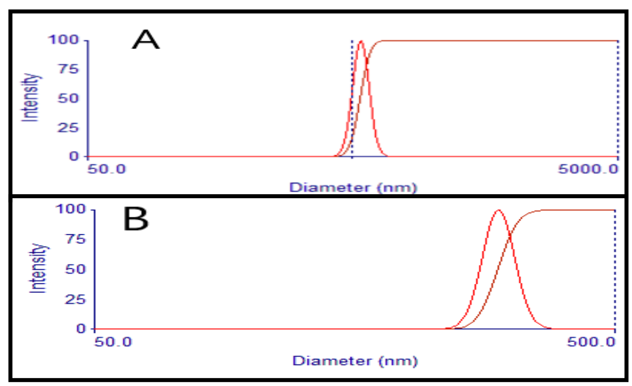
Figure 2: (A) Eggshell crushing; (B) Ball milling machine; (C) Sieve No. 35; (D) 50% Sodium hypochlorite; (E) Sieve No. 230; (F) Mechanical mixer

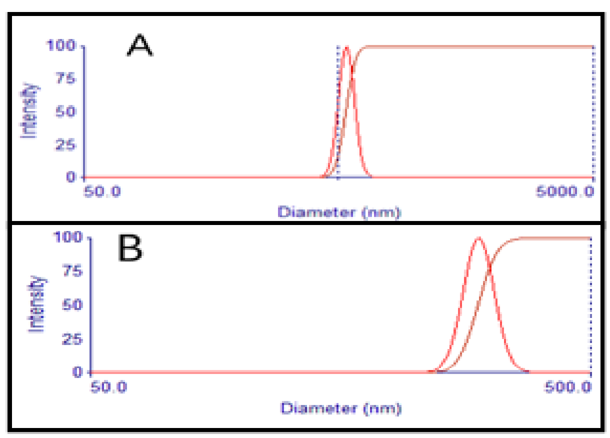


RESULTS AND DISCUSSION

Particle size analyzing method: The particle sizes of the prepared silica and calcium carbonate powders were investigated via laser particle size analyzer. The particle size of the RH-derived silica ranged between (480.4 – 606.1) nm with mean particle diameter of 541 nm as shown in Figure 3(A). While Figure 3(B) presented the eggshell derived $CaCO_3$ powder had a particle size between (266.4 - 336) nm and a mean particle diameter of 299.9 nm. The test was conducted in the Technology University, Center of Nanotechnology and Advances Researches.

Figure 3: Size distribution (A) Rh-silica; (B) Eggshell-Calcium Carbonate



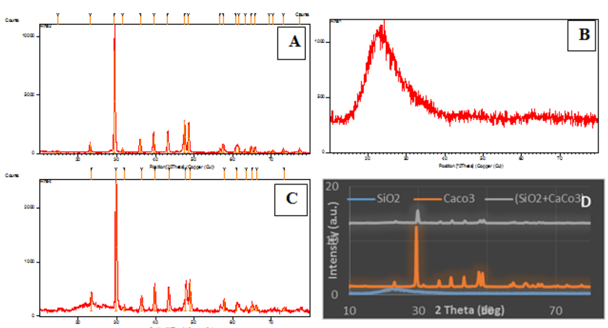


X-ray diffraction XRD: X-ray diffraction (XRD) was applied to detect the existing phases in the extracted (RH- derived and the eggshell-derived) powders and to determine the structural changes in the crystalline and amorphous phases of the composite. Samples were scanned with Cu Kα X-ray source in the 2θ range from 10° to 80° with 0.04° step size and a 5-s step interval [14]. Furthermore, the phases are recognized by means of matching the attained pattern with standard pattern. The XRD analysis of the extracted powders was performed at PAN analytical laboratories, Tehran, Iran. The data acquired from the XRD pattern in Figure 4(A) reveal the crystalline nature and phase composition of the naturally prepared eggshell-derived calcium carbonate powder.

The X-ray diffraction pattern of the synthesised calcium carbonate demonstrates sharp and well-defined peaks at 2θ values of 23.2º, 24.9º, 36.1º, 39.6º, 43.2º, 47.6º and 48.6º. However, peaks are also perceived at 2θ values of 31.6º, 57.8º, 61.5º, 65.4º and 73.3º. The sharp peaks of the diffractogram is a charecterestic feature of a high crystallinity of the prepared powder[15]. The results in Figure 4(B) shows the monocrystalline nature of SiO_2 which matches with the reference No. (01-076-0941). An amorphous peak was recorded at 23º which is in agreement with a study conducted by Martinez and colleagues in 2006[16], who prepared amorphous SiO_2 by the sol-gel procedure.

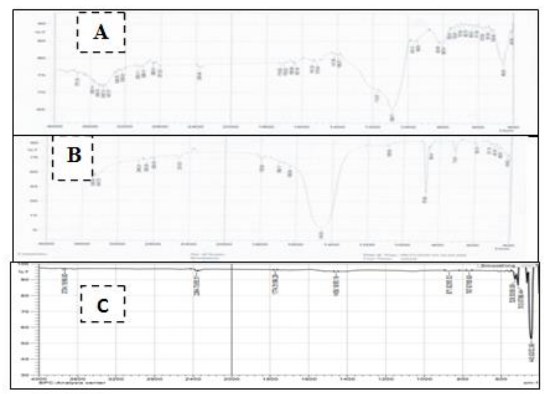
The single broad XRD reflection peak indicating the small size and of the particles of the prepared powder. The lack of impurity peak representative for the purity of the silica particles[17]. Figure 4(C&D) revealed the diffractograms of the three powders; silica, calcium carbonate and composite (mixed extracted powders). The diffractogram of the composite material exhibits compromized spectra between the silica and calcium carbonate powders[18].

Figure 4. XRD of (A) Eggshell-derived powder; (B) RH-derived powder; (C) The composite material;: (D The three powder



Fourier-transform infrared spectroscopy (FTIR): The powder samples were characterized by fourier-transform infrared (FTIR) analysis (Shimadzu prestige 21). Figure 5(A) shows FTIR spectra of the RH-derived silica. The band around ~ 806 cm^{-1} corresponds to Si-O bending vibration[16]. While the band nearby 1089 cm^{-1} indicates Si-O-Si asymmetric stretching vibration when the linking oxygen atom moves corresponding to the Si-Si lines directed contrary to their Si neighbor lines [19]. While, Figure 5(B) displays the FTIR spectra of the particles. The spectral statistics achieved for the eggshell-derived calcium carbonate samples exhibit a broad absorption peak of CO_3 ions at ~713 cm^{-1}, ~854 cm^{-1}, ~1084 cm^{-1}, ~1458 cm^{-1}, and~1795 cm^{-1} which have been stated to be the shared representative features and the essential styles of vibration of the carbonate ions present in calcium carbonate [15,19]. The composite powder spectrometer presented in Figure 5(C), demonstrated emergence of new spectra differentiated from the two original components; $CaCO_3$ and SiO_2.

Figure 5: FTIR analysis of the (A) Rice husk-derived silica; (B) Eggshell-derived calcium carbonate and (C) the composite $CaCO_3/SiO_2$



X-ray fluorescence analysis: The X-ray fluorescence (XRF) data was analyzed for calibration and verification of the element composition of the extracted powders; eggshell-derived and RH-derived as well as the composite of both powders[20]. Table 1 demonstrates the results of the chemical characterization of the rice husk-derived samples using XRF analysis. Results indicated that SiO_2 represent 99.4% of the assessed powder in addition to trace amounts of CaO and ferric ions[21]. On the other hand, the chemical composition of the eggshell-derived powder exhibits that calcium oxide (CaO) was the most profuse component. The great quantity of CaO is referred to the presence of $CaCO_3$, which is the main component of a hen eggshell[22]. While the chemical composition of the composite powder usually revealed that 70.2% of CaO derived from $CaCO_3$ with 28.7% of SiO_2.

Table 1: Elemental analysis of the Rh-derived, eggshell- derived and composite powders

Prepared powder	**Elements concentration (wt.%)**							
	SiO_2	**CaO**	**MgO**	**P_2O_5**	**S**	**K**	**Fe**	**Na**
Rh-derived	99.4	0.59	-	-	Trace	-	Trace	-
Eggshell- derived	-	98.2	1.33	0.45	Trace	Trace	Trace	Trace
Composite	28.7	70.2	1.0	Trace	Trace	-	-	Trace

CONCLUSIONS

Nowadays the development of novel composites derived from byproduct and biological waste has gained immense interest. Within the current study limitations, the biological SiO_2 microparticles were successfully prepared from sticky RHA through a simple acid pretreatment method, the absence of sharp peaks in the XRD pattern confirmed the amorphous nature of the material. $CaCO_3$ was successfully synthesized from avian eggshell via simple processes. The chemical, physical and morphological characterization using particle size analyzer, FTIR, XRD and XRF indicated that the formulated composite of silica and $CaCO_3$ can be used as coating material for ceramic implants with promising biological and mechanical properties.

Conflict of interest: The authors have no conflicts of interests relevant to this article.

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