Waste Management xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Conversion of biowastes to biomaterial: An innovative waste management approach

M. Bobby Kannan *, Karly Ronan

Discipline of Chemical Engineering, College of Science and Engineering, James Cook University, Townsville, Queensland 4811, Australia

ARTICLE INFO

Article history:
Received 31 January 2017
Revised 20 April 2017
Accepted 29 May 2017
Available online xxxx

Keywords:
Eggshell
Urine
Hydroxyapatite
Calcium phosphate
Biomaterial

ABSTRACT

The study suggests that biowastes (eggshells and urine) can be potentially used as precursors to produce hydroxyapatite (HAp) biomaterial in a simple chemical process. A batch reactor was used in this work to produce HAp powder from eggshells and synthetic urine (SU). Fine powder of calcined eggshells was dissolved in water to produce aqueous calcium hydroxide. The solution was then mixed with concentrated SU in stoichiometric amounts corresponding to HAp (Ca/P molar ratio ~ 1.67). The initial pH of the solution was alkaline (pH ~ 8.5) and particles formed rapidly with slight mixing. Stirring the turbid solution for a longer period (72 h) did not show any visual change, but the particle size decreased slightly. When the pH of the solution was adjusted to 5, the solution was initially clear, but particle formation was apparent after 48 h stirring. It was noticed that at a slow stirring speed (100 rpm), film formation occurred on the solution, whereas at a higher stirring speed (500 rpm) no such film formation was observed. X-ray diffraction (XRD) analysis confirmed that the particles (formed at 500 rpm) were an amorphous calcium phosphate (CaP). Alkaline treatment at 80 °C for 2 h converted the amorphous CaP into HAp. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of the particles (formed at 500 rpm) suggested that they are calcium-deficient HAp (Ca/P molar ratio 1.58).

1. Introduction

Waste production is a perpetuating problem; its management has been a high priority for many countries across the globe. Repurposing waste materials into valuable products will not only improve sustainable development, but promote effective waste management. In recent years, a significant amount of research work has been done to convert waste materials into valuable products, e.g., fertilizer like struvite synthesised from urine and biodiesel produced from waste cooking oil (Latifian et al., 2014; Tilley et al., 2008; Tangy et al., 2017; Hong et al., 2016). Strategies for producing sustainable materials and manufacturing process for various applications are vital for sustainable development.

Biomaterials are an essential element of regenerative medicine and have a vast range of applications in the biomedical industry. Their commercial demand is ever increasing as a result of an aging and expanding population (Habraken et al., 2016). Promoting the sustainable development of such materials is important in order to ensure that these materials can be made affordable and accessible by all patients in an environmentally considerate manner. In biomedical applications, e.g., orthopaedic and dental implants, hydroxyapatite (HAp) has become an integral biomaterial of reference (Habraken et al., 2016; Dorozhkin, 2009; Al-Sanabani et al., 2013). The calcium phosphate-based ceramic material is the primary constituent of many biological calcifications e.g., bone, teeth and enamel (Dorozhkin, 2009; Amjad, 1998; Asri et al., 2016; Kannan and Orr, 2011). For synthesising HAp, common chemicals such as calcium nitrate ($Ca(NO_3)_2$) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) have been generally used as sources of calcium and phosphate, respectively (Kuo and Yen, 2002; Savino and Yates, 2015; Kannan and Wallipa, 2013; Kesteven et al., 2015; Alabbasi et al., 2014). Producing HAp entirely from waste materials containing calcium and phosphate will enhance its environmental sustainability.

Eggshell waste is ~94% calcium carbonate ($CaCO_3$), and thus presents an attractive sustainable alternative as a calcium source for producing HAp (Stadelman, 2000). In 2014, over 7.7 million tons of eggshell waste was generated around the world (Rivera-Muñoz, 2011; WATT Global Media, 2015). Some previous research work has demonstrated the use of eggshell waste as a source of calcium for HAp synthesis, however, chemicals such orthophosphoric acid and diammonium phosphates were used for phosphate source. Urine is a ubiquitous biowaste that contains phosphorous, highlighting its potential to serve as a source of phosphate for pro-

* Corresponding author.
E-mail address: bobby.mathan@jcu.edu.au (M.B. Kannan).

http://dx.doi.org/10.1016/j.wasman.2017.05.045
0956-053X/

Table 1
Composition of synthetic urine (Chutipongtanate and Thongboonkerd, 2010).

Chemicals	g/L
Urea	12.012
Creatinine	0.452
Tri-sodium citrate dihydrate	1.470
Sodium chloride	3.155
Potassium chloride	2.236
Ammonium chloride	0.802
Calcium chloride dihydrate	0.441
Magnesium sulphate	0.492
Sodium bicarbonate	0.168
Sodium oxalate	0.0134
Sodium sulphate	1.278
Sodium di-hydrogen phosphate Dihydrate	0.561
Di-sodium hydrogen phosphate	0.056

ducing HAp. Integrating eggshells and urine into the process of producing HAp will not only significantly enhance the sustainability and affordability of the product, but also reduce biowaste accumulation.

In this study, an attempt was made to produce HAp powder entirely from biowastes in a batch reactor. Eggshell waste and synthetic urine (for simplicity) were used as the calcium and phosphate precursors for producing HAp powder. Since it has been reported in the literature that pH of the solution and stirring affect the formation of calcium phosphates in aqueous solutions (De Rooij et al., 1984; Pan et al., 2013), in this study the pH and stirring speed were altered to understand the particle formation process. Characterisation techniques were used to identify the chemical nature and composition of the produced powder.

2. Materials and methods

Eggshell waste and synthetic urine (SU) were used as the calcium and phosphate precursors, respectively, for producing HAp powder. Firstly, the inner membranes of the eggshells were removed, followed by scrubbing and cleaning the eggshells with distilled water, and then with methanol. In order to eliminate the odour and volatile contaminants, the eggshells were dried in an oven (Model: LABEC, ODWF14) for 24 h at 100 °C. A mortar and pestle was used to crush the dried eggshells into a fine powder. The crushed eggshell powder was then heat-treated in a furnace (Model: Carbolite Furnaces, ELF 10/14) at 450 °C (with a heating rate of 5 °C/min) for 2 h to remove any organic phases and pathogens. To obtain calcium oxide (CaO), the furnace temperature was increased to 900 °C (with a heating rate of 1 °C/min) and maintained for 3 h. The CaO powder was dissolved in distilled water to produce a saturated aqueous solution of calcium hydroxide ($Ca(OH)_2$). The phosphate precursor solution was prepared by concentrating (three times) the normal composition of SU shown in Table 1 (Chutipongtanate and Thongboonkerd, 2010).

The calcium and phosphate precursor solutions were mixed in stoichiometric amounts that correspond to HAp (i.e., Ca/P = 1.67). The mixed one litre solution contains ~0.6 g of CaO (equivalent to ~1.2 g of crushed eggshell powder) and 3 times the concentration of the SU. A schematic of the experimental setup is shown in Fig. 1. To maintain the solution temperature at 25 °C, the reactor was placed in a water bath. The solution was stirred continuously at two different stirring speeds, i.e., 100 rpm and 500 rpm, using a magnetic stirrer (Model: Heidolph Instruments, MR Hei-Tec) for a set period of 72 h. The initial pH of the solution was 8.5, and the pH was recorded every 24 h. In another set of experiments, the pH of the mixed solution was adjusted to 5 using 1 M hydrochloric acid and then stirred continuously. After 72 h, the particles were separated by centrifuging and then washed with distilled water and centrifuged again. The particles were then subjected to an alkaline treatment in 1 M NaOH at 80 °C for 2 h. After centrifuging the post-treated particles, they were dried in an oven at 80 °C for 1 h. The crystals, before and after alkaline treatment, were analysed using X-ray diffraction technique (XRD) (Model: Bruker, D2 Phaser, 2nd Gen). The elemental composition of the particles, after alkaline-treatment, was determined using an inductively coupled plasma mass spectrometer (ICP-MS) (Model: Varian 820-MS). The particles were dissolved in an acid for ICP analysis. The particle size analysis was carried out using a particle size analyser (Model: Malvern Mastersizer 3000 with Hydro EV). The morphology of the particles was analysed using a scanning electron microscope (SEM) (Model: Jeol, JSM 5410).

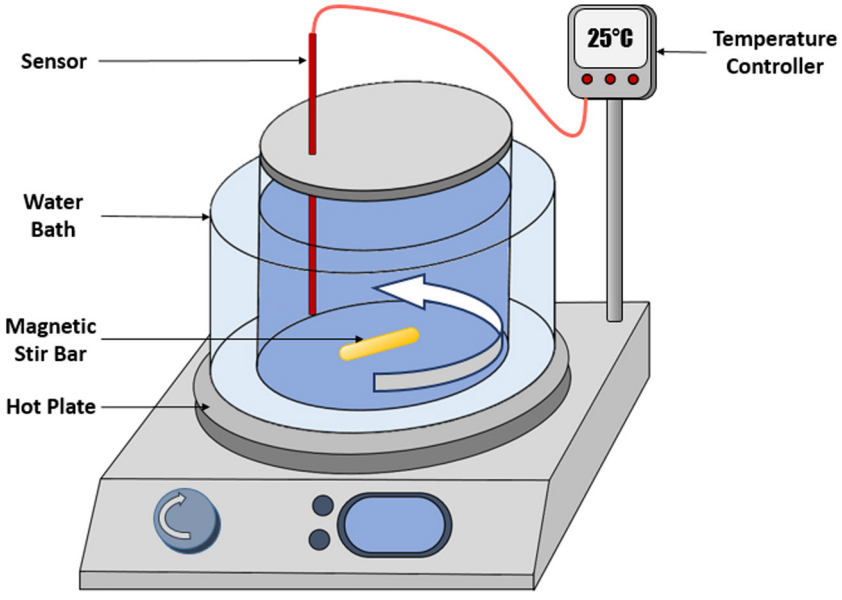

Fig. 1. A schematic diagram of the experimental setup.

Please cite this article in press as: Kannan, M.B., Ronan, K. Conversion of biowastes to biomaterial: An innovative waste management approach. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.05.045