RESEARCH PAPER

Binder-Free Direct Ink Writing Of Bovine-Bone Derived B-Type Carbonate Apatite Monoliths: A Preliminary Platform for Local Drug Delivery

JL Acevedo-Dávila[1], JD Flores-Valdez[2], MA Ávila-López[3], CM López-Badillo[4], M. Rodríguez-Reyes[5] and D. Vázquez-Obregón[6]

[1]Tecnológico Nacional de México
[2]Universidad Autónoma de Coahuila
[3]Centro de Investigación en Materiales Avanzados (CIMAV) / Tecnológico de Monterrey
[4]Universidad Autónoma de Coahuila
[5,6]Tecnológico Nacional de México
[1]Email: jorge.ad@saltillo.tecnm.mx, [2]Email: juanita.flores.valdez@hotmail.com, [3]Email: avila.manuel@tec.mx, [4]Email: clopezb@uadec.edu.mx, [5]Email: mario.rr@saltillo.tecnm.mx and [6]Email: dagoberto.vo@saltillo.tecnm.mx
[1]ORCID: 0000-0002-2439-2649, [2]ORCID: 0000-0002-7068-7480, [3]ORCID: 0000-0002-7496-7359, [4]ORCID: 0000-0001-6892-1541, [5]ORCID: 0009-0009-5977-3116 and [6]ORCID: 0009-0007-4830-3763

Received: 16th Dec, 2025; Revised: 8th Feb 2026; Accepted: 12th Feb, 2026; Available Online: 28th Feb, 2026

ABSTRACT
Additive manufacturing of calcium phosphate scaffolds has attracted growing attention for bone repair and localized drug delivery. Here we report the feasibility of printing monolithic structures by direct ink writing (DIW) using carbonate apatite powders obtained from bovine bone waste. Bone-derived powders were produced by thermal treatment at 850 °C, milled below 149 µm, and characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR-ATR), scanning electron microscopy (SEM), and particle size distribution (PSD). To obtain printable inks without polymeric binders, water:glycol ratios were explored and a low fraction of silica nanoparticles was incorporated as a shape-fidelity modifier. XRD and FTIR confirmed the formation of B-type carbonate apatite, while SEM revealed aggregates of acicular nanoscale particles (~100 nm). Stable DIW deposition was achieved mainly for the 70:30 (water:glycol) formulation containing 1 wt% silica nanoparticles, using 0.41–0.51 mm nozzles. These preliminary monoliths provide a sustainable platform that can be further optimized and functionalized for post-printing drug loading aimed at local therapy.
Keywords: *bovine bone waste; carbonate apatite; direct ink writing; 3D-printed monolith; silica nanoparticles; local drug delivery*
How to cite this article: Acevedo-Dávila JL, Flores-Valdez JD, Ávila-López MA, López-Badillo CM, Rodríguez-Reyes M, Vázquez-Obregón D, Binder-Free Direct Ink Writing of Bovine-Bone Derived B-Type Carbonate Apatite Monoliths: A Preliminary Platform for Local Drug Delivery. Int J Drug Deliv Technol. 2026;16(5s): 78-82. DOI: 10.25258/ijddt.16.5s.11
Source of support: Nil.
Conflict of interest: None

1. INTRODUCTION

Calcium phosphate bioceramics remain a cornerstone in bone substitute research due to their chemical affinity with mineralized tissues and their ability to support osteoconduction. In particular, carbonate-substituted apatites more closely resemble biological apatite and can exhibit enhanced biological response and resorbability compared with stoichiometric hydroxyapatite.[1,2,4,5] In parallel, porous calcium phosphate structures are increasingly explored as local drug delivery devices, where surface chemistry and architecture can be leveraged to adsorb and release antibiotics or other therapeutics.[16,17] Direct ink writing (DIW) offers a practical route to fabricate lattice-type monoliths with controlled macroporosity while preserving the ceramic nature of the material.[9,10,11]

From a circular-economy perspective, bovine bone waste is an abundant and inexpensive precursor for apatite-based powders, which can be obtained through cleaning, calcination, and milling.[2,14] However, printing binder-free ceramic inks from biogenic powders remains challenging because agglomeration, limited yield stress, and nozzle clogging can compromise filament continuity and shape retention.[12,13] This short communication outlines a preliminary workflow to obtain DIW monoliths from bovine-bone derived B-type carbonate apatite using minimal additives, and discusses their relevance as future drug delivery platforms.

**Author for Correspondence: jorge.ad@saltillo.tecnm.mx*

2. MATERIALS AND METHODS

2.1. Bovine bone-derived carbonate apatite powder. Raw bovine bone waste was cleaned and boiled in distilled water (~2 h) to remove residual organic matter, dried, and thermally treated at 850 °C for 4 h in an oxidizing atmosphere (heating rate 10 °C/min). After furnace cooling, the material was milled and sieved below mesh 100 (149 µm).

2.2. Physicochemical characterization. XRD was performed using a Malvern-PANalytical Empyrean diffractometer (Cu Kα, λ = 1.541874 Å, 45 kV, 40 mA; step 0.02°, 50 s/step). FTIR spectra were collected by ATR in the 4000–500 cm−1 range. PSD was measured by dynamic light scattering after dispersing 10 mg powder in 2 mL ethanol and ultrasonication (~3 min) (Nanotrac Flex, Microtrac MRB; refractive index 1.63; three runs of 90 s). SEM images were obtained using a Tescan Mira 3 microscope (12 kV, working distance ~12 mm).

2.3. Ink formulation and DIW printing. Printable pastes were formulated by mixing carbonate apatite powder with water:glycol mixtures at 100:0, 80:20, and 70:30 ratios. To enhance shape fidelity, 1 wt% silica nanoparticles was added to selected formulations. Monoliths were deposited through nozzles with inner diameters of 0.41 and 0.51 mm using a DIW/robocasting setup, following a layer-by-layer toolpath to generate lattice geometries.

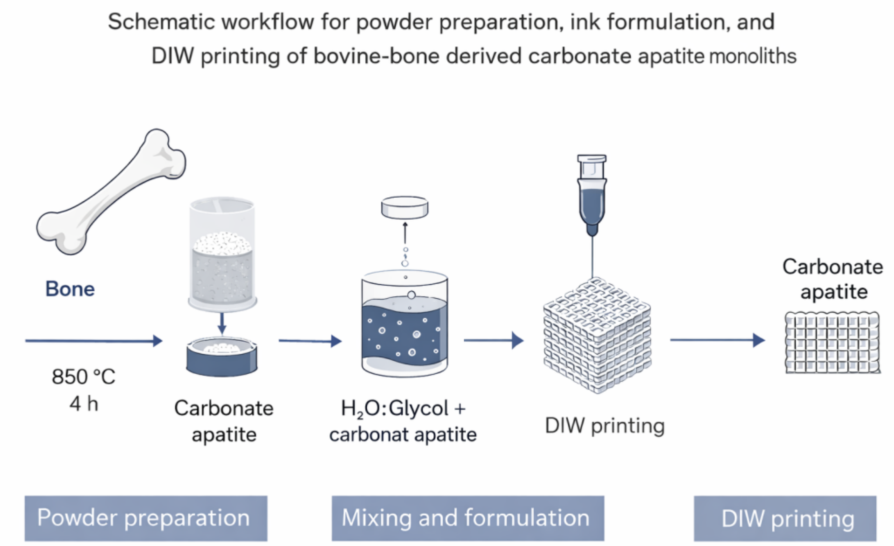


Figure 1. Schematic workflow for powder preparation, ink formulation, and DIW printing of bovine-bone derived carbonate apatite monoliths.

3. RESULTS AND DISCUSSION

3.1. Phase and functional group identification. XRD patterns of the calcined powder exhibited reflections characteristic of carbonate apatite, with prominent peaks around 2θ ≈ 31–33° that are typically assigned to apatite planes (e.g., 211, 112, and 300).[5,6] FTIR-ATR corroborated the apatite framework through phosphate bands near 1021 cm−1 (v3) and 958 cm−1 (v1), and carbonate bands at ~874 cm−1 (v2) and 1450–1418 cm−1 (v3), consistent with B-type substitution (CO3−2 replacing PO4−3).[4,5,6]

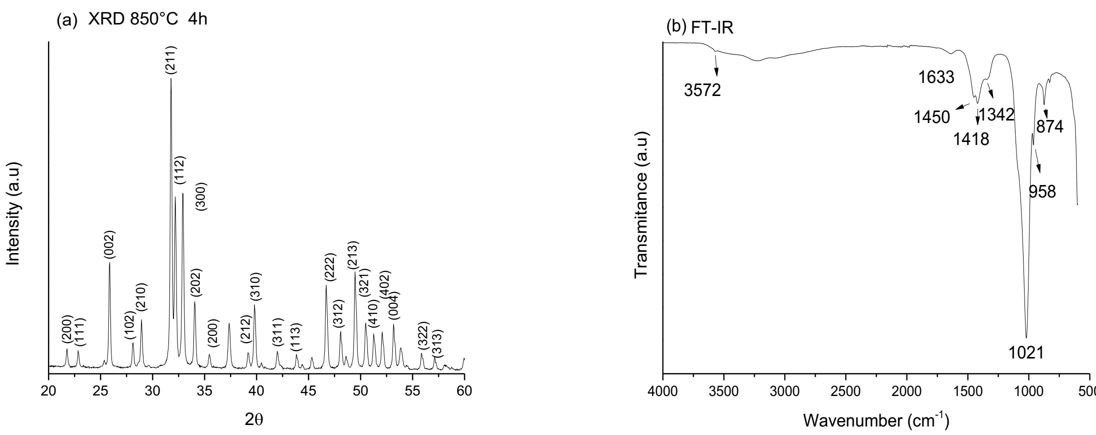


Figure 2. Representative (a) XRD pattern of bovine-bone derived carbonate apatite after calcination at 850 °C and (b) FTIR-ATR spectrum highlighting phosphate and carbonate bands consistent with B-type substitution.

3.2. Powder Morphology and Particle Size. SEM revealed aggregated particles with predominantly acicular morphologies. Although the powder was sieved below 149 µm, the primary features were nanoscale, with an estimated average dimension near 100 nm and a distribution extending to ~200 nm, which is compatible with bone-derived apatite powders.[7,14] Such fine features can increase surface area (beneficial for drug adsorption), but also promote agglomeration that may hinder extrusion and cause discontinuous filaments in DIW.[12,13]

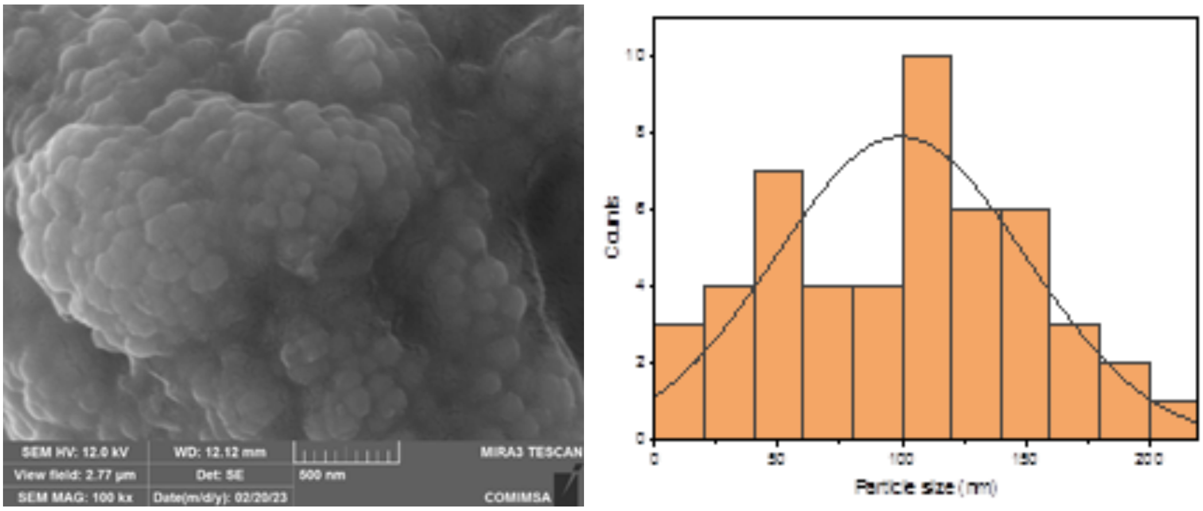
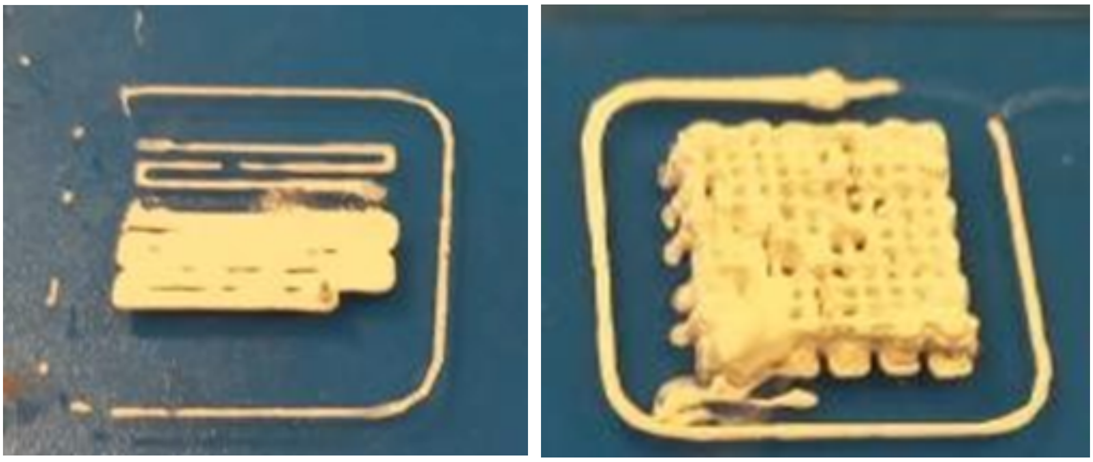


Figure 3. SEM micrograph and particle size distribution of the calcined bovine-bone derived powder showing aggregated acicular nanoparticles.

3.3. Printability window for binder-free monoliths. Trials using water-rich pastes showed limited printability and poor shape fidelity, likely due to insufficient yield stress and post-deposition relaxation. Increasing glycol content improved filament cohesion up to an optimum window; however, excessive glycol led to inks that were too viscous to extrude. The addition of 1 wt% silica nanoparticles to the 70:30 (water:glycol) composition improved printing consistency, producing the most stable monoliths without polymeric binders. Nozzle selection was also critical: 0.41–0.51 mm diameters minimized clogging and allowed continuous extrusion of the particle-rich paste.[12,13]



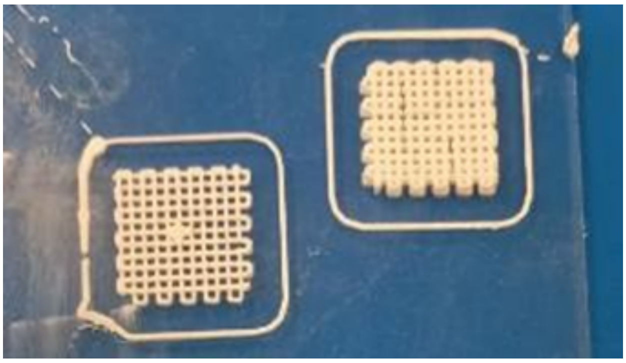


Figure 4. Photographs of DIW-printed monoliths obtained with different solvent ratios and nozzle diameters, highlighting the improvement achieved with the 70:30 (water:glycol) + 1 wt% SiO2 formulation.

From a drug delivery perspective, carbonate apatite monoliths are attractive because carbonate substitution can increase solubility and facilitate ion exchange under physiological conditions, potentially enabling sustained release and enhanced osteointegration.[4,6,16] Moreover, the interconnected macroporosity enabled by DIW can support capillary uptake of drug solutions and provide diffusion pathways for release.[10,11,16] Future work should quantify rheological parameters (yield stress, shear-thinning behavior, and recovery), dimensional changes after drying/sintering, and drug loading/release profiles using representative therapeutics (e.g., gentamicin) for infection control.[12,16,17]

4. CONCLUSION

This short communication demonstrates a preliminary route to fabricate DIW monolithic scaffolds from bovine-bone derived B-type carbonate apatite using minimal additives and no polymeric binders. The 70:30 (water:glycol) ink containing 1 wt% silica nanoparticles provided the most consistent printing performance when extruded through 0.41–0.51 mm nozzles. Given the bio-relevance of carbonate apatite and the architectural control offered by DIW, the resulting monoliths represent a promising low-cost platform for subsequent optimization and post-printing drug functionalization aimed at localized therapy.

ACKNOWLEDGMENTS

The authors acknowledge the support of their respective institutions and the laboratory facilities used for powder preparation, characterization, and additive manufacturing trials.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES (VANCOUVER STYLE)

1. Bermúdez García VS, Huaman Mujica K, Castañeda-Vía JA, Landauro CV, Quispe J, Tay Chu Jon LY. Obtención de hidroxiapatita a través de residuos biológicos para injertos óseos dentales. Rev Estomatol Herediana. 2021;31(2):111-116. doi:10.20453/reh.v31i2.3971.
2. Zhao R, Yang R, Cooper PR, Khurshid Z, Shavandi A, Ratnayake J. Bone grafts and substitutes in dentistry: a review of current trends and developments. Molecules. 2021;26(10):3007. doi:10.3390/molecules26103007.
3. Mainard D. Sustitutos óseos. EMC - Aparato Locomotor. 2014;47(2):1-11. doi:10.1016/S1286-935X(14)67558-4.
4. Barralet JE, Best SM, Bonfield W. Carbonate substitution in precipitated hydroxyapatite: an investigation into the effects of reaction temperature and bicarbonate ion concentration. J Biomed Mater Res. 1998;41(1):79-86. doi:10.1002/(SICI)1097-4636(199807)41:1<79::AID-JBM10>3.0.CO;2-C.
5. Fleet ME, Liu X, King PL. Accommodation of the carbonate ion in apatite: an FTIR and X-ray structure study of crystals synthesized at 2-4 GPa. Am Mineral. 2004;89(10):1422-1432. doi:10.2138/am-2004-1009.
6. Fleet ME, Liu X. Coupled substitution of type A and B carbonate in sodium-bearing apatite. Biomaterials. 2007;28(6):916-926. doi:10.1016/j.biomaterials.2006.11.003.
7. Dorozhkin SV. Calcium orthophosphates in nature, biology and medicine. Materials. 2009;2(2):399-498. doi:10.3390/ma2020399.
8. Bose S, Vahabzadeh S, Bandyopadhyay A. Bone tissue engineering using 3D printing. Mater Today. 2013;16(12):496-504. doi:10.1016/j.mattod.2013.11.017.
9. Smay JE, Cesarano J, Lewis JA. Colloidal inks for directed assembly of 3-D periodic structures. Langmuir. 2002;18(14):5429-5437. doi:10.1021/la0257135.
10. Lewis JA. Direct ink writing of three-dimensional ceramic structures. J Am Ceram Soc. 2006;89(12):3599-3609. doi:10.1111/j.1551-2916.2006.01382.x.
11. Franco J, Hunger P, Launey ME, Tomsia AP, Saiz E. Direct write assembly of calcium phosphate scaffolds using a water-based hydrogel. Acta Biomater.

2010;6(1):218-228. doi:10.1016/j.actbio.2009.06.031.

12. del-Mazo-Barbara L, Ginebra MP. Rheological characterisation of ceramic inks for 3D direct ink writing: a review. J Eur Ceram Soc. 2021;41(16):18-33. doi:10.1016/j.jeurceramsoc.2021.08.031.

13. Esslinger S, Gadow R. Additive manufacturing of bioceramic scaffolds by combination of FDM and slip casting. J Eur Ceram Soc. 2020;40(11):3707-3713. doi:10.1016/j.jeurceramsoc.2019.10.029.

14. Odusote JK, Danyuo Y, Baruwa AD, Azeez AA. Synthesis and characterization of hydroxyapatite from bovine bone for production of dental implants. J Appl Biomater Funct Mater. 2019;17:2280800019846930. doi:10.1177/2280800019846930.

15. Kolmas J, Groszyk E, Kwiatkowska-Różycka D. Substituted hydroxyapatites with antibacterial properties. Biomed Res Int. 2014;2014:178123. doi:10.1155/2014/178123.

16. Lara-Ochoa S, Ortega-Lara W, Guerrero-Beltrán CE, et al. Hydroxyapatite nanoparticles in drug delivery: physicochemical properties and applications. Pharmaceutics. 2021;13(10):1642. doi:10.3390/pharmaceutics13101642.

17. Rogers-Foy JM, Powers DL, LaBerge M. Hydroxyapatite composites designed for antibiotic drug delivery and bone reconstruction: a caprine model. J Investig Surg. 1999;12(5):263-275. doi:10.1080/089419399272386.