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Caesalpinia pulcherrima ash as a sustainable reinforcement in metallic biomaterials for biomedical applications: a review on mechanisms, compatibility, and prospects

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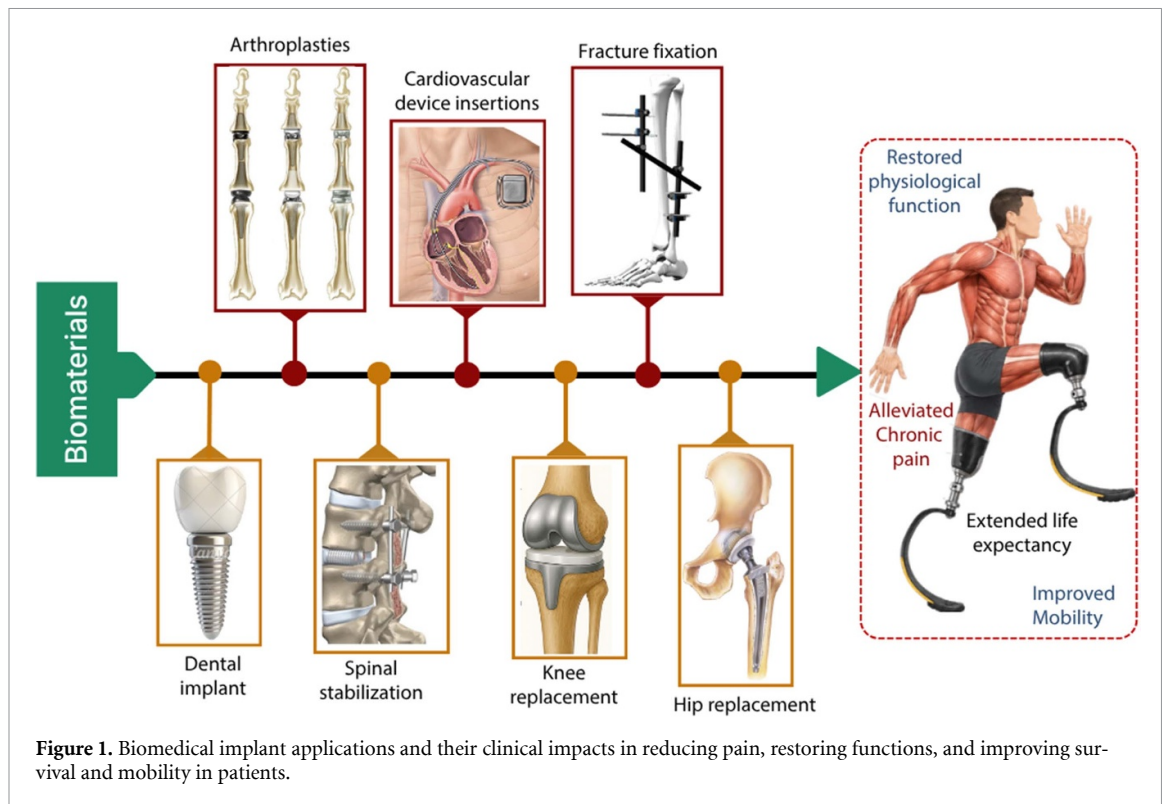
Keywords: agro-waste ash, oxide-based reinforcement, biomedical metal-matrix composites, matrix compatibility assessment, corrosion in simulated body fluid, sustainable biomaterials engineering

Abstract

Agro-waste-derived oxides are increasingly investigated as sustainable reinforcement phases in metal-matrix composites. However, their translation into biomedical metallic systems remains underexplored. *Caesalpinia pulcherrima* (Pride of Barbados) ash represents an oxide-bearing biomass derivative with a reported silica-rich composition. Yet, its suitability as a reinforcement in biomedical metal matrix composites (MMC) has not been systematically evaluated. This review assesses whether *Caesalpinia pulcherrima* ash (CPA) satisfies the chemical, mechanical, electro-chemical, and biological criteria required of reinforcements in biomedical metals (316L stainless steel, Ti-6Al-4V, Cr-Co-Mn alloys, magnesium systems). It develops a transferable reinforcement-selection framework for agro-waste residues. Available evidence indicates that CPA exhibits silica-rich oxide (91%) composition and predominantly amorphous phase characteristics consistent with oxide-based reinforcement behaviour. Comparative matrix compatibility screening indicates conditional plausibility in passive-film-forming metals such as stainless steel and titanium, whereas galvanic and electrochemical uncertainties persist for magnesium systems. However, key performance metrics, including mechanical strengthening, corrosion durability in simulated body fluids, ion-release control, and cytocompatibility, have not yet been experimentally validated for biomedical MMC applications. Accordingly, the principal translational gap lies in the absence of performance-qualified validation studies. The reinforcement-selection framework proposed in this work provides a systematic pathway for screening oxide-rich agro-waste ashes based on chemical stability, matrix compatibility, strengthening mechanisms, corrosion behaviour, and biological thresholds. Future research should prioritise interface characterisation, electrochemical durability testing, mechanical qualification, and biocompatibility assessment to advance sustainable oxide reinforcements toward biomedical deployment.

1. Introduction

The brisk advancement of biomedical implants represents one of the most transformative achievements in modern healthcare. Orthopaedic and load-bearing biomedical implants represent one of the most impactful technological interventions in modern medicine. With more than 2 million hip and knee replacement surgeries performed annually [1], joint replacement procedures are projected to exceed 5–6 million cases per year in major healthcare systems worldwide within the next two decades due to an ageing population and increased life expectancy [2]. Studies show that over 1 million joint arthroplasties are



conducted annually in the United States alone [3], while fracture fixation devices are implanted in several million trauma cases worldwide [4, 5]. Furthermore, dental implants exceed 12 million placements worldwide each year [6, 7]. These biomedical implant interventions have substantially restored mobility, alleviated chronic pain, and improved life expectancy and quality of life for both accident victims and the ageing population (figure 1). Implant survival rates commonly exceed 90% over 10–15 years in well-designed systems, evidence of a remarkable clinical success. However, complications remain significant as implant-associated infections account for about 2% of primary joint replacements and higher percentages in revision cases [8]. Likewise, wear-induced debris can trigger osteolysis and implant loosening [9]. At the same time, corrosion and ion release may provoke inflammatory or hypersensitivity reactions [10, 11], even as stress shielding due to elastic modulus mismatch often results in progressive bone resorption [12]. Revision surgeries, which are more complex and costly than primary procedures, continue to impose substantial economic and healthcare burdens. These persistent challenges explain the sustained global effort to develop advanced biomaterials that simultaneously improve corrosion stability, mechanical reliability, and biological compatibility.

Biomaterials are materials engineered to interact with biological systems for therapeutic or diagnostic purposes. They form the foundation for biomedical implant-associated technologies. Unlike conventional structural materials, biomedical materials are required to satisfy a complex and often competing set of functional requirements, including (1) possessing sufficient mechanical strength; (2) fatigue resistance to withstand cyclic physiological loading; (3) simultaneously maintaining chemical stability and corrosion resistance in aggressive body fluids rich in proteins, chloride ions, and changing pH environments; and (4) be biocompatible, i.e. perform the intended function without eliciting adverse systemic biological response. Studies have shown that, for load-bearing implants, the modulus of elasticity plays a decisive role [13]. Materials with stiffness significantly higher than that of cortical bone (typically 10–30 GPa) can divert stress away from surrounding tissue, leading to stress shielding and progressive bone degradation [14]. Biomaterial innovation, owing to its multidimensional requirements, remains an active, interdisciplinary field that requires further research to develop novel, improved material systems capable of balancing mechanical integrity, corrosion stability, and biological performance.

Sustainability in biomaterials has evolved over the past decade, as the transition toward circular manufacturing and resource-efficient material systems continues to stimulate a rapidly growing interest in renewable, bio-derived, and waste-valorised reinforcements capable of delivering functional performance, while reducing environmental impact. This is consistent with the United Nations sustainable development goals (SDGs) 3, 9, 12, and 13, which promote health, sustainable innovation, responsible resource

use, and climate action [15]. Agricultural residues and plant-derived biomass, traditionally regarded as low-value waste streams, have been reevaluated as chemically rich resources containing multi-oxide inorganic phases, silica precursors, alkaline earth elements, and functional phytochemicals [16]. Controlled calcination of biomass has been shown to yield ash streams composed of silicates, aluminates, calcium- and magnesium-based oxides [17], whose phase assemblage depends strongly on processing temperature and environment. Furthermore, research has demonstrated that plant extracts and phytochemical constituents can mediate nanoparticle synthesis [18], influence surface bioactivity [19], and contribute antibacterial functionality [20]. These developments have positioned agro-waste-derived materials not merely as environmental by-products but as emerging engineering inputs capable of modifying mechanical performance, corrosion response, and biological interaction in composite systems.

Metal matrix composites (MMCs) have emerged as a sustainable route for tailoring metallic biomaterials beyond what monolithic alloys can deliver, especially when the target is to simultaneously enhance wear resistance, mechanical reliability, and corrosion stability under physiological loading. In MMC design, particulate reinforcements are used to tune surface integrity [21], load transfer efficiency [22], and damage tolerance [23]. Recent literature increasingly shows that biomass-derived inorganic streams can serve as functional reinforcement candidates when their chemistry and phase assemblage are properly controlled. For example, biomass ash has been found to undergo strong mineral phase evolution with changing thermal history, implying that its final oxide assemblage, stability, and reactivity are processing-dependent and therefore engineerable [24]. In metal-facing environments, ash chemistry can also actively influence corrosion and phase stability at the metal interface, demonstrating that multi-oxide deposits are not inert and must be evaluated mechanistically [25]. From a performance perspective, ash inclusions have been reported to modify stiffness and strength responses in the composite systems, confirming that oxide-rich particulate fractions can act as true property modifiers rather than mere fillers [26, 27].

While agro-waste-derived reinforcements have gained considerable attention in recent years, their application has largely focused on structural and tribological MMCs, where improvements in hardness, wear resistance, and cost efficiency have been demonstrated [28, 29]. In contrast, their integration into metallic biomaterials remains relatively limited. Existing studies on sustainable reinforcements in biomedical contexts have predominantly focused on polymeric scaffolds [30], ceramic systems [31], and surface coatings [32], where bioactivity and controlled degradation are primary considerations. For instance, recent work on poly(lactic acid)(PLA) composites reinforced with cocoa bean shell particles demonstrates that agro-waste-derived fillers can significantly enhance mechanical stiffness while maintaining high biocompatibility, with cell viability exceeding 94% and haemolysis below clinically accepted thresholds [33]. More recent studies have extended the application of agro-waste-derived materials into bone tissue engineering systems. Rice husk ash (RHA), a silica-rich agricultural by-product, has been successfully incorporated into polycaprolactone (PCL) and hydroxyapatite (HA) -based composites for bone implant applications, where it contributed to improved physico-mechanical properties, enhanced biodegradability, and better structural integrity under physiological conditions [34]. Similarly, optimisation studies on PCL/HA/RHA systems have shown that agro-waste-derived reinforcements can be tailored to achieve desirable mechanical strength, porosity, and degradation behaviour suitable for bone regeneration [35]. Waste-derived aluminosilicate systems have also been explored for bone tissue applications due to their bioactivity, osteoconductivity, and chemical similarity to natural bone minerals [36]. These findings demonstrate that agro-waste is not only a sustainable filler but also an active contributor to scaffold performance and tissue integration.

Within ash-to-biomaterial translation pathways, agricultural waste ashes have been identified as silica-rich resources for bioactive glass manufacturing, demonstrating a recognised route by which plant-derived inorganic chemistry can be repositioned into biomedical-relevant oxide systems [37]. However, when viewed from a sustainability and engineering perspective, a major underutilised stream remains the ash itself. These plant residues are often discarded or openly burnt, producing inorganic by-products that are typically treated as environmentally low-value despite their potential to concentrate mineral oxides and silica-rich fractions. This presents an opportunity to reposition such ashes as functional reinforcement phases in advanced material systems, particularly where oxide stability, surface reactivity, and interfacial behaviour are critical design considerations.

In metallic implant systems, where long-term mechanical stability, corrosion resistance, and interfacial behaviour are critical, the adoption of agro-waste-derived reinforcement remains at an early stage. Although these materials exhibit potential chemical compatibility with passive oxide systems and may contribute to corrosion resistance [38], surface functionality [39, 40], and mechanical reinforcement [41, 42], their application in metal-based biomedical implants has not been sufficiently explored. This

disparity highlights a critical gap between advances in sustainable MMC development and their translation into biomedical systems, where performance requirements are significantly more stringent and governed by long-term stability, ion release, and interfacial integrity under physiological conditions. While silica-rich agro-waste materials, such as RHA, have been extensively investigated for biomedical applications, their evaluation has largely been limited to polymeric and ceramic systems. In contrast, *Caesalpinia pulcherrima* ash (CPA) represents an underexplored multi-oxide system whose compatibility with metallic biomaterials remains largely unaddressed, thereby providing an opportunity to assess emerging agro-waste reinforcements within a structured biomedical evaluation framework.

The limited engineering-level evidence currently available suggests that *Caesalpinia pulcherrima* seed ash can serve as a particulate phase in an aluminium-based hybrid composite, with measurable mechanical and electrochemical consequences [43], yet this is still far from biomedical translation. To the best of the authors' knowledge, no systematic body of work has yet established CPA under biomedical decision criteria, including safety-critical chemistry and leachability, corrosion behaviour in physiological media, ion release profiles, and cytocompatibility or antibacterial durability. This gap motivates the application-driven focus of this review. This study, therefore, focuses not on replacing established systems but on extending the scope of sustainable reinforcement research through a criteria-driven assessment of a less-studied candidate material. The central question guiding this review is: *Does CPA meet the functional requirements of biomedical MMC reinforcements?* To address this question, the different sections establish a mechanistic framework for reinforcement selection for biomedical applications and subsequently evaluate the physicochemical properties of CPA against those criteria.

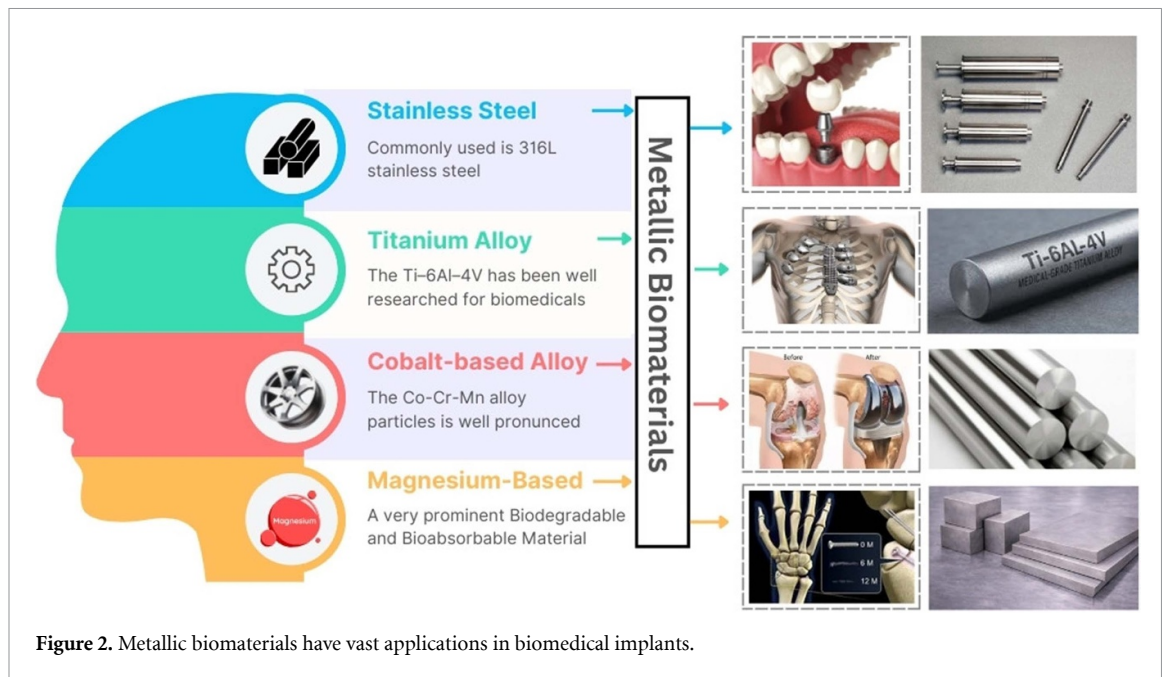
2. Metallic biomaterials for biomedical applications

Metallic biomaterials have been well researched for biomedical applications owing to their superior load-bearing, strength, fatigue resistance, and fracture toughness compared to ceramic and polymeric systems. Dental implants, fracture fixation devices, orthopaedic joint replacements, spinal stabilisation systems, and cardiovascular components all rely heavily on metallic substrates capable of sustaining complex cyclic loading in aggressive physiological environments (figure 2). However, no single metallic system simultaneously satisfies all mechanical, electrochemical, and biological requirements. The selection of a matrix material is therefore governed by a balance between strength, elastic modulus, compatibility with bone, corrosion resistance in chloride-rich body fluids, wear performance under articulation, manufacturability, and long-term biocompatibility [44–47]. Among the most extensively deployed systems are stainless steel, titanium and its alloys, cobalt-based alloys, and, more recently, biodegradable magnesium-based materials. Each class presents distinct advantages and limitations that have motivated continuous material modification strategies, including alloying, composite reinforcement, and surface engineering.

2.1. Stainless steel

Austenitic stainless steel, particularly AISI 316L, remains one of the most widely used metallic biomaterials for orthodontic components, fracture fixation devices, screws, bone plates, and other selected dental and orthopaedic applications. This is due mainly to its cost-effectiveness, availability, and balanced mechanical properties [48]. While AISI 304 stainless steel is also commonly used due to its good mechanical strength and general corrosion resistance, it lacks molybdenum, which is present in 316L [49]. The addition of molybdenum in 316L significantly enhances resistance to pitting and crevice corrosion in chloride-containing environments such as physiological fluids [50]. As a result, 316L exhibits superior corrosion stability under *in vivo* conditions and is therefore more widely adopted in biomedical implant applications, whereas 304 is less frequently considered for such environments due to its comparatively lower resistance to localised corrosion [51].

While conventional cast and wrought processing routes dominate clinical-grade production, emerging technologies such as powder injection moulding (PIM) and selective laser melting (SLM) are increasingly adopted for complex geometries and patient-specific implants. Studies have shown that the processing routes significantly influence grain structure, densification, and corrosion behaviour. For instance, boron-assisted PIM has been found to enhance densification to ~98.5% while maintaining acceptable cytocompatibility [52]. In contrast, additively manufactured 316L exhibits inherent porosity that can act as a corrosion initiation site during long-term immersion [53]. Mechanical properties of conventionally processed 316L typically include a yield strength of ~170–450 MPa, ultimate tensile strength of ~485–620 MPa, and an elastic modulus of ~190–210 GPa [54, 55], which is substantially higher than cortical bone (10–30 GPa) [54, 55], thereby predisposing implants to stress shielding. Severe plastic deformation



routes, such as multiaxial forging, can significantly increase strength (UTS up to $\sim 10,190$ MPa), though often at the expense of ductility [56]. At the same time, cold mechanical processing enhances strength through strain hardening without addressing corrosion limitations [57].

The corrosion resistance of 316L relies on the formation of a Cr_2O_3 passive film, but its stability is highly sensitive to surface integrity, coating quality, and microstructural heterogeneity. Long-term immersion studies reveal pore-driven localised corrosion and measurable Fe and Cr ion dissolution, especially in chloride- or acidic-rich environments [53]. Coating strategies such as TiO_2 films demonstrate that corrosion current density and pitting susceptibility are strongly dependent on film porosity, with dense coatings providing superior protection [58]. Molecular-scale surface modification using self-assembled organic inhibitors has achieved $\sim 90\%$ reductions in corrosion rate in simulated body fluid (SBF) [59], reinforcing the central role of surface engineering in corrosion control.

Furthermore, wear resistance and surface durability under physiological loading remain additional concerns. Studies have shown that surface finish significantly influences wear rate and electrochemical degradation [60], and tensile loading can induce microcracks and roughening, compromising passive film stability [61]. Ceramic-based reinforcement approaches, including nano-yttria-stabilised zirconia coatings and HA -enriched surfaces, have improved hardness (up to ~ 356 HV) and enhanced bioactivity [62, 63]. Functionally graded 316L/ β -tricalcium phosphate (β -TCP) systems have further demonstrated modulus tuning and improved hemocompatibility, although mechanical strengthening remains limited for high load-bearing applications [64]. While 316L stainless steel provides reliable baseline mechanical strength and established clinical performance, its high elastic modulus, wear sensitivity, susceptibility to localised corrosion, and reliance on processing-controlled densification continue to motivate composite reinforcement and surface stabilisation strategies in biomedical applications.

2.2. Titanium-based alloy

Titanium-based alloys, particularly Ti-6Al-4V, are widely regarded as the benchmark metallic biomaterial for permanent dental and orthopaedic implants. This is due to their excellent corrosion resistance, favourable strength-to-weight ratio, and improved elastic modulus compatibility relative to stainless steels [46]. Conventional wrought Ti-6Al-4V exhibits a yield strength typically in the range of ~ 800 – 900 MPa [65] and an elastic modulus of ~ 100 – 120 GPa [66]. This is lower than 316L but still substantially higher than cortical bone (10 – 30 GPa), leaving stress shielding a persistent concern. Modern production routes increasingly rely on additive manufacturing, especially SLM and laser powder bed fusion, enabling the fabrication of controlled porous architectures and gradient structures. Triply periodic minimal surface (TPMS) lattices with 80% – 95% porosity have demonstrated modulus tunability into the trabecular bone range while maintaining high yield strength and fatigue endurance approaching $\sim 60\%$ of yield stress [67, 68]. Bio-inspired porous Schwarz structures have achieved modulus values as low as ~ 2.25 GPa

while retaining corrosion resistance [69], highlighting architecture as a primary lever for mechanical compatibility.

Porosity design strongly influences osseointegration and fixation stability. Pore sizes around 600 μm have been reported to optimise bone ingrowth and mechanical fixation *in vivo* [53], and a porosity gradient in dental implants improves stress distribution and reduces stress concentrations under bite forces [70]. These findings demonstrate that structural design alone can partially mitigate modulus mismatch. However, additive manufacturing introduces surface heterogeneity, partially melted particles, and variability in oxide layers that may compromise biological performance and corrosion stability. Hybrid surface finishing via etching and electropolishing has been shown to reduce roughness and produce thicker, more homogenous TiO_2 layers that enhance stem-cell viability without inducing oxidative stress [71]. Despite titanium's stable TiO_2 passive film and excellent corrosion resistance in physiological media, challenges remain in fretting corrosion, tribocorrosion at modular junctions, and long-term wear under articulation. Micro-arc oxidation (MAO) coatings have improved fretting corrosion resistance by approximately $4.5\times$ under optimised conditions, though excessive coating porosity reduces hardness and stability [72]. Surface texturing has equally reduced friction coefficients and wear rates while enhancing cell adhesion [73], indicating that tribological performance is strongly surface-dependent rather than intrinsically optimal.

Multifunctional coatings, such as ZnO- HA composites, have further enhanced corrosion resistance, antibacterial activity, and osteointegration potential [74], while photothermal and heterojunction-based surface systems introduce antibacterial and antitumor functionality without altering the bulk structure [75, 76]. Alloying elemental-doping strategies have also been explored to modulate immune responses and osteogenesis, as demonstrated by Zn/Mg/Cu co-doped Ti-6Al-4V systems [77], yet ion release and microstructural changes require careful control. Similarly, advanced alloy systems, such as medium-entropy alloys, aim to optimise strength, corrosion resistance, and biocompatibility concurrently [78]. This complexity, however, increases processing and regulatory challenges. The literature indicates that while titanium alloys offer superior corrosion resistance and better modulus matching than stainless steels, their performance in wear, fretting corrosion, and multifunctional bioactivity increasingly depends on architectural design, surface engineering, and composite reinforcement approaches. Reinforcement strategies in Ti-based systems, therefore, must preserve modulus compatibility and fatigue endurance achieved through porous architecture while introducing enhanced wear resistance, antibacterial functionality, and controlled ion release.

2.3. Cobalt-based alloy

Cobalt-chromium-molybdenum (Co-Cr-Mo) alloys are widely used in high-load-bearing orthopaedic components, including knee prostheses, femoral heads, and modular joint systems. This is particularly due to their exceptional hardness, strength, and wear resistance. Elastic modulus values typically range from ~ 210 to ~ 230 GPa [79], exceeding those of both Ti alloys and cortical bone, which can contribute to stress shielding and stress concentration at implant-bone interfaces. Finite element analyses of knee systems consistently show that while Co-Cr-Mo provides superior load-bearing capacity, its high stiffness leads to localised stress regions under cyclic loading [80, 81]. As a result, modulus mismatch remains a persistent biomechanical concern in long-term implantation. However, despite Co-Cr-Mo's excellent wear performance, the alloy remains susceptible to tribocorrosion under physiological conditions. Combined mechanical wear and electrochemical attack significantly accelerate degradation in Ringer's lactate and other biological solutions [82]. *In vivo* analyses confirm synergistic wear-corrosion mechanisms driving surface deterioration and metal ion release [83]. Chromium ion and particulate release have been identified in periprosthetic tissues of failed metal-on-metal implants, linking tribocorrosion to biological complications [84]. Moreover, wear particles have been shown to induce an inflammatory cytokine response in osteocytes, including $\text{TNF-}\alpha$ production [85], reinforcing the clinical significance of debris generation.

Corrosion behaviour is environment-sensitive, with passive film stability varying across biological media [70], and even pharmaceutical exposure, such as calcium supplementation, has been shown to destabilise passive films and increase corrosion rates [86]. Surface damage and plastic deformation observed in simulator-tested metal-on-metal systems further confirm that intrinsic wear resistance is not immune to long-term degradation [87]. To mitigate these limitations, surface reinforcement approaches have demonstrated measurable benefits. For instance, tantalum-based coatings were observed to reduce ion release and cytotoxicity [88], while laser texturing combined with polymeric lubrication layers improved tribological behaviour [89]. Furthermore, mechanical performance is strongly microstructure-dependent. The cooling rate during casting was found to significantly influence dendritic refinement and hardness, with faster cooling rates promoting finer microstructures and increased hardness [90]. Severe

cyclic loading also drives crack initiation along microstructural features, particularly in additively manufactured variants [91]. Also, phase constitution plays a fundamental role; for instance, martensitic γ (FCC) to ϵ (HCP) transformation and precipitate formation markedly alter strength and deformation behaviour [92]. These findings demonstrate that grain refinement, phase control, and precipitate surface engineering are central to optimising fatigue resistance and structural integrity. While Co–Cr–Mo alloys provide superior mechanical strength and inherent wear resistance relative to stainless steel and titanium, their high elastic modulus, tribocorrosion-driven ion release, inflammatory response to wear debris, and fatigue-sensitive microstructural features continue to motivate the development of reinforcement and surface stabilisation strategies.

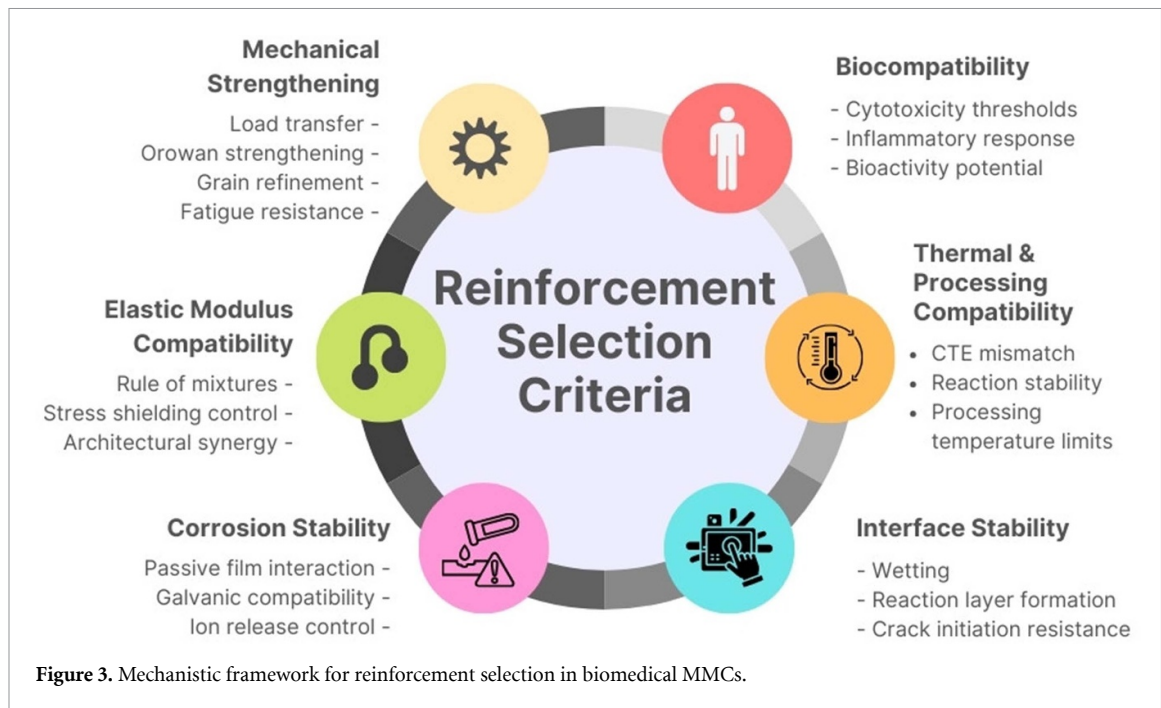
2.4. Magnesium-based systems

Magnesium, a biodegradable metallic biomaterial, has been used in bone pins, screws, temporary orthopaedic fixation devices, and cardiovascular stents. This is linked to the favourable density, biocompatibility, and elastic modulus ($\sim 40\text{--}45$ GPa) of the metal, which are closer to those of natural bone than those of stainless steel or cobalt-based alloys. The modulus proximity significantly reduces stress shielding. However, the magnesium system is limited by its inherent rapid corrosion in physiological environments, which can lead to premature mechanical failure, hydrogen gas evolution, and local alkalization. Studies have demonstrated that pure Mg corrodes too rapidly when used for structural applications [93], with degradation kinetics often exceeding the rate of tissue healing [94]. Corrosion rate, therefore, becomes the dominant performance determinant governing biocompatibility and implant longevity [95]. Furthermore, the processing route and grain refinement also influence corrosion resistance. Friction stir processing has been shown to refine grains, homogenise precipitates, and reduce corrosion current density by approximately one order of magnitude in simulated physiological media [96], while surface peening enhances surface integrity and biocompatibility by reducing localised corrosion [97]. Despite these advances, rapid surface degradation remains a challenge under physiological chloride exposure, necessitating protective or functional surface modifications. Polymer-based coatings effectively slow degradation kinetics [98], and multilayer nanosheet or bioadaptive coatings provide improved corrosion resistance, antibacterial function, and self-healing properties [99, 100].

Alloying strategies have also been widely investigated to moderate degradation while improving mechanical strength. Additions of Zn and Sr have not only enhanced strength but also influenced corrosion behaviour in a composition-dependent manner [101]. Also, Mg–Zn systems show improved mechanical response, but still face corrosion challenges [102]. Likewise, Ca-containing Mg alloys exhibit good biocompatibility but may accelerate corrosion if not microstructurally controlled [103]. Recent rare-earth additions, such as Er, modify second-phase distribution and reduce localised galvanic corrosion sites [104], while B and Sn additions refine microstructure and improve corrosion resistance and inflammatory balance [105]. Functional alloying has also been employed to impart antibacterial capability, such as Mg–Cu systems for osteomyelitis treatment. However, such additions can accelerate corrosion and alter ion release profiles [106]. These findings suggest that microstructure and second-phase engineering, rather than composition alone, dictate degradation behaviour. Furthermore, in magnesium-based biomaterials, while degradation is desirable, it must be precisely controlled to maintain mechanical integrity during tissue healing. Therefore, reinforcement strategies in Mg-based systems should focus on grain refinement, phase stabilisation, secondary-phase control, and surface-composition coatings to achieve a balanced synergy among strength, corrosion resistance, and biocompatibility.

3. Reinforcement selection criteria in biomedical MMCs

The comparative analysis presented in table 1 demonstrates that although metallic biomaterials provide the structural backbone of load-bearing implants, each system exhibits intrinsic mechanical, electrochemical, or biological limitations that have driven extensive reinforcement and surface engineering strategies. Each class (i.e. stainless steel, titanium alloys, cobalt-based alloys, and magnesium systems) exhibits specific performance limitations, including modulus mismatch, tribocorrosion-driven degradation, ion release, or uncontrolled biodegradation. The implication, therefore, is that reinforcement strategies in biomedical MMCs must be guided by well-defined functional requirements rather than compositional novelty alone. A reinforcement phase should not only enhance strength but also maintain corrosion stability in physiological environments, preserve or tune elastic modulus compatibility with bone, avoid cytotoxic ion release, remain thermally and chemically stable during processing, and provide a durable interface with the metallic matrix. Therefore, the suitability of any candidate reinforcement phase must



be evaluated against matrix-specific requirements, including modulus compatibility, corrosion stability, wear resistance, ion release control, and biological safety (figure 3).

3.1. Mechanical strengthening and load transfer mechanisms

In MMCs, strengthening arises from several mechanisms, including load transfer, Orowan strengthening, grain refinement, and fatigue resistance. For instance, fine, well-dispersed reinforcements can impede dislocation motion via Orowan strengthening, while load transfer from the ductile matrix to a stiffer reinforcement phase increases the composite's overall stiffness and yield strength [22]. Grain refinement may also occur through particle-stimulated nucleation during processing, leading to Hall-Petch strengthening [114]. However, reinforcement effectiveness depends on particle size, distribution uniformity, and interfacial bonding. Poor dispersion or clustering can create stress concentration sites that accelerate crack initiation under cyclic loading, as observed in fatigue-sensitive Co–Cr–Mo systems [91]. Mechanical strengthening thus remains one of the primary motivations for incorporating a reinforcement phase into metallic biomaterials.

Evidence from agro-waste-derived biomaterial systems supports this criterion. In PCL/RHA/Hap scaffolds, RHA -derived silica and HA increased compressive strength from about 3.5 MPa for pure PCL to 9.0–12.5 MPa, which falls within the trabecular bone strength range of 4–12 MPa. The same study reported more than 50% improvement in hardness and fracture toughness, attributed to silica-induced pore filling, crack shielding, and improved stress transfer across the interfacial region [34]. A related optimisation study also shows that RHA/HAP reinforcement increased compressive strength to 8.6–15 MPa and improved hardness and fracture toughness, with RHA content identified as a major factor controlling porosity, compressive strength, and hardness [35]. These findings provide literature-based validation that agro-waste-derived oxide reinforcements can satisfy mechanical-strengthening criteria when their content, dispersion, and matrix interaction are properly controlled.

For biomedical implants subjected to repetitive gait or joint articulation, reinforcements should improve strength and fatigue resistance without introducing brittle phases or microstructural heterogeneity that may likely compromise long-term durability. While systems such as Co–Cr–Mo exhibit high intrinsic strength, others, such as 316L stainless steel and magnesium alloys, require property enhancement to withstand cyclic physiological loading without premature deformation or fatigue failure. Processing-induced grain refinement has been shown to increase hardness and strength in Co–Cr–Mo alloys [90] and in 316L stainless steel through multiaxial forging [56]. Conversely, friction stir processing refines magnesium microstructure and improves corrosion-linked mechanical stability [96]. These observations confirm that microstructural control directly influences load-bearing capacity. Furthermore, bulk strengthening through severe plastic deformation often reduces ductility, indicating that reinforcement must enhance strength without compromising toughness. Moreover, from a biomedical perspective, strengthening must also be balanced against biological response. This is because excessively hard surfaces

Table 1. Comparative summary of major metallic biomaterials in biomedical applications.

Material system	Typical elastic modulus (GPa)	Typical strength level	Corrosion behaviour in physiological media	Wear/tribocorrosion behaviour	Primary limitation	Reinforcement driver
316L stainless steel	~190–210 [54, 55]	YS: ~170–310 MPa; UTS: ~485–620 MPa (can exceed 1000 MPa after severe deformation) [54, 55]	Passive Cr ₂ O ₃ film; susceptible to pitting in chloride-rich media; porosity increases Fe/Cr ion release [53, 58]	Moderate wear resistance; surface finish and loading-induced defects accelerate degradation [60, 61]	High modulus (stress shielding); localised corrosion; ion release [53, 54, 61]	Surface coatings (TiO ₂ , YSZ, HAp), densification, microstructural refinement, composite surface reinforcement [58, 62, 64]
Ti-6Al-4V and Ti alloys	~100–120 (can be reduced to 2–30 GPa via porous architectures) [66]	YS: ~800–900 MPa; high fatigue strength [65]	Excellent corrosion resistance via TiO ₂ film; fretting corrosion at modular junctions [71, 72]	Poor intrinsic wear resistance; tribocorrosion under articulation [72, 73]	Wear/fretting issues; stiffness is still higher than the bone, and there is limited antibacterial function [67, 71, 74]	Architectural design (TPMS), MAO coatings, ceramic composite coatings, multifunctional surface reinforcement [69, 73, 74]
Co–Cr–Mo alloys	~210–230 [79]	Very high strength and hardness; superior load-bearing capacity [90]	Good corrosion resistance but susceptible to tribocorrosion; Cr/Co ion release <i>in vivo</i> [82, 83]	Excellent wear resistance, but debris generation under Metal-on-Metal conditions [82, 87]	Very high modulus; tribocorrosion-driven ion release; inflammatory response [83–85]	Hard coatings (Ta, DLC), phase control, surface texturing, and microstructural refinement [88, 89]
Mg alloys	~40–45 (close to bone) [107, 108]	Lower than Ti/Co; improved via alloying and processing [109–111]	Rapid corrosion; hydrogen evolution; degradation rate often too high [93–95]	Wear is less dominant than corrosion; surface degradation governs performance [112, 113]	Uncontrolled degradation; early mechanical loss; alkalization [94, 95]	Alloying (Zn, Sr, Ca, rare earths), grain refinement (FSP), polymer/ceramic multilayer coatings, composite reinforcement for corrosion control [96, 98, 100]

have been found to increase wear debris generation under articulation [83], while particles can stimulate inflammatory pathways [85]. The implication is that mechanical reinforcement in biomedical MMCs must be controlled, uniform, and microstructurally compatible to ensure enhanced load-bearing performance without increasing debris-related complications.

3.2. Elastic modulus tailoring and stress shielding control

Elastic modulus mismatch between metallic implants and surrounding bone remains a primary cause of stress shielding and long-term bone resorption. As summarised in table 1, the elastic modulus of conventional metallic biomaterials varies widely but remains substantially higher than that of cortical bone (10–30 GPa). Austenitic stainless steel with ~190–210 GPa and Co–Cr–Mo alloys with ~210–230 GPa exhibit the greatest stiffness mismatch, while titanium alloys with ~100–120 GPa offer partial improvement, yet still exceed physiological requirements. This disparity alters load transfer across the implant–bone interface and promotes stress shielding, a phenomenon associated with bone resorption and long-term implant loosening. Finite element analyses of orthopaedic systems confirm that high-stiffness materials concentrate stress within the implant while reducing mechanical stimulation of adjacent bone [80, 81, 115].

Reinforcements for biomedical MMCs must therefore be selected with careful attention to elastic compatibility. The effective modulus should follow the rule-of-mixture relationships and rely strongly on reinforcement stiffness, volume fraction, and distribution. Introducing a high-modulus ceramic phase into an already stiff matrix may exacerbate stress shielding. In contrast, controlled reinforcement content or architecture–reinforcement synergy may enable modulus tuning without compromising strength. Evidence from agro-waste-derived scaffold systems supports this principle. In PCL/RHA/HAp composites, changes in RHA -derived silica and HAp contents altered porosity, density, and compressive response, showing that reinforcement loading can tune structural stiffness and load-bearing behaviour rather than only increase strength [34, 35]. This is important because the scaffold with excessive reinforcement content showed reduced porosity, whereas the controlled composition maintained porosity within ranges relevant to bone regeneration. Such findings demonstrate that sustainable reinforcement design must consider the stiffness–porosity–strength balance, not reinforcement content alone.

Recent advances demonstrate that structural design can significantly reduce effective stiffness. For magnesium-based systems, where modulus is already close to bone (~40–45 GPa), reinforcement must not over-stiffen the alloy but instead maintain load-sharing behaviour while improving corrosion stability [94]. Additively manufactured Ti-6Al-4V with TPMS architectures achieves modulus values approaching trabecular bone while maintaining adequate strength and fatigue resistance [67, 68]. Bio-inspired porous Schwarz structures have achieved effective modulus values as low as ~2.25 GPa [69], illustrating that architecture alone can serve as a stiffness-tuning strategy. Similarly, functionally graded systems incorporating TCP into 316L have been explored to reduce modulus mismatch and improve load transfer [64].

A broader review of sustainable bone-substituting biomaterials further confirms that recycled and agro-waste-derived inorganic materials are most effective when combined with architectural control, porosity design, and composite processing rather than used as simple fillers [116]. These findings suggest that modulus control goes beyond strengthening and can be achieved through structural, compositional, or composite design. Additionally, it requires balancing composite stiffness, architecture, and biological load transfer to preserve bone remodelling dynamics.

3.3. Corrosion stability and electrochemical compatibility

In biomedical MMCs, corrosion resistance is not merely a durability issue; it directly governs ion release, inflammatory response, and long-term biological safety [117]. Corrosion stability in physiological environments is, thus, a basic requirement for any reinforcement phase incorporated into biomedical MMCs. As highlighted in table 1, metallic biomaterials rely on passive oxide films for protection, yet these films remain vulnerable to localised breakdown, tribocorrosion, and micro-galvanic interactions. For instance, 316L stainless steel exhibits pitting susceptibility in chloride-containing media, particularly in the presence of porosity or surface defects [53, 58]. Likewise, Co–Cr–Mo alloys undergo synergistic wear–corrosion degradation under tribological loading, leading to passive film disruption and ion release [82, 83]. Magnesium systems present the most severe case, where rapid electrochemical degradation, hydrogen evolution, and alkalization dominate performance [94, 95]. These observations demonstrate that corrosion behaviour is highly sensitive to microstructure, surface condition, and environmental chemistry. Reinforcement phases must, therefore, not introduce compositional heterogeneity that undermines electrochemical stability, particularly in systems already prone to tribocorrosion or rapid degradation.

Evidence from biodegradable Mg-based composites reinforces this requirement. In Mg–Zn/HA composites, the addition of Zn reduced corrosion rate and hydrogen evolution compared with pure Mg and Mg/HA, with the Mg–Zn/HA system showing the lowest corrosion rate of 0.19 mm yr^{−1} and reduced H₂ evolution. This improvement was attributed to refined grains, uniform secondary-phase distribution, and protective Mg(OH)₂ and Ca-P apatite layer formation during immersion [118]. Similarly, Mg–3Zn/Ti–HA hybrid composites showed improved corrosion suppression relative to the unreinforced Mg–3Zn alloy, with the Mg–3Zn/1Ti/1.5HA composition displaying stronger evidence of bone-like apatite formation and enhanced corrosion resistance [119]. These studies show that bioactive ceramic reinforcements can improve corrosion behaviour by promoting protective surface layers and remain well distributed within the metallic matrix.

Furthermore, when a reinforcement phase is introduced into a metallic matrix, electrochemical compatibility becomes critical. Differences in electrode potential between the matrix and reinforcement may create galvanic coupling, accelerating localised corrosion at phase boundaries. Reinforcements containing electrochemically active elements or residual impurities can destabilise passive films or promote localised corrosion. This risk is particularly relevant in multi-phase systems or in porous architectures where electrolyte penetration is facilitated. Conversely, properly selected ceramic or oxide reinforcements can enhance corrosion resistance by acting as inert barriers, promoting passive film stability, or reducing defect density in surface layers. For instance, ceramic-based coatings and MAO layers have been shown to improve corrosion performance in titanium systems by stabilising surface oxides [120]. In contrast, surface inhibitors reduce corrosion current density in stainless steel [59].

Agro-waste and biomass-derived systems also provide useful validation for this criterion. Mg–Zn composites reinforced with eggshell particles showed improved corrosion resistance at controlled reinforcement levels, especially at 5 wt.% eggshell, due to the formation of protective Mg(OH)₂ and phosphate-rich surface layers during immersion in Hank's balanced salt solution [121]. However, excessive eggshell addition increased cathodic activity and reduced the corrosion benefit, demonstrating that reinforcement content and electrochemical balance are critical. Biomass-derived calcium silicate glasses produced from corn, sugarcane, and eggshell wastes also formed carbonated HA layers in SBF, while ion release and pH variation governed their degradation behaviour and bioactivity [122]. These findings confirm that sustainable oxide-rich reinforcements can support electrochemical stability and bioactive surface formation, but only when their dissolution, impurity content, and interfacial reactions are properly controlled. Therefore, reinforcement selection must ensure chemical inertness or controlled electrochemical behaviour in SBFs. Key criteria include: (1) resistance to localised corrosion initiation, (2) passive film compatibility, (3) avoidance of galvanic instability, and (4) suppression of excessive ion release.

3.4. Biocompatibility and ion release constraints

Reinforcement phases in biomedical MMCs must satisfy stringent biocompatibility requirements. Beyond mechanical and electrochemical performance, ion release and wear particle generation remain central determinants of biological response. It has been shown that tribocorrosion of Co–Cr–Mo alloys can lead to chromium ion and particulate release in periprosthetic tissues [83, 84], while wear particles have been shown to stimulate inflammatory cytokine production, including TNF- α , in osteocytes [85]. Similarly, rapid degradation of magnesium alloys alters local pH and releases Mg²⁺ and other alloying elements into surrounding tissues, directly influencing biocompatibility [95, 106]. These findings demonstrate that biological response is strongly coupled to electrochemical behaviour and material dissolution kinetics. Mechanistically, reinforcement-induced changes in surface chemistry, microstructure, and dissolution behaviour directly influence protein adsorption, cell adhesion, and inflammatory signalling. Therefore, reinforcement selection must ensure cytocompatibility under extract-testing conditions, minimise the inflammatory risk associated with wear debris, and avoid uncontrolled ion release during long-term immersion.

Recent studies on bio-derived and hybrid composites provide further insights into this interplay. In Mg–Zn/HA systems, controlled ion release combined with apatite layer formation improved cytocompatibility while maintaining degradation within acceptable limits [118]. Likewise, Mg–3Zn/Ti–HA hybrid composites demonstrated enhanced cell viability and reduced cytotoxicity compared to the base alloy, attributed to the stabilisation of degradation behaviour and bioactive HA-induced surface modification [119]. In another approach, the incorporation of silver nanoparticles into Mg/HA composites improved antibacterial performance but required strict compositional control to avoid cytotoxicity associated with excessive Ag⁺ ion release [123]. These examples highlight a critical balance: while bioactive reinforcements can promote osteogenic response and antimicrobial functionality, their dissolution kinetics and ion release profiles must remain within biologically acceptable thresholds.

Agro-waste-derived reinforcements also follow similar principles. Eggshell-reinforced Mg–Zn systems showed that moderate reinforcement levels improved immersion behaviour and biocompatibility due to controlled Ca-rich ion release, while excessive addition increased degradation rate and potential cytotoxicity [121]. Biomass-derived calcium silicate glasses released Ca^{2+} and Si^{4+} ions, promoting bioactivity and HA formation. However, their dissolution rate and pH evolution were found to directly influence cytocompatibility, requiring careful optimisation of composition and processing conditions [122]. Similarly, biosilicate obtained from Bermuda grass ash improved surface properties and tribological behaviour of Mg systems, but its biocompatibility depends on impurity control and stable interfacial bonding [124].

Polymer-based bio-composites further reinforce the importance of controlled degradation. In PLA composites reinforced with cocoa bean shell particulates, the natural filler influenced mechanical performance and degradation behaviour, with implications for ion release and biological response in biodegradable implant applications [33]. The study showed that filler dispersion and interfacial bonding governed degradation uniformity and prevented localised accumulation of degradation by-products, which could otherwise trigger adverse biological reactions. This aligns with broader observations that heterogeneous reinforcement distribution can lead to localised ion concentration gradients, influencing cellular response and inflammatory signalling.

In biomedical MMCs, biocompatibility is not achieved solely by mechanical stability. It requires electrochemical restraint, compositional purity, and biologically acceptable interfacial chemistry. Reinforcement phases must therefore be compositionally controlled, chemically non-toxic, and free of harmful trace elements. Impurities such as heavy metals or electrochemically unstable phases may elevate ion release beyond cytocompatibility thresholds. Conversely, controlled incorporation of bioactive elements can enhance osteogenic differentiation or antibacterial performance when properly regulated. For example, Sr/Ca-doped surface systems on Ti-6Al-4V have been shown to promote early osteogenic response while maintaining corrosion stability [125], illustrating that bioactivity and safety must be carefully balanced. However, excessive incorporation of reactive elements may destabilise coatings or accelerate corrosion, as observed in Ag-containing systems when processing limits are exceeded [126].

3.5. Thermal and processing compatibility

Reinforcement phases in biomedical MMCs must remain stable under the thermal and mechanical conditions required for matrix processing. Each metallic system highlighted in table 1 is manufactured through specific routes, including casting, PIM, SLM, hot rolling, and surface oxidation treatments. These processes involve elevated temperatures, rapid cooling cycles, or localised thermal gradients that can induce phase transformations, residual stresses, or interfacial reactions. For instance, the cooling rate significantly influences dendritic refinement and hardness in Co–Cr–Mo alloys [90], while sintering conditions alter microstructure and mechanical integrity in powder-processed systems [127]. Likewise, thermomechanical processing such as extrusion and rolling modifies grain structure and degradation behaviour in Mg-based alloys [103]. Reinforcements must therefore withstand these processing environments without decomposition, excessive oxidation, or undesirable chemical transformation that alters their functional role.

A reinforcement phase must, in addition, possess thermal stability at processing temperature and maintain chemical compatibility with the matrix. For example, RHA, a widely studied agro-waste reinforcement, undergoes controlled calcination (typically 500 °C–700 °C) to yield amorphous silica with high pozzolanic reactivity [116]. However, excessively high calcination temperatures can induce crystallisation into cristobalite or tridymite, reducing reactivity and altering interfacial bonding behaviour. Similarly, acid leaching prior to calcination is often required to remove alkali impurities that would otherwise promote unwanted reactions during composite processing. This highlights that reinforcement performance is not intrinsic alone but strongly dependent on pre-processing routes that define thermal stability, purity, and phase constitution.

A comparable principle applies to biomass-derived bioactive calcium silicate glasses, where melting and quenching conditions dictate network connectivity, dissolution kinetics and bioactivity [122]. Improper thermal processing can lead to phase separation or crystallisation, reducing bioactivity and compromising mechanical integrity. In magnesium-based systems, incorporation of such bioactive phases must be carefully controlled to avoid accelerated degradation due to thermal-induced microstructural heterogeneity or galvanic coupling. Studies on bioactive fluorcanasite-reinforced Mg composites demonstrate that controlled processing enables tunable mechanical properties and degradation rates, whereas poor thermal compatibility leads to interfacial instability and inconsistent performance [128].

Processing compatibility also extends to particle characteristics and dispersion behaviour. Reinforcement phases must maintain a stable particle size distribution, resist agglomeration, and remain uniformly dispersed during thermal cycling. Agglomeration is particularly problematic in bio-derived particulates due to their high surface energy and irregular morphology. For instance, biosilica derived from agricultural waste requires careful control of particle refinement and dispersion to ensure uniform load transfer and avoid defect clustering during processing [124]. Similarly, in squeeze-cast biowaste composites, microstructural evolution studies show that inadequate dispersion or thermal incompatibility leads to porosity and weak interfacial bonding, directly affecting mechanical and biological performance [129].

Another critical factor is the mismatch in the coefficient of thermal expansion (CTE) between the matrix and reinforcement. Significant CTE differences during cooling can generate residual stresses that may induce interfacial debonding, microcracking, or distortion. This effect is amplified in advanced processing routes such as SLM, where rapid solidification produces steep thermal gradients and non-equilibrium microstructures. In Ti-6Al-4V systems, such gradients can lead to metastable phase formation and the accumulation of residual stress [67], requiring reinforcements that are thermally stable and chemically inert under such extreme conditions. Similarly, in biodegradable Mg systems, reinforcement must not accelerate galvanic coupling or promote microstructural heterogeneity during processing, to prevent increased localised corrosion [104]. Thus, thermal and processing compatibility becomes a prerequisite for composite feasibility, ensuring that reinforcement phases retain structural integrity and do not introduce residual stresses or unstable reaction layers during fabrication.

Sustainable biomaterial processing further reinforces the importance of thermal compatibility. Recent advances in additive manufacturing of bio-based composites emphasise low-temperature processing routes and controlled thermal histories to preserve the functional integrity of natural reinforcements. For example, polymer-based systems such as PLA reinforced with lignocellulosic fillers rely on relatively low processing temperatures to prevent fibre degradation while maintaining dispersion and interfacial bonding. As reported for PLA/cocoa bean shell composites, thermal processing must be carefully controlled to avoid degradation of lignocellulosic constituents while preserving their bioactive and mechanical contributions [33]. This demonstrates that thermal compatibility is equally critical in both metallic and polymeric biomaterial systems, particularly when incorporating agro-waste-derived reinforcements. Therefore, thermal and processing compatibility are prerequisites for the successful integration of reinforcement phases in biomedical MMCs. Reinforcements must (i) retain structural and chemical stability at processing temperature, (ii) remain uniformly dispersed without agglomeration, (iii) exhibit compatible thermal expansion behaviour to minimise residual stresses, and (iv) avoid undesirable interfacial reactions or phase transformations.

3.6. Interface stability and interfacial reaction control

The long-term performance of biomedical MMCs is governed not only by matrix and reinforcement properties individually, but also by the stability of their interface. Effective load transfer, corrosion resistance, and fatigue durability all depend on strong and chemically stable interfacial bonding. Inadequate wetting, weak adhesion, or the formation of brittle reaction layers can create stress concentration sites that promote crack initiation under cyclic loading. For instance, cyclic loading has been shown to drive crack propagation along microstructural features in Co–Cr–Mo systems [91], demonstrating how interfacial heterogeneity may compromise fatigue resistance. Similarly, porosity-driven corrosion in additively manufactured 316L stainless steel highlights how structural discontinuities can act as electrochemical initiation sites [53]. Reinforcement-matrix compatibility, from a mechanistic lens, requires controlled interfacial reactions, minimal formation of brittle intermetallic compounds, and stable chemical bonding under physiological exposures.

Evidence from bio-derived composite systems reinforces this criterion. In RHA/PCL/HAp scaffolds, silica from RHA was reported to improve surface interfacial bonding through an energy-absorbing mechanism, which increased toughness and strengthened the scaffold structure [35]. In biodegradable Mg–Zn/HA systems, uniform distribution of MgZn secondary phases and fine grains reduced galvanic cell formation and controlled degradation. In contrast, clustered secondary phases created local pitting sites and weakened surface integrity, showing that interface stability is strongly governed by phase distribution and interfacial homogeneity [118]. Similar behaviour was observed in Mg-3Zn/Ti-HA hybrid composites, where Ti and HA incorporation promoted refined grain structure, protective oxide-layer formation, and bone-like apatite deposition during immersion. These interfacial products contributed to improved corrosion resistance and cytocompatibility [119].

Surface engineering studies further emphasise the importance of interface control. Substrate preparation significantly influences adhesion strength and coating morphology in 316L systems, where oxide-layer thickness and surface roughness govern mechanical interlocking and coating durability [130]. In

titanium alloys, MAO and surface finishing treatments improve oxide uniformity and corrosion resistance by stabilising the interface between substrate and protective layer [71, 131]. Excessive chemical reactivity may produce secondary phases that degrade corrosion resistance or mechanical performance, while insufficient bonding limits load transfer efficiency. These findings suggest that reinforcement effectiveness is inseparable from interfacial integrity.

For agro-waste-derived reinforcements, interfacial control is particularly important because ash particles often contain multiple oxide phases, trace impurities, and irregular surface morphologies. These features may improve mechanical interlocking and surface reactivity, but they may also create chemically heterogeneous zones if not properly processed. In PLA/CBS composites, FTIR analysis indicated blending rather than covalent bonding between the cocoa bean shell filler and PLA matrix, while the composite still maintained high cell viability and low haemolysis [33]. Although this example is polymer-based, it demonstrates that bio-derived reinforcements may remain functional even when bonding is primarily physical, provided dispersion and interfacial compatibility are controlled. For metallic systems, however, this requirement becomes more stringent because weak bonding or chemically unstable interfaces may accelerate galvanic corrosion, fatigue crack initiation, and particle detachment. Interfacial regions must therefore resist galvanic microcells that accelerate localised corrosion, particularly in chloride-rich environments. Reinforcement selection must consider wetting behaviour, residual stress development, interfacial reaction kinetics, and long-term electrochemical stability. In biomedical MMCs, the interface represents the critical zone where mechanical, chemical, and biological phenomena converge, ultimately determining composite durability and clinical reliability.

4. Physicochemical characteristics of CPA

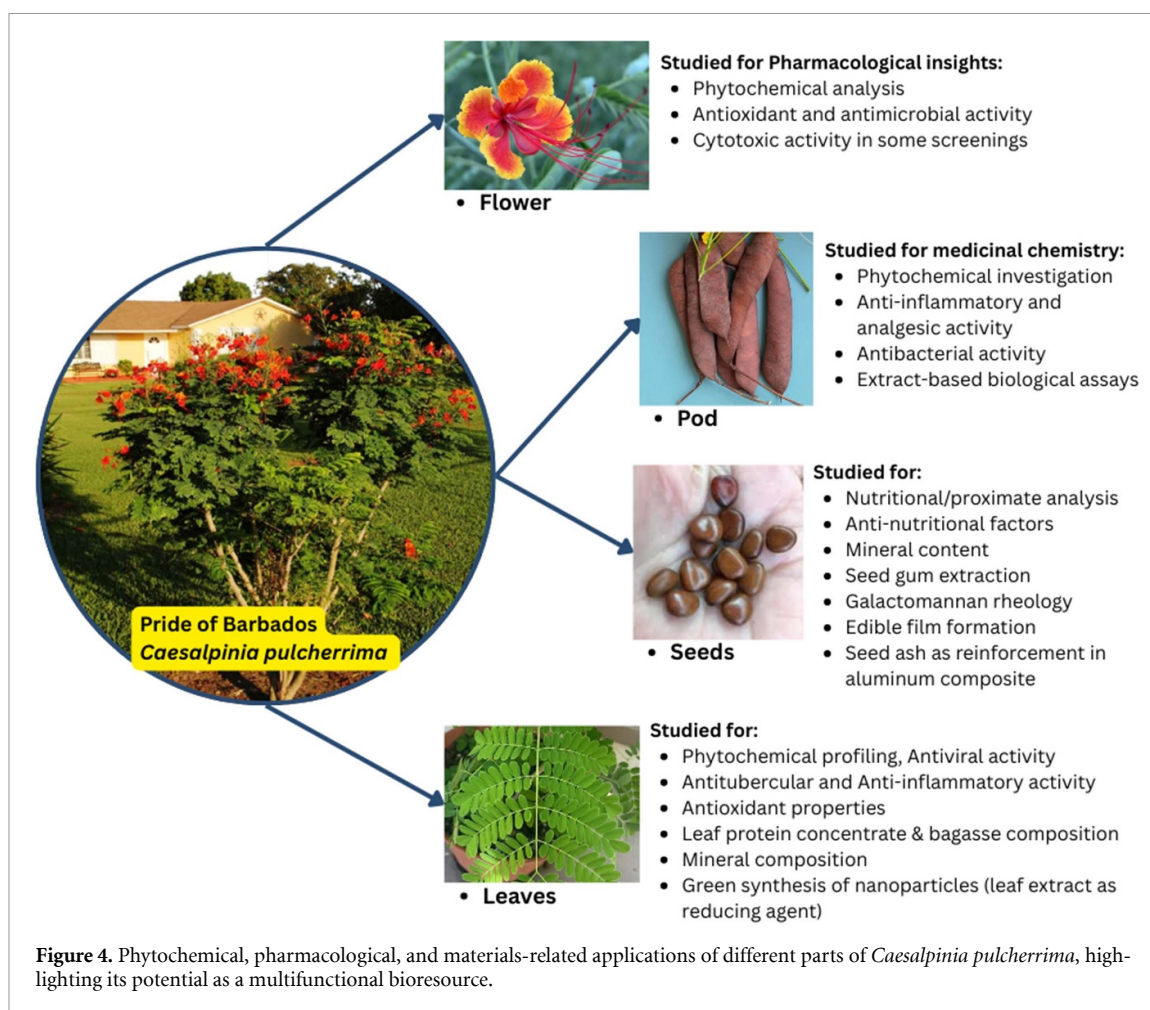
Caesalpinia pulcherrima, also known as Pride of Barbados (figure 4), is an ornamental and medicinal plant whose various parts (flowers, leaves, seeds, bark/root, and pods) have been extensively documented in the literature for diverse functional uses. Beyond its aesthetic value, the plant is consistently described as chemically active, while studies spanning phytochemistry and pharmacology, including antimicrobial and anti-inflammatory properties, as well as broader bifunctionality that has enabled plant-mediated synthesis of functional nanosystems [132, 133]. In parallel, materials-focused investigations of its seed-derived biopolymers have shown that *Caesalpinia pulcherrima* can yield structured biomaterial platforms, such as gums and galactomannans, with tunable rheology, film-forming capacity, and property trade-offs that depend on formulation variables [134, 135].

Having established the functional requirements for reinforcement selection in biomedical MMCs, the CPA is evaluated within the mechanistic framework presented in figure 3. By synthesising existing literature on materials derived from *Caesalpinia pulcherrima* and their ash characteristics, the decision framework is assessed against established biomedical reinforcement criteria. These includes: (i) the chemical composition, phase assemblage, and impurity profile of the ash under controlled processing conditions; (ii) the interaction potential of its multi-oxide chemistry with candidate metallic matrices such as stainless steels, titanium alloys, cobalt-based alloys, and magnesium systems; (iii) the strengthening, load-transfer, corrosion-modification, and bioactivity mechanisms that may arise from its incorporation; and (iv) the mechanical, electrochemical, and biological performance thresholds required for biomedical translation. This structural assessment provides a basis for evaluating whether CPA plausibly satisfies the functional requirements expected of biomedical MMC reinforcements and defines the compatibility conditions required to reposition it as a scientifically justified reinforcement candidate for metallic biomaterials.

4.1. Chemical composition and oxide chemistry

Oxide phases are widely preferred for biomedical reinforcement and surface-functionalization strategies because they are chemically stable in physiological electrolytes, can enhance corrosion resistance by stabilising passive films, and can support biocompatibility or bioactivity depending on composition and structure. This is evident in oxide-based surface systems, where corrosion resistance depends strongly on oxide integrity and microstructural continuity, such as TiO_2 on stainless steel [58] and ceramic zirconia-based layers [136]. In addition, bioactive oxide phases (Ca-P-rich ceramics) are frequently used to improve biological response and surface mechanical properties [63, 137].

Moreover, chemical stability in biomedical MMCs extends beyond the presence of oxides. Trace elements and impurity control are also critical. Reinforcement phases must be free from toxic heavy metals



such as Pb, Cd, or As, and must not introduce electrochemically unstable species that could accelerate galvanic corrosion when embedded in stainless steel, titanium, cobalt, or magnesium matrices. Beyond biomedical metals, broader biomass-to-oxide literature confirms that agricultural residues can yield multi-oxide products (SiO_2 , Fe_2O_3 , TiO_2 , MgO , Al_2O_3 , K_2O) whose functional performance depends on ash chemistry and processing conditions [16, 138].

For *Caesalpinia pulcherrima*, a systematic review of Scopus and Google Scholar datasets shows that several studies have quantified the mineral content of the biomass. These studies describe the *Caesalpinia pulcherrima* plant as chemically active, capable of accumulating alkaline, alkaline-earth, and transition elements that convert to oxide forms upon calcination. Although most studies focus on phytochemical and pharmacological properties [132, 133], mineral profiling across seed and leaf fractions confirms the presence of inorganic constituents that become concentrated in the ash phase after thermal treatment [139–142].

XRF study of CPA processed by controlled incineration (650 °C) reported a silica-dominated oxide system with SiO_2 (91.1 wt.%), accompanied by minor oxides including Al_2O_3 (~5 wt.%), Fe_2O_3 (~1 wt.%), K_2O (~2 wt.%), and CuO (0.34 wt.%), alongside trace constituents [143]. The resulting material exhibited an amorphous silica structure, confirmed by XRD, and contained siloxane (Si–O–Si) and silanol (Si–OH) functional groups, indicating a reactive oxide surface chemistry, confirmed by FTIR results from the study. Furthermore, the morphological features of the ash-derived silica particles were irregular and micron-sized (~1–2 μm), suggesting that load-transfer and interfacial interaction mechanisms would dominate over nanoscale strengthening effects, consistent with [144, 145] and influence passive film behaviour when incorporated into composite systems [146].

From a materials engineering perspective, this composition places CPA within the class of silica-rich, multi-oxide reinforcement systems, rather than as a pure or engineered bioactive ceramic. The high SiO_2

content suggests potential for mechanical reinforcement, passive film stabilisation, and interfacial modification in metallic matrices, while the presence of secondary oxides may influence local electrochemical behaviour and bonding characteristics. Unlike conventional biomedical ceramics such as HA or β -TCP, which are designed for osteoconductivity and controlled degradation, CPA-derived oxides are better interpreted as structural and interfacial modifiers, whose performance depends on dispersion, purity, and interactions with the host matrix. Engineering-level reinforcement evidence reported in [43] further shows that *Caesalpinia pulcherrima* seed ash can function as a particulate phase in aluminium-based hybrid composites, indicating the presence of thermally stable inorganic phases with measurable mechanical and electrochemical responses.

4.2. Comparative positioning of CPA against established biomedical ceramic reinforcements

To contextualise the suitability of CPA as a reinforcement candidate in biomedical metallic systems, it is necessary to compare its oxide chemistry and functional role with established ceramic reinforcements such as silica, HA, β -TCP, and bioactive glass. These materials are widely used in biomedical applications. This is due to their well-defined performance characteristics, including corrosion resistance, bioactivity, osteoconductivity, and controlled degradation behaviour [147].

Silica-based systems, for instance, are recognised for their ability to form HA layers in physiological environments. They also contribute to surface reactivity and corrosion resistance [147, 148]. In contrast, calcium phosphate ceramics such as HA and β -TCP are valued for their direct biological interactions. This includes osteoconduction and controlled resorption during bone regeneration [149, 150].

HA exhibits strong structural similarity to natural bone. This enables excellent biocompatibility and osteoconductive behaviour. However, its relatively low mechanical strength limits its use in load-bearing applications [151]. β -TCP complements this by offering higher biodegradability and controlled dissolution. This allows gradual replacement by natural bone tissue [149].

Bioactive glass systems extend these capabilities further. They promote rapid surface mineralisation and strong interfacial bonding with biological tissues. This behaviour is driven by dissolution and reprecipitation of the silica-calcium-phosphate network [148, 152]. Collectively, these materials show that effective biomedical reinforcements are not defined solely by composition. Their ability to mediate interfacial reactions, ion exchange, and biological integration is equally important.

In comparison, CPA represents a multi-oxide, biomass-derived system in which silica is the dominant phase. CPA contains ~ 91 wt.% SiO_2 , making it a silica-rich material. However, unlike engineered SiO_2 or bioactive glass, CPA retains minor oxide phases that may influence interfacial and electrochemical behaviour. From a chemical standpoint, this composition supports oxide stability and suggests potential for passive film reinforcement in metallic matrices (table 2). However, unlike HA, β -TCP, or bioactive glass, CPA does not possess a well-defined or engineered bioactive composition. Its functional relevance, therefore, lies primarily in reinforcement and interface modification. In this role, oxide stability and surface interactions may enhance corrosion resistance and mechanical performance.

The comparison presented in table 2 further highlights an important distinction. Established ceramic reinforcements have benefited from decades of optimisation in composition, purity, and biological performance. In contrast, CPA remains an under-characterised system in the biomedical context. Although plant-derived constituents of *Caesalpinia pulcherrima* have demonstrated antioxidant, antimicrobial, and cytocompatible behaviour in non-metallic systems [153, 154]. These properties have not been translated or validated within their ash-derived inorganic phase for biomedical applications.

4.3. Phase structure and mineral evolution

In biomedical metal matrix systems, phase structure is critical because crystalline or amorphous states directly influence chemical stability, corrosion behaviour, mechanical interaction, and bioactivity. Oxide phases govern passive film stability in stainless steel and titanium systems, where structural defects can initiate localised corrosion [58]. Likewise, ceramic coatings such as yttria-stabilised zirconia depend on controlled sintering to preserve phase integrity and electrochemical performance [136]. In bioactive reinforcement systems, HA crystallinity influences hardness, solubility, and biological response [63, 137]. Beyond conventional biomedical ceramics, biomass-derived oxide systems yield crystalline or amorphous silica, magnetite, and mixed-oxide phases depending on calcination temperature and precursor chemistry [138]. These precedents demonstrate that phase assemblage and mineral evolution under thermal treatment determine whether a candidate reinforcement phase can function reliably in biomedical environments.

For *Caesalpinia pulcherrima*, direct ash-phase evidence is reported in [143], where calcination at 650°C produced silica-rich ash exhibiting predominantly amorphous structure in XRD analysis. FTIR spectra show Si–O–Si and Si–OH bonding, indicating formation of siliceous oxide networks.

Table 2. Comparative evaluation of CPA and conventional ceramic reinforcements in biomedical systems.

Reinforcement	Primary composition	Dominant functional role	Key strength	Limitation	Relevance to CPA	References
Silica	SiO ₂ (amorphous/crystalline)	Chemical stability. Passive film support, surface reactivity	Promotes hydroxyapatite formation; enhances corrosion resistance	Brittle; limited intrinsic bioactivity	CPA is silica-dominated and aligns closely in oxide stability and surface behaviour	[152, 155]
HA	Ca ₁₀ (PO ₄) ₆ (OH) ₂	Bioactivity, osteoconductivity	Excellent biocompatibility; strong bone bonding	Low mechanical strength for load-bearing use	CPA lacks intrinsic bioactivity; differs in biological function	[156, 157]
β-TCP	Ca ₃ (PO ₄) ₂	Biodegradable scaffold, ion release	Controlled resorption; supports bone regeneration	Faster degradation; limited long-term stability	CPA is more chemically stable but lacks controlled degradation	[148, 158]
Bioglass	SiO ₂ -CaO-P ₂ O ₅ systems	High bioactivity, surface mineralisation	Rapid hydroxyapatite layer formation; strong tissue bonding	Brittle; composition-sensitive dissolution	CPA lacks an engineered bioactive network; may contribute to surface stabilisation	[152, 155]
Other ceramics (e.g., YSZ, Al ₂ O ₃)	ZrO ₂ , Al ₂ O ₃	Wear resistance, structural reinforcement	High hardness and chemical stability	Limited bioactivity; potential interfacial mismatch	CPA may offer a low-cost alternative with multi-oxide interface effects	[158, 159]
<i>Caesalpinia pulcherrima</i> ash	Multi-oxide (SiO ₂ -dominant)	Reinforcement, interface modification	Sustainable; potential corrosion resistance; oxide stability	No validated bioactivity; limited biomedical data	Candidate system requiring mechanistic and biological validation	[153, 154]

Mineral profiling across seed and leaf fractions further indicates the presence of calcium-, magnesium-, potassium-, and iron-associated constituents [139–142]. Upon controlled incineration, these elements are expected to convert into corresponding oxide phases (e.g. CaO, MgO, Fe₂O₃), indicating that CPA is likely a multi-oxide system rather than a purely silica material. Additionally, engineering composite evidence suggests that CPA can survive metallurgical processing without structural collapse [43]. This observation indirectly supports the phase stability at elevated temperatures. However, systematic crystallographic quantification of ash-phase assemblage under biomedical processing routes remains limited.

4.4. Morphology, particle size, and density

Particle morphology, size distribution, and surface characteristics are critical in biomedical MMCs because they govern load-transfer efficiency, interfacial bonding, dispersion stability, and corrosion localisation. In oxide-reinforced biomedical systems, nano- or micron-scale ceramic phases influence hardness, surface integrity, and biological response depending on particle architecture [63, 137]. Surface topography and coating morphology directly influence adhesion and electrochemical stability in metallic implants [130]. Similarly, porosity and microstructural heterogeneity have been linked to corrosion initiation and accelerated degradation in additively manufactured stainless steel [53]. In biomass-derived systems, oxide nanoparticles and micron-scale siliceous structures obtained from agricultural residues demonstrate morphology-dependent functionality in catalytic and composite applications [138]. This evidence establishes that particle geometry, surface structure, and dispersion potential are fundamental determinants of reinforcement performance in biomedical metallic environments.

Literature study has shown that *Caesalpinia pulcherrima*-derived ash exhibits irregularly shaped particles with sizes ranging from approximately 1–2 μm, as observed by SEM [143]. The XRD and FTIR results indicate that these particles represent consolidated oxide residues following organic burnout.

The micron-scale dimension of CPA places it within the typical size range of particulate reinforcements used in composite systems. Engineering validation further shows that these ash particles can be incorporated into metallic matrices during stir casting, indicating structural persistence during processing [43]. Although detailed particle-size distribution and surface-area measurements specific to CPA are not extensively reported in the literature, available evidence suggests the formation of thermally stabilised, irregular micron-scale oxide particulates that may possess mechanical interlocking potential when embedded in metallic systems.

4.5. Thermal stability and processing compatibility

Thermal stability is a core requirement for reinforcement phases intended for biomedical MMCs, as fabrication routes such as powder metallurgy, casting, additive manufacturing, and surface modification expose materials to elevated temperatures and thermal cycling. Reinforcements must retain phase integrity and avoid producing deleterious reaction products that weaken interfaces or compromise corrosion resistance. In oxide-based biomedical systems, corrosion protection and adhesion depend strongly on maintaining structurally continuous and defect-controlled oxide layers, as shown for TiO₂-based surface protection [58] and zirconia-based ceramic coatings [136]. Similarly, the thermal history influences crystallinity and functional response in Ca–P bioactive systems [63, 137]. In biomass-derived oxide streams, thermal treatment governs mineral evolution and residual carbon removal, producing silica- or multi-oxide phases with processing-dependent stability [138]. These studies support the need to evaluate reinforcement candidates not only by composition but by their ability to remain stable under realistic manufacturing conditions.

Findings related to *Caesalpinia pulcherrima* residues indicate direct evidence of controlled calcination behaviour, reporting ash generation through incineration for variable durations and noting low residual carbon under optimised conditions. The resulting oxide-rich products remain stable during alkaline extraction and acid precipitation, retain siliceous functional groups, and indicate the formation of a thermally consolidated inorganic network. Additionally, the literature indicates that *Caesalpinia pulcherrima* seed ash can withstand metallurgical processing and serve as a particulate reinforcement phase [43]. The ash served as a particulate phase in a metallic composite, leading to measurable changes in its properties. These findings indicate that *Caesalpinia pulcherrima*-derived ash can withstand moderately high-temperature processing without complete degradation of its oxide structure. However, systematic data on high-temperature phase transitions, thermal expansion behaviour, and interfacial reaction products of CPA under biomedical alloy processing routes are limited in the literature.

4.6. Impurity profile and leachability risk

Impurity control and ion-release behaviour are critical in biomedical MMCs because implants operate in electrolyte-rich physiological environments where even trace elements may dissolve and interact with surrounding tissues. Localised corrosion, passive film instability, and adverse biological responses have been associated with metal ion release and electrochemical heterogeneity [84, 160]. Surface defects, compositional heterogeneity, and environmental interactions can accelerate degradation processes [53, 86]. In biomass-derived oxide systems, thermal processing concentrates mineral constituents, producing multi-oxide ashes whose impurity spectrum depends on plant uptake and soil chemistry [138]. Therefore, beyond primary oxide composition, trace elements and leachability characteristics must be assessed before any biomass-derived ash can be considered for biomedical reinforcement applications.

Studies on *Caesalpinia pulcherrima* report measurable elemental constituents within the seed and leaf fractions, indicating the presence of mineral species that convert to oxides upon calcination [139, 142]. Silica-rich inorganic residue, with reduced residual carbon, has been reported under optimised thermal conditions [143]. However, detailed trace-element quantification relative to biomedical safety thresholds, as well as systematic ion-leaching studies in simulated physiological media, remain largely unreported. This represents a critical gap that must be addressed before CPA can be considered for biomedical MMC application.

5. Reinforcement criteria assessment and matrix compatibility framework

This section builds on the findings established in section 4 regarding the physicochemical characteristics of *Caesalpinia pulcherrima*-derived ash, including its silica-rich oxide chemistry, amorphous XRD response, and micro-scale particle morphology. The CPA is evaluated against biomedical reinforcement decision criteria, and a matrix-compatibility framework is developed for stainless steels, titanium alloys,

cobalt-based alloys, and magnesium systems. Benchmark reinforcement logic from established oxide systems is used to define decision thresholds and compatibility expectations.

5.1. Chemical and thermodynamic compatibility

In evaluating CPA against established biomedical reinforcement criteria, the first screening dimension concerns chemical composition, phase assemblage, and impurity profile under controlled processing conditions. Oxide phases are widely preferred in biomedical metallic systems due to their chemical stability, passivity, and relative biological tolerance. The corrosion-protection role of TiO₂ films on 316L [58], together with the improved performance of YSZ-coated stainless steel [136] and HAp-modified surfaces [63]. It demonstrates that stable oxide systems can improve corrosion resistance while maintaining biocompatibility. Similarly, biowaste-derived ceramic phases, such as HA, can be synthesised from eggshell [137]. This reinforces the broader principle that oxide-based reinforcements are chemically favourable in physiological environments when phase purity and interfacial integrity are controlled.

Available evidence indicates that CPA-derived ash contains a silica-rich fraction, with reported SiO₂ contents ranging from 73 to 95 wt.% depending on processing conditions [143]. XRD patterns show predominantly amorphous structures, while SEM analysis reveals irregular micron-scale particles. Earlier compositional studies of the plant and its residues suggest that the biomass contains mineral elements that can concentrate into oxide phases upon calcination [139–141]. These observations establish the chemical plausibility of CPA as an oxide-bearing reinforcement candidate.

From a thermodynamic standpoint, silica-rich oxides are chemically stable in neutral physiological media and are unlikely to undergo rapid dissolution under passive conditions. However, unlike biomedical-grade oxides such as TiO₂ or YSZ, CPA has not undergone systematic quantification of trace impurities, heavy-metal screening, or leachability assessment in SBFs. Thus, while its bulk oxide chemistry satisfies phase stability criteria, its impurity profile remains insufficiently characterised for safety-critical applications.

With respect to interaction potential with metallic matrices, the multi-oxide chemistry of CPA suggests possible compatibility with passive metals such as stainless steel and titanium, where oxide-oxide interfacial continuity could theoretically be maintained. In contrast, for reactive systems such as magnesium, local alkalinisation and galvanic coupling risks require validation. This is particularly important given the highly negative standard electrode potential of magnesium (−2.37 V vs SHE), which makes it anodic relative to most oxide and ceramic phases, thereby increasing susceptibility to galvanic corrosion in multiphase systems under physiological conditions [118, 119]. At the level of chemical and thermodynamic screening, CPA satisfies the oxide-stability plausibility criterion but does not yet meet impurity control and leachability requirements necessary for biomedical qualification. Further controlled calcination studies, trace element analysis, and simulated physiological exposure testing are required before definitive classification as a chemically compliant reinforcement candidate can be made.

5.2. Mechanical compatibility

The CPA was assessed for mechanical compatibility, specifically modulus alignment, load-transfer plausibility, and thermal expansion coherence with candidate metallic matrices. Biomedical metals such as stainless steel (~190–200 GPa), cobalt-based alloys (~210–230 GPa), and titanium alloys (~100–120 GPa) exhibit elastic moduli significantly higher than cortical bone (5–30 GPa), leading to stress shielding concerns [64, 81]. Magnesium-based systems (~40–45 GPa) are closer to bone but suffer from rapid degradation and strength limitations [94, 161].

Reinforcement strategies in biomedical MMCs, therefore, aim either to enhance strength without excessive stiffness increase or to tailor effective modulus through controlled particulate incorporation. From a compositional standpoint, silica-rich oxides are inherently stiff phases (SiO₂ modulus typically >60–70 GPa in bulk form), suggesting that CPA particulates could contribute to load transfer when well bonded within a metallic matrix. The reported micron-scale morphology (1–2 μm) [143] indicates that classical load-transfer strengthening would dominate rather than the nanoscale Orowan mechanism. However, the absence of direct modulus measurements for calcined CPA and of interfacial shear strength data prevents a quantitative prediction of reinforcement efficiency.

Thermal expansion mismatch between oxide particles and metallic matrices may introduce residual stresses during processing, particularly in stainless steel and cobalt systems, where coefficient mismatch may promote interfacial decohesion if bonding is weak. Thus, while CPA satisfies the theoretical

load-bearing criterion of possessing a stiffer oxide phase relative to magnesium and potentially comparable stiffness relative to bone, its mechanical compatibility remains inferential rather than experimentally validated.

When briefly related to candidate matrices, stainless steel and cobalt alloys can exhibit strength enhancement with modest modulus variation when CPA volume fraction is controlled, but embrittlement risk may arise from particle clustering. Titanium alloys may tolerate oxide reinforcement provided fatigue resistance is preserved. Magnesium systems may benefit from strength augmentation; however, particle-induced stress concentrations may accelerate localised corrosion if mechanical integrity is compromised. At the level of mechanical screening, therefore, CPA demonstrates conceptual plausibility under a load-transfer framework but lacks quantitative modulus, fracture toughness, and fatigue-interface validation required for biomedical applications.

5.3. Corrosion and electrochemical compatibility

The CPA was assessed for corrosion and electrochemical compatibility, specifically galvanic stability, passive film interaction, and local chemical environment modification under physiological conditions. Biomedical metallic systems rely on surface passivation for durability. Stainless steel depends on a stable Cr_2O_3 layer, titanium alloys on TiO_2 , and cobalt-based alloys on mixed oxide films, while magnesium systems degrade through active anodic dissolution [53, 58, 161]. Reinforcement phases introduced into these matrices must therefore neither destabilise passive films nor create galvanic microcells that accelerate localised corrosion.

Available physicochemical evidence indicates that CPA contains silica-rich oxide phases that are chemically inert in neutral aqueous environments. In principle, silica and other stable oxides can act as corrosion barriers when properly integrated, as demonstrated by ceramic surface reinforcement strategies such as YSZ and HAp coatings [63, 136]. However, unlike engineered coatings with controlled density and adhesion, CPA has not been evaluated for electrochemical behaviour in SBF or phosphate-buffered saline (PBS). The presence of trace mineral elements [139, 140] introduces uncertainty regarding galvanic coupling potential, particularly if residual metallic impurities remain after calcination.

Without electrochemical impedance spectroscopy, potentiodynamic polarisation, or ion release studies, the corrosion-modification mechanism remains hypothetical. When considered across matrices, stainless steel and cobalt alloys require assurance that CPA does not disrupt passive film continuity or increase pitting susceptibility under chloride exposure, especially given the pore-sensitivity documented in additively manufactured 316L [53]. Titanium systems may tolerate oxide inclusions if interfacial stability is preserved, but surface discontinuities could impair repassivation kinetics. Magnesium matrices exhibit the greatest electrochemical sensitivity; embedded oxide particulates can either locally buffer alkalization or, conversely, intensify galvanic differentials, depending on impurity chemistry. At the level of electrochemical screening, CPA demonstrates theoretical plausibility as a corrosion barrier based on its oxide stability, but lacks direct physiological corrosion testing, ion release profiling, and galvanic interaction studies necessary to meet biomedical electrochemical performance thresholds.

5.4. Strengthening pathways

The CPA was evaluated against the mechanistic reinforcement criteria, including load transfer, dislocation interaction, grain refinement, corrosion-barrier contribution, and potential bioactivity effects. In biomedical MMCs, strengthening is typically achieved through one or more mechanisms: (a) direct load transfer from matrix to stiffer reinforcement, (b) Orowan strengthening via dislocation bypass around fine particles, (iii) grain refinement through heterogeneous nucleation or deformation-induced microstructural control, and (iv) surface biofunctional modification when oxide phases interact with physiological media.

Based on reported morphology, *Caesalpinia pulcherrima*-derived silica particles are predominantly micron-scale and irregular [143]. At this scale, load-transfer strengthening is the dominant plausible mechanism rather than Orowan looping, which is more effective at the nanoscale. If adequate interfacial bonding is achieved, the inherent stiffness of silica-rich oxides could allow partial redistribution of stress from the metallic matrix to the reinforcement phase. However, reinforcement efficiency would depend strongly on particle dispersion, volume fraction, and interfacial shear strength—parameters that have not yet been quantified for CPA in biomedical systems. Without controlled particle-size refinement or surface modification, clustering could negate the strengthening benefits and introduce stress-concentration sites.

Microstructurally, oxide particulates can act as heterogeneous nucleation sites during solidification or thermochemical processing, potentially contributing to grain refinement. Grain refinement has been

shown to improve mechanical strength and corrosion resistance in magnesium systems subjected to processing refinement [96, 104]. This suggests that particulate-assisted microstructural control could be beneficial if properly engineered. Whether CPA can serve as an effective nucleation catalyst, however, remains untested and requires experimental verification. In addition to mechanical strengthening, oxide phases may contribute to corrosion-barrier effects and modulate surface bioactivity.

Silica-based systems have been explored in biomedical contexts for their potential involvement in apatite formation and surface reactivity [138]. Though such functionality is strongly dependent on surface chemistry and controlled dissolution kinetics. For CPA specifically, no studies have yet demonstrated apatite-forming ability, antibacterial durability, or cytocompatibility under physiological exposure.

From a performance standpoint, reinforcement-driven strengthening in oxide- and ceramic-based systems is typically reflected in measurable improvements in hardness, compressive strength, and wear resistance. For example, silica-rich and ceramic-reinforced biomaterial systems have demonstrated hardness improvements in the range of 20%–50%, compressive strength values within the trabecular bone region (~ 4 –15 MPa), and enhanced resistance to wear and surface degradation depending on reinforcement dispersion and volume fraction [34, 35, 118]. In Mg-based composites, reinforcement with HA and related ceramic phases has also been associated with improved strength retention and reduced degradation-induced mechanical loss [119]. These trends suggest that, if appropriately engineered, CPA may similarly contribute to strength enhancement and surface stability. However, the magnitude of such improvements remains contingent on interfacial bonding, particle distribution, and processing control. Thus, while CPA satisfies conceptual strengthening mechanisms under the load-transfer and grain-refinement framework, its mechanical efficiency and biofunctional contribution remain unvalidated.

6. Translational outlook and future directions for agro-waste reinforcements in biomedical MMCs

The comparative matrix compatibility assessment summarised in table 3 demonstrates that reinforcement viability is matrix-dependent and performance-threshold driven. The table positions CPA within a conditional compatibility landscape across stainless steel, titanium, cobalt-based, and magnesium systems. Compatibility is not uniform; it varies with passive film behaviour, galvanic susceptibility, modulus alignment, and interface stability. While chemical plausibility is evident, particularly in matrices governed by passive-oxide stability, gaps in mechanical, electrochemical, and biological validation persist across all systems. The assessment criteria established in this study (section 4), therefore, shift the discussion from compositional feasibility to translational readiness. This section further evaluates the biomedical performance outlook of CPA based on current evidence. It extends the reinforcement-selection framework to other agro-waste ashes with similar oxide-phase characteristics. The translation gaps and priority validation pathways required to progress from chemical plausibility to biomedical qualification are also identified.

6.1. Biomedical performance outlook and translational gap

The screening assessment suggests that CPA satisfies several preliminary oxide-based plausibility criteria for biomedical metal-matrix composite reinforcement. However, it remains unvalidated against performance thresholds required for clinical translation. In biomedical applications, modulus mismatch between metallic implants and bone remains a primary driver for reinforcement engineering. Stainless steel and cobalt alloys exhibit elastic moduli far exceeding those of cortical bone [64, 81], leading to stress shielding and long-term bone resorption. Titanium alloys partially mitigate this mismatch, while magnesium systems offer closer modulus alignment but suffer from rapid degradation [94, 161]. Incorporation of oxide particulates, such as CPA, could enhance strength through load transfer without significantly increasing bulk stiffness if the volume fraction and dispersion are controlled. However, without quantified elastic modulus, fracture toughness, and fatigue-interface data for CPA-metal systems, the influence of CPA on stress redistribution remains inferential.

Wear resistance and surface integrity are equally critical in orthopaedic and dental applications. Surface degradation under cyclic loading can accelerate passive film breakdown and ion release, particularly in stainless steel systems where pore-driven corrosion has been documented [53]. Oxide-based reinforcement strategies, such as YSZ and HAP coatings, have demonstrated improvements in hardness and surface stability [63, 136]. The CPA may serve as a conceptual surface-functional reinforcement candidate if integrated into hybrid or graded MMC systems. However, no tribological or nanoindentation studies have been conducted in biomedical matrices, leaving wear-performance implications undefined.

Table 3. Comparative matrix compatibility assessment of *Caesalpinia pulcherrima* ash as a biomedical MMC reinforcement candidate.

Criterion	Stainless steel (316L)	Titanium alloys	Cobalt-based alloys	Magnesium systems	Validation gap
Chemical stability & phase compatibility	Likely compatible with passive Cr ₂ O ₃ film if impurities are controlled; risk of pitting if trace elements disrupt passivity [53, 58]	Oxide–oxide interface plausible with TiO ₂ passive layer; chemical inertness favourable [58, 136]	Similar passive oxide logic as stainless steel; impurity-induced localised corrosion must be excluded [82, 85, 160]	High sensitivity to local chemistry; oxide inclusion may alter local pH and galvanic balance [94, 95, 161]	No biomedical-grade trace impurity quantification; no leachability testing in SBF/PBS
Mechanical compatibility (modulus & load transfer)	Potential strength enhancement; minimal modulus tailoring unless volume fraction optimised [64, 81]	May enhance strength; fatigue interface behaviour must be validated [67–69]	High stiffness matrix; risk of embrittlement if dispersion is poor [79–81]	Could improve strength; stress concentration risk under rapid degradation [94, 161]	No modulus measurement of ash; no interfacial shear data; no fatigue validation
Thermal & interfacial compatibility	Thermal expansion mismatch may induce residual stresses during processing	Oxide compatibility is thermodynamically plausible; bonding behaviour is unknown [58, 136]	Similar CTE concerns as stainless steel; interfacial reaction data are absent [91, 130]	CTE mismatch + active corrosion could destabilise the interface	No coefficient of thermal expansion data; no interfacial reaction studies
Corrosion & electrochemical interaction	Must not disrupt passive film; porosity sensitivity documented [53, 58]	Should preserve TiO ₂ repassivation; surface continuity critical [71, 72]	Passive film stability required; impurity-driven microcells possible [82, 83]	Highest galvanic risk; rapid degradation sensitivity [94, 95, 161]	No EIS, polarisation, ion-release, or galvanic coupling studies
Expected strengthening mechanisms	Classical load transfer dominant; clustering risk [22]	Load transfer plausible; limited Orowan unless refined	Similar to stainless steel; dispersion critical	Load transfer + possible grain refinement benefit [96, 104]	No experimental strengthening study in biomedical matrices
Bioactivity & biological interaction potential	No direct bioactivity evidence; surface modification required	Possible silica-related surface reactivity; untested [125]	No direct evidence; cytocompatibility unknown [83–85]	Must avoid toxic ion synergy during degradation [95, 106]	No cytocompatibility, antibacterial, or apatite formation data

Electrochemical performance remains the most significant translational uncertainty. In passive metals, long-term corrosion resistance depends on film stability and resistance to chloride-induced pitting [53, 58]. In magnesium systems, degradation kinetics directly influence biocompatibility and hydrogen evolution [161]. Although CPA exhibits silica-rich oxide stability [143], its behaviour under physiological immersion, particularly with respect to ion release, galvanic interaction, and local pH modification, has not been systematically investigated. Without electrochemical impedance spectroscopy, polarisation analysis, and controlled leachability profiling, the corrosion-modification potential of CPA remains hypothetical.

Biological performance considerations introduce further translational requirements. Successful biomedical reinforcement must demonstrate cytocompatibility, absence of toxic leachables, and, where applicable, osteogenic or antibacterial functionality. Biowaste-derived oxides, such as HA synthesised from eggshell, demonstrate that sustainable mineral sources can support positive cell viability and bioactivity when properly processed [137]. However, for CPA, no *in-vitro* cytotoxicity, antibacterial durability, or apatite-forming ability studies have been reported in the literature. Thus, while the botanical origin and phytochemical profile of the *Caesalpinia pulcherrima* suggest bioresource richness [139], biological safety cannot be inferred from plant chemistry alone, it must be experimentally validated.

Therefore, the biomedical performance outlook for CPA is promising but experimentally limited. It satisfies oxide-stability plausibility and conceptual strengthening logic, but does not yet meet the mechanical, electrochemical, and biological performance thresholds required for translation into load-bearing or long-term implant systems.

6.2. Implications for other agro-waste ashes and their prospect as reinforcement in biomedical MMCs

Although this review centres on CPA, the reinforcement-selection framework developed in this study is applicable to other agro-waste ashes that are increasingly appearing in biomedical composite research. Recent studies demonstrate that biomass-derived silica, calcium-rich ashes, and hybrid oxide systems

Table 4. Influence of processing conditions of agro-waste ash composition and biomedical relevance.

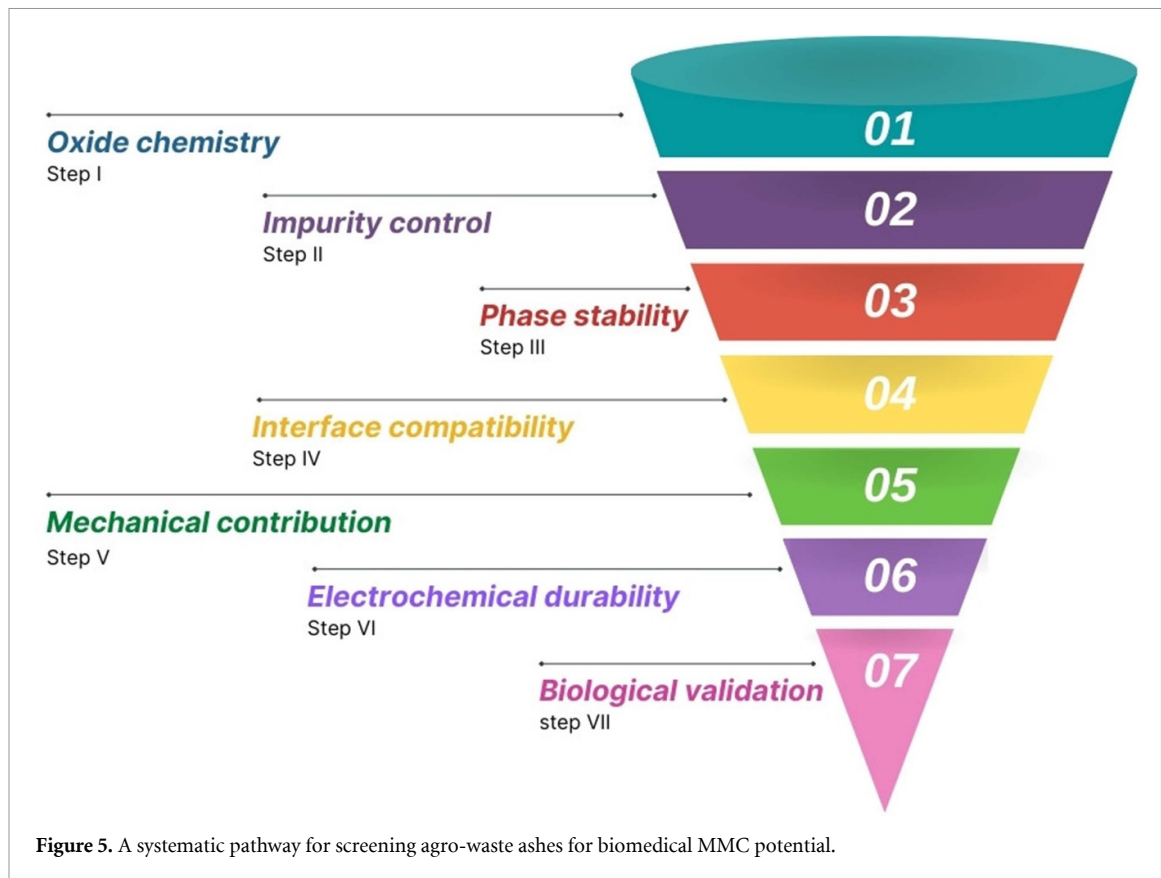
Ash type	Processing/calcination conditions	Dominant phase/output	Biomedical relevance	References
Rice husk ash	~600 °C calcination	Amorphous SiO ₂	Silica nanoparticles for bone scaffolds; bioactive and biocompatible	[163]
Eggshell ash	~800 °C calcination	CaO → HAp precursor	Used in hydroxyapatite synthesis for bone regeneration	[137]
Cocoa bean shell	Thermal treatment (carbonisation, not strictly calcined)	Carbon-rich biofiller	Reinforcement in biodegradable polymer biomaterials	[33]
Bermuda grass ash	Burning + alkaline fusion (70 °C) + hydrothermal (100 °C) + drying (150 °C)	Biosilica (processed SiO ₂)	Improves the mechanical and tribological behaviour in Mg systems	[124]
Cockle shell ash	800 °C–900 °C calcination	CaO	Biomedical CaO precursor; optimal at ~900 °C	[164]
Tilapia fish bone ash	800 °C–1000 °C calcination	Hydroxyapatite	Bone substitute; dense structure at ~1000 °C	[165]
Limestone-derived HAp	700 °C–1100 °C calcination	Hydroxyapatite	Implant coatings; lower temp improves antibacterial behaviour	[166]

can be engineered into implant-relevant composites when their chemistry, phase stability, and degradation behaviour are explicitly validated under physiological conditions. For instance, RHA -derived silica combined with HA in polymeric scaffolds achieved trabecular-bone-relevant porosity and compressive strength while maintaining near-neutral pH during immersion testing [34]. This observation indicates that waste-derived silica can transition from an environmental residue to a mechanically contributing biomedical phase, provided that dissolution kinetics and mechanical windows are controlled.

Similarly, controlled incorporation of bio-silica into composite systems has shown that filler loading strongly influences water uptake, porosity, and mechanical integrity [162]. These findings reinforce an important translation principle: that oxide presence alone is insufficient; reinforcement performance depends on phase dispersion, interface continuity, and a balance of degradation. This directly supports the criteria-based evaluation model proposed in this review. Furthermore, calcium-rich agro-waste residues have also demonstrated biomedical viability when processed into HA or CaP-based systems. Eggshell-derived CaO converted into nano- HA and embedded in chitosan matrices improved compressive strength, corrosion stability, and cell viability for orthopaedic applications [137]. Likewise, sustainable calcium-phosphate systems sourced from shells and agricultural residues are increasingly discussed as feedstocks for additive manufacturing of bone scaffolds [116]. These examples show that agro-waste residues become viable biomedical reinforcements not by virtue of origin, but by satisfying chemical purity, phase stability, and biological performance thresholds.

Importantly, the oxide composition of agro-waste-derived ashes is not intrinsic, but strongly dependent on processing conditions, particularly calcination temperature and pre-treatment. As shown in table 4, different agro-waste sources exhibit distinct phase evolution pathways under thermal exposure. For example, RHA calcined at ~600 °C retains predominantly amorphous silica suitable for biomedical applications, whereas calcium-rich sources such as cockle shell and eggshell require higher temperatures (~800 °C–900 °C) to form stable CaO or HA phases. In contrast, Bermuda grass-derived biosilicate follows a non-conventional route involving controlled burning, alkaline fusion, and hydrothermal processing rather than direct high-temperature calcination, highlighting that processing pathways can vary significantly depending on feedstock chemistry [124]. These variations demonstrate that ash composition, crystallinity, and impurity profile are inherently processing-dependent, and therefore must be treated as controllable variables in reinforcement design rather than fixed material properties. Consequently, the applicability of any agro-waste ash, including *Caesalpinia pulcherrima*, depends not only on its inherent composition but also on how it is processed, purified, and integrated into the composite system.

Beyond calcium systems, broader surveys of biomass-assisted nanostructures show that agricultural residues can yield amorphous SiO₂, Fe₃O₄, MnO₂, TiO₂, MgO, and Al₂O₃ phases with tunable nano-architectures [138]. Although many of these studies emphasise catalytic or adsorptive applications, the underlying oxide-phase logic aligns with established biomedical coating and reinforcement strategies (e.g. TiO₂, YSZ, HAp systems), suggesting that properly purified and characterised agro-waste oxides could be used in hybrid metallic biomaterials. More importantly, some biomedical-oriented composite studies



demonstrate that agro-waste-derived fillers can contribute to mechanical reinforcement without catastrophic degradation when interface design and porosity are controlled [63, 136]. These reinforce the idea that reinforcement success depends on: (i) chemical stability of the oxide phase, (ii) controlled interfacial bonding, (iii) absence of toxic trace elements, and (iv) stability of passive films under physiological conditions.

Agro-waste residues can be converted into biomedical composite systems by processing them into chemically stable oxide phases and validating the resulting materials using mechanical, electrochemical, and biological testing protocols. However, most agro-waste studies remain in either polymer scaffold systems or surface coating formats rather than in bulk load-bearing metallic MMC architectures. While this reveals a translational opportunity, from a materials engineering perspective, the transition from structural MMC applications to biomedical MMC systems requires an additional validation layer: (i) ion-release profiling in SBFs, (ii) cytotoxicity and hemocompatibility testing, (iii) long-term electrochemical stability, and (iv) galvanic interaction assessment with metallic substrates. Figure 5 provides a logical pathway for agro-waste ash reinforcement-based studies to adopt, rather than a trial-based approach. The implication, therefore, is that agro-waste residues that satisfy these sequential gates (figure 5) may transition from low-value biomass ash to scientifically justified reinforcement candidates in metallic biomaterials.

6.3. Translational gaps and priority validation for CPA

Unlike several agro-waste-derived silica and calcium systems that have progressed to scaffold fabrication, corrosion testing, and cytocompatibility assessment [34, 116, 137], CPA remains limited to compositional characterisation and isolated hybrid composite observations [43, 143]. From a materials engineering perspective, the following critical gaps remain:

- *Chemical and impurity validation:* Although bulk oxide composition has been reported, biomedical-grade trace impurity quantification, ion-release kinetics, and long-term dissolution stability under physiological conditions are undocumented.
- *Interface and matrix compatibility:* No direct interface characterisation exists for CPA incorporated into stainless steel, titanium, cobalt, or magnesium matrices. Reaction-layer formation, galvanic interaction risks, and passive-film stability remain limited.

- *Mechanical qualification*: There are no fatigue, fracture, or modulus-tuning studies for CPA -reinforced metallic systems under physiologically relevant loading conditions.
- *Electrochemical durability*: There are no published data on long-term corrosion performance in SBFs, particularly under cyclic or stress-assisted conditions, nor are there galvanic interaction maps with stainless steel, titanium, cobalt, or magnesium matrices.
- *Biological screening*: Cytotoxicity, hemocompatibility, inflammatory response, and antibacterial durability data are absent for CPA in metallic composites.

These gaps indicate that CPA has not yet progressed from chemical characterisation toward performance-qualified biomedical reinforcement status. The absence of integrated validation is particularly striking given the accelerating momentum in sustainable materials engineering. Agro-waste research has established applications in structural MMCs, cementitious systems, adsorption technologies, and bio-silica scaffold fabrication. However, the transition into metallic biomedical MMC systems remains underexplored, despite strong chemical and sustainability justifications.

7. Conclusion

This review set out to evaluate whether CPA plausibly satisfies the functional requirements expected of biomedical metal-matrix composite reinforcements. To achieve this, the study systematically examined its physicochemical characteristics, assessed its compatibility against established reinforcement-selection criteria, and analysed its translational readiness within broader agro-waste biomedical contexts. By integrating compositional data, mineralogical reports from the phytochemical literature, and comparative insights from oxide-based biomedical systems, the review developed a structured decision framework that links oxide chemistry interface compatibility, mechanical contribution, electrochemical stability, and biological validation thresholds. Based on available evidence, the CPA satisfies chemical validation criteria: it exhibits oxide-bearing composition, silica-rich fractions, and phase characteristics that are conceptually aligned with established bioactive or corrosion-resistant oxide systems. However, it does not yet satisfy mechanical, electrochemical, and biological performance thresholds required for translation into load-bearing or long-term biomedical metallic composites.

This principal limitation lies not in compositional promise but in the absence of integrated experimental validation across interface stability, corrosion behaviour in simulated physiological media, fatigue reliability, ion-release profiling, and cytocompatibility assessment. Therefore, while *Caesalpinia pulcherrima* indicates potential as a reinforcement candidate in biomedical MMCs, its ash content still requires extensive experimental validation as a reinforcement-based engineering material. The reinforcement-selection framework developed in this study can be used to screen other agro-waste ashes for biomedical MMC applications. By progressing systematically from oxide chemistry to impurity control, interface evaluation, mechanical qualification, electrochemical durability, and biological confirmation, sustainability-driven materials research can move beyond compositional reporting toward performance-based biomedical validation. The larger implication is that agro-waste residues with stable oxide fractions may hold untapped potential in advanced metallic biomaterials, provided that they are subjected to rigorous, criteria-aligned evaluation. Future investigations should therefore prioritise integrated validation pathways that align sustainable resource utilisation with the scientific standards required for biomedical deployment.

Data availability statement

The data cannot be made publicly available upon publication because no suitable repository exists for hosting data in this field of study. The data that support the findings of this study are available upon reasonable request from the authors. No new data was generated in the study.

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Conflict of interest

The authors confirm the absence of any financial or personal interests that could have affected the findings presented in this research.

Ethical statement

This study is a review article and does not involve human participants or animal experiments. All images used are schematic representations; therefore, ethical approval was not required.

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