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Review

Sustainable Stabilizer Derived from Calcium- and Phosphorus-Rich Biowaste for Remediation of Heavy Metal-Contaminated Soil: A Critical Review

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Abstract: Soil pollution by heavy metals (HMs) is a major environmental problem around the world. The addition of biowaste-based stabilizers for HM remediation has recently gained attention due to its relatively low cost and eco-risk, abundance, ease of operation, and quick remediation results. Among these stabilizers, shell (crustacean shell, bivalve shell, and eggshell), starfish, and bone-based stabilizers are particularly attractive because of their high Ca and P contents, allowing for highly efficient HM immobilization and simultaneous supplement of nutrients to the soil. However, a comprehensive review focusing on these stabilizers is currently missing. Therefore, this review attempts to summarize the HM immobilization efficiency of these stabilizers and the mechanisms associated with HM stabilization, and perform an operation cost estimation and cost comparison. Cost comparisons among different stabilizers are widely ignored in reviews due to the lack of reliable cost estimation tools or methods. However, for practical application in soil remediation, cost is one of the most important factors to consider. Thus, a simple but reasonable cost estimation method is developed and discussed in this review. Bivalve shell-based stabilizers demonstrated the most promising results for the immobilization of soil HMs in terms of higher performance and lower cost. Current research limitations, challenges, and recommendations regarding possible future research directions are also provided.

Keywords: heavy metals; stabilizer; biowaste; soil remediation; shell; starfish; bone; cost estimation

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Citation: Datta, D.K.; Biswas, T.; Castonguay, E.; Ni, P. Sustainable Stabilizer Derived from Calcium- and Phosphorus-Rich Biowaste for Remediation of Heavy Metal-Contaminated Soil: A Critical Review. *Sustainability* **2024**, *16*, 8841. https://doi.org/10.3390/su16208841

Academic Editors: Hongbiao Cui, Ru Wang, Yu Shi, Haiying Lu and Lin Chen

Received: 30 June 2024
Revised: 17 September 2024
Accepted: 10 October 2024
Published: 12 October 2024

1. Introduction

Soil contamination by heavy metals (HMs), including Pb, Zn, Cu, Cd, Cr, Ni, Hg, As, and Sb, is a serious threat to food systems, human health, and environmental safety [1–6]. Accelerated industrialization and urbanization due to the ever-growing population have made HM-induced soil contamination an even more critical global concern [6–10]. According to Tu et al. (2020) [11], more than 100,000 sites in the United States are suffering from HM contamination. In Europe, 37.3% of total contaminated land sites are affected by HMs, whereas the fraction is as high as 80% in China [12]. The persistence of HMs in these contaminated sites can destroy soil health and deplete soil resources [13]. For example, HMs can alter the diversity of microbial communities and their enzyme activity, leading to disturbances in soil nutrient cycling, reduced bioavailability of nutrients, and, ultimately, the degradation of soil health [14,15]. Moreover, mobile forms of HMs in soil can accumulate in plants and leach into the groundwater, which poses the risk of HM exposure to humans through the food chain and drinking water sources [4,15,16]. Such factors reinforce the need to immediately treat HM-contaminated soils to ensure food security and both human and environmental health safety.

Throughout the past two decades, various techniques have been investigated for HM soil remediation, such as phytoremediation, extraction, sorption, oxidation, electrochemical treatment, and chemical leaching [13,17–19]. These treatments can be divided into two groups based on the setting required for their application: ex situ and in situ HM remediation [20]. Ex situ HM treatment requires the removal of the surface and subsurface soil, which is both costly and destructive for soil ecology [20,21]. This method is also inconvenient for treating large-scale lands [22]. On the contrary, in situ HM treatment methods have gained more popularity due to their low cost, preservation of original soil structure and environment, and the practicality of taking place on-site [20]. In situ remediation of HMs can be achieved through either mobilizing or immobilizing the HMs [13]. The mobilization approach includes the transformation of HMs into bioavailable forms that can be removed using bioremediation and phytoremediation [23]. However, such a technique presents potential risks of HM leaching into the groundwater and the possibility of plant or microbial toxicity in the surrounding environment [24]. The immobilization of HMs works to limit the solubility and bioavailability of soil HMs by converting them into unavailable forms through the addition of soil amendments. These stabilizers also provide active sites to strongly bind or adsorb HMs, therefore reducing their mobility. In turn, the uptake of these potentially toxic elements by crops is restricted and the risk of human exposure through the food chain is lowered. Simultaneously, immobile HMs have reduced leachability through soil pores, which limits their exposure to groundwater and helps maintain the water quality. Thus, the immobilization technique has been adopted as an effective in situ remediation strategy [25,26].

The application of liming agents, phosphate minerals, industrial wastes such as steel slag and red mud, and organic matter such as livestock waste and discarded plant fractions have all been reported in the literature as soil amendments for HM stabilization [4,13]. However, materials like steel slag and red mud can act as a source of HMs themselves [25,27], worsening the existing contamination scenario. Moreover, most liming agents used in HM stabilization are cement-based, which, despite their good stabilization performance, raises additional contamination and harmful gas release concerns [28,29]. Phosphate-based minerals like hydroxyapatite can efficiently stabilize HMs in soil through adsorption, dissolution precipitation, and ion exchange [30–32]. The high production cost of hydroxyapatite, however, inhibits its large-scale application [32]. Thus, abundantly available natural waste resources have the potential to be a sustainable and cost-effective solution for HM-contaminated soils. Recent studies have shown that annual waste shell production from crustaceans (e.g., crab, shrimp, lobster, and crawfish/crayfish), bivalves (e.g., oyster, cockle, mussel, and scallop), and eggs are 6–8, 13, and 8 million tons, respectively [33–35]. Additionally, globally expanding meat industries produce an inordinate amount of bone waste, which is expected to reach 40 million tons within the next decade [5]. These huge quantities of waste have created a disposal and recycling dilemma. It has been documented that the haphazard dumping of waste oyster and crawfish shells has led to deteriorating environmental conditions and a foul odor for surrounding communities [36,37]. Similar conditions can arise from improper livestock bone disposal with an additional concern of pathogen growth [5]. However, crustaceans, bivalves, and eggshells are rich in Ca [38–40], and livestock bone wastes can be a dependable organic P source [5]. Hence, the disposal and recycling issues associated with these biodegradable wastes can be combatted by using them as sustainable and low-cost alternatives to cement, industrial byproducts, and phosphate-based stabilizers. Starfish can be another effective stabilizing agent for soil HM immobilization. In some communities, like Korea, starfish are seen as harmful marine organisms because of their predation of shellfish, causing economic loss to Korea's aquaculture [41]. Invasive starfish species are also a concern for aquatic ecology and are often caught in large quantities by oyster fishermen to control their population [37]. High $CaCO_3$ content in these captured starfish, in combination with the need to reduce their presence in ocean ecosystems, would make them a good option for HM soil remediation [37,42].

The rich $CaCO_3$ and P contents and low eco-risk of these shell and bone materials are precisely what has piqued researchers' interest for their use as soil HM stabilizers in the past fifteen years. $CaCO_3$ can facilitate HM precipitation by increasing the concentration of OH^- ions in soil, thus raising soil pH and lowering levels of dissolved HMs [32,43].

Additionally, the exchange of Ca^{2+} ions with divalent HM ions can result in HM immobilization through the formation of metal-carbonate precipitates [12,44]. P materials have also been reported to effectively stabilize HMs via precipitation through mineral formation and surface complexation [32,45,46]. Studies have shown that, aside from Ca and P, chitin in crustacean shells can successfully immobilize HMs through complex formation or chelation [6]. Therefore, the composition of these shells, starfish, and bone-based materials makes them exceptional amendments not only for HM immobilization in soil but also for nutrient supply for enhanced soil health and crop production.

A wide range of reviews have been published regarding different types of stabilizers for soil HM immobilization, including industrial byproducts, organic amendments, chemical additives, and biochar. However, reviews on bone-based stabilizers are limited, and there are no reviews on shell- and starfish-based amendments for soil HM stabilization, to the best of our knowledge. The advantages of shell, starfish, and bone-based HM stabilizers are apparent—high HM stabilization potential, large availability, low cost, easy processing, negligible ecological impact, and added soil nutrition. Hence, a comprehensive understanding of these materials' efficacy, mechanisms, performance comparison, and cost assessment are of critical importance. Additionally, a majority of the reviews on stabilizer application for the remediation of soil HMs did not incorporate a cost assessment aspect in their discussion. As a result, it is difficult to determine an ideal stabilizer for practical application. Thus, a performance and cost comparison among the stabilizers is necessary for the implementation of effective remediation in real world scenarios. Current research gaps should also be addressed to develop a more extensive knowledge of HM remediation techniques using these stabilizers. Therefore, the broader goal of this review is to provide insight into the applicability of shell, starfish, and bone-based stabilizers for effective HM stabilization, while the specific objectives are to: (1) assess these stabilizers' immobilization trend for HMs, (2) discuss the mechanisms behind HM stabilization, (3) compare the performance and cost of the stabilizers, and (4) identify the research gaps and potential future undertakings required for improving the use and performance of these stabilizers.

2. In Situ Stabilization of HMs by Phosphorus- and Calcium-Rich Biological Waste

Stabilizers that contain both phosphorous and calcium, when applied to soils, are known to behave as a slow-release fertilizer, providing extra nutritional value to plants and fostering healthier soil conditions [5,47–50]. Seafood shells, eggshells, starfish, and livestock-bone-derived stabilizers are included in this category. To fully evaluate this remedial option, a thorough investigation of their performance is discussed below.

2.1. Shell-Based Stabilizing Agents

Shell-based stabilizing agents include crustacean shell (e.g., crawfish/crayfish, crab, and shrimp), bivalve shell (e.g., oyster, cockle, mussel, and scallop), and eggshell materials that are applied as HM stabilizers in soils. Wasted shells are known to produce biogenic amines through environmental degradation which can lead to the formation of malodor as well as create potential environmental and human health concerns [36,51]. Processing waste shells for in situ HM stabilization can serve dual purposes—to reduce the hazards present in current shell disposal practices and to provide a solution for HM-contaminated soils. Summaries of the studies using shell-based stabilizing agents can be found in Table 1. Additional context regarding the cost estimation index values can be found in Section 4.

Many factors contribute to the heavy metal stabilization ability of shell-based stabilizers. These include their composition (polysaccharides, alkalinity, Ca, Mg, P), pretreatment of material through pyrolysis and calcination, as well as soil conditions and stabilizer–soil interactions. Polysaccharides are one common component in crustacean and bivalve shells [52,53]. It has been reported that chitin, an N-containing polysaccharide found in crayfish shell (CFS), has a remarkable HM and metalloid (e.g., As, Sb) binding ability through complex formation or chelation [5–7,54,55]. Researchers have also added chitin to modify stabilizers for As stabilization performance enhancement. In one study, the availability of As was reduced by 29.8% with the addition of chitin in shell-based stabilizers [6]. The protonated amine surface functional groups of chitin produce a positive charge on its surface, allowing for electrostatic attraction with As anions and the potential formation of ion pairs and chelation [54,56]. Thus, increased polysaccharide content and specifically chitin presence has been shown to increase this material's stabilization ability for both HMs and metalloids.

The compositions of crayfish shell (CFS) and crab shell (CS) are somewhat comparable [57–59]. Consequently, similar HM stabilization mechanisms are observed for both types of stabilizers. A gradual increase in Ca^{2+} and Mg^{2+} ions released from crab shell (CS) has been reported with increasing Pb^{2+} concentration in aqueous solution [60], suggesting the likelihood of ion exchange mechanisms contributing to the immobilization of HMs. Researchers have tried further modifications of crustacean shells to improve their efficacy, such as magnetic microsphere development using shrimp shell (SS) [19]. It showed promisingly higher efficiency toward immobilizing soil HMs, when compared to the performance of unmodified CFS and CS. It should be noted that the concentrations of HMs used for evaluating the SS-derived magnetic microsphere's performance were notably higher than that of CFS and CS (Table 1), indicating SS-derived magnetic microsphere as an advantageous option for treating HM-contaminated soils. However, positive charge development on the SS magnetic microsphere surfaces is observed in highly acidic conditions as it has an isoelectric point (IEP) of 5.7. Such a feature can compromise its HM adsorption capacity in acidic soils with pH lower than 5.7 because of the electrostatic repulsion [61,62].

The alkaline nature of these materials also impacts their HM stabilization ability. Bivalve shells contain a significantly greater amount of $CaCO_3$ (>95%) compared to crustacean shells (30–80%) [57,58,63–67], which makes them very useful for HM stabilization and pH restoration in problematic soils like acidic soil. Studies found that oyster shell (OS), cockle shell (COS), scallop shell (SCS), and mussel shell (MS) powders or meals can significantly reduce soil HM leaching, which is primarily attributed to their alkaline character (Table 1). The precipitation of HMs can also occur by increasing soil pH, induced by the alkalinity of shell-based stabilizers [68,69]. However, increased soil pH can also induce a negative charge formation on the soil particle surfaces. This can lead to the development of repulsive forces between ions such as AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^{-}$, $Sb(OH)_6^{-}$ (the dominant form of Sb in soil solution) and the soil surface, making these metalloids more mobile [70–74]. Difficulties regarding As and Sb stabilization were also observed in soils treated with crustacean shells due to soil pH increase and P release from the stabilizers [6,15]. OS-based stabilizers did, however, demonstrate reduced leaching potential of As when used in combination with rice straw biochar. A 62.3% reduction in HM concentrations was seen within just 2 days [75]. Such a result likely occurred due to the shift in soil pH to a point where $HAsO_4^{-}$ was dominant, leading to the adsorption of As (V) onto oxide mineral and clay surfaces [75,76]. Eggshell (ES) also contains high amounts of $CaCO_3$, at 93–97% on average, in the form of calcite polymorph [40]. Such high Ca content acts as the primary HM stabilization factor by increasing soil pH, leading to a higher availability of negatively charged surface sites [8]. In summary, the alkalinity of shell-based stabilizers and the resulting change in soil pH can affect factors like stabilizer surface charge, HM leachability, and distribution of As metalloid species, which govern the sorptive interaction between labile As species and the stabilizer [75].

The pretreatment of shell-based stabilizers, such as pyrolysis, has also been shown to impact HM stabilization efficacy. For example, CFS-based stabilizers undergoing pyrolysis [1,6–8,15,36] have demonstrated promising performances in stabilizing soil Pb content. In the reported cases, the application of this CFS-based stabilizer at a 1% w/w dose reduced the availability of Pb by 2.9–47.6% in soils within 45–50 days. In such studies, pyrolysis of the stabilizer at 300 °C led to the dominance of aliphatic C in the material, whereas increasing pyrolysis temperature to 500 and 700 °C resulted in the thermal decomposition of aliphatic C and the formation of fused-ring aromatic C structures [36]. Higher pyrolysis temperatures also increased the ash content and facilitated the formation of O-containing functional groups, enhancing the electrostatic attraction between the positive HM ions and the stabilizer surface [6]. In acidic soils, the higher pyrolysis temperatures produced a favorable CFS biochar with elevated Pb stabilization potential.

Pretreatment of crab shell (CS) stabilizers has also been evaluated (Table 1). Without significant pretreatment, pristine powered CS used at 6% w/w showed a good HM stabilization efficiency within 8 days of application. Results indicated more than 70% of the initial concentration was immobilized for most of the HMs [77]. However, pyrolyzing the CS powder for only 30 min at 990 °C led to remarkable HM stabilization performance enhancement. A dose of only 4% w/w CS upon pyrolysis achieved more than 85% stabilization of the majority of the HMs in a similar period [77]. Pyrolysis of the CS also led to the formation of oxidized C functional groups and aromatic rings on the surface of pyrolysis products, improving their HM binding potential through surface complexation and electrostatic attraction [5].

Calcination effects on HM stabilization ability have been evaluated in various studies by modifying pristine bivalve shell powders or meals. Calcination at higher temperatures was performed to activate CaO by transforming the $CaCO_3$ content through CO_2 removal [16,41]. Park et al. (2023) [41] observed improved HM immobilization performance using calcined shells. The author proposed the reason to be the formation of calcium silicate hydrates (CSHs) and calcium aluminum hydrates (CAHs), which demonstrated low solubility, thus restricting mobility. A significant increase in the quantity of soil-available P can occur under the influence of CSHs and CAHs, which can facilitate the immobilization of HMs through precipitation [78]. Moreover, CSH and CAH surfaces present various surface functional groups, including carboxyl, hydroxyl, and carboxylate [79,80]. Such functional groups immobilize exchangeable forms of HMs by providing a higher number of sorption sites [80].

Improved HM stabilization has also been reported for calcined eggshell (ES) soil amendments. Enhanced ion exchange processes, precipitation of metal oxide and hydroxide, and carbonate-mineral co-precipitation were all observed in soils with the addition of pristine ES stabilizers alone [81,82]. However, ES performance was further increased following calcination [8]. Calcination of ES converts almost all of the $CaCO_3$ content to reactive CaO. As a result, rapid dissociation of Ca^{2+} from CaO becomes possible, which enhances the ion exchange capacity for a greater degree of HM fixation [8,83]. Furthermore, calcination can increase the porosity of ES, providing more sites for HM immobilization through sorption [8,84]. In general, heat-treating the stabilizers prior to application helps to improve HM stabilization ability in most cases.

The particle size of shell-based stabilizers also appeared to have an important effect on HM immobilization, which was investigated by only a handful of researchers. An increase in the mesh size or reduction in particle size improved the immobilization efficiency of HMs (Table 1). As stabilizers with small particle sizes offer higher effective surface areas, there are more surface sites available for binding and stabilizing HMs [41].

Despite the overall success of shell-based stabilizers in HM immobilization, there are some instances in which these materials did not prove as efficient. It was observed that the mobilization and availability of As and Sb metalloids in soil increased when shell-based powder and biochar were applied (Table 1). Such an observation can be attributed to the rich P content of shell-based powder and biochar [6,15]. Since P, As, and Sb are in the same group of the periodic table, the presence of P can trigger the desorption of As and Sb from the soil through competition for binding sites [85–87]. Additionally, an inconsistent trend for Cu was observed by Ahmed et al. (2012) [88]. Even though they determined leaching for Pb was reduced, the mobilization of Cu increased upon ES addition to the soil, which is also inconsistent with other investigations on ES for HM stabilization listed in Table 1. It should be noted that dissolved organic carbon (DOC) leaching from soil increased with an increase in ES doses, which likely led to the formation of DOC-Cu complexes and induced Cu immobilization [88,89]. Thus, soil properties and interactions between the soil and stabilizer are vital in such cases in governing HM stabilization characteristics.

2.2. Starfish-Derived Stabilizing Agents

Starfish (SF) has been used as an alternative to seafood shells for soil HM immobilization (Table 1). A high Ca content with small amounts of other nutrients has led to its application to soil for acid neutralization [90,91]. Significant quantities of $CaCO_3$ makes it capable of stabilizing HMs through the same mechanisms as bivalve shells [42]. Such likeness between bivalve shells and starfish may have prompted the idea of its application for soil HM remediation. Powdered SF possesses notable HM stabilization capabilities as exhibited in Table 1. Fine SF powder effectively reduced the leachability of most HMs above 90%, including acute hazards like Hg [41,92]. Natural SF contains SO_3 and S, which leads to the formation of insoluble compounds of Hg, making it an advantageous stabilizer for Hg [92,93]. Lim et al. (2017) [94] reported that natural SF can facilitate the immobilization of HMs like Mn and Zn by forming $MnHPO_4$ and $Zn_3(PO_4)_2{\cdot}4H_2O$, respectively, due to its P content. However, similar to the shell-based stabilizers, untreated SF-based amendments are also limited in their As immobilization ability [94]. Researchers indicated that residual organic tissues of natural SF can contribute to increasing the soil organic matter (OM) content [94]. The decomposition of OM resulting in the elevation of DOC concentration in soil can eventually cause competitive adsorption between As and DOC [95]. Such events can lead to counterproductive scenarios such as the mobilization of As [95].

The activation of CaO through the calcination of SF improved its stabilization capability for HMs to nearly 100%, including As, while Hg stabilization potential did not change significantly. The formation of ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) has been reported upon the addition of calcined SF to the soil [94]. This compound can trigger the ionic substitution of Ca^{2+} with Pb^{2+}, Co^{2+}, Cd^{2+}, and Zn^{2+}. It can also facilitate an "association" mechanism, where Ca^{2+} forms compounds with $AsO_4{}^{3-}$ and $SeO_4{}^{2-}$. As a result, HMs are immobilized due to their incorporation into the structure of ettringite [94]. Moreover, calcined SF stabilizers have high pH values. Therefore, the development of alkaline conditions in the soil following the addition of such stabilizers leads to an effective stabilization of HMs due to the formation of insoluble compounds [95]. Calcination also resulted in a change in S and SO_3 content in the stabilizer, of which some part of it gets converted to $SO_4{}^{2-}$ [92,93,95]. This change actually provides an enhancement in As stabilization potential. Anionic species of As ($AsO_4{}^{3-}$, $HAsO_4{}^{2-}$, $H_2AsO_4{}^{-}$) can get exchanged with $SO_4{}^{2-}$, helping to bind As strongly and reducing its bioavailability [93,94]. As mentioned earlier, as a result of decreases in S and SO_3 content, improved Hg immobilization cannot be achieved by using calcined SF compared to natural SF [92,94].

The effect of particle size for SF stabilizers is similar to what has been observed for shell-based stabilizers (Table 1). Higher specific surface area was achieved by screening the stabilizers through a finer mesh and a facilitated interaction with abundant surface functional groups led to the enhanced stabilization of HMs [41,92].

2.3. Livestock-Bone-Based Stabilizing Agents

Livestock bones make an attractive stabilizer for soil HM remediation because of the appreciable amounts of Ca, Mg, and P in their composition [96,97]. More specifically, apatite and hydroxyapatite in bone and bone chars provide these materials with high HM immobilization efficiency [5,96]. HM stabilization via pyromorphite or metal-phosphate compound formation can be facilitated by abundant P supply from livestock bone powder application [16,96]. Moreover, Zheng et al. (2022) [20] found cow bone meal to be significantly high in organic matter content (288.50 g/kg) compared to oyster shell (7.21 g/kg). Organic matter in bone meal can immobilize HMs by forming stable complexes due to the presence of chemical functional groups on organic matter surfaces [20,98]. Mei et al. (2022) [99] also reported hydroxyapatite as the main component of bone char, along with plenty of organic functional groups that indicate its chemical makeup. The bone char showed a rapid and strong chemical adsorption potential for HMs through precipitation, ion exchange, and surface complexation. In their study, they observed the release of calcium and phosphate ions simultaneously as HM adsorption occurred. This positive correlation between Ca^{2+} release and HM adsorption indicated a prevalence of the ion exchange process. The dominant use of this mechanism enabled bone char to reach a chemical equilibrium within just 2 h of application [99]. Gruden et al. (2017) [46] similarly observed a noticeable decrease in Pb, Zn, and Cd mobility upon application of bone char. Sorption via surface complexation was reported as an important immobilizing mechanism in addition to precipitation and ion exchange. Bone char has been deemed a suitable amendment for HM removal due to its ability to form strong phosphate complexes with different HMs, and such complex formation potential is greater for HMs like Pb and Cd [46,100–102]. The specific details of the bone-based stabilizers mentioned above are summarized in Table 1.

Improvements in the performance of bone meal for HM stabilization, however, have been sought out by some researchers through oxalic acid activation [7,103]. Liu et al. (2022) [7] demonstrated better Pb immobilization capacity as well as an increase in available P supply by 3.62 times in oxalic acid-activated bone meal, compared to unprocessed bone meal. Additionally, Ca^{2+} release from the activated bone meal was significantly higher than that from the non-activated material [7]. The elevated release of phosphate and calcium ions upon oxalic acid treatment possibly increased Pb stabilization through precipitation and ion exchange, respectively. However, there is no apparent influence of oxalic acid activation of bone meal on the stabilization of Cd and Cu in soil [7,103]. Oxalic acid activation of bone meal results in a low pH, compared to its unprocessed counterpart. As a result, this activated bone meal cannot sufficiently produce an alkaline soil environment, which is preferable for the stabilization of HMs like Cd and Cu [7,45,103,104]. Acid activation of bone meal may also prevent dissolution-precipitation from being the main mechanism for Cd immobilization [7]. A similar phenomenon has been observed by researchers for Cd removal through sulfur-modified bone char, where bone char without modification exhibited better Cd removal [105]. Such results indicate bone meal modification by oxalic acid or sulfur to be an unreasonable approach when the stabilization of multiple HMs is of interest.

The particle size effect for livestock-bone-based stabilizers complies with the trend observed for shell-based and starfish-derived stabilizing agents. A greater degree of stabilization is observed for stabilizers composed of smaller sized particles [96]. To reiterate, this outcome is related to the increased surface area of the smaller particles, resulting in more available binding sites for the HMs.

Table 1. Summary of common P- and Ca-rich biowaste stabilizers.

Stabilizer Name	Synthesis Process	Major Composing Materials or Surface Functional Groups	Target HMs	Dose	Concentration of HMs in Treated Soil	Stabilizing Time and Method	Stabilizing Efficiency	Ref
Shell-Based Stabilizers								
Crawfish shell biochar	Crawfish shells rinsed with tap water, oven dried at 105 °C, followed by oxygen-limited pyrolysis at 650 °C for 2 h	C-O-C, -OH, C=O, >C=C<	As and Pb	1% *w*/*w*	As: 141.3 mg/kg Pb: 736.2 mg/kg	50-day pot experiment	Increased bioavailable As by 1.5% and decreased bioavailable Pb by 2.9%	[15]
Crawfish shell powder	Crawfish shells rinsed with tap water, oven dried at 80 °C for 24 h, followed by grinding and sieving	N-H, O-H, C=O, C-H, C-C, olefins	As and Pb	1% *w*/*w*	As: 141.3 mg/kg Pb: 736.2 mg/kg	50-day pot experiment	Increased availability of As by 25.7% and reduced availability of Pb by 18.8%	[6]
Chitin and crawfish shell biochar composite	Crawfish shells rinsed with tap water, oven dried at 80 °C for 24 h, followed by pyrolysis at 650 °C for 2 h, then ground and mixed with chitin using 1:1 ratio at 200 rpm for 2 h	N-H, O-H, C=O, C-H, C-C, and olefins	As and Pb	1% *w*/*w*	As: 141.3 mg/kg Pb: 736.2 mg/kg	50-day pot experiment	Reduced availability of As and Pb by 29.8% and 46.5%, respectively	[6]

Table 1. *Cont.*

Stabilizer Name	Synthesis Process	Major Composing Materials or Surface Functional Groups	Target HMs	Dose	Concentration of HMs in Treated Soil	Stabilizing Time and Method	Stabilizing Efficiency	Ref
Crayfish shell biochar	Crayfish shells air-dried at 60 °C followed by heating at a rate of 15 °C/min in the presence of N_2 at 300 °C, 500 °C, and 700 °C, respectively	Methyl and methylene C, aliphatic-C, O-alkyl-C, anomeric-C, aromatic-C, carboxyl-C, and amide	Pb	0.5–5% *w*/*w* for all biochars produced at three different temperatures	Pb: 480 mg/kg	45-day incubation experiment	Reduction in DTPA extractable Pb in acidic soil by 2.71–6.04%, 1.87–12.55%, and 9.57–16.48%, and in saline soil by 1.00–11.09%, 1.92–10.38%, and 1.15–5.18% applying crayfish shell biochar produced at 300 °C, 500 °C, and 700 °C, respectively	[36]
Crawfish shell biochar	Crawfish shells rinsed with tap water, oven dried at 80 °C for 24 h, followed by pyrolysis at 650 °C for 2 h	N-H, O-H, C=O, and olefins	As and Pb	1% *w*/*w*	As: 141.3 mg/kg Pb: 736.2 mg/kg	50-day pot experiment	Increased availability of As by 32.6% and reduced availability of Pb by 47.6%	[6]
Waste shrimp shell magnetic microsphere	Waste shrimp shells washed and air-dried, submerged in 1.5% HCl for 20 h for decalcification and insoluble materials removed using DI water, then placed in 10% NaOH for 2 h and afterward washed using DI water followed by submerging respectively in 5% potassium permanganate and 5% oxalic acid solution for 1 h, then decolorized samples dried in oven for 12 h at 60 °C to extract chitin chitosan; obtained product deacetylated for 8 h at 60 °C in 50% NaOH, and residue purified with DI water, dried at 80 °C and ground and sieved through 180 mesh, and, finally, 1 g shrimp shell powder dissolved in 50 mL 2% acetic acid and mixed with 1 g MnFe2O4 followed by ultrasonic treatment for 15 min and subsequent addition of 5 mL 30% glutaraldehyde for crosslinking for 12 h at 45 °C and then washed by ethanol and dried at 60 °C for 12 h	N-H coupled with H-O, C-H, N-H, C=O	Cu and Cd	10% *w*/*w*	Cu: 335,700 mg/kg Cd: 4350 mg/kg	7-day batch experiment	Cu and Cd reduction in soil by 75.5% and 81.6%, respectively	[19]
Crab shell powder	Seafood processing plant discarded crab shells air-dried and crushed into powder followed by sieving through 0.5 mm mesh	* NR	Pb, Zn, Cu, Cr, and Ni	2–6% *w*/*w*	Pb: 844 mg/kg Zn: 4260 mg/kg Cu: 4530 mg/kg Cr: 327 mg/kg Ni: 305 mg/kg	4–8-day incubation experiment	Stabilization efficiency of >80, >70, >70, >95, and >60% for Pb, Zn, Cu, Cr, and Ni, respectively at a dose of 6% *w*/*w* after 8-day curing	[77]
Pyrolyzed crab shell powder	Seafood processing plant discarded crab shells air-dried and crushed into powder followed by sieving through 0.5 mm mesh and pyrolyzed at 400 °C for 0.5 h	* NR	Pb, Zn, Cu, Cr, and Ni	2–6% *w*/*w*	Pb: 844 mg/kg Zn: 4260 mg/kg Cu: 4530 mg/kg Cr: 327 mg/kg Ni: 305 mg/kg	4–8-day incubation experiment	Stabilization efficiency of >60, >75, >90, >90, and >70% for Pb, Zn, Cu, Cr, and Ni, respectively at a dose of 6% *w*/*w* after 8-day curing	[77]

Table 1. *Cont.*

Stabilizer Name	Synthesis Process	Major Composing Materials or Surface Functional Groups	Target HMs	Dose	Concentration of HMs in Treated Soil	Stabilizing Time and Method	Stabilizing Efficiency	Ref
Baked crab shell powder	Seafood processing plant discarded crab shells air-dried and crushed into powder followed by sieving through 0.5 mm mesh and baked 990 °C for 0.5 h in a muffle furnace	* NR	Pb, Zn, Cu, Cr, and Ni	2–6% *w*/*w*	Pb: 844 mg/kg Zn: 4260 mg/kg Cu: 4530 mg/kg Cr: 327 mg/kg Ni: 305 mg/kg	4–8-day incubation experiment	Stabilization efficiency of >85, >90, >95, >50, and >90% for Pb, Zn, Cu, Cr, and Ni, respectively at a dose of 4% *w*/*w* after 8-day curing	[77]
Waste oyster shell	Raw oyster shells pulverized and sieved through 0.853 mm mesh	SiO_2, Al_2O_3, Na_2O, MgO, K_2O, CaO, Fe_2O_3, SO_3, MnO	Pb	1–10% *w*/*w*	Pb: 2800 mg/kg	28-day incubation experiment	Approximately 85% reduction in Pb leachability with 10% *w*/*w* dose	[37]
Calcined oyster shell	Raw oyster shells pulverized and sieved through 0.853 mm mesh followed by calcination at 900 °C for 2 h	SiO_2, Al_2O_3, Na_2O, MgO, K_2O, CaO, Fe_2O_3, SO_3, MnO	Pb	1–5% *w*/*w*	Pb: 2800 mg/kg	28-day incubation experiment	Approximately 68% reduction in Pb leachability with 5% *w*/*w* dose	[37]
Oyster shell powder	Oyster shells crushed and ground using ball milling to obtain powders with particle size < 6.5 µm	O-C-O, C-O, C=O, O-H, $-CH_3$	Pb and Cd	5% and 10% *w*/*w*	Cd: 638 mg/kg Pb: 1092 mg/kg	28-day incubation experiment	Approximately 96% and 97% decrease in the dissolution of Pb and Cd, respectively, and >98% reduction in Pb and Cd leachability with a dose of 10% *w*/*w*	[28]
Oyster shell meal	Oyster shells thoroughly washed and dried at 70 °C followed by mechanical pulverization and screening through #100 mesh	Ca and C	Pb, Cd, Zn, and Cu	0.1–3% *w*/*w*	Pb: 193.45 mg/kg Cd: 4.16 mg/kg Zn: 353.88 mg/kg Cu: 147.07 mg/kg	108-day incubation experiment	Reduced bioavailability of Pb from >65% to <5%, Cd from >70% to <5%, Zn from >55% to <10%, and Cu from >60% to <5% at 3% *w*/*w* dose	[20]
Oyster shell powder	Industrially obtained oyster shell powder with a $CaCO_3$ content of 89.3%	SiO_2, Al_2O_3, Na_2O, MgO, K_2O, CaO, Fe_2O_3, MnO, P_2O_5	Pb, Zn, Cu, Cd, and Ni	1–10% *w*/*w*	*Mine soil*: Pb: 0.64 mg/kg Zn: 102.78 mg/kg Cu: 3.95 mg/kg Cd: 0.32 mg/kg Ni: 0.43 mg/kg	2-h batch experiment	*Mine soil*: Reduction in leachability by >80% for Pb, 33.2% for Zn, 76% for Cu, 42.4% for Cd, and >70% for Ni with 5% *w*/*w* dose	[106]
					Sandy soil: Pb: 1.58 mg/kg Zn: 201.06 mg/kg Cu: 44.70 mg/kg Cd: 0.92 mg/kg Ni: -		*Sandy soil*: Reduction in leachability by >80% for Pb, 50% for Zn, 86% for Cu, and 50% for Cd with 5% *w*/*w* dose	
					Hand contaminated soil: Pb: 301.65 mg/kg Cu: 3.95 mg/kg		*Hand contaminated soil*: Reduction in leachability by 53% for Pb and 61% for Cu, with 10% *w*/*w* dose	
Waste oyster shell	Oyster shell collected from local oyster farm air-dried, crushed, ground, and sieved through 0.3 mm mesh to obtain fine powder	$CaCO_3$	As	2–4% *w*/*w*	15,076.8 ± 726.4 mg/kg	2-day column leaching experiment	62.3% reduction in As leaching to porewater when 2% *w*/*w* waste oyster shell applied with 2% *w*/*w* rice straw biochar	[75]

Table 1. *Cont.*

Stabilizer Name	Synthesis Process	Major Composing Materials or Surface Functional Groups	Target HMs	Dose	Concentration of HMs in Treated Soil	Stabilizing Time and Method	Stabilizing Efficiency	Ref
Calcined oyster shell	Collected waste oyster shells dried, pulverized, and screened through #20 mesh followed by roasting at 900 °C for 2 h	CaO, MgO, Na_2O, P_2O_5, Al_2O_3, SiO_2, K_2O, Fe_2O_3, SO_3, TiO_2	Pb and Cu	3–10% *w*/*w*	Pb: 11,900 mg/kg Cu: 1270 mg/kg	28-day incubation experiment	Reduction in Pb and Cu leachability by >98% and >95%, respectively, at 10% *w*/*w* dose	[16]
Cockle shell	Cockle shells cleaned to remove foreign materials and immersed in flowing water to wash salts, then washed with distilled water, naturally dried followed by crushing and screening through #10 and #20 mesh	$CaCO_3$	Pb, Zn, and Cu	0–10% *w*/*w*	Pb: 514.6 mg/kg Zn: 852.7 mg/kg Cu: 667.7 mg/kg	28-day incubation experiment	Leaching reduction efficiency of 97.8% for Pb, 54.2% for Zn, and 92.8% for Cu with 10% *w*/*w* dose of cockle shell screened with #10 mesh, and 99.6% for Pb, 71.8% for Zn, and 96.3% for Cu with 10% *w*/*w* dose of cockle shell screened with #20 mesh	[41]
Calcined cockle shell	Cockle shells cleaned to remove foreign materials and immersed in flowing water to wash salts, then washed with distilled water, naturally dried followed by crushing and screening through #10 mesh and calcination at 900 °C for 2 h	CaO	Pb, Zn, and Cu	0–10% *w*/*w*	Pb: 514.6 mg/kg Zn: 852.7 mg/kg Cu: 667.7 mg/kg	28-day incubation experiment	Leaching reduction efficiency of 99.9% for Pb and 98.1% for Zn with 6% *w*/*w* dose, and 95.4% for Cu with 10% *w*/*w* dose	[41]
Calcined cockle shell powder	Cockle shells collected from a local market waste washed with hot water to remove organics and impurities, then dried at 105 °C for 48 h followed by crushing, grinding, and screened through a #20 mesh, then calcinated at 900 °C for 4 h	CaO, MgO, Na_2O, P_2O_5, SiO_2, SO_3, Al_2O_3, Fe_2O_3	Cd, Pb, and Zn	1–5% *w*/*w*	Cd: 151 mg/kg Pb: 18,134 mg/kg Zn: 23,847 mg/kg	28-day incubation experiment followed by 8-day freeze-thaw and wetting-drying cycles	Up to 85%, 85%, and 91% reduction in Cd, Pb, and Zn	[107]
Scallop shell	Scallop shells cleaned to remove foreign materials and immersed in flowing water to wash salts, then washed with distilled water, naturally dried followed by crushing and screening through #10 and #20 mesh	$CaCO_3$, $MgCO_3$	Pb, Zn, and Cu	0–10% *w*/*w*	Pb: 514.6 mg/kg Zn: 852.7 mg/kg Cu: 667.7 mg/kg	28-day incubation experiment	Stabilization efficiency of 98.9% for Pb, 64.7% for Zn, and 96.8% for Cu with 10% *w*/*w* dose of scallop shell screened with #10 mesh, and 99.5% for Pb, 75.5% for Zn, and 98.2% for Cu with 10% *w*/*w* dose of scallop shell screened with #20 mesh compared to initial leaching concentration	[41]
Calcined scallop shell	Scallop shells cleaned to remove foreign materials and immersed in flowing water to wash salts, then washed with distilled water, naturally dried followed by crushing and screening through #10 mesh and calcination at 900 °C for 2 h	CaO	Pb, Zn, and Cu	0–10% *w*/*w*	Pb: 514.6 mg/kg Zn: 852.7 mg/kg Cu: 667.7 mg/kg	28-day incubation experiment	Stabilization efficiency of >99.9% for Pb, >99.9% for Zn, and 98.5% for Cu with 10% *w*/*w* dose	[41]
Mussel shell	Mussel shells collected from local restaurant washed in boiling water and dried at 105 °C followed by griding to fine powder of <1 mm	CaO, MgO, Na_2O, P_2O_5, Al_2O_3, SiO_2, K_2O, Fe_2O_3, MnO, TiO_2	Pb and Sb	5% *w*/*w*	Pb: 3970.65 mg/kg Sb: 67.48 mg/kg	175-day incubation experiment	Up to 99% reduction in Pb, whereas increase in Sb leaching	[108]

Table 1. *Cont.*

Stabilizer Name	Synthesis Process	Major Composing Materials or Surface Functional Groups	Target HMs	Dose	Concentration of HMs in Treated Soil	Stabilizing Time and Method	Stabilizing Efficiency	Ref
Mussel shell powder	Waste mussel shells collected from several restaurants washed with warm water several times for impurity removal, then dried for 48 h in a forced air oven, ground, and homogenized by sieving through 1 mm mesh	C, N, Ca, Na, K, Mg	Pb	5% *w*/*w*	Pb: 11,100 mg/kg	7-day incubation experiment	Bioavailability reduction by 92.5% compared to the unamended soil	[109]
Baked eggshell powder	Waste eggshells crushed and roasted at 900 °C for 0.5 h in a muffle furnace	* NR	Pb, Zn, Cu, Cr, and Ni	2% *w*/*w*	Pb: 844 mg/kg, Zn: 4260 mg/kg, Cu: 4530 mg/kg, Cr: 327 mg/kg, Ni: 305 mg/kg	4-day incubation experiment	Stabilization efficiency of approximately 50, >35, >45, >50, and >40% for Pb, Zn, Cu, Cr, and Ni, respectively	[77]
Eggshell	Eggshells collected from university dining facilities washed thoroughly, dried at 40 °C, pulverized, and sieved through a #100 mesh	$CaCO_3$, MgO, Na_2O, P_2O_5, Al_2O_3, SiO_2, K_2O, Fe_2O_3, MnO, TiO_2	Cu, Zn, and Cd	0–1% *w*/*w*	Cu: 185.61 mg/kg Zn: 245.79 mg/kg Cd: 0.64 mg/kg	30-day pot incubation experiment	Reduction in availability of Cu, Zn, and Cd by 10.4, 3.01, and 2.20 times, respectively	[9]
Eggshell	Locally sourced inorganic eggshells washed vigorously with distilled water for residue removal, then oven dried at 105 °C followed by grinding in an electric grinder	N, C, Ca, Mn, Fe	Pb, Zn, and Cd	5% *w*/*w*	Pb: 700 mg/kg, Zn: 900 mg/kg Cd: 20 mg/kg	84-day leaching experiment	Reduction in Pb, Zn, and Cd leaching by 28%, 70%, and 83%, respectively, after 84 days	[82]
Eggshell waste	Eggshells collected from a restaurant washed with distilled water for impurity removal, the oven dried at 105 °C for 72 h followed by pulverizing and screening through 1 mm mesh	$CaCO_3$	Cd and Pb	0–5% *w*/*w*	Cd: 11.27 mg/kg Pb: 1233.21 mg/kg	80-day pot experiment	Up to 67.9% and 93.2% reduction in Cd and Pb, respectively, at 5% *w*/*w* dose	[25]
Eggshell powder	Eggshell collected from local restaurants washed a few times with hot water, oven-dried at 105 °C for 72 h, ground and passed through 1 mm sieve	$CaCO_3$, CaO, MgO, Na_2O, P_2O_5, Al_2O_3, SiO_2, K_2O, Fe_2O_3, MnO, TiO_2	Pb	0–30% *w*/*w*	Pb: 4626 mg/kg	28-day incubation experiment	>80% reduction in Pb leaching at a dose of 30% *w*/*w*	[8]
Calcined eggshell powder	Eggshell collected from local restaurants washed a few times with hot water, oven-dried at 105 °C for 72 h, ground and passed through 1 mm sieve followed by calcination at 900 °C for 6 h in a furnace	CaO, MgO, Na_2O, P_2O_5, Al_2O_3, SiO_2, K_2O, Fe_2O_3, MnO, TiO_2	Pb	0–30% *w*/*w*	Pb: 4626 mg/kg	28-day incubation experiment	>95% reduction in Pb leaching at a dose of 30% *w*/*w*	[8]
Eggshell powder	Eggshell collected from a local restaurant rinsed several times with hot water (95 °C), oven-dried at 105 °C for 72 h, mechanically ground and passed through 1 mm sieve	$CaCO_3$, CaO, MgO, Na_2O, P_2O_5, Al_2O_3, SiO_2, K_2O, Fe_2O_3, MnO, TiO_2	Pb and Cu	0–15% *w*/*w*	Pb: 4626 mg/kg Cu: 225 mg/kg	24-h batch leaching experiment	>45% reduction in Pb solubility, whereas 180% increase in Cu solubility at 2.5% *w*/*w* dose	[88]
Starfish-based stabilizers								
Starfish	Natural starfish soaked in tap water for one day to remove impurities and salts followed by multiple rinses with deionized (DI) water, then air-dried in sun for 7 days, ground to prepare powder, and screened through 2 mm mesh	SiO_2, Al_2O_3, Na_2O, MgO, K_2O, CaO, Fe_2O_3, SO_3, MnO	Pb	1–10% *w*/*w*	Pb: 2800 mg/kg	28-day incubation experiment	Approximately 50% reduction in Pb leachability with 10% *w*/*w* dose	[37]

Table 1. *Cont.*

Stabilizer Name	Synthesis Process	Major Composing Materials or Surface Functional Groups	Target HMs	Dose	Concentration of HMs in Treated Soil	Stabilizing Time and Method	Stabilizing Efficiency	Ref
Starfish	Natural starfish cleaned to remove foreign materials and immersed in flowing water to wash salts, then washed with distilled water, naturally dried followed by crushing and screening through #10 and #20 mesh	$CaCO_3$, $MgCO_3$	Pb, Zn, and Cu	0–10% *w*/*w*	Pb: 514.6 mg/kg Zn: 852.7 mg/kg Cu: 667.7 mg/kg	28-day incubation experiment	Leaching reduction efficiency of >99.9% for Pb, 83.4% for Zn, and 95.6% for Cu with 10% *w*/*w* dose of starfish screened with #10 mesh, and >99.9% for Pb, 85% for Zn, and 95.8% for Cu with 10% *w*/*w* dose of starfish screened with #20 mesh compared to control leaching concentration	[41]
Calcined starfish	Natural starfish cleaned to remove foreign materials and immersed in flowing water to wash salts, then washed with distilled water, naturally dried followed by crushing and screening through #10 mesh and calcination at 900 °C for 2 h	CaO	Pb, Zn, and Cu	0–10% *w*/*w*	Pb: 514.6 mg/kg Zn: 852.7 mg/kg Cu: 667.7 mg/kg	28-day incubation experiment	Stabilization efficiency of >99.9% for Pb, >99.9% for Zn, and 97.7% for Cu with 10% *w*/*w* dose	[41]
Starfish	Natural starfish desalted by washing in tap water for 24 h, then several times DI water rinse, afterward air-dried in sun for 7 days followed by crushing and grinding to obtain fine powder and sieved through #10 and #20 mesh	$CaCO_3$, $MgCO_3$	Hg	0–10% *w*/*w*	Hg: 23.1 mg/kg	28-day incubation experiment	Approximately 36%-79% and 94% stabilization with 10% *w*/*w* dose of starfish powder sieved through #10 mesh and #20 mesh, respectively	[92]
Calcined starfish	Natural starfish desalted by washing in tap water for 24 h, then several times DI water rinse, afterward air-dried in sun for 7 days, then crushing and grinding to obtain fine power and sieved through #10 followed by calcination at 900 °C for 2 h in an electric furnace	CaO, MgO, CaS	Hg	0–5% *w*/*w*	Hg: 23.1 mg/kg	28-day incubation experiment	Approximately 64–91% reduction in leachability with 5% *w*/*w* dose	[92]
Natural starfish	Starfish collected from seaside rinsed multiple times with DI water to remove salt and impurities, then air-dried, ground to fine powder, and sieved through #20 sieve	SiO_2, Al_2O_3, MgO, K_2O, CaO, Fe_2O_3, TiO_2, P_2O_5	Pb and Zn	0–10% *w*/*w*	Pb: 980 mg/kg Zn: 890 mg/kg	28-day incubation experiment	Reduction in leachability by 58% and 51% for Pb and Zn, respectively with 10% *w*/*w*	[42]
Calcined starfish	Starfish collected from seaside rinsed multiple times with DI water to remove salt and impurities, then air-dried, ground to fine powder, sieved through #20 sieve and finally calcinated at 900 °C for 2 h in an electric furnace	SiO_2, Al_2O_3, MgO, K_2O, CaO, Fe_2O_3, TiO_2, P_2O_5	Pb and Zn	0–5% *w*/*w*	Pb: 980 mg/kg Zn: 890 mg/kg	28-day incubation experiment	Reduction in leachability by 93% and 76% for Pb and Zn, respectively with 5% *w*/*w*	[42]
Natural starfish	Starfish collected from fish market rinsed multiple times with DI water and heated in water at 95 °C for several hours to remove impurities, then air-dried, ground, and sieved using 2 mm sieve	CaO, MgO, P_2O_5, K_2O, SiO_2, Fe_2O_3, Na_2O, TiO_2, MnO, Al_2O_3	Pb, Zn, and As	0–10% *w*/*w*	Pb: 1198.60 mg/kg Zn: 394.65 mg/kg As: 127.13 mg/kg	432-day incubation experiment	Leachability of Pb and Zn reduced by 100%, whereas As leaching increased by almost 10.8 times at an application rate of 10% *w*/*w*	[94]

Table 1. *Cont.*

Stabilizer Name	Synthesis Process	Major Composing Materials or Surface Functional Groups	Target HMs	Dose	Concentration of HMs in Treated Soil	Stabilizing Time and Method	Stabilizing Efficiency	Ref
Calcined starfish	Starfish collected from fish market rinsed multiple times with DI water and heated in water at 95 °C for several hours to remove impurities, then air-dried, ground, and sieved using 2 mm sieve followed by calcination at 900 °C for 2 h in a muffle furnace	CaO, MgO, P_2O_5, K_2O, SiO_2, Fe_2O_3, Na_2O, TiO_2, MnO, Al_2O_3	Pb, Zn, and As	0–10% *w*/*w*	Pb: 1198.60 mg/kg Zn: 394.65 mg/kg As: 127.13 mg/kg	432-day incubation experiment	Leachability of Pb, Zn, and As reduced by 100% at an application rate of 10% *w*/*w*	[94]
Bone-based stabilizers								
Cow bone meal	Cow bones thoroughly washed and dried at 70 °C followed by mechanical pulverization and screening through #100 mesh	Ca and P	Pb, Cd, Zn, and Cu	0.1–3%	Pb: 193.45 mg/kg Cd: 4.16 mg/kg Zn: 353.88 mg/kg Cu: 147.07 mg/kg	108-day incubation experiment	Reduced bioavailability of Pb from >60% to <5%, Cd from >70% to <5%, Zn from >60% to <10%, and Cu from >60% to <5% at 3% *w*/*w* dose	[20]
Ox bone powder	Raw ox bone crushed and roasted at 990 °C for 0.5 h in a muffle furnace	* NR	Pb, Zn, Cu, Cr, and Ni	2% *w*/*w*	Pb: 844 mg/kg Zn: 4260 mg/kg Cu: 4530 mg/kg Cr: 327 mg/kg Ni: 305 mg/kg	4-day incubation experiment	Stabilization efficiency of >55, >40, >50, >50, and >45% for Pb, Zn, Cu, Cr, and Ni, respectively	[77]
Cow bone	Cow bones collected from local restaurant washed in boiling water and dried at 105 °C followed by grinding to fine powder of <1 mm	CaO, MgO, Na_2O, P_2O_5, Al_2O_3, SiO_2, K_2O, Fe_2O_3, MnO, TiO_2	Pb and Sb	5% *w*/*w*	Pb: 3970.65 mg/kg Sb: 67.48 mg/kg	175-day incubation experiment	Up to 93% reduction in Pb, whereas increase in Sb leaching	[108]
Waste cow bone	Waste cow bones collected from restaurants dried at 105 °C, then pulverized, and screened through #20 mesh	CaO, MgO, Na_2O, P_2O_5, Al_2O_3, SiO_2, K_2O, Fe_2O_3, MnO, TiO_2	Pb and Cu	3–10% *w*/*w*	Pb: 11,900 mg/kg Cu: 1270 mg/kg	28-day incubation experiment	Reduction in Pb and Cu leachability by >98% and >86%, respectively, at 10% *w*/*w* dose	[16]
Cow bone	Cow bones collected from local restaurants submerged in boiling water for organic impurity removal, then dried at 105 °C for 24 h, ground, and homogenized to <1 mm particle size by sieving	C, N, Ca, Na, K, Mg	Pb	5% *w*/*w*	Pb: 11,100 mg/kg	7-day incubation experiment	Bioavailability reduction by 84.8% compared to the unamended soil	[109]
Bone char	Waste pork bones repeatedly heated in water bath for 3 h at 95 °C for three times, then drained bones oven-dried, ground to approximately 1 mm size using a universal cutting mill followed by pyrolysis at 550 °C for 2 h in the presence of N_2	PO_4^{3-}, -OH, CO_3^{2-}, C=O, C-N, N-H, C-H	Cu, Zn, Pb, and Cd	0–5% *w*/*w*	* NR	60-day incubation experiment	Reduction in leachability by 91.2, 38.6, 67.6, and 54.3% for Cu, Zn, Pb, and Cd, respectively at 5% *w*/*w*	[99]
Livestock bone powder	Synthesis process not reported, sieved through #10 and #20 mesh to obtain two different sizes of powder	CaO, MgO, Na_2O, P_2O_5, Al_2O_3, SiO_2, K_2O, Fe_2O_3, SO_3	Cu and Pb	2–10% *w*/*w*	Cu: 667.7 mg/kg Pb: 514.6 mg/kg	7- and 28-day incubation experiment	Approximately 90% and >99% leachability reduction for Cu and Pb, respectively, with a 10% *w*/*w* dose of #10 mesh sieved powder, and 92% and 99% for Cu and Pb, respectively, with a 10% *w*/*w* dose of #20 mesh sieved powder after 28-day incubation	[96]

Table 1. *Cont.*

Stabilizer Name	Synthesis Process	Major Composing Materials or Surface Functional Groups	Target HMs	Dose	Concentration of HMs in Treated Soil	Stabilizing Time and Method	Stabilizing Efficiency	Ref
Oxalic acid activated bone meal	Commercially available bone meal produced by crushing, heating, and defatting of bones screened through 2 mm sieve, mixed in a beaker with 1 mol/L oxalic acid at 2:1 liquid solid ratio, cured 20 ± 2 °C and 95% humidity for 6 days, then filtered and oven-dried at 60 °C	CaO, P_2O_5, SiO_2, Al_2O_3, Fe_2O_3	Pb and Cd	0–15% *w*/*w*	Pb: 10,000 mg/kg Cd: 2500 mg/kg	7–90-day incubation experiment	99.7% of Pb and 83.6% of Cd immobilization after 7 and 90 days of curing, respectively at 15% *w*/*w*	[7]
Bone meal	Commercially available bone meal produced by crushing, heating, and defatting of bones screened through 2 mm sieve	CaO, P_2O_5, SiO_2, Al_2O_3, Fe_2O_3	Pb and Cd	0–15% *w*/*w*	Pb: 10,000 mg/kg Cd: 2500 mg/kg	7–90-day incubation experiment	>99% of Pb and 79.4% of Cd immobilization after 7 and 90 day of curing, respectively at 15% *w*/*w*	[7]
Fish bone biochar	Collected waste fishbones dried at 60 °C, ground, and pyrolyzed at 400 °C and 600 °C in tightly sealed stainless steel container, then cooled, crushed, and screened through 2 mm sieve	C=C, C=O, PO_4^{3-}, O-H, C-H, COO-	Pb, Cu, Zn, and Cd	1.5% and 3% *w*/*w*	* NR	35-day pot experiment	Pb, Cu, Zn, and Cd immobilization of 40%, 61.7%, 48.3%, and 32.7% with biochar pyrolyzed at 400 °C and 43%, 66.2%, 55.6%, and 33.8% with biochar pyrolyzed at 600 °C, respectively	[110]

* NR = not reported; *w*/*w* = weight by wight (stabilizer to soil).

3. Mechanisms for HM Stabilization by Shell, Starfish, and Livestock-Bone-Derived Stabilizers

3.1. Precipitation

All kinds of stabilizers included in this review contain a considerable quantity of $CaCO_3$, which plays a pivotal role in the stabilization of HMs in soil. One major mechanism for the stabilization of most HMs is precipitation (see Figure 1). Precipitation can be defined as the transformation of dissolved HMs to solids [5]. For example, Sun et al. (2021) [36] observed a rise in soil pH upon the addition of CFS biochar. Thereafter, the precipitation of Pb through the formation of cerussite ($PbCO_3$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) under the basic condition occurred. It is known that aqueous Pb^{2+} species are predominant at an acidic pH and start to precipitate as the pH approaches neutrality [111]. The following reactions (Equations (1)–(3)) can be used to explain Pb stabilization through precipitation by the stabilizers discussed in this review [36]:

$$Pb^{2+} + HCO_3^- + OH^- \rightarrow PbCO_3 \downarrow + H_2O \tag{1}$$

$$3Pb^{2+} + 2HCO_3^- + 4OH^- \rightarrow Pb_3(CO_3)_2(OH)_2 \downarrow + 2H_2O \tag{2}$$

$$CaCO_3 + Pb^{2+} \rightarrow PbCO_3 \downarrow + Ca^{2+} \tag{3}$$

Oxides of Fe and Mn can play a similar role as that of $CaCO_3$ [100,112]. The availability of HMs such as Pb can be reduced due to its incorporation into the Fe and Mn oxide structure and co-precipitation [19,71]. Shell, starfish, and bone-based stabilizers can contain a substantial amount of these oxides (Table 1). The subsequent release of Fe and Mn oxides after the application of these stabilizers may reduce the availability of HMs through precipitation, especially if the materials are calcinated or pyrolyzed. Additionally, pyrolysis of livestock bones may lead to the formation of mineral fractions like hydroxyapatite [5], which can further assist the precipitation of HMs as displayed in Equations (4)–(7) [113,114]:

$$Ca_{10}(PO_4)_6(OH)_2 + 14H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2H_2O \tag{4}$$

$$10Pb^{2+} + 6H_2PO_4^{-} + 12H_2O \rightarrow Pb_{10}(PO_4)_6(OH)_2 + 14H^{+} \quad (5)$$

$$Ca_{10}(PO_4)_6(OH)_2 + XPb^{2+} \rightarrow Ca_{10-X}Pb_X(PO_4)_6(OH)_2 + XCa^{2+} \quad (6)$$

$$Ca_{10}(PO_4)_6(OH)_2 + XCd^{2+} \rightarrow Ca_{10-X}Cd_X(PO_4)_6(OH)_2 + XCa^{2+} \quad (7)$$

Hg, however, acts differently than other HMs such as Pb. Its immobilization cannot be achieved by applying Ca compounds. Rather, it has been reported that Hg stabilization can be accomplished by forming insoluble HgS through its reaction with S or S-containing compounds as follows (Equations (8)–(10)) [115,116]:

$$Hg + S \rightarrow HgS \quad (8)$$

$$Hg^{2+} + H_2S \rightarrow HgS + 2H^{+} \quad (9)$$

$$Hg + Na_2S_5 \rightarrow HgS + Na_2S_4 \quad (10)$$

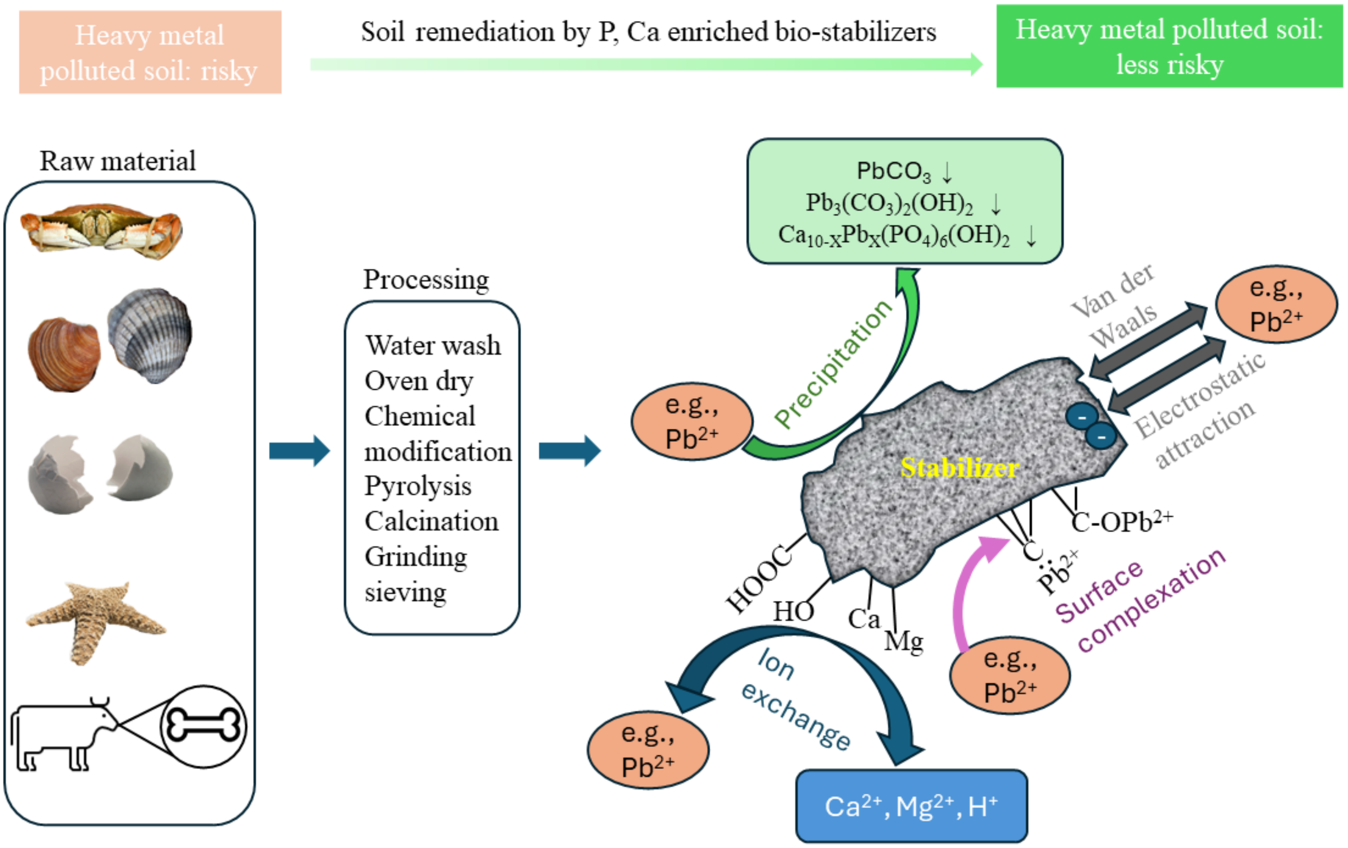

Figure 1. Possible mechanisms behind heavy metal remediation in soil by P- and Ca-rich biowaste stabilizers.

3.2. Ion Exchange

Ion exchange is another major mechanism through which HMs may become immobilized in soil. As is shown in Figure 1, this mechanism involves divalent ions such as Ca^{2+} and Mg^{2+} that are present in shell, starfish, and livestock-bone-based stabilizers to be exchanged with the major HM ions, leading to soil HM stabilization [32]. Surface functional groups of the stabilizer are capable of releasing protons such as -COOH and -OH and can also facilitate HM immobilization through ion exchange [36]. Pyrolysis temperature can be significant in determining the presence of functional groups, as acidic functional groups are destroyed at higher pyrolysis temperatures [117,118]. Azeem et al. (2022) [5] reported a negative relationship between the cation exchange capacity (CEC) of biochar and pyrolysis temperature. A decrease in the CEC of biochar with increasing pyrolysis temperature was observed and can be attributed to the destruction of surface functional groups and aromatization of C [119]. As the number of surface functional groups is reduced, so is the total number of sites for cation exchange [120]. Though calcination and pyrolysis treatments may help to increase electrostatic interactions between HMs and stabilization surfaces, as discussed in Section 2, these processing techniques may demonstrate lower HM stabilization capability via ion exchange. Equation (11) explain the mechanism for HM stabilization through cation exchange, as reported by Ok et al. (2011) [121]:

$$CaCO_3 + Cd^{2+} \rightarrow CdCO_3 + Ca^{2+} \tag{11}$$

3.3. Surface Complexation

Surface complexation is another accepted mechanism for HM stabilization and refers to the formation of coordination complexes where metals bind to ligands on the surface of the stabilizer material (see Figure 1). Evidence of this mechanism is seen in biochar with high surface area and surface functional groups that are responsible for capturing HMs like Pb and Cd [5,46]. Crawfish shell (CFS) biochar contains amines and hydroxyl functional groups, which play the roles of donor ligands and chelation sites for Pb adsorption [6,122]. Abundant C=O bonds present on CFS biochar surfaces can form C-O-Pb and/or C=O-Pb complexes, resulting in a high removal efficiency of Pb [6,36].

Functional groups of shell- and bone-based biochar are controlled by pyrolysis temperature and the feedstock chemical composition. As previously mentioned, lower pyrolysis temperatures result in biochar with acidic functional groups, whereas higher pyrolysis temperatures result in biochar with basic and more graphite-like aromatic functional groups [5,36,123,124]. Sun et al. (2021) [36] found that Pb^{2+} was predominantly adsorbed by CFS biochar produced at high temperatures, specifically 500 °C and 700 °C, through complexation with surface groups such as -COO-, -O-, and C-π interactions (Equations (12)–(14)).

$$>C\text{-}COOH + Pb^{2+} + H_2O \rightarrow >C\text{-}COOHPb^{2+} + H_3O^+ \tag{12}$$

$$>C\text{-}OH + Pb^{2+} + H_2O \rightarrow >COPb^{2+} + H_3O^+ \tag{13}$$

$$\equiv C{:} + Pb^{2+} \rightarrow \equiv C{:}Pb^{2+} \tag{14}$$

Biochar produced from shell, starfish, and bone materials is expected to have functional groups such as -OH, -COOH, and R-OH. These functional groups can engage in surface complexation and ion exchange, effectively capturing HMs by releasing Ca^{2+} and Mg^{2+} [5,125]. According to Azeem et al. (2022) [5], the dominant mechanism for As removal is surface complexation with N-containing functional groups. Chitin in crustacean shells is rich with N- and O-containing functional groups, which make it desirable for HM removal via strong complex formation [36,126]. In the applications of cow bone biochar to soil, the surface complexation mechanism is responsible for the reduced availability of Zn and Cd. The transformation of these HMs from an exchangeable to an oxidizable fraction through interactions with aromatic C structures in cow bone biochar is a great example of the metal complexation process in these stabilizers [127].

3.4. Physical Adsorption and Electrostatic Attraction

Physical adsorption corresponds to the mechanism of attaching compounds to the material's surface by weak intermolecular bonds such as electrostatic and Van der Waals interactions [128,129]. All stabilizers considered in this review are alkaline by nature and increase soil pH upon their addition to soil, leading to the development of negative surface charge due to increased availability of OH^- ions [4]. Electrostatic attraction, therefore, occurs between the negatively charged stabilizer surface and positive HM ions [130]. However, it has been documented by many researchers that As and Sb mobilization increases after applying these alkaline stabilizers (Table 1). As and Sb are considered metalloids that exist as anions by combining with O and H (e.g., ${AsO_3}^{3-}$ and ${Sb(OH)_6}^-$).

Due to their prevalence as negative ions, they repel the negatively charged stabilizer surfaces. However, Chen et al. (2023) [6] showed that modifying CFS using chitin can develop a positive charge on the stabilizer surface, encouraging electrostatic attraction between the stabilizer surface and anions. Besides electrostatic attraction, the porous structure of stabilizers can aid in physical adsorption of ions through diffusion. Pyrolysis or calcination of stabilizers at high temperatures can generate a larger specific surface area and pore volume, which further facilitates the physical attachment of ions to the stabilizer surface [5,131].

It has been established that pH impacts the mechanism of precipitation by influencing the solubility and speciation of metals in solution. pH also regulates the surface charges and functional groups of stabilizing materials. At low pH, the surface groups of the stabilizer may be protonated due to the abundance of H^+, resulting in electrostatic repulsion between the positive surface charge of the stabilizer and Pb^{2+} [132]. Pb mostly remains as Pb^{2+} species at pH < 6, and it persists as $PbOH^+$, $Pb(OH)_2$, and $Pb(OH)_3{}^-$ in the range of pH 6–12 [111]. Hence, higher pH levels promote the adsorption process by creating more available bonding sites as a result of the deprotonation of the functional groups on the stabilizer surface. Additionally, the more bioavailable forms of Pb are transformed into stable metal–organic complexes under these conditions [15,100].

4. Performance and Cost Comparison

Heavy metal remediation efficiency and operation cost are two crucial factors in the practical applications of these stabilizers. Due to the significant variety in the facilities used for stabilizer synthesis, such as different types of ovens, grinding equipment, and synthesis procedures used for processing the raw materials, it is almost impossible to provide the specific cost for each type of stabilizer mentioned in this review. This is also likely the reason why previous reviews on soil stabilizers did not discuss cost comparison, to the best of our knowledge [4,5,12,13,26,47,49,52,57,58,64,67,87,130]. Therefore, it became our motivation to develop a reasonable but simple cost estimation method to allow for cost comparison among these stabilizers.

To simplify the cost assessment, the following method, shown in Table 2, was used. First, each process associated with the production of the stabilizers discussed in this review were listed in Table 2 as items 1–28. Then, each item was ranked on a scale of 1–6, based on the cost affiliated with each item. An index value of 1 refers to a low cost, while a 6 refers to a high cost, relative to the other items. These index values were assigned based on the authors' experiences and general knowledge about the items listed in the table.

To provide a clear example of this ranking process, refer to items 1 and 2 in Table 2. The items of "raw materials" and "water wash" were assigned index values of 1 because raw materials and water are both readily available and have low costs [33–35]. Additionally, water washing is a simple treatment that does not require other equipment or complicated processes. The highest cost index was assigned to item 28 of Table 2, for "time cost of 200–500 days". The reasoning for this is the high labor cost associated with longer treatment times. It should be noted that the cost index values assigned in Table 2 may vary between different regions globally. For example, in developed countries, the time cost may carry more weight, while in the developing countries treatment processes may be more expensive. The time cost in this case is set to meet the situations in developed countries.

Using Equation (15) shown below, the total estimated cost of applying a specific soil stabilizer (P) was calculated by summing together the index values for all items (i_n) required to produce and use the stabilizer. n is item # shown in Table 2.

$$P = \sum_1^n i_n \tag{15}$$

Table 1 describes the items needed for the production and application of each stabilizer and Table 2 lists the items (#1–28) and their corresponding cost index values. For example, the first row in Table 1 has an estimated total cost of 10 for the crawfish shell biochar. The items required to produce this material are #1—raw material, #2—tap water wash,

#5—oven drying at 60–105 °C, #6—pyrolysis or calcination using furnace at 300–900 °C, #18—dose cost 1% w/w, and #25—time cost 50-day pot experiment. The cost index values for these items, according to Table 2, are 1, 1, 1, 3, 1, and 3, respectively. Therefore the sum of these values is 10, which represents the estimated total cost for the production and application of this crawfish shell biochar. An Excel 2024 spreadsheet, found in the Supporting Information, includes final cost estimates for each type of stabilizer that is included in Table 1.

Table 2. Cost index of common items used in stabilizer manufacturing processes.

Item	Item#	Cost Index
Raw material (e.g., crustacean shell, bivalve shell)	1	1
Water wash	2	1
Boiling water wash (95–100 °C)	3	2
Ethanol wash	4	1
Oven drying (60–105 °C)	5	1
Pyrolysis or calcination using furnace (300–900 °C)	6	3
HCl treatment	7	1
Chitin treatment	8	1
NaOH treatment	9	1
Potassium permanganate treatment	10	1
Oxalic acid treatment	11	1
Deacetylation	12	1
Ground or pulverization and sieving for granular products	13	1
Ground or pulverization and sieving for fine powder	14	2
Acetic acid treatment	15	1
Crosslinking treatment	16	1
Defatting treatment	17	1
Dose cost:		
0–1% w/w	18	1
2–6% w/w	19	2
7–10% w/w	20	3
11–15% w/w	21	4
16–30% w/w	22	5
Time cost:		
0–10 days	23	1
11–30 days	24	2
31–50 days	25	3
51–100 days	26	4
101–200 days	27	5
200–500 days	28	6

Note: These index values were assigned based on the authors' experiences and general knowledge about the items listed in the table.

As a visualization tool and basis for comparison, Figure 2 displays the cost and performance data of the five main types of stabilizers discussed in this review. Cost values for Figure 2 were obtained via the process described above and Equation (15), while the performance data were obtained directly from Table 1 and taken as the Pb or Cd bioavailability reduction rate in soil. These data can be found in the Excel file included in the Supporting Information. Figure 2a plots the cost index values with heavy metal bioavailability reduction rates, which were collected from soil leaching tests [8,41,85,105] and used to quantify stabilizer performance. The ideal stabilizer candidate should cost less but perform better in the heavy metal stabilization process, as shown in the red circle (>80% metal reduction; <10 cost index). Figure 2b,c show violin plots of the HM bioavailability reduction rate and cost index per stabilizer type, respectively, for convenient comparison across groups. Kernel Smooth curve types were used for violin plots.

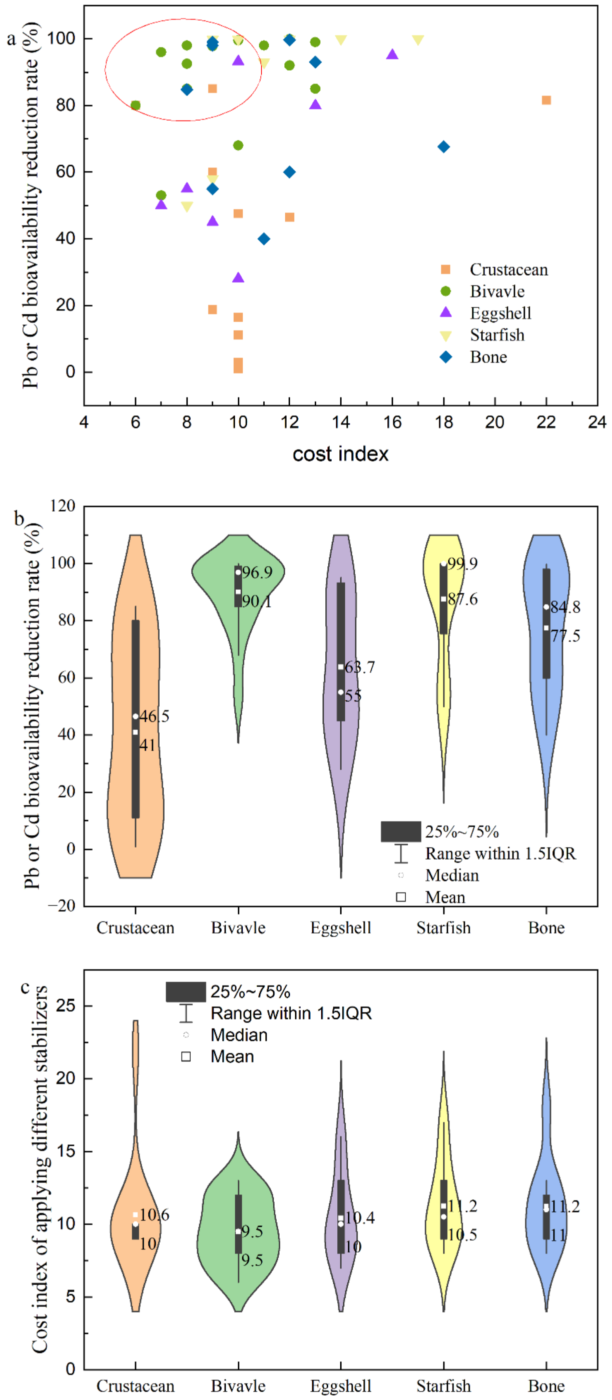

Figure 2. Performance and cost comparison among the five types of biowaste-based stabilizers. (**a**) Performance versus cost among the collected stabilizers; (**b**) performance comparison of the stabilizers via violin plot; (**c**) cost comparison of the stabilizers via violin plot.

From Figure 2b,c, it is clear that stabilizers made from bivalve shells most closely meet ideal stabilizer cost and performance goals. The performance for bivalve-based stabilizers is higher compared to the other stabilizer types, with a mean and median of specific Pb or Cd reduction rate of 96.9% and 90.1%, respectively. Though starfish-based amendments have a similar performance in terms of median and mean value, the data have greater variability than the bivalve shell-based products. This high variability in performance is also observed in stabilizers derived from crustacean shells, eggshells, and bone raw materials (Figure 2b), suggesting the performance of bivalve shell-based stabilizers is more reliable and consistent.

Similar advantages of bivalve shell-derived products are also shown in the cost in Figure 2c. The median and mean cost index values of bivalve shell-based stabilizers (both 9.5) are lower than the rest of the stabilizer types. Additionally, there is much less variability in bivalve stabilizer cost index values, in contrast to the alternatives. Based on these factors, bivalve shells appear to be the best raw material contender for stabilizer production used in heavy metal soil remediation applications.

5. Conclusions and Future Perspectives

Cost-effective stabilizers are the key to overcoming the current obstacle of heavy metal contamination in soil. This review summarizes the past several years of research on green and sustainable biowaste-based stabilizers. Additionally, a straightforward, effective cost estimation method and further cost comparison among various types of stabilizers was introduced and discussed for the very first time. Bridging this gap in the literature may help promote more efficient and affordable stabilizer development in the soil HM remediation field. Given the analysis in this work, bivalve shells appear to be the most promising raw materials among the different types of biowastes. The stabilization mechanisms of this material include precipitation, surface complexation, ion exchange, electrostatic interaction, and physical adsorption. Generally, these biowaste-based stabilizers are abundant in phosphorus and lime content, present minimal ecological risk, can operate at low cost, and have high performance in metal immobilization. However, most of the investigations have been performed on a lab-scale, and the assessment of heavy metal stabilization capacity is confined to the heavy metal leachability, bioavailability, and mobility. Additionally, the majority of HMs investigated are limited to Cu, Cd, Cr, Pb, Zn, Ni. Studies including other HMs are either not available or very rare. Furthermore, research on heavy metal accumulation in crops or plants grown in stabilizer-amended soil is minimal. Finally, the long-term impacts and efficacy of applying these biowaste-based stabilizers are not clear. Based on these findings, the following research areas are suggested:

(1) Expansion of the list of heavy metals to be studied. Several studies reported the increase of arsenic and antimony bioavailability in the soil after adding biowaste-based stabilizers; thus, these metalloids should be a particular future focus.
(2) Completion of pilot-scale testing on diverse, contaminated land with a well-prepared risk control plan. More factors need to be considered when testing is translated from a lab setting to a real-world scenario. Considerations like the effect on soil microbe activity and the potential effect on the groundwater need to be evaluated when scaling up these experiments. Monitoring of P and N in the soil and surface runoff water after precipitation events may also be necessary. Additionally, the heavy metal accumulation in the leaves and seeds of the planted crops is also an important factor in the pilot-scale testing. In general, field conditions are highly variable, so a wide range of tested conditions would be beneficial in understanding the effectiveness of these stabilizers.
(3) Long-term evaluation of the effectiveness of the stabilizers in heavy-metal-polluted soil and risk monitoring. This process will be time-consuming. In order to reduce the time cost, it may be helpful to develop simulation methods or mathematical models using artificial intelligence platforms such as Gemini 1.5 by Google, Azure Quantum by Microsoft, and ChatGPT-4o by Open AI that can speed up the long-term assessment of using P- and Ca-rich biowaste-based stabilizers.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su16208841/s1, Table S1: The summary of the determined cost index and heavy metal bioavailability reduction rate for the five P, Ca-riched bio-wastes.

Author Contributions: D.K.D.: writing—original draft, validation, methodology, investigation, formal analysis, data curation; T.B.: writing and editing, data curation; E.C.: writing and editing. P.N.: writing—review and editing, validation, methodology, formal analysis, data curation, supervision,

project administration, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: The authors thank the University of Missouri REP program and Missouri Water Center for the financial support.

Data Availability Statement: The data have been made available and shared in Tables 1 and 2.

Conflicts of Interest: The authors declare no conflicts of interest.

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