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MICROBIAL-INDUCED CALCITE PRECIPITATION" AS A POTENTIAL SUSTAINABLE TECHNIQUE FOR POLLUTED SOIL BIOREMEDIATION: A REVIEW

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Abstract: Industrialization and population growth have increased the emission and buildup environmental heavy metals. These components' bioaccumulations as exposure have been related to a range of illnesses and cancer, and the mechanical and physical properties of soil are altered. The "Microbial Induced Calcite Precipitation" is environmentally green, friend and sustainable method. This review focused on the metal remediation technology's effects and how to make them sustainable and more environmentally friendly. Many bacteria that produces urease, bacillus is a more common type. Bacteria, with sizes ranging from 0.5 to 3.0µm, are the most common microbes found in soils. It is critical to examine the type of soil, Bacterial size, and size of pore throat. The calcium carbonate majority tend to coat the surface of soils with coasrse particles in state of the contact points in soils with particles smaller than bacterial size (heterogeneous and limited precipitation). The bacterial concentration appears to affect crystal shape, calcium carbonate formation, and the cementation effect of geomaterials. Calcite precipitation takes place most when the pH is between 7.5 and 9.5. Calcite is formed three times at 50°C, while the unconfined compressive strength is only 60% of that at 25°C.Calcium carbonate can be immobilized or formed into undissolved compounds by binding free ions to the calcium carbonate's surfaces, resulting in a form of non-toxic and chemically stable.

Keywords: *Bioremediation, Microbial-induced carbonate precipitation (MICP), heavy metals*

1. Introduction

The advancement of industrialization and the extraction of natural resources, there has been a significant increase in the discharge of heavy metals into the environment. One of the main challenges facing the world is the contamination of soils, groundwater, sediments, surface water, and air with harmful heavy metals and toxic chemicals [1,2]. A contaminant is a chemical element, ion, or compound that has the potential to endanger human health or the environment, primarily due to its toxic properties [3,4].

Heavy metal poisoning of soil is is universal problem that threatens the ecology and health of human. In addition to uncommon geological reasons, heavy metal pollutants are injected unintentionally into soils through waste treatment and other activities, the electronical industry, mining, the use of fossil fuels, war and military education, agricultural, irrigation and chemical [5]. The immobilization of heavy metals using chemical, physical, and biological

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ways to improve the chemical and physical properties of soil has piqued the interest of researchers [6]. However, as a result of operational costs and the degradation of soil qualities, these procedures are relatively expensive [7]. Bioremediation, on the other hand, which detoxifies pollutants using microorganisms, has emerged as something of a simple, effectively cost and ecologically friendly solution for polluted soil repair [8,9]. Biochemical reaction which occurs inside a soil for producing calcite precipitate to affect engineering qualities of soil is referred to as a bio-mediated approach of soil improvement. Meanwhile, using interdisciplinary understanding of microbiology, chemistry and civil engineering to modify soil engineering features within subsurface [10]. For precipitating calcium carbonate into the matrix of soil, the approach uses soil microbial activities known as "Microbial-induced-calcite-precipitation" (MICP). Calcium carbonate formed binds together soil particles (clogs and cementing soils), improving soil strength and decreasing hydraulic conductivity. MICP is a viable choice for improving the soil-supporting capabilities of both existing and new structures, and it has been used in a wide range of civil engineering applications [11]. This review focused on the metal remediation technology's effects and how to make them sustainable and more environmentally friendly.

2. Microbially Induced Calcite Precipitation (MICP)

Recent improvements in bioremediation techniques have resulted in the ultimate goal of effectively restoring damaged areas in an eco-friendly and low-cost manner. Indigenous microorganisms found in contaminated environments hold the key to resolving the majority of the problems related with polluting material biodegradation and bioremediation, provided that the environmental circumstances are favorable for their growth and metabolism [12]. Pollutant kind, depth and degree of contamination, location, type of environment, cost, and environmental policies are some of the selection variables considered while choosing a bioremediation technique [13, 14]. Regardless of the fact that bioremediation techniques are vary, performance criteria “nutrient concentrations, oxygen, pH, temperature, and other abiotic parameters” that effect the efficacy of bioremediation processes are also considered. [15]. Bio mineralization based on "microbially induced carbonate precipitation" (MICP) is a new technology that has been intensively researched because of its potential applications in heavy metal contamination immobilization [16]. MICP has gained popularity in recent years for applications such as calcareous stone restoration, wastewater treatment, selective plugging for enhanced oil recovery, concrete strengthening and crack remediation, improvement in sandy soil strength/stiffness, foundation settlement reduction, liquefaction mitigation, soil permeability, dust control, and soil erosion prevention [17]. Bioremediation [18, 19, 20, 21], can be utilized to address a wide range of environmental issues, including radioactive pollution and heavy metal remediation [22]. " Table 1" illustrates examples of using MICP in heavy metal stabilization.

Table 1. Examples of using MICP in heavy metal stabilization

Heavy metal	Bacterial	Removal rate	final products	Ref
Cd, Pb , Cu	Mixture of four bacterial strains isolated from an abandoned mine soil	Pb(II):98.5%; Cu(II):67.2%; Cd(II): 42.4%, 98%, 79%, 65%	Precipitation of heavy metals to PbCO3, CuCO3,and CdCO3	[23,24] (Kang et al.,2016, Bhattachar a et al., 2018)
Pb	Leclercia adecarboxylata , isolated from heavy metal contaminated soils		Complexation of EPS.to lead Precipitation of lead ions intoCa10(PO4)6(OH)2 and (Pb5(PO4)3Cl).	[25] (Teng et al.,2019)
Cr, Cu,Zn	Bacillus subtilis, isolated from industrial contaminated soil	Cr(III): 99.95%; Cu(II):95.90%; Zn(II): 86.59%	Precipitation and co-precipitation: Cu2(OH)2CO3, ZnCO3, NiCr2O4, FeCr2O3,Zn5(CO3)2(OH) 6 CaCO3.	[26] (Maity et al.,2019)
Cd	Bacillus cereus, isolated from Cd contaminated soil	29.25%	Bio sorption of bacteria to Cd Precipitation: CdS and Cd·xH3O4P (cadmium phosphate)	[27] (Li et al., 2018)
As	Clostridium sp.	100%, 30%, 15% (6 days) 100%, 100%, 100% (20 days)	Precipitation: Fe(III) oxides. Fe(III)-As: adsorption of As to the biogenic Fe(III) oxides. Redox: As(III) is oxidized to the low-toxicity As(V).	[28] (Li et al., 2016)
Cu	Rahnella sp., isolated from Cu-contaminated dark brown soil	Cu(II): 83 mg/kg in soil Remediation for 5, 10, 30 days	Precipitation: rod-shaped Cu3(OH)3PO4 crystal.	[29] (Zhao et al.,2019)
Cu, Zn, Pb	Mixture of Desulfosporosinus meridie and Acidithiobacills ferrooxidans	Cu: 100%, Zn: 100%, Pb:84.62%	Precipitation: black metal sulfides	[30] (Liu et al., 2017)

2.1. Mechanism of (MICP)

Enzymes such as urease, carbonic anhydrase, and asparaginase activate MICP [31]. The bacterial mineralization process can be summarized as follows: The negative charge on the cell surface adsorbs Ca^{2+} from the surrounding solution in bacterial metabolism. After adding urea to the bacteria, urease secreted by the cells decomposes urea to create CO_3^{2-} and NH_4^+ plasma, and Ca^{2+} interacts with CO_3^{2-} to form calcium carbonate crystals on cell surface [32,33]. Because urea is a nitrogen supply for many different organisms, carbonate synthesis via ureolytic pathway has been reported to be most efficient in terms of energy, ubiquitous, and simple, has a high potential for calcification [16]. The metabolic processes

Including ureolytic-driven MICP are depicted in Eqs. (1–4). Urea is hydrolyzed by the urease enzyme into carbamate and ammonia, which are further hydrolyzed to liberate ammonia and carbonic acid. Because these bacteria precipitate Ca as $CaCO_3$, they could be used to efficiently collect other heavy metals and create carbonates-containing immobilized heavy metals [34, 35, 36, 37], as illustrated in the figure (1).

as pH and temperature influence calcite formation [38, 39, 40, 41].

2.2.1. Soil Particle Size

Soil is particularly difficult to treat among the several geometerials which could be possibly treated through MICP due to the complicated nature of soil parameters like particle size, mineral content, relative density and gradation.

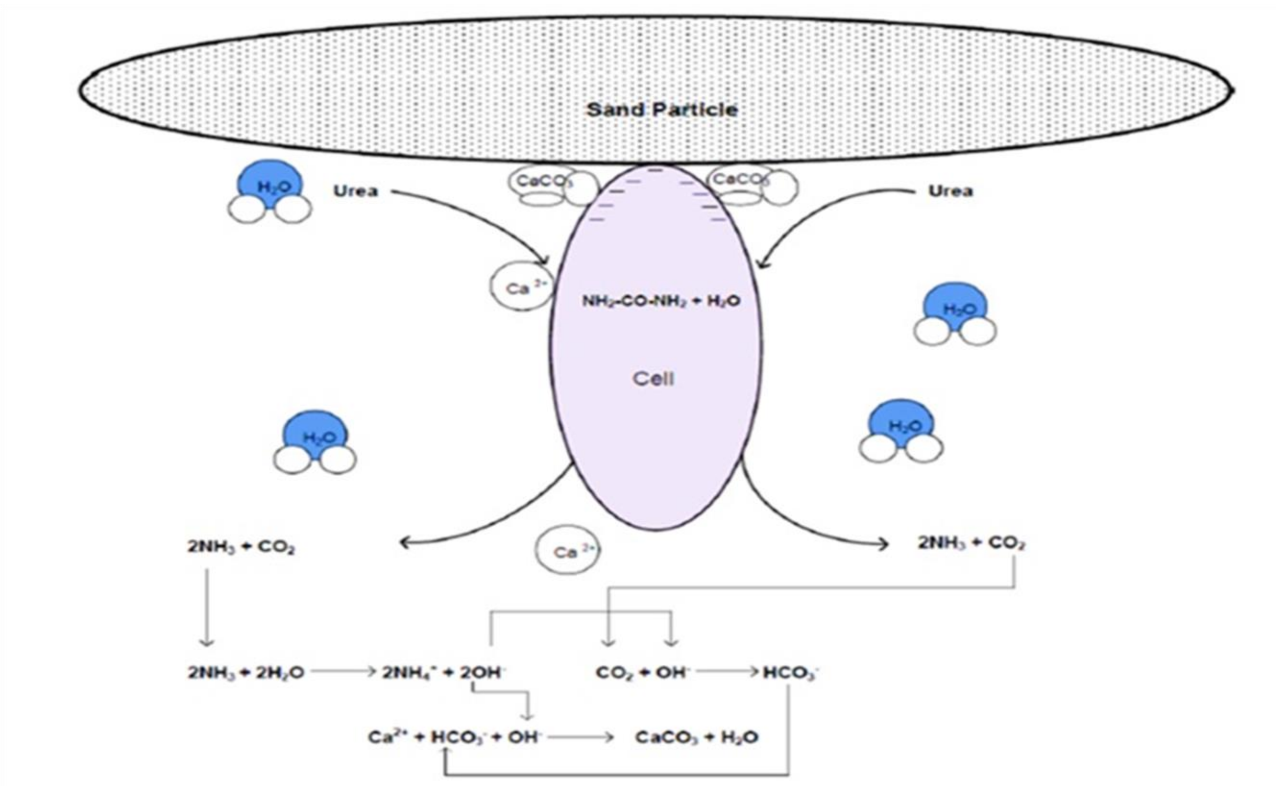

Figure1. Depicts the overall chemical reaction process that takes place in the soil matrix

$$(NH_2)_2CO+H_2O\rightarrow 2NH_3+CO_2 \quad (1)$$

$$2NH_3+2H_2O\leftrightarrow 2NH_4^{+}+2OH^{-} \quad (2)$$

$$CO_2+2OH-\leftrightarrow HCO_3^{-}+OH^{-}\leftrightarrow CO_3^{2-}+H_2O \quad (3)$$

$$Ca^{2+}+CO_3^{2-}\leftrightarrow CaCO_3\,(s) \quad (4)$$

2.2. Factors that Affect MICP

Urease activity and the amount of $CaCO_3$ precipitated are influenced by a number of factors. This production rate is affected by soil properties, bacterial species, and cementation solution concentrations. Extrinsic variables such

Mineral content may alter the pore fluid's chemical and thermodynamic qualities, resulting in additional nucleation sites for precipitation of calcium carbonate. As a result, MICP thrives in soils with a wide range of mineral compositions [42].

S. Pasteurii was employed to cement five distinct sands (rich in feldspar, quartz, iron oxide and calcite) and the shear wave velocity of cemented sands was measured. It was revealed that different mineral compositions had a substantial effect on the rate of calcium carbonate precipitation, sand rich in calcite having the fastest precipitation rate. Another crucial soil feature that influences MICP efficiency is particle size. The size of soil particles is proportional to the size of the pore throats in the soil matrix, that regulates whether bacteria may freely and evenly flow in soil matrix. Bacillus and Sporosarcina are generally about 1-5 μm in size. As a result, soils having particles smaller than the size of bacteria (as, clay) may inhibit free flow of bacteria in the matrix of soil, resulting in calcium carbonate precipitation that is restricted and heterogeneous [43]. Particles that are larger, such as(gravel and coarse sand and so on) have fewer intergranular interactions and a greater intergranular distance. Rather of coating the contact points, the bulk of calcium carbonate coatings the surface of coarse particles, potentially reducing total cementation efficiency.

2.2.2. Bacteria

Microbial activity is thought to be a major contributor to the formation of soil carbonate deposits, and because bacteria are the only live organisms present in the MICP system, it is thought to be one of the most influential components in the precipitation process. It may have an effect on various parameters and may also have an effect on certain parameters. Currently recognized microbial mineralizing bacteria include urease-producing bacteria, oxidizing bacteria, denitrifying bacteria, sulfate-reducing bacteria and others. Urease-producing bacteria, in particular, have been widely studied and employed because they are inexpensive, relatively easy separation and cultivation, strong mineralization and cementation effect, and ease of control over the reaction mechanism [33].

2.2.2.1 Type of bacteria

The type of bacteria influences thecrystal form, morphology, and deposition rate of calciumcarbonate [44] [Bacillus megaterium showed the highest urease activity, followed by Bacillus thuringiensis Bacillus cereus, Clostridium, and Bacillus subtilis.When Bacillus megaterium and Bacillus sphaericus were cocultured, they exhibited the effects of nitrogen fixation and synergism. Bacillus sphaericus was the most suitable for biodegradation in practice various environmental conditions [45]. S. pasteurii, eg, has been used in heavy metal contamination, remediation, soil enhancement and concrete remediation [18]. B. megaterium, on the other hand, has been employed to increase the hardness of concrete and the durability of construction materials [43, 46].

2.2.2.2 Size and shape of Bacteria

Bacteria, with sizes ranging from 0.5 to 3.0 μm, are the most common microbes found in soils. A key factor is the urease-producing bacteria's geometric compatibility with the soil into which they are injected affects MICP because it impacts the pace of the bacteria movement inside soil. Microbes are transported through soil by either passive diffusion or self-propelled movement between soil particles and through pore throats. Small size of pore throat will hinder free movement inside soil depending on the size of microorganisms and compaction of soil. Bacteria with sizes ranging (0.3 to 2) μm can readily travel inside sandy soil with sizes particle ranging (0.05 to 2.0) mm. However, fine with substantial amount (clay and silt) in soil have an inhibiting effect on bacterial migration. As a result, before beginning the MICP process, it is critical to examine pore throat size, size of bacteria and soil type [2].

2.2.3. Bacterial solution concentration

Bacterial cells have two important jobs in creation the crystals of calcium carbonate during the MICP process. First and foremost, bacteria operate as sites of nucleation sites for calcium carbonate crystal formation. Second, on the cells surface of bacteria, there are negative ion groups and the extracellular polymeric sub-stances (EPS) may act as calcium carbonate crystal nucleation sites and influence crystal shape and morphology [47,48,49]. Bacterial cell aggregation and flocculation also influence the calcium carbonate growth pattern at nucleation location. As a result, the bacterial concentration appears to affect crystal shape, calcium carbonate formation, and the cementation effect of geomaterials [43].

2.2.4. Concentration of cementation reagent

Ather element that influences precipitation of calcite is cementation reagent concentration, which is required for calcite precipitation. A limited number of research have been conducted to investigate the influence of cementation reagent concentration upon geotechnical parameters of various soils [50,51]. The results of a study by [52] demonstrate a strength increase with increasing the concentration reagent to 0.5M, followed by a decrease in strength within levels greater than 0.5M [53]. Discovered that the best cementation reagent concentration for MICP treated residual soil is 0.25M. [41] Discovered that lower concentrations of cementation reagents (≤0.25M) resulted in greater unconfined compressive strength values. Based on these few investigations, at lower cementation reagent concentrations, MICP is more effective.

2.2.5 pH

Calcite formation begins when urea is decomposed by the urease enzyme under favorable conditions, which are often alkaline. Calcite precipitation is most common when the pH is between 7.5 and 9.5, according to several research [10]. the highest pH for calcite precipitation, 7 for Bacillus Megaterium, 8 for Bacillus sphaericus, and (9.1,9.3,9.5) for "Sporosacina pasteurii" in general, the synthesis of ammonia by urea hydrolysis raises the pH medium through the MICP process. The pH rise is buffered by bicarbonate from microbial respiration and urea hydrolysis.

During MICP treatment monitoring the effluent pH is critical for maintaining the most favorable conditions to calcite synthesis since carbonate tends to dissolve rather than precipitate at very low pH [2]. B. licheniformis, Bacillus cyclobacillus, Bacillus lateralis, and Bacillus filamentosa all have optimal growth pH levels of around 9.5 [54].

2.2.6. Temperature

Calcite precipitation is temperature sensitive, just as any other enzymatic activity since it impacts microorganism proliferation, rate of nucleation, activity of urease and calcium carbonate solubility. The change of temperature will affect the crystal sizeand the cementation mode of purpose calcium carbonatebetween soil particles [19, 31]. Studies have shown that the catalytic activity of urease was the strongest at 20∼37°C [55]. [56] investigated the influence of room temperature (25°C) and higher temperature (50°C) of MICP-treated sand on strength . Calcite created at 50°C was found to be approximately 3 times more abundant than calcite created at normal temperature. However, at 50 °C, the unconfined compressive strength (UCS) is only 60% of that at 25 °C.

3. Immobilization of Heavy Metals

Metals (including metalloids) are abundant in nature, and can be found in rocks, soils, and water. Although modest amounts of particular metals are necessary for the health of humans and other organisms [57]. As the concentration of heavy metal ions increases, the mechanical and physical properties of the soil alter, and the unconfined compressive strength progressively declines. This is due to the seepage of heavy metal ions into the clay soil. As a result, the cohesive force between soil particles decreases, as does the effective contact area, lowering the unconfined compressive strength. Heavy metal ions contaminated clay soil disrupts the internal equilibrium of soil particles, alters their connectivity and electric field, weakens the cementation surface, and raises the permeability coefficient [58]. Land disposal is the most frequent kind of waste disposal done by many countries, which is a waste containment system intended to regulate and avoid contamination of the ground. This disposal encompasses all waste products, whether hazardous or non-hazardous, such as industrial wastes and municipal wastes. In some circumstances, heavy metals will escape into the environment due to defective landfill design. As a result, operators must guarantee that leachate from the burial of trash does not seep and harm neighboring ground and surface water [4]. Because of their high toxicity, metals such as "As, Cd , Pb ,Cr ,and Hg" classified as human carcinogenic by the Environmental Protection Agency (EPA), as they can induce systemic failures or multiple organ damage at very low exposure levels, removing or eliminating them from polluted environmental matrices is critical. Metals could not be biodegraded or eliminated, although their mobility in the environment can be reduced [59]. Metal microbiological immobilization is defined a reduction in metal mobility caused by a change in the chemical physical or condition of the metal [60]. The fundamental processes for metal immobilization include pH change and/or redox reactions, solubility increase or decrease via complex formation or precipitation, and adsorption[61].Metals and metalloids' mobility and toxicity are determined by their oxidation states, which meaning that alter the redox potential of the matrix being treated might impact the microbial processes which lead to their stabilization[62,63] .This immobilization is influenced by a number of parameters, including the specific properties of each metal, concentration, temperature and pH . Calcium carbonate generated can be immobilized or create undissolved compounds, with ions that are free, bound to surfaces of the CO_3 to produce a non-toxic and chemically stable form [64].

4. Conclusions

This study provides an overview to bioaccumulation of heavy metal and how exposure to them has been linked to various diseases and cancer. The mechanical and physical qualities of the soil are altered. MICP is emerging as a method for immobilizing hazardous metals via ureolytic microbes (bacteria). Pollutant kind, depth and degree of contamination, location, type of environment, cost, and environmental policies are some of the selection variables considered while choosing a bioremediation technique. Urease hydrolysis becomes the most popular $CaCO_3$ precipitation technique used by researchers since it is simple and easy to control. The heavy metals are detoxified by converting them from soluble to insoluble forms using the MICP process.The type of bacteria influences the crystal form, morphology, and deposition rate of calcium carbonate .Bacteria with sizes ranging (0.3 to 2) µm can readily travel inside sandy soil with sizes particle ranging (0.05 to 2.0) mm. Calcite precipitation takes place most when the pH is between 7.5 and 9.5.The created calcite increased with increasing temperature up to 50 °C while the higher strength found at room temperature.

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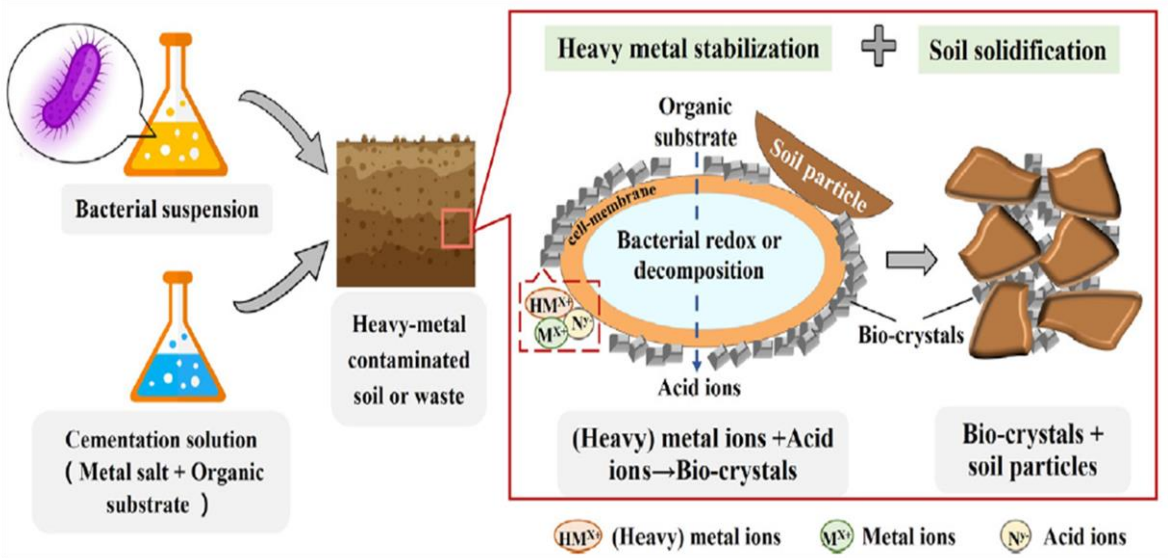
Conflict of interest

The publication of this article causes no conflict of interest.



Fig**ure2.** Process of soil bioremediation by MICP

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