REVIEW

Clay Mineral Nanoparticles for Heavy Metal Remediation in Soil: A Comprehensive Review of Current Trends and Future Directions

Rinky Yadav[1], Manju Devi[2], and Deepti Singh Vashishth[3*]

1   Department of Environmental Science, Alpine group of Institutions, Dehradun, India
2   Department of Entomology, College of Horticulture and forestry Thunag, Mandi H.P.
3   Department of Environmental Science, Graphic Era (Deemed to be University), Dehradun, India

Corresponding Email: deepti8694@gmail.com

Abstract

Heavy metal contamination in soil represents a critical global environmental challenge due to the fact that it poses substantial threats to ecological integrity and to human health. Remediation methods that are common like land filling and also excavation often is environmentally damaging and also costly. Because of this, alternatives that are revolutionary along with sustainable we must explore. Nanomaterials of a highly promising class have emerged these are clay mineral nanoparticles for in-situ remediation of soils contaminated by heavy metals. This is a review that endeavors toward the provision of a full overview of the state of current knowledge. It is about the use of clay mineral nanoparticles in the cleanup of heavy metal soil. This review closely examines the diverse types of clay minerals people employ, the various strategies people use to modify and functionalize them for remediation efficiency improvement, and the detailed mechanisms governing all interactions with a wide heavy metal contaminant spectrum. Furthermore, we explore here a critical analysis into all of the key factors that do largely influence remediation efficiency, which then include nanparticle size and surface charge characteristic in addition to the complexities of solution chemistry.   Acknowledging the practical implementation aspects, the review also meticulously addresses the inherent challenges and limitations associated with the real-world application of clay mineral nanoparticles for soil remediation, specifically focusing on scalability, cost-effectiveness, stability, durability, and potential environmental and health risks. Finally, we propose a series of well-defined future research directions aimed at overcoming these limitations and further optimizing the performance of clay mineral nanoparticle-based remediation technologies, paving the way for sustainable and efficient solutions to heavy metal soil pollution.

Keywords:Adsorption, Clay mineral nanoparticles, Environmental sustainability, Heavy metal remediation, Soil pollution

1. Introduction

The escalating global industrialization and agricultural intensification have inadvertently led to a pervasive environmental problem: heavy metal contamination in soil (Alloway, 2013; Sharma et al. 2023). Heavy metals, defined as elements with a density greater than 5 g/cm³, encompass a range of elements including arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), and zinc (Zn), among others (Tchounwou et al. 2012). These contaminants, originating from diverse anthropogenic sources such as mining activities, industrial effluents, agricultural inputs (e.g., fertilizers and pesticides), and improper waste disposal, accumulate in soil matrices, posing significant and multifaceted risks (Bradl, 2005; Kabata-PendiasandPendias, 2001). The persistence of heavy metals in the soil environment stems from their non-biodegradable nature and long residence times, leading to chronic exposure and bioaccumulation within food chains, ultimately impacting both human health and ecosystem sustainability (Järup, 2003).

The adverse effects of heavy metal contamination on human health are well-documented and include a wide

spectrum of ailments ranging from developmental disorders and neurological damage to various forms of cancer and organ dysfunction (ATSDR, 2019; WHO, 2018). Furthermore, heavy metals exert detrimental impacts on soil ecosystems, disrupting microbial communities, inhibiting plant growth, and reducing overall soil fertility, thereby compromising agricultural productivity and ecological balance (Githinji, 2019).

Conventional remediation technologies employed to address heavy metal-contaminated soils often fall short of providing sustainable and cost-effective solutions. Chemical methods, such as soil washing and chemical leaching, can be energy-intensive, generate secondary pollutants, and often alter soil physicochemical properties, potentially impacting soil health (Mulligan et al. 2001). Phytoremediation, although considered a more environmentally friendly approach, is often slow, metal-specific, and may not be effective for highly contaminated sites. Therefore, the urgent need for innovative, efficient, and sustainable remediation technologies for heavy metal-contaminated soils is paramount.

Over the past few years, nanotechnology, and specifically the application of nanomaterials, has emerged as a revolutionary field with immense potential for environmental remediation. Clay mineral nanoparticles have gained significant attention as a promising technology for heavy metal remediation in soil (Brigatti et al. 2006; Carretero et al. 2002). Clay minerals, naturally occurring hydrous aluminosilicates with layered structures, posess inherent properties that make them particularly well-suited for adsorption-based remediation processes (Brigatti et al. 2006; Bergaya and Lagaly 2013). These properties include a large surface area, negative charge, and layered structure, allowing them to interact with and preventing pollutants from spreading (Murray, 2006). When clay minerals are reduced to the nanoscale, their surface area and reactivity increase, enhancing their ability to clean up pollutants (Lin and Xing, 2007).

- **Natural Abundance and Cost effective:** Clay minerals are better approach for environmental remediation due to their natural abundance and affordability. This makes them a practical and cost-effective solution for big cleanup projects.

- **Environmental Compatibility:** Clay minerals are also a safe choice for the environment because they don't harm the environment, are compatible with living things and won't create new pollution problems. This

makes them a reliable and eco-friendly solution for cleaning up pollutants (Sposito, 2008).

- **High Adsorption Capacity:** Because clay particles have a large surface area and a negative charge that attracts the positively charged heavy metal ion, making it easy for them to trap and remove these pollutants (Bhattacharyya and Gupta, 2008).

- **Versatility in Modification:** Modified clay nanoparticles to target specific heavy metals by altering their surface properties and attaching molecules that selectively bind to those metals, enhancing their removal efficiency. This will result in better finding and removing of exact pollutants they are designed to target.

- **Potential for In-Situ Remediation:** The tiny size of clay particles allows them to spread easily through the soil and move deep into the soil without getting stuck. This means we can cleanup pollutants right where they are, without having to dig up a lot of soil. This approach saves money, and minimizes disruption to the environment (Theng, 2012).

2. Types of Clay Minerals:

Clay minerals a big part of earth surface. They are made up of tiny layers of aluminum, silicon and oxygen atoms, and they are incredibly small measured in nanometers. They are made up of two main building blocks that is tetrahedral sheets which are made up of silicon atom surrounded by four oxygen atoms and octahedral sheets which are made up of aluminum, magnesium and iron atoms surrounded by six oxygen atoms or hydroxyl groups (Feininger et al. 2013).

Studies have shown that montmorillonite, kaolinite, bentonite and sepiolite for their ability to prevent and remove heavy metals, having unique properties.

2.1. Kaolinite:

Kaolinites got a 1:1 structure, low cation exchange capacity, small surface area, and a non-expandable framework, with its surface charge shifting based on pH levels (Murray, 2006).

It effectively removes heavy metals from polluted soil via electrostatic attraction and surface bonding, despite its relatively low ion-exchange capacity. Nano-kaolinite outperforms its regular counterpart due to increased surface area, and modifications with organic compounds

increases its removal capabilities (Ajala et al. 2024; Unuabonah et al. 2008).

2.2. Montmorillonite:

Montmorillonite's 2:1 structure gives it unique properties, such as high cation exchange capacity and interlayer expansion, making it effective for applications like heavy metal removal and wastewater treatment. it has a unique structure, with two layers of tetrahedral sheets sandwiched an octahedral sheet. This structure gives montmorillonite a higher capacity to exchange ions and a larger surface area compared to kaolinite. Montrmorillonite have a special ability to expand and contract, as well as substitution, often involving ions like aluminum, magnesium, or ion, creates charge imbalances that contribute to its high cation exchange capacity (Mitchell and Soga, 2005). These substations, where aluminum replaces silicon and magnesium replaces aluminum create a permanent negative charge on the montmorillonite layers. The negative charge of montmorillonite is balanced by positively charged ions like sodium, calcium and potassium, which are located between the layers. Montmorillonite is highly effective at removing heavy metals from contaminated environments due to its exceptional ability to absorb (Bhattacharyya and Gupta, 2008). Montmorillonite nanoparticles excel at removing heavy metals like cadmium, copper, chromium, lead and zinc from soil and water. Modifying the interlayer space with organic and inorganic materials can enhance its selectivity for specific heavy metals remediation (Goncharuk et al. 2010).

2.3. Bentonite:

Distinctive properties Bentonite's, such as interlayer expendability, low permeability, and high adsorption capacity, make it a valuable resource for various environmental applications, including landfill liners, wastewater treatment, and soil remediation. Moreover, bentonite nanoparticles derived from natural bentonite available have shown promising results in heavy metal remediation. These nanoparticles offer a cost-effective and readily available alternative to pure monmorillonite nano clays. Furthermore, modification strategies like surface modification and intercalation, commonly used for montmorillonite, can also be applied to bentonite to enhance its heavy metal removal efficiency, increasing capacity in environmental remediation (Bhattacharyya and Gupta, 2008).

2.4 Halloysite:

Halloysite's unique tubular structure, sets it apart from other clay minerals like kaolinite. Its moderate cation exchange capacity and variable surface charge, influenced by pH, make it a useful material for various applications. The differing functional groups on its inner and outer surface, allowing it to interact with ions and molecules in definite ways (Theng et al. 2012).

Halloysite nanotubes (HNTs) are naturally offering a large surface area for heavy metal adsorption. Their unique shape allows for loading special materials inside the tubes to increase remediation efficiency. Modifying HNTs with organic molecules and polymers can further improve their potential for targated remediation applications (Yuan et al. 2015).

3. Transformation and Functionalization:

Various technique is used to modify clay mineral nanoparticles, improving their cleanp efficiency and selectivity for specific heavy metals.

3.1. Surface Modification with Organic Compounds:

Organic modifiers like polymers, surfactants, chelating agents, and biochar alter the surface properties, improving the nanoparticles' ability to effectively remove pollutants.

- **Polymers:** polymers by introducing functional groups like amine, carboxyl, hydroxyl, and thiol that bind to heavy metal ions can enhance clay mineral nanoparticles heavy metal removal capabilities. Natural polymers like chitoson and synthetic polymers like polyacrylamide and polyacrylic acid have been used to modify clay minerals, improving their adsorption capacity and stability in water and soil, making them more effective for environmental remediation (Barbooti et al. 2019; Tsai et al. 2016).

- **Surfactants:** surfactant with them with both water-loving (hydrophilic) and water-repelling (hydrophobic) characteristics, can alter clay mineral nanoparticles surface properties, that can lead to altering their interaction with heavy metals. Certain surfactants such as cetyltrimethylammonium bromide, can even reverse the surface charge increases adsorption of specific heavy metals (Zhu et al.2005). Anionic surfactants, such as sodium dodecyl sulfate (SDS), can further enhance the negative surface charge of clay

minerals, improving the adsorption of cationic heavy metals through increased electrostatic attraction (Chen et al. 2011). Non-ionic surfactants, like as Triton X-100, can enhance the dispersion and wetting properties of clay mineral nanoparticles, improving their mobility and interaction with heavy metals in soil, which can lead to more effective remediation (Zhang et al. 2017).

- **Chelating Agents:** chelating agents like EDTA, DTPA, and humic acid can be used to modify clay mineral nanoparticles, notably enhancing their adsoption capacity for specific heavy metals. These agents from stable complexes can sequestre or bind and isolate metal ions, allowing for efficient removal of contaminats. By immobilizing chelating agents onto the clay mineral surface through covalent or non-covalent bonding, highly effective binding sites are created. This modification enables the nanoparticles to demonstrate high efficiency in removing heavy metals from contaminated site, making them a promising tool for environmental remediation (Kloprogge and Kloprogge 2019; Bao et al. 2014).

- **Biochar:** biochar-modified clay nanoparticles create a potent nanocomposite for heavy metal remediation. Biochar's porous structure, high surface area, and functional groups (such as carboxyl, hydroxyl, and phenolic groups) enhance the adsorption capacity of clay minerals (Thies et al. 2009). With biochar facilitating metal absorption and clay minerals providing stability and uniform distribution (Yang et al. 2024; Gao and Goldfarb, 2021).

3.2. Ion Exchange and Intercalation:

Ion exchange and intercalation modify clay mineral's structure and chemistry by ions exchange or inserting molecules between layers, modofying their heavy metal adsorption properties. This enables altered clay minerals for effective heavy metal remediation.

- **Ion Exchange:** Ion exchange replace existing ions between clay mineral layers with new ones, boosting heavy metal removal. Adding transition metal ions like Fe3, Mn2, or Cu2 can result in modified clays that capture heavy metals through combined effects and electron transfer reaction (redox) reactions. Intercalation with organic cations, such as alkylammonium ions, expands interlayes space and

alters hydrophobicity, affecting pollutant adsorption and heavy metal transport (Mudzielwana et al. 2019).

- **Intercalation:** Intercalation inserts molecules or materials between clay mineral layers, transforming properties like space between layers, surface area, and chemistry. This makes better heavy metal uptake. For instance, introducing metal oxides like iron or manganese result in materials capable at sequestering heavy metals like arsenic and chromium through chemical reactions (Kosuge et al. 2000).

3.3. Nanocomposite Formation:

Combining clay mineral nanoparticles with materials like metal oxides, carbon nanotubes, graphene, or polymers creates hybrid nanocomposites that enhance heavy metal remediation by improving their grab onto and hold a larger number of heavy metals, specific target, stability, and it might be easier to resuse these materials after they've absorbed metals, or easier to recover the captured metals.

- **Clay-Metal Oxide Nanocomposites:** clay-metal oxide nanocomposites, made from integrating clay minerals with metallic oxides, titanium dioxide, or zinc oxide, demonstrate enhanced heavy metal adsorption and photocatalytic activity. The metal oxides provide extra binding locations and taken part in redox reactions, while clay minerals offer structural support and stability. These nanocomposites are effective for removing heavy metals, such as arsenic and chromium, and can also enable light-activated catalytic ability of organic contaminants (Chen et al. 2008).

- **Clay-Carbon Nanotube/Graphene Nanocomposites:** incoprating clay mineral nanoparticles with carbon nanotubes (CNTs) or graphene sheets or carbon sheets result in the formation of nanocomposites with enhanced properties, including high surface area, high electrical conductivity, and enhanced structural integrity, making them suitable for various applications. These nanocomposites demonstrate grater adsorption capacity. Clay minerals help disperse CNTs and grapheme, preventing aggregation and improving accessibility for heavy metal adsorption. Clay-CNT/ graphene nanocomposites exhibit enhanced adsorption capacity for heavy metals like lead, cadium and copper, making them effective for

environmental cleanup applications (Novoselov et al. 2004).

- **Clay-Polymer Nanocomposites:** clay polymer nanocomposites are made from integrating clay mineral nanoparticles with organic polymers, leading to enhanced mechanical properties, robustness, andability for controlled release. The polymers serve as binders and matrices, increasing mechanical strength and preventing caly nanoparticle aggression. Meanwhile, clay minerals enhance the thermal and mechanical properties. These nanocomposites can be shaped into various forms, such as films, beads, or fibers, fit for different environmental restoration application. For instance, clay alginate nanocomposite beads can efficiently remove heavy metals from wastewater, while clay-polymer nanocomposite films can serve as permeable reactive barriers for in-situ groundwater and soil remediation (Abara et al. 2024).

3.4. Interactions with Heavy Metals:

Nano-sized clay particles interact with heavy metals through several key mechanisms including adsorption and desorption, complexation and precipitation, and redox reactions. Adsorption is the principal way by which these nanoparticles remove heavy metal ions accumulate at the solid-liquid interface. Desorption on the other hand is the opposite process, where adsorbed heavy metal ions are released back into the solution. understanding the dynamics of both adsorption and desorption is crucial for evaluation the longterm effectiveness and stability of clay mineral nanoparticles-based remediation technologies, ensuring the contaminants are securely immobilized and do not reenter the environment (Ugwu et al. 2019).

- **Adsorption Mechanisms:** Heavy metal adsorption onto clay mineral nanoparticles is influence by a combining of physical and chemical interactions, including electrostatic attraction, ion exchange, complexation, and surface precipitation, which collectively determine the adsorption capacity and specificity of the nanoparticles.

- **Electrostatic Interactions:** clay mineral nanoparticles typically have a net negative surface charge which attracts positively charged heavy metal cations like lead, cadmium, and copper through electrostatic attraction, influenced by

factors like charge density and ionic strength of the surrounding solution (Sposito, 2008).

- **Surface Complexation:** Surface complexation occurs when heavy metal ions from chemical bonds with functional groups on clay mineral surfaces, such as silanol (Si-OH), aluminum (Al-OH), and edge hydroxyl groups. This process can be inner-sphere, with water molecules in between. Inner sphere complexation is typically stronger and has higher adsorption affinity. Surface complexation is highly dependent on pH, with different functional groups binding best at different pH levels (Ray and Okamoto, 2003).

- **Ligand Exchange:** Ligand exchange involves the replacement of ligands (e.g., H_2O, OH^-) coordinated to surface metal centers of clay minerals with heavy metal anions (e.g., arsenate, chromate) or organic ligands complexed with heavy metal cations. Ligand exchange can be particularly important for the adsorption of oxoanionic heavy metals onto clay minerals and for the removal of heavy metals in the presence of complexing agents. The effectiveness of ligand exchange depends on the relative affinity of the ligands for the surface metal centers and the heavy metal ions (Sparks, 2003).

- **Interlayer Adsorption:** For expanding clay minerals like montmorillonite, heavy metal ions can also be adsorbed into the interlayer space between the clay mineral layers. Interlayer adsorption can occur through ion exchange with interlayer cations, complexation with interlayer water molecules, or direct intercalation into the interlayer space. Interlayer adsorption can significantly enhance the overall adsorption capacity of expanding clay minerals due to the increased surface area available within the interlayer space (Theng, 2012).

- **Adsorption Isotherms and Kinetics:** Adsorption isotherms and kinetics are used to quantitatively describe the adsorption behavior of heavy metals onto clay mineral nanoparticles. Adsorption isotherms describe the equilibrium relationship between the concentration of heavy metal ions in solution and the amount of heavy metal adsorbed onto the nanoparticles at a constant temperature. Adsorption kinetics describe the rate at which heavy

metal adsorption occurs and the time required to reach equilibrium.

- **Desorption Mechanisms:** Desorption is the process by which heavy metal ions are released from clay mineral nanoparticles back into the solution. This can happen due to change in chemistry, such as pH, ionic strength, or presence of competing ligands. Desorption can be detrimental in remediation in remediation if it releases heavy metals back into the environment. However, controlled desorption can be beneficial for regenerating and reusing clay mineral nanoparticles or recovering valuable heavy metals, enhancing the sustainability of remediation technologies (Ugwu et al. 2019).

3.5. Complexation and Precipitation Reactions:

Beside adsorption, clay mineral nanoparticles can also remove heavy metals through complexation and precipitation reactions. Complexation forms soluble or insoluble complexes between heavy metal ions and ligands in the solution or on the clay surface. Precipitation creates insoluble solid phases containing heavy metals, which can be easily separated from the surrounding soil (Ray and Okamoto, 2003; Gaskova et al. 2008)

- **Complexation Reactions:** Clay mineral nanoparticles can act as supports for complexing agents, facilitating the formation of heavy metal complexes. Complexation can occur in solution or at the clay mineral surface. Soluble complexation can enhance the mobility of heavy metals, potentially hindering remediation. However, surface complexation, where heavy metal ions form stable complexes with functional groups on the clay mineral surface, can enhance adsorption and immobilization. Clay mineral nanoparticles modified with chelating agents, as discussed previously, utilize surface complexation as the primary mechanism for heavy metal removal (Reich et al. 2010).

- **Precipitation Reactions:** Clay mineral nanoparticles can promote heavy metal precipitation by providing nucleation sites for precipitation or by altering the solution chemistry to favor precipitation. Precipitation of heavy metals can occur through various mechanisms, including:

  o **pH-Induced Precipitation:** Increasing the pH of the soil solution can promote the precipitation of heavy metal hydroxides and carbonates, which

are generally less soluble than heavy metal ions at neutral and alkaline pH conditions. Clay mineral nanoparticles can act as pH buffers and provide nucleation sites for precipitation, enhancing the precipitation efficiency.

  o **Sulfide Precipitation:** Introducing sulfide ions into the soil solution can induce the precipitation of highly insoluble heavy metal sulfides (e.g., PbS, CdS, ZnS). Clay mineral nanoparticles can act as carriers for sulfide ions and facilitate the precipitation process. Sulfide precipitation is particularly effective for immobilizing heavy metals under reducing conditions.

  o **Phosphate Precipitation:** Phosphate ions can react with heavy metal ions to form insoluble heavy metal phosphates (e.g., $Pb_3(PO_4)_2$, $Cd_3(PO_4)_2$) (Ma, Cao, & Chen, 1994). Clay mineral nanoparticles can facilitate phosphate-induced precipitation by providing nucleation sites and promoting phosphate adsorption. Phosphate precipitation is a promising approach for long-term immobilization of heavy metals in soil due to the low solubility and high stability of heavy metal phosphates.

3.6. Redox Reactions:

Redox reactions involve the transfer of electrons between chemical species, resulting in changes in oxidation states. Clay mineral nanoparticles, particularly when modified with redox-active materials, can participate in redox reactions with heavy metals, leading to their detoxification or immobilization.

- **Redox Reactions of Chromium:** Chromium exists in soil primarily in two oxidation states: Cr (VI) and Cr (III). Cr (VI) is highly toxic and mobile, while Cr(III) is less toxic and less mobile. Reduction of Cr(VI) to Cr(III) is a detoxification strategy for chromium remediation. Clay mineral nanoparticles modified with reducing agents, such as iron nanoparticles, biochar, or organic matter, can facilitate Cr(VI) reduction through electron transfer reactions Clay minerals themselves, particularly iron-containing clay minerals like bentonite, can also contribute to Cr(VI) reduction under certain conditions (Fendorf et al. 2000).

- **Redox Reactions of Arsenic:** Arsenic exists in soil primarily in two oxidation states: As(V) and As(III). As (III) is generally more toxic and mobile than As(V).

Oxidation of As(III) to As(V) can reduce arsenic mobility and facilitate its adsorption onto clay mineral nanoparticles. Modification of clay mineral nanoparticles with oxidizing agents, such as manganese oxide or iron oxide, can facilitate the oxidation of As(III) to As(V), thereby enhancing arsenic remediation. Clay iron oxide nanocomposites can participate in redox reactions, exhibiting versatility in assenic removal by adapting to varying redox conditions, which enables efficient remediation strategies (Lizama et al. 2011).

Understanding the interaction mechanisms between clay mineral nanoparticles and heavy metals is key to designing effective remediation strartegies. Adsorption is often primary for cationic heavy metals, while complexation, precipitation, and redox reactions also play significant roles, depending on the specific heavy metal and solution conditions.

3.7. Factors Influencing Remediation Efficiency:

The effectiveness of clay mineral nanoparticles in heavy metal remediation depends on factors like particle size, surface area, surface charge, zeta potential, solution chemistry, and pH. These properties influence nanoparticle reactivity and interactions with heavy metals, impacting remediation efficiency (Nel et al.2006).

- **Particle Size:**Reducing clay mineral particle size to the nanoscale (<100nm) significantle increases surface area. Smaller nanoparticles have more surface atoms, providing more adsorption sites (Katz, 2019). Studies show clay mineral nanoparticles adsorb heavy metals better than bulk clay minerals due to increased surface area. However, optimal particle size varies depending on clay type, heavy metal and soil properties. Very small nanoparticles (<10nm) may agglomerate, reducing effective surface area and dispersibility. Therefore, controlling particle size distribution is crucial for maximizing remediation efficiency (del Mar Orta et al. 2020).

- **Surface Area:**the specific surface area (SSA) of clay mineral nanoparticles measured by techniques like Brunauer-emmet-Teller (BET) nitrogen adsorption, is a direct indicator of adsorption capacity. Clay minerals with higher specific surface area (SSA) generally exhibit greater heavy metal adsorption capacity. For example, montmorillonite's high SSA (700-800 m²/g) enables superior adsorption compared to kaolinite

and halloysite which have lower SSA values, modification techniques like intercalation and exfoliation can increase SSA, enhancing remediation performance. However, surface chemistry and active site availability also significantly influence adsorption capacity (Bergaya, et al. 2013).

3.8. Surface Charge and Zeta Potential:

Surface charge and zeta potential are crucial in controlling the electrostatic interactions between clay mineral nanoparticles and heavy metal ions. The surface charge of clay minerals comes from substitutions within their crystal lattice and the ionization of surface hydroxyl groups. Zeta potential measures the electrical potential at the nanoparticle surface in a colloidal suspension, indicating the net surface charge and stability of the nanoparticle dispersion.

- **Surface Charge:** Natural clay mineral nanoparticles typically exhibit a negative surface charge at neutral to alkaline pH, attracting positively charged heavy metal cations and facilitating adsorption. The surface charge is influenced by pH, ionic strength, and can be modified through strategies like surfactant modification to enhance adsorption capacity for target heavy metals (Sposito, 2008).

- **Zeta Potential:** the surface charge of natural clay mineral nanoparticles is predominantly negative at neutral to alkaline pH to osomorphic substitutions and sesorption of surface hydroxyl groups, thereby facilitating electrostatic attraction and adsorption of positively charged heavy metal cations. The surface modification strategies, such as surfactant intercalation, eto enhance adsorption capacity for specific heavy metal ions (Gonzaga et al. 2018).

3.9. Solution Chemistry and pH:

Solution chemistry parameters, including pH, ionic strength, competing ions and organic matter, significantly influence the remediation efficiency of clay mineral nanoparticles. pH affects surface charge and heavy metal speciation, ehile ionic strength and cpmpeting ions impact electrostatic interactions and adsorption selectively. Organic matter intercalation with nanoparticles and heavy metals further complicate remediation performance, highlighting the need to consider these factors in remediation strategies (Theng, 2012).

- **pH:** soils pH a crucial role in determining the surface charge of clay mineral nanoparticles, speciation of heavy metals, and the dominant adsorption mechanisms, ultimately impacting the effectiveness of heavy metal remediation (Venema et al. 1996). At low pH, clay surfaces become positively charged, reducing cationic heavy metal adsorption but enhancing anionic heavy metal adsorption. Athigh pH, clay surfaces become negatively charged, enhancing cationic heavy metal adsorption but reducing anionic heavy metal adsorption. Heavy metal speciation also depends on pH. The optimal pH range for remediation using clay mineral nanoparticles varies depending on the clay type, heavy metal contaminant, and modification strategy (Sposito, 2008; Sparks, 2022).

- **Ionic Strength:** Ionic strength, reflecting the concentration of electrolytes in the soil solution, can influence electrostatic interactions between clay mineral nanoparticles and heavy metal ions. Increasing ionic strength can screen the electrostatic attraction between negatively charged clay mineral surfaces and positively charged heavy metal cations, reducing adsorption efficiency. Conversely, increasing ionic strength can enhance the adsorption of anionic heavy metals onto positively charged modified clay mineral nanoparticles. The effect of ionic strength on remediation efficiency depends on the specific ionic composition of the soil solution and the surface charge characteristics of the clay mineral nanoparticles.

- **Competing Ions:**The presence of other ions in the soil solution, such as Ca^{2+}, Mg^{2+}, Na^+, and K^+, can compete with heavy metal ions for adsorption sites on clay mineral nanoparticles, decreasing remediation efficiency (Appelo and Postma, 2004).

- **Organic Matter:**Soil organic matter (SOM) is a complex mixture organic compounds that interacts with both clay mineral nanoparticles and heavy metals, affecting remediation performance in multiple, intricate ways.

4. Challenges and Limitations:

Although clay mineral nanoparticles show great promise for heavy metal remediation for soil, several challenges and limitations impede their widespread adoption. Overcoming these hurdles is essential to transform laboratory successes into practical, cost-effective field scale remediation solutions. Key challenges include:

- **Scalability and Cost-Effectiveness:**

The widespread adsorption of clay mineral nanoparticles for heavy metal remediation faces several challenges. Scalable synthesis of nanoparticles with controlled size, size, and modification remains difficult and costly. Moreover, maintaining uniformity and efficiency during large-scale modification and functionalization is crucial. Additionally, developing effective and affordable methods for dispersing nanoparticles in large soil volumes poses a significant hurdle, necessitating further research and innovotaion to overcome tese limitations.

- **Stability and Durability:**

Nanoparticle aggregation and agglomeration in soil,can reducing their effective surface area and mobility, compromising remediation efficiency. Moreover, potential leaching of nanoparticles and adsorbed heavy metals due to rainfall or irrigation poses environmental risks. The durability of nanoparticles under varying conditions, such as temperature fluctuations, freeze-thaw cycles, and microbial activity, also raises concerns about their long-term effectiveness and stability in soil remediation applications.

5. Conclusion

Clay mineral nanoparticles exhibit significant potential for sustainable and efficient remediation of heavy metal contamination in soil, owing to their inherent properties and versatility in modification strategies. Laboratory-scale studies have demonstrated remarkable performance in removing and immobilizing a wide range of heavy metals. However, several challenges must be overcome before large-scale field application can be realized, including scalability, cost-effectiveness, stability, durability, and potential environmental risks. To fully harness the potential of clay mineral nanoparticle-based remediation technologies, future research should prioritize innovative nanoparticle design, mechanistic understanding, scale-up methodologies, comprehensive field testing, and thorough sustainability assessments, ultimately contributing to the development of cleaner and healthier soil environments for future generations.

Exploring novel eco-friendly modification strategies using bio based materials and green chemistry, developing nanoparticles with tailored properties for specific heavy

metals and soil conditions, designing stimuli-responsive functionalities for targated remediation, creating multifunctional nanoparticles that combine heavy metal remediation with other soil health enefits like nutrient delivery or microbial enhancement, and investigating scale-up and field testin methodologies, all while conductiong thorough sustainability assessments and environmental impact studies.

Furthermore, investigating sustainable and scalable methods for nanoparticles synthesis and modification using renewable resources and energy-efficient processes is crucial.

Employing advanced spectroscopic and microscopic techniques to uncover the detailed mechanism of heavy metal interactions with clay mineral nanoparticles in realistic soil conditions. Utilizing molecular modeling and simulation n to predict and optimize nano-particle properties and remediation performance. Conducting long-term fate and transformation studies to investigate the stability and environmental impact of nanoparticle and adsorbed heavy metals in soil environment.

To bridge the gap between laboratory research and real word implementation, Future studies should prioritize pilot. Scale studies to evaluate Nanoparticle remediation performance and cost-effectiveness under controlled field conditions. Field demonstrations at contaminate sites will assess practical feasibility and scalability. Additionally, optimizing application methods such as spray application or soil amendment techniques is necessary for efficient and cost-effective nanoparticle dispersion in large soil volumes. Finally exploring synergistic integration with existing remediation technologies like phytoremediation or bioremediation can enhance overall remediation effectiveness.Conducting comprehensive life cycle assessments to evaluate the environmental footprint and sustainability of nanoparticle production, application and disposal.

Author Contributions: Conceptualization – Rinky Yadav and Deepti Singh Vashishth; Data curation, Investigation, and Methodology – Rinky Yadav and Manju Devi; Supervision, Validation, and Visualization – Deepti Singh Vashishth; Writing – Rinky Yadav Editing – Deepti Singh Vashishth.

Conflicts of Interest: The authors declare no conflict of interest. This study was conducted independently, free from financial or personal relationships that could influence the results.

Institutional/Ethical Approval: This article does not contain any studies with human and animal participants performed by any of the authors.

References

1. Abara, H., Saadani, H., Allaoui, B., Akachar, S., Hadri, M., Ahrouch, M., Barhoun, A. &Draoui, K. (2024). Eco-friendly Cadmium Removal Using Novel Modified Clay/Alginate Floatable Beads: A Sustainable Solution for Water Pollution Mitigation. *Arabian Journal for Science and Engineering*, 1-16.)

2. Abollino, O., Giacomino, A., &Malandrino, M. (2008). Interaction of metal ions with montmorillonite and bentonite: A review. Applied Clay Science, 38(3-4), 277-287.

3. Agency for Toxic Substances and Disease Registry (ATSDR). (2019). Priority list of hazardous substances*. U.S. Department of Health and Human Services.

4. Ajala, M. A., Abdulkareem, A. S., Kovo, A. S., Tijani, J. O., &Ajala, E. O. (2024). Synthesis of Ag2O-TiO2-kaolinite clay nanocomposite for efficient removal of Mn2+, Fe3+, Cu2+, and Pb2+ and pathogens in mining wastewater. *Water, Air, & Soil Pollution*, *235*(1), 42.

5. Alloway, B. J. (2013). *Heavy metals in soils: Trace metals and metalloids in soils and their bioavailability*. Springer Science & Business Media.

6. Appelo, C. A. J., & Postma, D. (2004). *Geochemistry, groundwater and pollution*. CRC press.

7. Ba, K., He, L. L., Tang, H., Gao, J. Q., Zhu, S. F., Li, Y., & Sun, W. N. (2014). Use of Chitosan-modified Bentonite for Removal of Cu 2+, C l-and 2, 4-Dichlorophenoxyacetic Acid (2, 4-D) from Aqueous Solution. *Kemija u Industriji*, *63*.

8. Barbooti, M. M., Al-Dabbagh, B. D., &Hilal, R. H. (2019). Preparation, characterization and utilization of polyacrylic acid–kaolin composite in the removal of heavy metals from water. *International Journal of*

Environmental Science and Technology, *16*(8), 4571-4582.

9. Bergaya, F. B. K. G., &Lagaly, G. (2013). General introduction: clays, clay minerals, and clay science. In *Developments in clay science* (Vol. 5, pp. 1-19). Elsevier.

10. Bhattacharyya, K. G., & Gupta, S. S. (2008). Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Advances in colloid and interface science*, *140*(2), 114-131.

11. Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of colloid and interface science*, *277*(1), 1-18.

12. Bradl, H. (Ed.). (2005). Heavy metals in the environment: origin, interaction and remediation (Vol. 6). Elsevier.

13. Brigatti, M. F., Galan, E., Theng, B. K. G., Bergaya, F., &Lagaly, G. (2006). Handbook of clay science. *Developments in Clay Science*, *1*, 19-86.

14. Cao, X., & Harris, W. (2010). Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. Bioresource Technology, 101(14), 5222-5228.

15. Carretero, M. I. (2002). Clay minerals and their beneficial effects upon human health. A review. *Applied clay science*, *21*(3-4), 155-163.

16. Chen, D., Chen, J., Luan, X., Ji, H., & Xia, Z. (2011). Characterization of anion–cationic surfactants modified montmorillonite and its application for the removal of methyl orange. *Chemical engineering journal*, *171*(3), 1150-1158.

17. Chen, D., Cheng, Y., Zhou, N., Chen, P., Wang, Y., Li, K., Huo, S., Cheng, P., Peng, P., Zhang, R., Wang, L., Liu, Y.,&Ruan, R. (2020). Photocatalytic degradation of organic pollutants using TiO2-based photocatalysts: A review. *Journal of Cleaner Production*, *268*, 121725.

18. del Mar Orta, M., Martín, J., Santos, J. L., Aparicio, I., Medina-Carrasco, S., & Alonso, E. (2020). Biopolymer-clay nanocomposites as novel and ecofriendly adsorbents for environmental remediation. *Applied Clay Science*, *198*, 105838.

19. Feininger, T. (2013). An introduction to the rock-forming minerals In The Canadian Mineralogist, 51 (4), 663–664.

20. Fendorf, S., Wielinga, B. W., & Hansel, C. M. (2000). Chromium transformations in natural environments: the role of biological and abiological processes in chromium (VI) reduction. *International Geology Review*, *42*(8), 691-701.

21. Gao, L., & Goldfarb, J. L. (2021). Characterization and adsorption applications of composite biochars of clay minerals and biomass. *Environmental Science and Pollution Research*, *28*(32), 44277-44287.

22. Gaskova, O. L., & Bukaty, M. B. (2008). Sorption of different cations onto clay minerals: Modelling approach with ion exchange and surface complexation. *Physics and Chemistry of the Earth, Parts A/B/C*, *33*(14-16), 1050-1055.

23. Githinji, P. M. (2019). *Surface Water Quality Assessment in Ng'ethu Water Works, Chania Catchment, Kenya* (Doctoral dissertation, JKUAT-IEET).

24. Goncharuk, V. V., Puzyrnaya, L. N., Pshinko, G. N., Bogolepov, A. A., &Demchenko, V. Y. (2010). The removal of heavy metals from aqueous solutions by montmorillonite modified with polyethylenimine. *Journal of Water Chemistry and Technology*, *32*, 67-72.

25. Gonzaga, V. D. A. M., Chrisostomo, B. A., Poli, A. L., & Schmitt, C. C. (2018). Preparation, characterization and photostability of nanocomposite films based on poly (acrylic acid) and montmorillonite. *Materials Research*, *21*, e20171024.

26. Järup, L. (2003). Hazards of heavy metal contamination. *British Medical Bulletin*, *68*(1), 167-182.

27. Joussein, E., Petit, S., Churchman, J., Theng, B., Righi, D., &Delvaux, B. J. C. M. (2005). Halloysite clay minerals—a review. *Clay minerals*, *40*(4), 383-426.

28. Kabata-Pendias, A., &Pendias, H. (2001). *Trace elements in soils and plants* (3rd ed.). CRC press.

29. Katz, E. (2019). Synthesis, properties and applications of magnetic nanoparticles and nanowires—A brief introduction. *Magnetochemistry*, *5*(4), 61.

30. Khoury, H. N. (2019). Review of clays and clay minerals in Jordan. *Arabian Journal of Geosciences*, *12*(23), 706.

31. Kloprogge, J., &Kloprogge, J. (2019). Interactions of the kaolin minerals with complex organic molecules. *Spectroscopic Methods in the Study of Kaolin Minerals and Their Modifications*, 321-415.

32. Kosuge, K., & Singh, P. S. (2000). Mixed-oxide pillared silicates from H-ilerite by intercalation. *Chemistry of materials*, *12*(2), 421-427.

33. Lin, D., & Xing, B. (2007). Phytotoxicity of nanoparticles: inhibition of seed germination and root growth. *Environmental pollution*, *150*(2), 243-250.

34. Lizama, K., Fletcher, T. D., & Sun, G. (2011). Removal processes for arsenic in constructed wetlands. *Chemosphere*, *84*(8), 1032-1043.

35. Mitchell, J. K., & Soga, K. (2005). *Fundamentals of soil behavior* (Vol. 3, p. 558). New York: John Wiley & Sons.

36. Mudzielwana, R. (2019).*Synthesis and potential application of Fe3+/Mn2+ bimetal and hexadecyltrimethylammonium bromide (HDTMA-Br) modified clayey soils for arsenic removal in groundwater* (Doctoral dissertation).

37. Mulligan, C. N., Yong, R. N., & Gibbs, B. F. (2001). Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Engineering geology*, *60*(1-4), 193-207.

38. Murray, H. H. (2006).*Applied clay mineralogy: occurrences, processing and applications of kaolins, bentonites, palygorskitesepiolite, and common clays* (Vol. 2). Elsevier.

39. Nel, A., Xia, T., Madler, L., & Li, N. (2006). Toxic potential of materials at the nanolevel. *science*, *311*(5761), 622-627.

40. Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D. E., Zhang, Y., Dubonos, S. V., Gregorieva, I. V., &Firsov, A. A. (2004). Electric field effect in atomically thin carbon films. *science*, *306*(5696), 666-669.

41. Ray, S. S., & Okamoto, M. (2003). Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in polymer science*, *28*(11), 1539-1641.

42. Reich, T. J., Das, S., Koretsky, C. M., Lund, T. J., & Landry, C. J. (2010). Surface complexation modeling of Pb (II) adsorption on mixtures of hydrous ferric oxide, quartz and kaolinite. *Chemical Geology*, *275*(3-4), 262-271.

43. Schwertmann, U., & Cornell, R. M. (2008). *Iron oxides in the laboratory: preparation and characterization*. John Wiley & Sons.

44. Sharma, J. K., Kumar, N., Singh, N. P., & Santal, A. R. (2023). Phytoremediation technologies and their mechanism for removal of heavy metal from contaminated soil: An approach for a sustainable environment. *Frontiers in Plant Science*, *14*, 1076876.

45. Sparks, D. L. (2003). Environmental soil chemistry: An overview. *Environmental soil chemistry*, *2*, 1-42.

46. Sparks, D. L., Singh, B., &Siebecker, M. G. (2022). *Environmental soil chemistry*. Elsevier.

47. Sposito, G. (2008). *The chemistry of soils*. Oxford University Press.

48. Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2012). Heavy metal toxicity and the environment. *Molecular, clinical and environmental toxicology: volume 3: environmental toxicology*, 133-164.

49. Theng, B. K. G. (2012). *Formation and properties of clay-polymer complexes* (Vol. 4). Elsevier.

50. Theng, B. K. (2024).*The chemistry of clay-organic reactions*. CRC Press.

51. Thies, J. E., Rillig, M. C., Lehmann, J., & Joseph, S. (2009). Biochar for environmental management: Science and technology. *Edited Lehmann J, Joseph S, Earthscan, Sterling, VA, USA*, 85-106.

52. Tsai, W. C., Ibarra-Buscano, S., Kan, C. C., Futalan, C. M., Dalida, M. L. P., & Wan, M. W. (2016). Removal of copper, nickel, lead, and zinc using chitosan-coated montmorillonite beads in single-and multi-metal system. *Desalination and Water Treatment*, *57*(21), 9799-9812.

53. Ugwu, I. M., & Igbokwe, O. A. (2019). Sorption of heavy metals on clay minerals and oxides: a review. *Advanced sorption process applications*, *2019*, 1-23.)

54. Unuabonah, E. I., Adebowale, K. O., Olu-Owolabi, B. I., Yang, L. Z., & Kong, L. (2008). Adsorption of Pb (II) and Cd (II) from aqueous solutions onto sodium tetraborate-modified kaolinite clay: equilibrium and thermodynamic studies. *Hydrometallurgy*, *93*(1-2), 1-9.

55. Venema, P., Hiemstra, T., & van Riemsdijk, W. H. (1996). Multisite adsorption of cadmium on goethite. *Journal of Colloid and Interface Science*, *183*(2), 515-527.

56. World Health Organization (WHO). (2018). Ambient (outdoor) air pollution.

57. Yang, X., Zhou, Y., Hu, J., Zheng, Q., Zhao, Y., Lv, G., & Liao, L. (2024). Clay minerals and clay-based materials for heavy metals pollution control. *Science of The Total Environment*, 176193.

58. Yuan, P., Tan, D., &Annabi-Bergaya, F. (2015). Properties and applications of halloysite nanotubes: recent research advances and future prospects. *Applied Clay Science*, *112*, 75-93.)

59. Zhang, W., Zhang, F., Han, Z., Lü, X., Lin, D., & Werner, D. (2017). Effect of clay minerals on transport of surfactants dispersed multi-walled carbon nanotubes in porous media. *Acta GeologicaSinica-English Edition*, *91*(1), 135-144.