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Adsorbents Based on Modified Clay Minerals for Heavy Metals Removal

Abstract: The escalating global issue of heavy metal contamination in water resources necessitates the development of efficient and sustainable remediation technologies. Adsorption using modified clay minerals has emerged as a promising approach due to the natural abundance, low cost, and inherent adsorption capacity of clays, which can be significantly enhanced through various modification techniques. This review explores the fundamentals of clay minerals as adsorbents, detailing their structure, properties, and natural adsorption capabilities. It synthesizes current research on the mechanisms of heavy metal adsorption onto modified clay minerals, including ion exchange, surface complexation, and electrostatic attraction, highlighting the influence of modification on these processes. Various methods for enhancing adsorption, such as chemical (acid activation, pillaring, organic modification, metal oxide functionalization, polymer modification), physical (thermal treatment), biogenic, and mechano-chemical treatments, are discussed. The investigation examines the efficacy of modified clay minerals in removing various heavy metals, including lead, cadmium, mercury, and arsenic, along with the principal elements affecting adsorption effectiveness, such as pH, temperature, adsorbent dosage, and contact time. The review also addresses the challenges, limitations, and future directions in the application of these materials for heavy metal removal, emphasizing the ongoing need for cost-effective, selective, and environmentally friendly solutions. Key researchers whose works are utilized in this review include Lamrani et al., Adekeye et al., Sarkar et al., Bhatnagar et al., and Pylypenko et al., whose contributions have significantly advanced the understanding and application of modified clay minerals in wastewater treatment. The results of this study are intended for environmental scientists, engineers, researchers, and policymakers seeking sustainable solutions for heavy metal pollution remediation.

Keywords: modified clay minerals, heavy metals, adsorption, wastewater treatment, environmental remediation, clay modification.

Abbreviations:

CEC is cation exchange capacity.

Introduction

The increasing contamination of water resources by heavy metals poses a significant global environmental and health crisis, demanding urgent and effective remediation strategies (*Hu et al., 2024*; *Bhatnagar et al., 2010*; *Fu & Wang, 2010*; *Rafique et al., 2022*). Industrial activities, agricultural practices, and urbanization are primary sources of pollutants like lead, cadmium, mercury, arsenic, chromium, and copper, which are toxic and non-degradable, leading to bioaccumulation and adverse health effects (*Fu & Wang, 2010*; *Lamrani et al., 2025*; *Rafique et al., 2022*). Existing wastewater treatment methods often have limitations in terms of cost, efficiency at low contaminant levels, and the generation of toxic by-products. Adsorption using modified clay minerals has emerged as a promising alternative due to the abundance, low cost, and modifiable adsorption capacity of clay materials (*Adekeye et al., 2019*; *Sarkar et al., 2018*). This review aims to explore the potential of modified clay minerals for heavy metal removal, discussing their fundamentals, modification techniques, adsorption mechanisms, performance, influencing factors, challenges, and future directions. The findings are intended for environmental scientists, engineers, researchers, and policymakers involved in developing sustainable water treatment solutions.

Results

Fundamentals of Clay Minerals as Adsorbents

Clay minerals, composed mainly of silica, alumina, and iron, possess layered structures that contribute to their high surface area and cation exchange capacity (CEC) (*Adekeye et al., 2019*; *Sarkar et al., 2018*). These phyllosilicates, such as kaolinite, montmorillonite, and bentonite, exhibit a net negative surface charge due to isomorphic substitution, attracting positively charged heavy metal ions. Key properties like high surface area, significant CEC, porosity, and surface reactivity enable natural clay minerals to adsorb pollutants through mechanisms including ion exchange, surface complexation, electrostatic attraction, and direct bonding (*Adekeye et al., 2019*; *Sarkar et al., 2018*; *Bhatnagar et al., 2010*). Thus, the inherent structural and chemical characteristics of clay minerals make them effective natural adsorbents for heavy metals.

Mechanisms of Heavy Metal Adsorption onto Modified Clay Minerals

Modifying clay minerals enhances their heavy metal removal capabilities by augmenting natural adsorption mechanisms and introducing new interaction processes (*Adekeye et al., 2019*; *Sarkar et al., 2018*). The introduction of functional groups like -OH, -COOH, and -NH_2 through modification facilitates hydrogen bonding with contaminants (*Hu et al., 2024*). Modification can also increase the CEC and enhance the negative surface charge, leading to stronger electrostatic attraction for heavy metal ions. Surface complexation is significantly influenced by modification, allowing heavy metal ions to form stable complexes with introduced functional groups. Furthermore, modifications can create mesoporous structures, increasing surface area and binding sites. Certain techniques can introduce functional groups that form strong covalent bonds or chelating complexes with heavy metals. Modifications using nZVI can facilitate redox reactions for heavy metal removal, while cationic surfactants can enable the adsorption of anionic heavy metal species (*Adekeye et al., 2019*; *Sarkar et al., 2018*). Thus, the diverse modification strategies significantly improve the efficiency of heavy metal adsorption by clay minerals.

Methods for enhancing adsorption: modifying clay minerals

Various techniques are employed to modify clay minerals for enhanced heavy metal adsorption. Chemical modification includes acid activation to increase surface area and porosity, pillaring and intercalation to enhance structural properties, modification with organic compounds to alter surface properties (*Bhatnagar et al., 2010*), salt modification to introduce specific functional groups (*Adekeye et al., 2019*), metal oxide functionalization to increase surface area and introduce reactive sites (*Sarkar et al., 2018*), and polymer modification to create hybrid composites. Physical modification primarily involves thermal treatment like calcination to alter clay structure and increase porosity. Biogenic modification uses organic biomass to enhance adsorption (*Adekeye et al., 2019*), while mechano-chemical treatment employs mechanical force to alter clay properties (*Sarkar et al., 2018*). Thus, a wide array of chemical and physical methods can be used to tailor clay mineral properties for improved heavy metal adsorption.

Performance Analysis of Modified Clay Minerals in Heavy Metal Removal

Modified clay minerals have shown significant effectiveness in removing various heavy metals. For lead (Pb), carbon-modified montmorillonite and activated bentonite–alginate composite beads have demonstrated high adsorption capacities and removal rates (*Hu et al., 2024*). For cadmium (Cd), MgO-modified biochar composites and MoS_2/bentonite composites have shown enhanced adsorption. In removing mercury (Hg), montmorillonite with thiol groups and (chitosan-polyvinyl alcohol)/bentonite composites have shown strong ability to adsorb it (*Hu et al., 2024*; *Adekeye et al., 2019*; *Sarkar et al., 2018*). Montmorillonite and nZVI-supported smectite composites have been effective for arsenic (As) removal (*Hu et al., 2024*). Research by Pylypenko and colleagues has further demonstrated the effectiveness of Fe/Ti-pillared montmorillonite for cobalt, chromium, and uranium removal (*Pylypenko et al., 2014a*), Al- and Al/Fe-pillared clays for chromium and uranium removal (*Pylypenko et al., 2014b*), and Zr/Al-pillared montmorillonite for uranium and chromium removal (*Pylypenko et al., 2014a*). Composites of montmorillonite with iron oxide are effective for chromium (VI) removal (*Pylypenko & Spasonova, 2020*), and nanoscale iron composites show sorption of Cu(II), Cd(II), Co(II), Zn(II), and Cr(VI) ions (*Kovalchuk et al., 2021*). Granular composites based on laponite have also been developed for the removal of methylene blue and uranium (VI) (*Pylypenko, 2023a*; *Pylypenko et al., 2023b*; *Pylypenko, 2024*). Thus, modified clay minerals exhibit promising performance across a range of heavy metal contaminants (*Table 1*).

Factors Influencing Adsorption Efficiency

The efficiency of heavy metal adsorption by modified clay minerals is influenced by several environmental parameters. pH is a critical factor affecting both the surface charge of the adsorbent and the speciation of heavy metals, with optimal adsorption often occurring at moderate pH levels (*Lamrani et al., 2025*). Temperature can also influence adsorption, with its effect varying depending on whether the process is endothermic or exothermic (*Adekeye et al., 2019*). Adsorbent dosage generally shows a positive correlation with removal efficiency up to an optimal point. Contact time is crucial for reaching adsorption equilibrium. Initial heavy metal concentration affects the adsorption capacity and removal efficiency. Ionic strength and the presence of competing ions can also impact adsorption by affecting surface charge and competition for binding sites (*Bhatnagar et al., 2010*). Thus, optimizing these environmental parameters is essential for maximizing the effectiveness of modified clay adsorbents.

Discussion

The research on modified clay minerals for heavy metal removal has shown significant advancements, yet several challenges remain. The cost-effectiveness and environmental impact of different modification techniques vary, and achieving high selectivity for specific heavy metals in complex wastewater is still a hurdle. The regeneration and disposal of spent adsorbents loaded with heavy metals also present economic and environmental considerations. Variability in the properties of natural clay sources can lead to inconsistencies in adsorbent performance (*Adekeye et al., 2019*; *Sarkar et al., 2018*). Therefore, the central research problem revolves around optimizing modification techniques to enhance the efficiency, selectivity, and sustainability of clay-based adsorbents for heavy metal removal from diverse wastewater sources. Key questions for further discussion include: How can modification methods be made more cost-effective and environmentally benign? What strategies can be employed to improve the selectivity of modified clays for specific heavy metals in complex matrices? What are the most efficient and sustainable methods for the regeneration and disposal of heavy metal-laden clay adsorbents? Addressing these questions will be crucial for the broader application of modified clay minerals in environmental remediation.

Conclusion

The analysis of existing studies underscores the considerable potential of modified clay minerals as adsorbents for the extraction of heavy metals from aqueous solutions. Various modification techniques enhance the natural adsorption capabilities of clays, leading to improved performance in removing pollutants like lead, cadmium, mercury, and arsenic. The effectiveness of these adsorbents is influenced by factors such as pH, temperature, adsorbent dosage, and contact time, necessitating careful optimization for practical applications. While challenges related to cost, selectivity, and regeneration remain, ongoing research focuses on developing more sustainable and efficient modification methods, exploring novel materials, and investigating hybrid treatment systems. Furthermore, modified clay mineral adsorbents offer a long-term and effective option for heavy metal removal from aqueous solutions. Continued research and development in this area are expected to yield even more efficient and environmentally friendly materials and processes, contributing significantly to the global efforts in combating water pollution and protecting human health and ecosystems.

Conflict of interest

The author declares that there is no conflict of interest.

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Appendix

Table 1. Performance of modified clay mineral adsorbents for heavy metal removal

Clay Mineral	Modification Method	Target Metal	Max Adsorption Capacity (mg/g)	Removal Efficiency (%)	Key Conditions	Reference
Montmorillonite	Carbon modification	Pb(II)	263.83	–	–	(*Sarkar et al., 2018*)
Bentonite	Activated, alginate composite beads	Pb(II)	250.5	High	Acidic conditions	(*Hu et al., 2024*)
Montmorillonite /Carbon	Carboxylation (-COOH)	Pb(II)	247.85	–	Langmuir model fit	(*Adekeye et al., 2019*)
Bentonite	MgO-modified biochar	Cd(II)	Significantly higher than pristine biochar	–	Ion exchange, chemical bonding	(*Hu et al., 2024*)
Bentonite	MoS_2 composite	Cd(II)	89.45	–	Hydrothermal method	
Attapulgite	Magnetic composite (ATPCFS-CSEs)	Cd(II)	127.79	>88% (after 5 cycles)	–	
Montmorillonite	AEPE grafting	Hg(II)	46.1	–	pH 4	
Hectorite			54.7	–	pH 4	
Montmorillonite	Thiol-functionalization (ISH)	Hg(II)	141.55	–	–	
Bentonite	(Chitosan–polyvinyl alcohol) composite	Hg(II)	460.18	–	–	(*Adekeye et al., 2019*; *Sarkar et al., 2018*)
Montmorillonite	Untreated	As(V)	–	99.5%	River water	(*Hu et al., 2024*)
Montmorillonite	Untreated	As(III)	–	68.2%	River water	
Smectite	nZVI-supported	As(V)	23.12	–	Wide pH range, negligible iron release	
Halloysite Nanotubes	Zirconia-loaded	As(III)	36.08	–	Hydroxyl groups, large surface area	
Montmorillonite	Ti-pillared	As(III)/As (V)	–	Effective	–	(*Adekeye et al., 2019*)
Fe/Ti-pillared Montmorillonite	Pillaring	Co(II)	4.42	–	pH 6	(*Pylypenko et al., 2014a*)
		Cr(VI)	5.8	–	pH 6	
		U(VI)	70.2	Effective	pH 6	
Al-pillared Clay	Pillaring	Cr(VI)	1.35	–	pH 6	(*Pylypenko et al., 2014b*)
Al/Fe-pillared Clay	Pillaring	Cr(VI)	23.5	–	pH 6	
Al-pillared Clay	Pillaring	U(VI)	38.08	–	pH 6	(*Pylypenko et*

Al/Fe-pillared Clay	Pillaring	U(VI)	71.65	–	pH 6	*al., 2014a*)
Zr/Al-pillared Montmorillonite	Pillaring	U(VI)	67.6	–	pH 6	(*Pylypenko et al., 2014b*)
		Cr (VI)	10.87		pH 6	
Montmorillonite /Iron Oxide	Composite	Cr(VI)	3.28	–	pH 6	(*Pylypenko & Spasonova, 2020*)
Nanoscale Iron Composite	Composite	Cu(II)	16.01	–	pH 6	(*Kovalchuk et al., 2021*)
		Cd(II)	10.34	–	pH 6	
		Co(II)	6.13	–	pH 6	
		Zn(II)	12.62	–	pH 6	
		Cr(VI)	2.44	–	pH 6	
Laponite/Sodium Alginate	Composite	Methylene Blue	7.04	–	pH 6	(*Pylypenko, 2023a*)
Laponite/Zr/Fe-Alginate	Composite	U(VI)	75.8	–	Sulfate solutions	(*Pylypenko et al., 2023b*)
		Cr(VI)	1.54	–	pH 6	(*Pylypenko, 2024*)