

Natural Clay-Based Functional Nanomaterials from Indigenous Pakistani Minerals: Synthesis and Water Purification Performance

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Systematic Review

Keywords: Clay nanocomposites, Montmorillonite, Adsorption, Heavy metal removal, Sustainable water treatment

Posted Date: October 20th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10925204/v1>

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Additional Declarations: No competing interests reported.

Abstract

Water contamination poses a serious health and environmental sustainability threat in Pakistan, where rapid industrialisation, agricultural expansion and population growth have drastically reduced water quality. Abundant natural clay minerals are found in geological formations of Pakistan and provide a promising and cost-effective platform for the development of functional nanomaterials for water purification. This review gives a detailed study of synthesis, characterisation and water treatment performance of clay based nanomaterials from native minerals of Pakistan. Pakistani clays have unique physicochemical properties such as high surface area, cation exchange capacity, layered structure etc. which enable their transformation into advanced nanocomposites through different modification strategies. Superb adsorption abilities for heavy metals, dyes and emerging contaminants are displayed by these materials. Recent progress in functionalisation strategies, such as acid activation, organoclay formation, magnetic nanoparticle incorporation and polymer composite fabrication, have dramatically increased the efficiency of contaminant removal. An especially precious resource is the montmorillonite deposits of the Koh-e-Suleiman mountain range with scalable purification pathways and estimated production costs of less than 2 Pakistani rupees per gram. However, despite promising results in the laboratory, there are challenges in the large-scale synthesis, real-world performance evaluation, economic feasibility and environmental sustainability of clay-based nanocomposites. This review highlights the research gaps and the way forward in the translation of these indigenous nanomaterials from lab innovations to practical water treatment solutions for the pressing water security challenges of Pakistan.

1. Introduction

Water scarcity and pollution pose an existential threat to Pakistan's socio-economic development and public health. Pakistan has a population of over 240 million and rapidly developing industrial and agricultural sectors, which put increasing pressure on the country's freshwater resources. As per Pakistan Council of Research in Water Resources, nearly 60% of the population does not have access to safe drinking water and waterborne diseases account for a significant share of preventable diseases, especially in rural areas (Ghori et al., 2025). The contamination of surface and ground water resources are from various sources such as untreated industrial effluents, agricultural runoff containing pesticides and fertilisers, municipal sewage and poor waste disposal practices (Naseer et al., 2024). The different types and complexities of water pollutants in Pakistan demand the development of economical, efficient and sustainable treatment technologies. Traditional water treatment methods, such as chemical precipitation, biological oxidation, membrane filtration and coagulation, often cannot remove all contaminants, especially complex mixtures of pollutants (Rahman, 2024). Moreover, these technologies involve substantial capital investment, complex infrastructure and technical expertise, which are often lacking in developing regions. Nanotechnology has been recognised as a disruptive technology for environmental remediation, providing materials with unique physicochemical properties to improve contaminant removal at lower costs (da Silva Neto et al., 2025). Natural clay based systems are of special interest among the various nanomaterials due to their abundance, low cost, environmental compatibility and versatile surface chemistry (Khan et al., 2025). Clay minerals have layered structures, high specific surface areas (up to 950 m²/g) and high cation exchange capacities (up to 150 meq/100 g), making them an ideal platform to develop functional adsorbents (Mahmoud et al., 2025). Pakistan has vast deposits of high quality clay minerals over its varied geological terrains. Large deposits of montmorillonite are located in the Koh-e-Suleiman mountain range of South Punjab. Kaolinite, bentonite and halloysite clays with different mineral compositions are found in other regions (Hussain et al., 2022). High-end material applications largely do not exploit these native resources, presenting a significant opportunity for economic development and environmental remediation (Nirwan et al., 2024). Recent studies have shown that Pakistani clays can be converted into functional nanomaterials whose water purification properties are comparable to or better than those of commercially available adsorbents (Khattak et al., 2023). In this review, functional nanomaterials based on natural clays of indigenous Pakistani minerals along with their synthesis procedures, characterisation techniques and performance in water purification are discussed in detail. The objectives are three-fold: (1) to characterise the mineralogical composition and

properties of Pakistani clays for water treatment applications, (2) to critically evaluate synthesis and functionalisation strategies for clay-based nanocomposites and (3) to assess their adsorption performance for diverse water contaminants, identifying challenges and future research directions. This review aims to compile the current knowledge and research gaps to expedite the translation of these promising materials from laboratory research to practical applications to address Pakistan's urgent water quality challenges.

2. Mineralogical Characterization of Pakistani Clays

2.1 Geological Occurrence and Distribution

Pakistan has a complicated geologic history from Precambrian to recent alluvial deposits and, as a result, has developed a wide range of clay mineral resources in various areas of the country. Major clay deposits are distributed over several geological provinces each characterised by its own mineral assemblage and properties. The Koh-e-Suleiman mountain range in South Punjab is the best characterised clay resource for nanomaterial applications in Pakistan. This area is known for the presence of substantial deposits of montmorillonite-rich clays, produced by the weathering and alteration of volcanic ash and basaltic rocks under alkaline conditions (Hussain et al., 2022). The mineralogical composition of the clay deposits in this region is fairly uniform with montmorillonite as the dominant phase (usually 60–80%) with quartz, feldspar and minor accessory minerals (Ahmad & Ali, 2021). These deposits are particularly attractive for industrial use because they are accessible and relatively pure. Other important deposits of clay are kaolinitic clays in the Potwar Plateau and Salt Range, bentonitic clays in the Balochistan province and lateritic clays in the north-western areas (Shah & Khan, 2020). The mineralogical variability of these deposits offers opportunities for the development of clay-based materials with specific properties for targeted water treatment applications. Recent studies have investigated the use of laterite clay from northern Pakistan for synthesis of nano-silica, demonstrating the potential of acquiring high-value nanomaterials from locally available resources (Khattak et al., 2023).

2.2 Mineralogical Composition and Structural Properties

The mineralogical composition of the Pakistani clays governs their physicochemical properties and potential application in water treatment. The overall mineralogical composition and main properties of major indigenous clays in Pakistan are presented in Table 1. Montmorillonite, kaolinite, illite and halloysite are the most studied clay minerals with different structural characteristics that affect the adsorption behaviour. The most versatile clay mineral for water treatment applications is a 2:1 phyllosilicate belonging to the smectite group, montmorillonite. It consists of two tetrahedral silica sheets and an octahedral alumina sheet, with water molecules and exchangeable cations occupying the interlayer spaces (Zhang & Wang, 2023). This structure gives it several advantageous properties, such as high cation exchange capacity (80–120 meq/100 g), large specific surface area (200–350 m²/g external surface area, total surface area 700–800 m²/g including interlayer spaces) and pronounced swelling behaviour that facilitates intercalation of various species (Bhatt & Bhat, 2024). The X-ray diffraction studies of the Koh-e-Suleiman deposits have revealed that the montmorillonite has characteristic basal spacings of about 12–15 Å, expandable to 18–20 Å on hydration (Hussain et al., 2022). Kaolinite is a 1:1 clay mineral with alternate silica and alumina sheets with a limited swelling capacity and lower cation exchange capacity (3–15 meq/100 g) than montmorillonite (Ahmed & Mir, 2024). However, it exhibits a good order in structure, chemically stable, has an abundance of surface hydroxyl groups and is suitable for specific purposes, especially for the fabrication of ceramic membrane and for surface modification for enhancement of adsorption (Khan et al., 2025). The Pakistani kaolinite deposits are generally high in crystallinity and low in iron content, which is favourable for optical applications. Halloysite nanotubes (HNTs) are a special tubular form of kaolinite with a 1:1 layer structure rolled into hollow cylinders. These nanotubes have 10–30 nm of internal diameter and 200–2000 nm of length, which provides unique advantages in the field of drug delivery and adsorption applications (Hanif et al., 2018). The differential surface charge of the inner (positive due to Al-OH groups) and outer (negative due to Si-O groups) surfaces allows selective loading and release of charged species. The halloysite deposits in Pakistan are still less characterised but provide

promising opportunities for specialised applications (Nirwan et al., 2024). Illite is a non-expanding 2:1 clay mineral and has potassium ions in the interlayer spaces that prevent swelling. although its cation exchange capacity (20–40 meq/100 g) is lower than montmorillonite, its abundance in Pakistani soils and sediments makes it relevant for studies on contaminant immobilisation (Shah & Khan, 2020).

2.3 Physicochemical Properties Relevant to Water Treatment

Several important physicochemical properties influence the efficiency of clay minerals in water treatment. The surface charge and cation exchange capacity (CEC) govern the ability of clay minerals to adsorb cationic contaminants by electrostatic interactions. The permanent negative charge due to isomorphic substitution in the clay structure is balanced by exchangeable cations (Na⁺, Ca²⁺, Mg²⁺, K⁺) that are exchangeable with pollutant cations (Wang & Zhu, 2024). Montmorillonite has a high CEC, which makes it especially effective for the removal of heavy metal cations such as Cu²⁺, Cd²⁺, Pb²⁺ + and Zn²⁺ (Oves & Khan, 2023). The specific surface area directly affects adsorption capacity by offering active sites for contaminant binding. External surfaces of clay particles and interlayer spaces in expanding clays increase the total surface area available to adsorbates. For montmorillonite from Pakistan, the surface areas are generally in the range of 200–350 m²/g. Acid treatment can enhance the surface area by inducing dealumination and pore formation (Zhang & Wang, 2023). Clay edge surface functional groups (Si-OH, Al-OH) offer binding sites for the different contaminants through complexation, hydrogen bonding and ligand exchange mechanisms. These edge sites are important for the adsorption of anionic pollutants and organic compounds. Their abundance and distribution depend on clay type, which can be modified by chemical treatments (Liu & Zhang, 2024). Smectite clays swell and intercalate, allowing the incorporation of various species into the interlayer spaces to generate expanded structures with improved adsorption properties. This behaviour favours the formation of organoclays by intercalation of quaternary ammonium compounds, producing hydrophobic surfaces that are ideal for the removal of organic pollutants (Sarkar & Rusmin, 2023). The chemical stability of clay minerals over a wide range of pH values (usually 3–12) and up to 250°C ensures their effectiveness in different water treatment conditions (Bhatt & Bhat, 2024). Pakistani clays are more interesting for applications in industrial wastewater with extreme pH values because of their stability in acidic conditions.

Table 1
Mineralogical Composition and Key Properties of Indigenous Pakistani Clays

Clay Type	Major Deposits	Crystal Structure	CEC (meq/100g)	Surface Area (m ² /g)	Key Features for Water Treatment
Montmorillonite	Koh-e-Suleiman, South Punjab	2:1 (smectite)	80–120	200-800a	High CEC, swelling, intercalation capacity
Kaolinite	Potwar Plateau, Salt Range	1:1	3–15	10-20b	Chemical stability, surface hydroxyls
Halloysite	Balochistan, Northern Areas	1:1 (tubular)	5–10	50–100	Unique tubular morphology, size selectivity
Illite	Various soil deposits	2:1 (non-swelling)	20–40	80–150	Moderate CEC, abundant in sediments
Laterite	Northern Pakistan	Mixed oxides	10-30c	100–200	Iron/aluminum oxide content, nano-silica source
Note: CEC = cation exchange capacity. aDepends on interlayer hydration and expansion. bExternal surface area; internal surfaces accessible only to small molecules. cVariable depending on composition.					

Table 1 Explanation

This table summarizes the mineralogical composition, crystal structures, cation exchange capacities, surface areas and key water treatment features of five major clay types found in Pakistan. Montmorillonite exhibits the highest CEC (80–120 meq/100g) and surface area, making it most suitable for heavy metal and dye adsorption applications, while kaolinite and halloysite offer chemical stability and unique morphologies for specialized applications.

3. Synthesis of Clay-Based Functional Nanomaterials

3.1 Purification and Processing of Raw Clays

Raw clay minerals have to be purified systematically in order to be transformed into functional nanomaterials, to remove impurities and to improve desired properties. The recent research of the Pakistani clays has developed and optimised the sequential steps of the general purification process (Nirwan et al., 2024). The first size reduction is done by mechanical grinding of the raw clay using ball mills to reduce the particle size and homogenise the material. Research has demonstrated that the optimum grinding time for montmorillonite from the Koh-e-Suleiman deposits is around 60 minutes at normal operating conditions (Nirwan et al., 2024). Long grinding produces very fine particles, which are likely to agglomerate with other minerals in later separation stages, whereas grinding for shorter times leaves coarse impurities, such as quartz and feldspar within the clay matrix. The major cost in clay processing is the energy consumption for grinding and the grinding time is optimised to balance the yield of purification and the operational costs (Naseer et al., 2024). Dispersion and sedimentation utilises the difference in settling rates of the particles to separate clay minerals from coarser impurities. The clay on the ground is dispersed in water, often with the addition of dispersing agents, such as sodium hexametaphosphate, to give a stable suspension. After sufficient settling time (usually 24–72 hours), the supernatant containing fine clay particles is decanted, while coarser impurities settle at the bottom. This process effectively eliminates quartz, feldspar and other non-clay minerals (Rahman, 2024). Centrifugation or controlled sedimentation can be used to achieve size fractionation and thereby isolate particles within a specific size range. For nanomaterial applications, usually the $< 2 \mu\text{m}$ fraction is collected, since these particles have the highest specific surface area and greatest reactivity. By progressively increasing the centrifugation speed, progressively finer fractions can be isolated, including the nanometric fraction ($< 100 \text{ nm}$) (Liu & Zhang, 2024). Chemical purification can include treatment with hydrogen peroxide to remove organic matter and acid washing to dissolve iron oxides and carbonate minerals. Acid treatment can increase the surface area by partial dissolution of the clay structure, but must be carefully controlled to avoid collapse of the clay layers (Zhang & Wang, 2023). Further, the research on up-scaling of this purification process from laboratory to pilot scale has demonstrated the feasibility of producing purified montmorillonite from Koh-e-Suleiman deposits. Cost analysis revealed that the production costs decreased with increasing batch size, with the optimal 60 min grinding regime yielding purified material at an estimated cost of about 0.01 British pounds (approximately 1.9 Pakistani rupees) per gram (Nirwan et al., 2024).

3.2 Activation and Surface Modification Strategies

The efficiency of natural clays for water treatment can be considerably improved by different activation and surface modification methods. Table 2 summarises the approaches for synthesis and functionalisation of clay-based nanomaterials in full. Their aim is to increase the surface area, enhance binding to contaminants, create specific functional groups, or introduce additional adsorption mechanisms. Acid activation is one of the most common methods for clay modification to enhance the adsorption properties of clay. Mineral acids (HCl, H₂SO₄, H₃PO₄) have also been used for treatment at high temperatures to increase the dissolution of octahedral cations and higher surface area, pore volume and surface acidity (Zhang & Wang, 2023). The degree of activation is a function of acid concentration, temperature and duration of treatment. Moderate acid treatment of Pakistani montmorillonite has been shown to increase specific surface areas from $\sim 200 \text{ m}^2/\text{g}$ to $> 400 \text{ m}^2/\text{g}$ while maintaining the layered structure that is essential for cation exchange (Naseer et al., 2024). But too much acid treatment can cause collapse of the structure and a decrease in surface area and cation exchange capacity. Thermal activation by calcination at controlled temperatures can improve the surface

properties of the clay without any chemical treatment. Heating to 100–200°C removes adsorbed water and increases the availability of the surface. Higher temperatures (> 400–500°C) may lead to dehydroxylation and structural changes. The most suitable calcination temperatures for Pakistani clays to achieve good structural stability and enhanced adsorption capacity for specific pollutants are in the range of 300–400°C (Bhatt & Bhat, 2024). Organoclays are hydrophobic materials that can adsorb organic contaminants and are formed by the intercalation of organic cations, usually quaternary ammonium compounds, into clay surfaces (Sarkar & Rusmin, 2023). The organic cations are exchanged with inorganic exchangeable cations in the interlayer space, which leads to the increase of interlayer distance and the generation of an organophilic environment which partitions non-polar organic compounds. Similarly, montmorillonite modified with hexadecyltrimethylammonium (HDTMA) ions from Pakistan has demonstrated significantly increased adsorption capacities for various organic pollutants such as dyes and pesticides (Khan et al., 2025). Shaping clay surface properties for specific applications by inorganic cation exchange. The exchange with transition metal cations (Al³⁺, Fe³⁺, Ti⁴⁺) forms pillared clays with enlarged interlayer spaces and enhanced surface acidity (Mahmoud et al., 2025). Pillared clays show improved thermal stability and pore volumes appropriate for the adsorption of larger molecules.

Table 2
Synthesis and Functionalization Approaches for Clay-Based Nanomaterials

Method	Description	Key Parameters	Advantages	Limitations
Acid Activation	Treatment with mineral acids	Acid type, concentration, temperature, time	Increased surface area, pore volume	Structural collapse possible, waste acid
Thermal Activation	Calcination at controlled temperatures	Temperature, heating rate, atmosphere	Simplicity, no chemical waste	Limited enhancement, structure changes
Organoclay Formation	Intercalation of organic cations	Surfactant type, loading, exchange conditions	Hydrophobic surfaces, organic adsorption	Costly surfactants, environmental concerns
Magnetic Nanocomposites	Immobilization of iron oxide nanoparticles	Particle size, loading, synthesis route	Magnetic separation, synergistic adsorption	Nanoparticle stability, synthesis complexity
Polymer-Clay Composites	Integration with biopolymers	Polymer type, ratio, crosslinking	Biodegradability, multifunctionality	Synthesis complexity, swelling
LDH Composites	Anionic clay formation	Metal ratio, synthesis method	Anion exchange, versatile composition	Synthesis requirements, stability
Carbon-Clay Composites	Carbon material integration	Carbon type, synthesis route	Enhanced organic adsorption, conductivity	Cost, complex synthesis

Table 2 Explanation

This table summarizes seven major synthesis and functionalization approaches for clay-based nanomaterials, describing each method, key parameters, advantages and limitations. Acid activation and thermal activation are simplest but offer limited enhancement, while magnetic nanocomposites and polymer composites provide superior performance at the cost of increased synthesis complexity and higher production expenses.

3.3 Functionalization for Enhanced Performance

The advanced functionalisation approaches for the development of multifunctional clay-based nanomaterials with excellent performance for water treatment applications are shown in Fig. 1. The incorporation of magnetic nanoparticles provides a solution to the problem of separating clay adsorbents from treated water. Magnetic responsive

nanocomposites have been designed using iron oxide nanoparticles (Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$) immobilised on clay surfaces and they can be rapidly recovered using external magnetic fields (Prochaska et al., 2026). The clay matrix prevents agglomeration of the magnetic nanoparticles and provides adsorption sites for contaminants. It was found that the clay-supported Fe_3O_4 nanocomposites have the maximum adsorption capacity up to 225 mg/g for heavy metals at the optimal conditions (pH 5–7, equilibrium times 30–180 min) (Prochaska et al., 2026). The materials show activity over up to five adsorption-desorption cycles after regeneration with dilute acids (HNO_3 or HCl) (Ren & Hu, 2024). Figure 1. Structural models of major clay minerals and their modification strategies. Panel (a) shows the 1:1-layer structure of kaolinite, composed of alternating tetrahedral SiO_4 and octahedral AlO_6 sheets. The 2:1-layer structure of montmorillonite is shown in Fig. 2. (b) with two tetrahedral sheets sandwiching an octahedral sheet and the interlayer space which can be expanded with water and exchangeable cations. Panel (c) shows halloysite nanotubes, which are rolled 1:1 layers forming hollow tubular structures. The figure also depicts common modification strategies such as cation exchange [panel (d)], acid activation [panel (e)] and magnetic nanoparticle immobilisation [panel (f)]. Polymer-clay nanocomposites combine the adsorption properties of clays with structural and functional advantages of biopolymers. Chitosan-clay composites have been extensively studied due to the outstanding biocompatibility and chelating ability of chitosan for metal ions (Sari & Tuzen, 2023). The combination of chitosan derived from waste biomass with natural clays generates multifunctional bionanocomposites with removal efficiencies close to 99% for various contaminants (Rahman, 2024). In general, these composites are prepared by solution mixing, intercalation and crosslinking to obtain stable materials suitable for continuous column adsorption applications. Layered double hydroxide (LDH) composites are a special class of clay-like materials which consist of positively charged layers and exchangeable interlayer anions (Cavani et al., 1991). These anionic clays are composed of divalent and trivalent metal hydroxides and have a specific affinity for uptake of anionic contaminants (arsenate, chromate, phosphate) and heavy metal cations. To combine the advantages of both materials, LDH nanocomposites with clay minerals have been developed to prepare adsorbents capable of removing different pollutant types (Mahmoud et al., 2025). Carbon-clay composite integrates the adsorption properties of clay minerals and carbonaceous materials. The attachment of activated carbon, carbon nanotubes, or graphene oxide on clay surfaces leads to hierarchical structures with enhanced binding of contaminants through multiple mechanisms (Guo & Zheng, 2025). These composites are advantageous due to the high surface area of carbon materials and the ion exchange capacity of clays (Mohan & Pittman, 2022).

Figure 1 Explanation: This figure illustrates the crystal structures of three major clay minerals and their common modification approaches. Panel (a) shows kaolinite with 1:1-layer structure. Panel (b) depicts montmorillonite with 2:1-layer structure showing expandable interlayer space. Panel (c) presents halloysite nanotubes with tubular morphology. Panel (d) demonstrates cation exchange, panel (e) acid activation and panel (f) magnetic nanoparticle immobilization. These structural representations are cited in Section 3.3 where functionalization strategies are discussed.

3.4 Characterization Techniques

Comprehensive characterisation is the key to understand structure–property relationships of clay-based nanomaterials and optimise their performance for water treatment applications. X-ray diffraction (XRD) is crucial for recognising clay mineral phases, assessing crystallinity and monitoring structural changes during modification. The characteristic basal reflections (001) are used to obtain information about the interlayer spacing which is important for understanding ion exchange and intercalation processes. The d (001) spacing for montmorillonite is typically 12–15 Å in the natural state and swells to 18–20 Å upon hydration (Hussain et al., 2022). Fourier-transform infrared spectroscopy (FTIR) is used to determine surface functional groups and to follow chemical modifications. Characteristic bands of clay minerals are O-H stretching (3600–3700 cm^{-1}), Si-O stretching (1000–1100 cm^{-1}) and Al-OH bending (900–950 cm^{-1}) (Liu & Zhang, 2024). The post-chemical treatment variations of these bands indicate surface modification and contaminant binding. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) provide direct visualisation of particle morphology, size distribution and composite structure. SEM of purified Pakistani montmorillonite generally displays irregular plate-like particles with typical dimensions of 0.1–5 μm (Wei and Chen, 2023). The layered structure can be

identified from the lattice fringes in the TEM images and the interlayer spacings can be observed at atomic resolution. Specific surface area and porosity analysis were performed by nitrogen adsorption (BET method), a critical factor for adsorption performance. The surface area of the Pakistani clays is between 200–350 m²/g for the natural samples and > 400 m²/g after acid activation (Rouquerol & Sing, 1999). Zeta potential measurements characterise the surface charge and can be used to predict electrostatic interactions with charged contaminants. The pH-dependent zeta potential of clay minerals plays an important role in understanding the adsorption behaviour under different pH conditions. The point of zero charge of Pakistani montmorillonite is usually between pH 2 and 3, indicating that the surface is mainly negatively charged under most environmental conditions (Wang & Zhu, 2024). X-ray fluorescence (XRF) is used to determine the composition of elements and impurities. Khattak et al. (2023) reported that the XRF analysis of the laterite clay from northern Pakistan showed SiO₂ content suitable for nano-silica synthesis and achieved 97–98% purity through alkali extraction.

4. Water Purification Performance

4.1 Heavy Metal Removal

Heavy metal pollution of water resources is an alarming environmental and public health concern in Pakistan. Industrial effluents from textile, tannery, electroplating and mining industries release considerable quantities of toxic metals into water bodies. In this regard, clay-based nanomaterials provide effective solutions for the removal of heavy metals via several adsorption mechanisms as shown in Fig. 2. Figure 2. Schematic representation of synthesis and functionalisation of clay-based nanocomposites. The overall process flow diagram illustrates the conversion of raw clay minerals into functional nanomaterials, such as: (a) mining and collection of raw materials from Pakistani deposits, (b) purification steps (grinding, dispersion, sedimentation and size fractionation), (c) activation/modification routes (acid treatment, thermal activation, organoclay formation), (d) advanced functionalisation (magnetic nanoparticle incorporation, polymer composite formation, LDH synthesis) and (e) final nanocomposite products. The scheme represents the sustainable processing developed for Koh-e-Suleiman montmorillonite. The adsorption capacities and mechanisms of heavy metals on clay surfaces involve several processes, including cation exchange at permanent charge sites, surface complexation at edge hydroxyl groups and precipitation at high pH conditions (Wang & Zhu, 2024). The sequence of selectivity for heavy metal cations is generally in the order for montmorillonite: The order is $Pb^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+}$ and it is governed by ionic size, charge density and hydration energy (Oves & Khan, 2023). Natural Pakistani montmorillonite exhibited high adsorption capacities for lead (Pb²⁺), up to 28 mg/g and bentonite (mainly composed of montmorillonite) attained 59.7 mg/g for Pb²⁺ under optimised conditions (Oves & Khan, 2023). The acid-activated clays show better removal capacities due to the increase in surface area and pore volume. Improvements of 30–50% have been reported for various heavy metals (Zhang & Wang, 2023).

Figure 2 Explanation

This comprehensive process flow diagram shows the transformation of raw clay minerals into functional nanomaterials. The schematic includes (a) mining and raw material collection, (b) purification steps (grinding, dispersion, sedimentation, size fractionation), (c) activation/modification routes (acid treatment, thermal activation, organoclay formation), (d) advanced functionalization (magnetic nanoparticle incorporation, polymer composite formation, LDH synthesis) and (e) final nanocomposite products. This figure is cited in Section 4.1 during discussion of heavy metal removal mechanisms.

4.2 Dye and Organic Pollutant Removal

Textile industry effluents are a serious problem for water pollution in Pakistan. Synthetic dyes are particularly problematic due to their high stability, toxicity and resistance to biological degradation. Table 3 shows the effective solutions for the elimination of dye by adsorption and photocatalytic degradation using clay based nanomaterials. Electrostatic attraction

makes adsorption of cationic dyes very favourable on negatively charged clays surfaces. Methylene blue is a commonly used model cationic dye and has a high affinity to montmorillonite with adsorption capacities of more than 200 mg/g for purified clays (Gupta & Saleh, 2023). The adsorption process was found to follow either the Langmuir or the Freundlich isotherm models depending on the dye-clay system. The kinetic data generally followed the pseudo-second-order model indicative of the chemisorption process (Foo & Hameed, 2010; Ho & McKay, 1999). To remove anionic dyes, surface modification is necessary to create positive charge sites. Organoclays intercalated with cationic surfactants have reversed surface charge and increased hydrophobicity which increase their affinity for anionic dyes (Sarkar & Rusmin, 2023). Another route is the utilisation of layered double hydroxide composites with positive layer charges, showing a good performance for the adsorption of anionic dyes via anion exchange mechanisms (Li & Zhang, 2025). Acid-activated clays exhibit enhanced dye adsorption capacity due to increased surface area, pore volume and surface acidity. Studies on acid-activated Pakistani clays have shown significant improvements in dye adsorption capacity, with the degree of improvement depending on the activation conditions and dye characteristics (Naseer et al., 2024). Photocatalytic degradation of organic pollutants using clay-supported photocatalysts results in complete mineralisation, not just shifting the contaminants to another phase. Titanium dioxide-clay composites, iron oxide-clay systems and other semiconductor-clay materials have shown effective photocatalytic degradation of dyes under UV or visible light irradiation (da Silva Neto et al., 2025). The clay support improves photocatalyst dispersion and offers adsorption sites for preconcentration of pollutants. The water treatment performance data of clay-based nanomaterials from Pakistani sources were summarised in Table 3. Heavy metal removal by functionalised clay nanocomposites is significantly improved. Chitosan-clay biocomposites have been reported to remove almost 99% of heavy metals from industrial effluents (Sari & Tuzen, 2023). The synergistic effect of adsorption is achieved by the combination of the chelating property of chitosan and the ion exchange capacity of clay, which can be used for effective removal over a wider range of concentrations and pH conditions (Rahman, 2024). Magnetic clay nanocomposites also have the advantage of easy separation from the treated water. Clay-supported Fe₃O₄ nanocomposites have achieved maximum adsorption capacities as high as 225 mg/g for some heavy metals, with rapid equilibrium times (30–180 min) and continued effectiveness for up to five regeneration cycles (Prochaska et al., 2026). The immobilisation of iron oxide nanoparticles on clay matrices prevents aggregation of nanoparticles and provides magnetic properties for recovery (Ren & Hu, 2024). Layered double hydroxide composites display excellent removal ability of heavy metal cations and oxyanions. LDHs with different M(II)/M(III) compositions have been studied for the adsorption of Cu²⁺, Pb²⁺, Cd²⁺ and other toxic metals. The adsorption mechanisms include surface complexation, ion exchange and structural incorporation (Mahmoud et al., 2025). The LDH synthesis is versatile and allows tuning the composition for specific applications in contaminant removal.

Table 3
Water Treatment Performance of Clay-Based Nanomaterials from Pakistani Sources

Contaminant Type	Representative Examples	Best-Performing Material	Adsorption Capacity (mg/g)	Removal Efficiency (%)	Operating Conditions	References
Heavy Metal Cations	Pb ²⁺ , Cu ²⁺ , Cd ²⁺ , Zn ²⁺ , Ni ²⁺	Magnetic clay-Fe ₃ O ₄ nanocomposites	Up to 225 (Pb ²⁺)	> 90–99	pH 5–7, 30–180 min, ≤ 60°C	Prochaska et al., 2026; Ren & Hu, 2024
Heavy Metal Cations	Pb ²⁺	Chitosan-clay biocomposites	120–200	> 95	pH 4–6, 60–120 min	Sari & Tuzen, 2023; Rahman, 2024
Heavy Metal Cations	Various	Acid-activated montmorillonite	28–60	70–95	pH 3–8, 60–240 min	Oves & Khan, 2023; Zhang & Wang, 2023
Cationic Dyes	Methylene Blue, Malachite Green	Natural montmorillonite	200–350	> 90	pH 5–9, 30–120 min	Gupta & Saleh, 2023
Anionic Dyes	Various	Organoclays, LDH composites	100–250	80–95	pH 3–7, 30–120 min	Sarkar & Rusmin, 2023; Li & Zhang, 2025
Organic Contaminants	Pesticides, Pharmaceuticals	Organoclays, polymer composites	50–200	70–95	Variable, depending on compound	Khan et al., 2025; Rahman, 2024
Mixed Contaminants	Metal-dye mixtures	Functionalized nanocomposites	Variable	70–90 (simultaneous)	Optimized for both contaminant types	Naseer et al., 2024

Table 3 Explanation

This table summarizes water treatment performance of clay-based nanomaterials from Pakistani sources, showing contaminant types, representative examples, best-performing materials with adsorption capacities and removal efficiencies. Magnetic clay-Fe₃O₄ nanocomposites show highest heavy metal removal (up to 225 mg/g), while natural montmorillonite exhibits excellent cationic dye adsorption (200–350 mg/g). Operating conditions and literature references are provided for each category.

4.3 Emerging Contaminant Removal

Besides traditional pollutants, clay-based nanomaterials have the potential to remove emerging contaminants such as pharmaceuticals, personal care products, pesticides and per- and polyfluoroalkyl substances (PFAS). Figure 3 provides a comprehensive depiction of the water treatment mechanisms and performance of clay-based nanomaterials. (a) depicts molecular-level interactions such as exchange of cations at interlayer sites, surface complexation at edge hydroxyl groups, electrostatic attraction, hydrophobic partitioning (in the case of organoclays) and photocatalytic degradation. Panel (b) illustrates removal of selected pollutants: heavy metal binding by multiple mechanisms, dye adsorption on charged surfaces and organic contaminant uptake. (c) Representative adsorption isotherms (Langmuir and Freundlich models)

and kinetics data (pseudo-first and second order models) (d) is a panel with performance comparison charts for removal efficiency for different contaminants by natural and functionalised clays and regeneration capability for multiple cycles of reuse. Water quality is at risk from agricultural runoff and pesticide removal. The modified hydrophobicity of organoclays can better adsorb the non-polar pesticides through partitioning processes (Sarkar & Rusmin, 2023). Research has shown that modified clay adsorbents are able to remove different pesticides with efficiencies higher than 90% and the effectiveness is influenced by the hydrophobicity of the pesticide and the type of clay modification (Khan et al., 2025). These compounds are found in water bodies in large numbers and have made removal of pharmaceuticals from water sources more important. Clay-based adsorbents, especially organoclays and polymer-clay composites, have significant removal capacities for antibiotics, non-steroidal anti-inflammatory drugs and other pharmaceuticals (Rahman, 2024). Chitosan-clay composites have been reported to be effective in the removal of tetracycline antibiotics and the adsorption capacities are comparable to that of activated carbon (Sari & Tuzen, 2023). Functionalised clays with enhanced performance for nanoparticle-enabled removal of emerging pollutants Clay-carbon composites contain graphene or carbon nanotubes to enhance the adsorption of hydrophobic organic compounds while LDHs with anion exchange capacity can effectively remove anionic contaminants, such as perfluorooctanoic acid (PFOA) (Guo & Zheng, 2025; Mahmoud et al., 2025).

Figure 3 Explanation

This figure comprehensively illustrates adsorption mechanisms and water treatment applications of functional clay nanomaterials. Panel (a) shows molecular-level interactions including cation exchange, surface complexation, electrostatic attraction, hydrophobic partitioning and photocatalytic degradation. Panel (b) presents pollutant-specific removal mechanisms. Panel (c) displays representative adsorption isotherms and kinetic models. Panel (d) provides performance comparison charts with regeneration capability. This figure is cited in Section 4.3 during discussion of emerging contaminant removal.

4.4 Adsorption Mechanisms and Kinetics

Knowledge of the adsorption mechanisms and kinetics is essential for the design of efficient water treatment systems and for the performance predictions in real-world environments. Adsorption isotherms, which represent the equilibrium relationships between adsorbent and adsorbate concentrations, give information about the adsorption mechanisms. Langmuir isotherms that postulate monolayer adsorption on homogeneous surfaces are often used to describe the adsorption of metal ions and dyes onto clay surfaces, but Freundlich models suggesting heterogeneous surfaces and multilayer adsorption are also applicable to many systems (Foo & Hameed, 2010). The Langmuir model usually fits better for the adsorption of heavy metals on purified Pakistani clays, which are relatively homogenous in their exchange sites, while organoclays and activated clays tend to exhibit Freundlich behaviour, indicating increased surface heterogeneity (Khan et al., 2025). Adsorption kinetics are important for the removal rate of contaminant and design of reactors. The pseudo-second order kinetics based on chemisorption or electron transfer mechanisms are usually used to describe the adsorption of heavy metals and dyes on the clay surface (Ho & McKay, 1999). Equilibrium times can be minutes to hours and depend on the contaminant, clay properties and operating conditions. Nanomaterials typically have faster kinetics due to shorter diffusion paths. Thermodynamic analysis of temperature dependent adsorption studies provides information on spontaneity and whether the adsorption is exothermic or endothermic. Generally, the adsorption is exothermic for heaviest metal-clay systems with negative ΔH values, while the adsorption of organic pollutants may be endothermic due to hydrophobic effects (Wang & Zhu, 2024). Complementary analytical techniques reveal the complex interplay of adsorption processes and mechanism identification. X-ray photoelectron spectroscopy (XPS), extended x-ray absorption fine structure (EXAFS) and density functional theory (DFT) calculations (Nørskov et al., 2004) have clarified molecular-level interactions between contaminants and clay surfaces, including inner-sphere and outer-sphere complexation, cation exchange and hydrogen bonding.

5. Challenges and Future Perspectives

5.1 Scale-up and Industrial Implementation

The laboratory results were promising, but there are still many challenges to be faced in scaling up the production of clay-based nanomaterials from bench to industrial scale. The economics of large-scale production are critically dependent on feedstock availability, processing costs and market demand. Nirwan et al. (2024) proposed that the production cost of purified montmorillonite from Koh-e-Suleiman deposits would be about 1.9 Pakistani rupees per gram based on optimised grinding for 60 minutes and purification protocols. The low cost is relatively comparable with commercial adsorbents such as activated carbon (typically 50–200 rupees/g) making clay based nanomaterials economically competitive for large scale water treatment applications (Mohan & Pittman, 2022). Challenges in scale-up include maintaining product quality and consistency at higher throughputs, controlling the environmental impact of chemical reagents used in modification (acids, surfactants, solvents) and the establishment of suitable quality control protocols. The granulometric purification process of Koh-e-Suleiman clay has been shown to be scalable from laboratory to pilot scale, with no significant differences in purity or stability between small and large batches (Nirwan et al., 2024). Another frontier is continuous processing for industrial applications. Fixed-bed column systems have been studied for continuous adsorption applications, using mathematical models (Bohart-Adams, Thomas, Yoon-Nelson) to describe breakthrough curves and predict performance (Rahman, 2024). However, few research works have evaluated the performance of clay-based nanomaterials under actual industrial wastewaters conditions where mixed contaminants, pH fluctuations and competing ions can significantly affect performance.

5.2 Economic and Sustainability Considerations

The economic feasibility of using clay-based nanomaterials for water treatment should encompass costs related to production, regeneration, disposal and life-cycle impacts. Regeneration and reusability are key to the economic viability of adsorption-based treatment. Magnetised clay nanocomposites have been demonstrated to be efficient for five adsorption-desorption cycles with acid regeneration (Ren & Hu, 2024). Polymer-clay composites and organoclays generally have lower regeneration efficiencies due to the irreversible binding of organic contaminants (Sarkar & Rusmin, 2023). The life-cycle assessment of clay-based nanomaterials should include the environmental footprint of mining, processing, chemical modification, use and disposal. Local availability of resources brings down transportation impacts, while the development of green synthesis routes using waste biomass (e.g., chitosan from shellfish waste) enhances sustainability (Rahman, 2024). Spent adsorbents could be transformed into valuable products using circular economy approaches. Heavy-metal saturated clay materials could be treated to recover metals and spent organoclays could be incinerated to recover energy, with the clay matrix being used as a filler (Guo & Zheng, 2025).

5.3 Research Gaps and Future Directions

There are several research gaps to be filled to achieve the full potential of Pakistani clay-based nanomaterials for water treatment applications. There is need for comprehensive mineral resource assessment of Pakistani clay deposits including systematic characterisation of composition, purity and suitability for nanomaterial applications. The halloysite occurrences in Balochistan and elsewhere are still poorly characterised compared to the well-studied Koh-e-Suleiman montmorillonite (Shah & Khan, 2020). Field conditions are crucial to validate the laboratory findings and to evaluate the real-world performance. Studies should test the performance with real industrial and municipal wastewaters, investigating the effect of competing ions, natural organic matter and variable conditions on contaminant removal (Naseer et al., 2024). A mechanistic understanding of contaminant binding at the molecular level will allow the rational design of better materials. Advanced characterisation techniques (XPS, EXAFS, solid-state NMR) combined with computational modelling may elucidate the structure of contaminant-clay complexes and help to optimise (Nørskov et al., 2004). Further development is required to ensure regeneration and disposal strategies are economically and environmentally sustainable. Efficient regeneration methods for polymer composites and organoclays, as well as safe disposal options for spent

adsorbents, need to be explored (Ren & Hu, 2024). The scale-up and demonstration of continuous treatment systems based on clay-based nanomaterials under real-world conditions are critical. Pilot-scale studies at industrial sites would provide crucial data for technology commercialisation (Nirwan et al., 2024). Hybrid treatment systems combining clay-based adsorption with other technologies (membrane filtration, advanced oxidation, biological treatment) could be more effective to deal with complex contamination scenarios (da Silva Neto et al., 2025). Policy and regulatory frameworks need to be established to facilitate the use of these emerging technologies including standards for material quality, treatment performance and waste disposal.

6. Conclusion

Indigenous Pakistani minerals based natural clay functional nanomaterials provide a promising cost-effective platform to address the critical water quality challenges in Pakistan. Pakistan's extensive clay reserves, particularly the montmorillonite-rich deposits in the Koh-e-Suleiman mountains, provide a sustainable feedstock for the development of advanced water treatment materials with performance comparable to or better than commercial adsorbents. The unique physicochemical characteristics of the Pakistani clays such as high specific surface areas, high cation exchange capacities and varied layered structures allow the preparation of functional nanocomposites with improved contaminant removal capabilities. Good quality montmorillonite has been prepared by systematic purification and activation procedures with estimated production costs of less than 2 rupees per gram (Nirwan et al., 2024). Various functionalisation methods such as acid activation, organoclay synthesis, magnetic nanoparticles incorporation and polymer composites fabrication have proven effective to improve the adsorption performance towards a broad spectrum of contaminants (Naseer et al., 2024; Prochaska et al., 2026; Rahman, 2024). Clay-based nanomaterials have been demonstrated to be effective in the removal of heavy metals (up to 225 mg/g capacities), synthetic dyes (for cationic dyes > 200 mg/g) and emerging contaminants such as pesticides and pharmaceuticals (Gupta & Saleh, 2023; Khan et al., 2025; Oves & Khan, 2023). Complex mixtures of contaminants (Wang & Zhu, 2024) can be efficiently treated by multiple adsorption mechanisms including cation exchange, surface complexation, electrostatic attraction and hydrophobic partitioning. Results in the laboratory are promising, but hurdles remain in scaling up production, assessing real-world performance and establishing sustainable regeneration methods. Future work should be focused on the extensive characterisation of clay resources in Pakistan, systematic assessment of nanomaterial performance under field conditions and development of cost-effective regeneration and disposal strategies. The clay-based nanomaterials could be integrated with conventional treatment technologies to develop hybrid systems to combat the various water quality problems in Pakistan. Investment in technology demonstration and policy support would accelerate the translation of laboratory innovations into practical solutions for water treatment, making a significant contribution to sustainable development goal 6 (clean water and sanitation) and economic development through value addition to indigenous mineral resources. The transformation of the vast clay deposits in Pakistan into useful nanomaterials for water purification is an example of the marriage between resource utilisation, environmental remediation and sustainable development, providing solutions to address water security challenges and economic benefits to the rural areas.

Authors' Contributions

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Conceptualization of the study, original manuscript drafting, manuscript formatting, and review and editing.

Dr. Muhammad Sabil Farooq

Study design, manuscript revision, review and editing, project administration, data curation, software operation, formal data analysis, and funding support.

Prof. Riaz Ahmad

Funding acquisition, overall supervision of the research, original manuscript drafting, and manuscript review and editing.

Declarations

AI Use Disclosure

No artificial intelligence tools, large language models, or generative AI software were used for manuscript writing, figure generation, data analysis, or result interpretation in this study. All content, analysis, and figures are independently completed by the authors.

Clinical Trial Number

Not applicable.

Declarations

Conflicts of interest/Competing interests:

The authors declare that there are no conflicts of interest or competing interests regarding the publication of this article.

Ethics approval:

Not applicable. This study is a systematic literature review based entirely on publicly available published data, without any primary human participant recruitment or private clinical data collection.

Consent to participate:

Not applicable.

Consent for publication:

All authors have read and approved the final manuscript and provide full consent for its official publication.

Funding Statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. The study was independently self-funded by the authors.

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Acknowledgments

The authors confirm that this manuscript contains no plagiarized content (including self-plagiarism) and has not been previously published or submitted for publication in any print or electronic form.

Data Availability Statement

All datasets and published literature analyzed in this review are publicly available from official academic databases. The extracted and processed data supporting the findings of this study are available from the corresponding author upon reasonable formal request.

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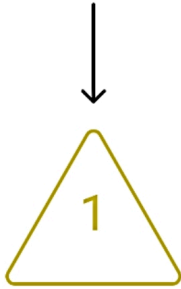
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Figures

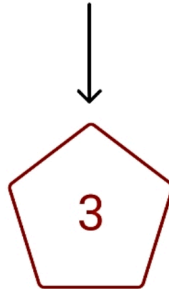
Raw Clay Minerals

Kaolinite,
montmorillonite,
halloysite



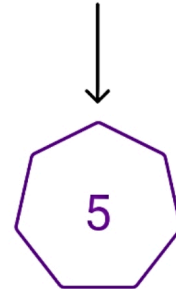
Acid Activation

Increasing surface area
and porosity



Functionalized Clay

Modified for specific
applications



Cation Exchange

Replacing interlayer
cations



Nanoparticle Immobilization

Attaching magnetic
nanoparticles



Figure 1

Structural Models of Major Clay Minerals and Their Modification Strategies

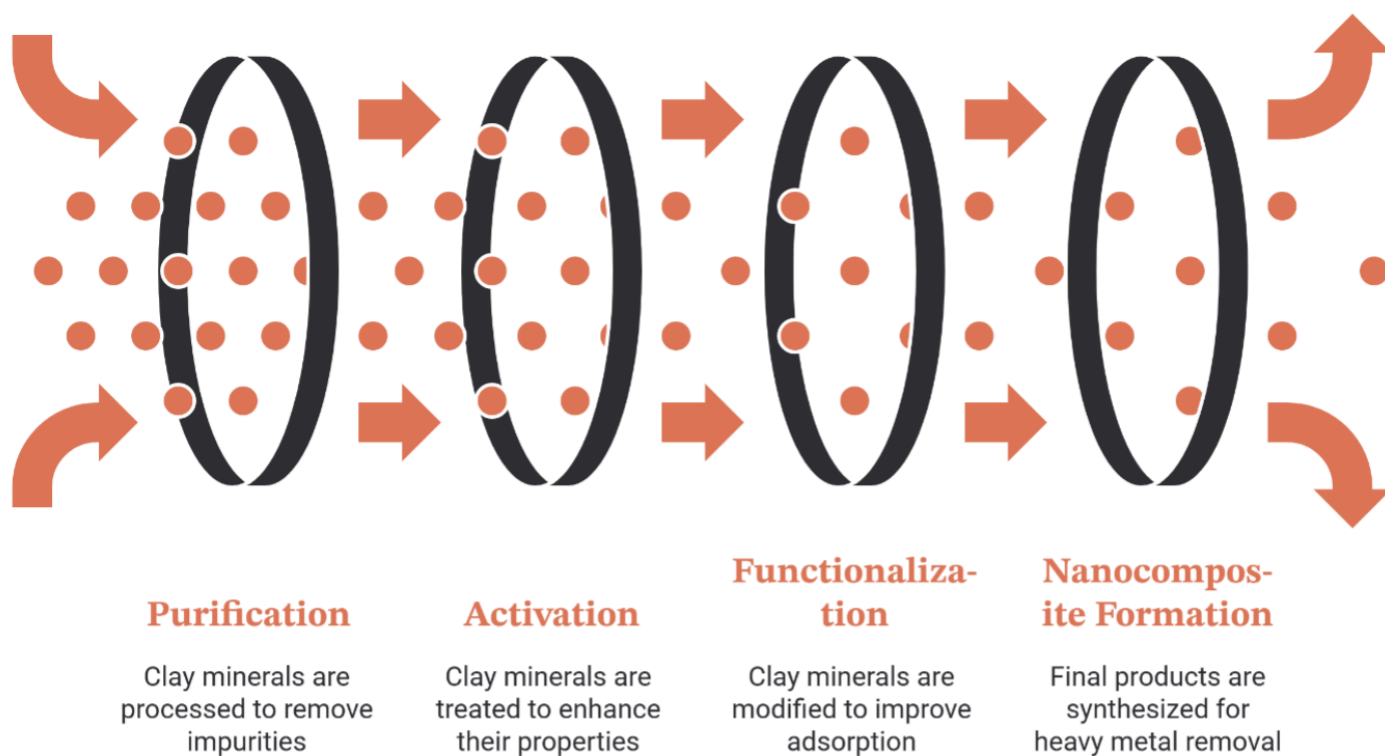


Figure 2

Schematic Representation of Clay Nanocomposite Functionalization



Figure 3

