

Harnessing clays and clay composites for efficient removal of pharmaceutical contaminants from water: A review

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ABSTRACT

The increasing prevalence of pharmaceutical residues, particularly antibiotics, in water supplies poses a serious risk to both the environment and human health. The limited biodegradability of antibiotics and the inadequacy of conventional wastewater treatment methods to eliminate them contribute to the emergence of antibiotic-resistant bacteria. Adsorption using natural clays, a cost-effective and efficient technique, has emerged as a promising solution for removing these pollutants. Modified clay composites, in particular, have shown significant potential due to advancements in surface modification and hybridization techniques. This review explores the latest developments in the generation of modified clay minerals to eliminate antibiotics from water, emphasizing upcoming trends and approaches to enhance adsorption capacity. Techniques such as intercalation with organocations or metal-pillared clay minerals and acid activation and thermal treatment can improve adsorption properties like surface area, capacity, stability, and mechanical strength. Furthermore, the development of clay and its composites offers advantages in its adsorption capacity, recovery, and physicochemical properties compared to modified and unmodified clay and clay minerals.

1. Introduction

The world's rapidly growing demand for water is one of humanity's most urgent issues in the 21st century. A serious drinking water crisis is affecting most people on Earth due to the damage and pollution caused by the unsustainable use of nearly all natural water resources. Recent investigations have documented the presence of micropollutants, including pharmaceuticals, their metabolic byproducts, and transformation derivatives, at concentrations reaching the milligram-per-liter range in diverse aquatic ecosystems [1]. Research has identified over 80 different types of pharmaceutical compounds (used in hospitals and other healthcare facilities) in water bodies across many developed countries. These compounds include hormones, antibiotics, tranquilizers, antidepressants, painkillers, and nonsteroidal anti-inflammatory drugs [2]. These pharmaceutical substances are synthetic or naturally occurring molecules that have been shown to act in the bodies of humans and animals through specific mechanisms [3].

Antibiotics are among the most extensively utilized pharmaceuticals worldwide, specifically developed to eliminate or suppress the proliferation of bacteria, thereby serving as critical agents in treating bacterial infections. Recently, the presence of antibiotics in the environment has garnered significant attention due to their potential threats to human health and ecosystems [4–7]. Global antibiotic consumption has surged significantly, increasing by 65% from 21.1 billion defined daily doses (DDDs) in 2000 to 34.8 billion DDDs in 2015 [8]. Projections suggest that this trend will persist, with estimates indicating up to a 200% increase by 2030, reaching approximately 42 billion DDDs. This escalating consumption has led to the continuous release of pharmaceuticals, such as tetracycline, diclofenac, enrofloxacin, and ibuprofen, into aquatic environments via wastewater treatment plants and hospital effluents. The persistent discharge of these compounds into surface and groundwater systems has contaminated clean water sources, highlighting pharmaceuticals as critical emerging pollutants threatening environmental and public health [9,10]. Studies by Langbehn et al. [11] and Ashiq et al. [12] indicate that antibiotics are typically not biodegradable and are difficult to remove from wastewater in conventional wastewater treatment plants (WWTPs). As a result, they are regarded as a growing problem due to the harm these compounds

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cause to ecosystems when they enter the water supply and encourage the development of resistant bacteria [12].

Recent research has focused on developing cost-effective and environmentally sustainable strategies to treat various sectors' substantial volumes of industrial wastewater. These approaches aim to safeguard clean water resources and mitigate the disposal of highly polluted effluents into aquatic ecosystems. Therefore, several treatment techniques, such as membrane filtration, flotation-coagulation, electrocoagulation, and biological treatment, have been applied to treat wastewater [13–16]. Despite the high treatment efficiency of these technologies, several issues commonly accompany them, including high energy consumption, high costs, and difficulties in scaling up [17].

Adsorption is gaining popularity in scientific communities due to its unique effectiveness, low cost, and manageability. Additionally, a wide variety of adsorbents can be used and regenerated when appropriate desorption procedures are applied. Researchers have utilized many adsorbent materials, including fly ash [18], geopolymers [5,19], clay or functionalized clay [20–22], fly ash-based zeolites [4], and waste/biowaste [23–26] in wastewater treatment [24,27,28]. However, they are still searching for an inexpensive, easy-to-use adsorbent with high adsorption capacity that is also environmentally safe. Using natural clays as efficient adsorbents to remove pollutants from wastewater has attracted significant interest [4,5,29]. The adsorptive ability of clay/clay composites to absorb organic and inorganic water contaminants has been extensively studied. The physicochemical properties of clays and clay minerals, such as swelling capacity and ion exchange capacity, along with their unique two-dimensional (2D) layer structure, allow them to effectively adsorb a wide range of organic and inorganic water contaminants [14].

The adsorption capacity of clays and clay minerals is determined by a complex interaction of factors, including surface charge, specific surface area, and swelling properties. However, the intrinsic crystal structure and the predominance of negative surface charge in natural clays often constrain their applicability in industrial processes [30]. Consequently, modifying clay minerals has enhanced their adsorption affinity for pharmaceutical compounds. The main objective of this review is to provide a comprehensive analysis of the effective use of modified clay-based materials in removing pharmaceutical pollutants from water. This study focuses on recent research concerning clay modification techniques and developing clay composites with various components. Finally, it highlights the challenges in areas such as introducing new functional groups to clay minerals, combining different modification methods, utilizing adsorbent mixtures, and conducting pilot-scale and real wastewater studies.

2. Clay/clay minerals modification techniques

Several studies have demonstrated that pre-treating clays can significantly increase their ability to adsorb pollutants [4,21,22,31–34]. This pretreatment process

increases the clay's surface area, pore volume, and the number of active adsorption sites. Consequently, the clay's surface properties transition from hydrophilic to hydrophobic and organophilic, facilitating the adsorption of non-polar, nanoscale organic molecules. Utilizing clays and their components addresses disposal challenges and provides a cost-effective resource for wastewater treatment. Additionally, clays offer further benefits as adsorbents due to their low production costs, eliminating the need for regeneration [35].

Several approaches have been utilized to modify clay minerals to improve their ability to adsorb antibiotics, as illustrated in Figure 1. These methods include using metal-pillared clay minerals, blending multiple clay minerals with biochar, applying techniques like thermal activation, and creating new clay-based nanocomposites with biopolymers and organocations. These modifications are designed to introduce various surface functional groups, enhance specific surface area, and optimize pore sizes of the adsorbent materials. With the appropriate adsorption properties, clay minerals can significantly increase adsorption capacity and porosity through chemical and physical treatments [36]. This section discusses the various pre-treatment techniques for clay/clay minerals. Additionally, it highlights the synthesis techniques for modified clay minerals and the corresponding parameters involved.

2.1. Chemical Treatment

This technique modifies clays through pillaring and intercalation using organic and mineral acids, bases (alkalinization), salts, and metal oxides, as shown in Figure 2. The activation and functionalization of clays are typically achieved through chemical treatments [37].

2.1.1. Pillared clays

Pillaring is a versatile technique for improving mechanical and thermal stability, increasing specific surface area and porosity, and enhancing the catalytic performance of clay minerals [4]. Due to this pillarization, clay minerals become useful adsorbents for environmental preservation [38]. The primary reason for developing pillared clay (PILC) is the lack of persistent porosity in unmodified clay minerals. For instance, smectite clay can swell when wet, but when heated or dehydrated, the layers separate, leaving the surface unavailable for chemical reactions. Stable pillars with large pore capacities are created in the interlayer spaces to address this issue. Regardless of being hydrated or dehydrated, PILC retains its porosity. Pillared interlayered clay minerals, analogous to zeolites, are synthesized by exchanging cations within clay layers with larger mineral cations. These cations are derived from the hydrolysis of metal oxides or their salts, forming metal hydroxyl cation polymers or oligomers. Subsequent heat treatment induces dehydration and dehydroxylation, transforming these substances into stable metal oxide clusters. These clusters function as pillars, separating the silicate layers and creating interstitial spaces with molecular dimensions [39].

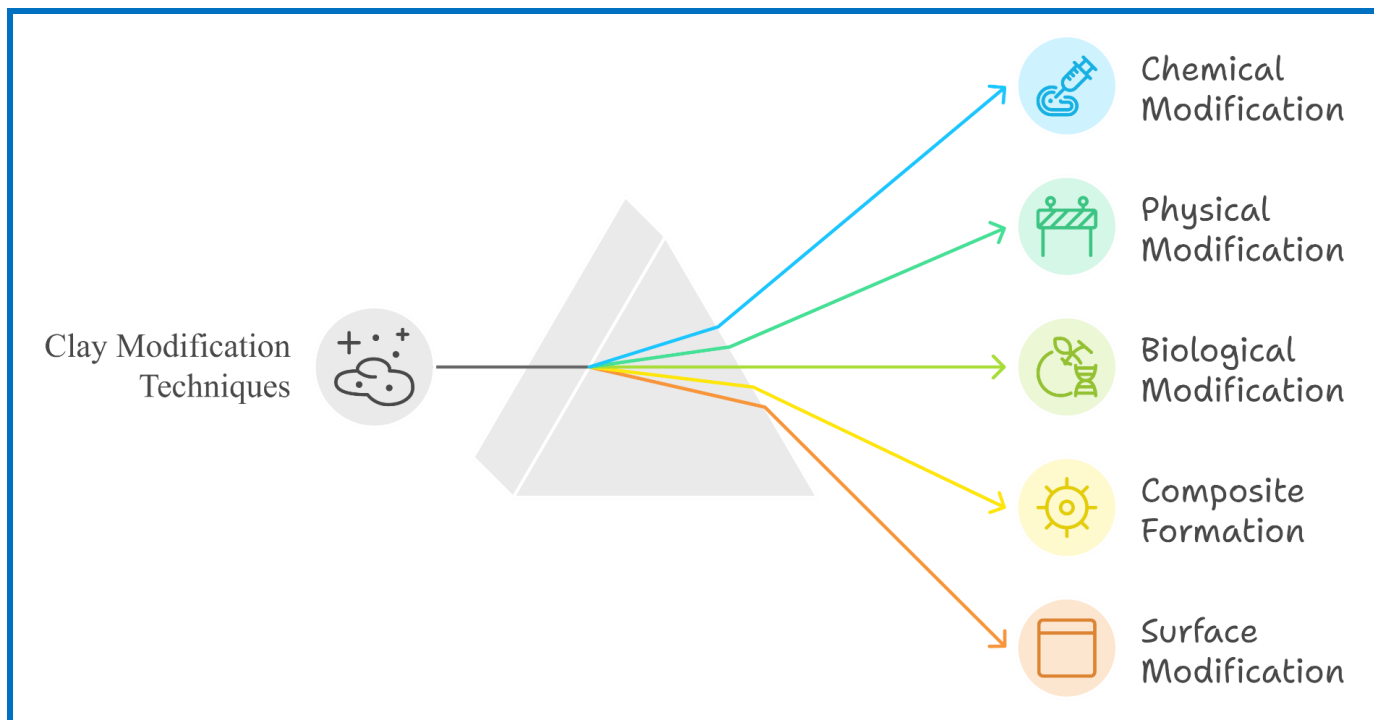


Figure 1. Common clay modification techniques.

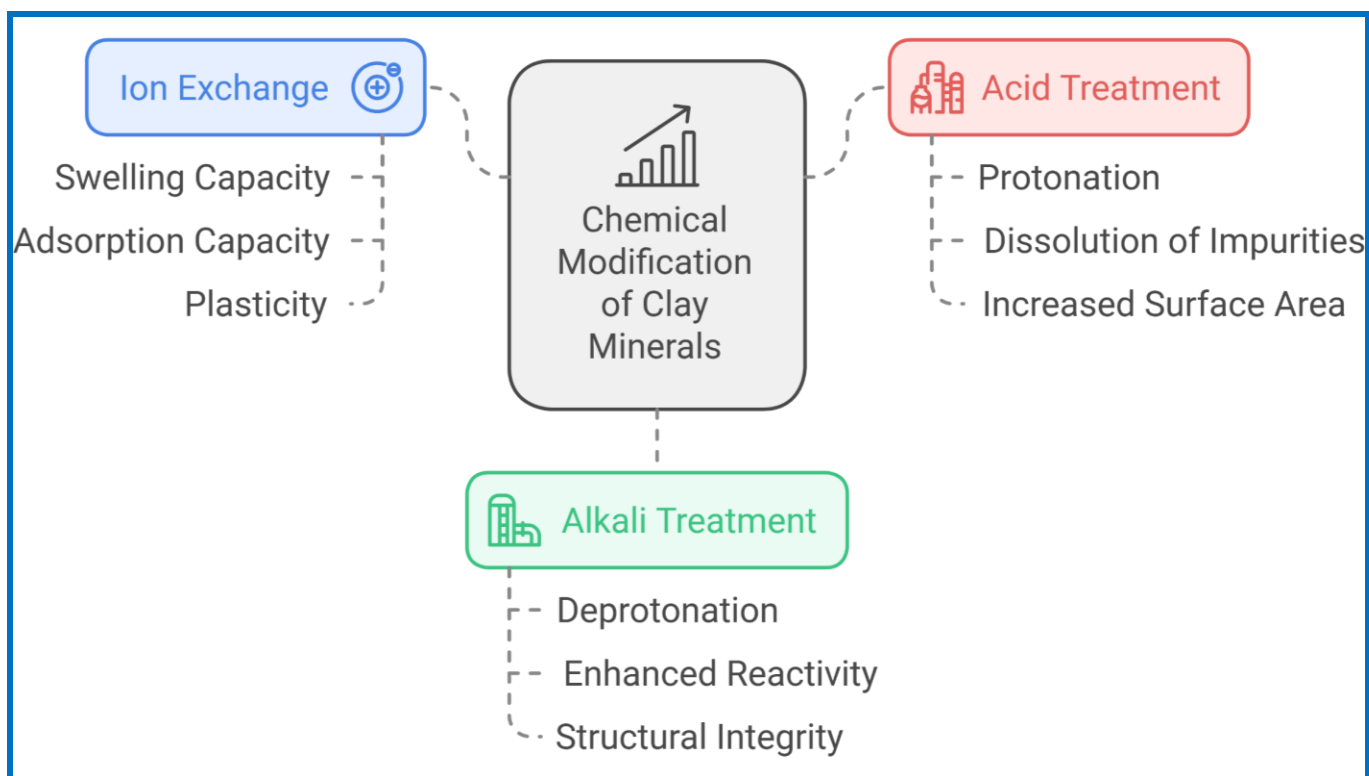


Figure 2. Chemical Modification of Clay Minerals.

Eugenia et al., (2017) investigated the adsorption of ciprofloxacin (CPX) in its anionic form (CPX^-) on pillared clays (PILC) in basic pH conditions [40]. Their research focused on manufacturing four pillared clay minerals (Si, Fe, Al, and Zr) with bentonite and different oligocations. The silica solution serves as the pillaring agent for

preparing silica pillared clay (Si-PILC). Trinuclear acetate-hydroxo iron (III) nitrate acts as the pillaring agent in synthesizing iron pillared clay (Fe-PILC). Aluminum pillared clay (Al-PILC) is synthesized by the basic hydrolysis of $AlCl_3 \cdot 6H_2O$ solution with NaOH solution. Zirconium pillared clay (Zr-PILC) uses $ZrOCl_2 \cdot 8H_2O$ as the pillaring agent.

Among these, Si-PILC and Fe-PILC exhibited maximum CPX adsorption capacity of 100.6 and 122.1 mg/g under the studied conditions [40]. This could be attributed to their micro and mesoporous structures, which are larger than those of Al-PILC and Zr-PILC, and the formation of novel adsorption sites due to the metal atoms in the pillars. The proposed adsorption mechanism includes van der Waals interactions between CPX⁻ and the accessible adsorption sites on the PILC surfaces and creating inner-sphere complexes [40].

Chauhan *et al.* (2020) studied the incorporation of tetrameric Zr-polyoxocations into the layered structure of smectite clay, followed by their pillarization into Zr-pillared interlayered clay (Zr-PILC) to enhance the clay's adsorptive removal efficiency of amoxicillin (AMOX), imipramine (IMP), paracetamol (PCM), and diclofenac sodium (DIF-S) [38]. Tetrameric zirconium polycations of the [Zr₄(OH)₈(H₂O)₁₆]⁸⁺ type were added to the space between layers, and upon calcination, they were converted into ZrO₂ pillars. The clay's adsorption capability was increased by 238 - 2078% for a range of PPCPs with modification. For these PPCPs, Zr-PILC's maximal adsorption capacity follows the order DIF-S > IMP >> PCM > AMOX. The chosen PPCPs are rapidly adsorbed; in just 15 minutes, over 75% to 80% of their adsorption capability is reached. The changes in clay after intercalation were examined using a range of surface and structural analytical methods. The findings support a growth in microporosity, surface area, and acidic sites, which enhance and control Zr-PILC interactions with electron-rich PPCPs molecules [38].

2.1.2. Acid Activation

Acid activation is a commonly used technique to enhance the properties of clay, including specific surface area, porosity, surface acidity, and cation exchange capacity (CEC). This process involves treating clay minerals with relatively high concentrations of inorganic acids, typically at elevated temperatures. Mineral acid solutions are often used for this purpose, leading to the partial dissolution of cations and an increase in the clay's surface acidity, specific surface area, and porosity. Commercially available acid-activated clay minerals, often untreated, are commonly used in adsorption research. When replaceable cations are substituted with H⁺ ions through such treatments, SiO₄ groups are largely retained, while Al³⁺ and other cations are released from both tetrahedral and octahedral positions [41]. This process generally increases the surface area and acidity of the clay minerals, eliminating mineral impurities and partially dissolving the outer layers [35].

The effectiveness of acid treatment on the surface area and porous structure of clays depends on several factors, such as the specific clay mineral composition, the presence of other minerals, the overall chemical makeup, the nature of interlayer cations, the type of acid, the treatment temperature and duration, and additional environmental conditions. In kaolinite, octahedral Al³⁺ ions are primarily released when exposed to acid, transforming its crystalline structure into amorphous metakaolin and increasing the number of Al-OH and Si-OH interactions without

significantly altering the overall composition of the mineral. Clay minerals undergo complex modifications under acidic conditions, affecting their surface properties [42].

Maged *et al.* (2020) focused on the acid activation method to enhance the adsorptive capacity of natural bentonite (NB) for removing ciprofloxacin (CIP) from water [32]. An HCl solution was used as the modifying agent for the bentonite, and the resulting sorbent is referred to as acid-activated bentonite (AAB). According to BET surface area analysis, AAB exhibited more than double the surface area of NB. Kinetic experiments revealed that CIP sorption onto AAB and NB primarily occurs through chemisorption mechanisms involving ion exchange and surface complexation. The maximum monolayer sorption capacity of AAB was determined to be 305.20 mg/g, significantly higher than that of NB (126.56 mg/g) [32].

Moreover, hydrochloric acid was applied to one section of the natural clay and distilled water to another for the adsorption of two of the most commonly used medications globally: paracetamol (PA) and metformin (MF). The adsorption of PA and MF onto acid-treated clay (ATC) and water-treated clay (WTC) was most accurately represented by the Freundlich isotherm model [43]. The adsorption mechanism was physisorption, exothermic, and spontaneous [43]. Both WTC and ATC demonstrated high efficacy in eliminating PA and MF from tap water, groundwater, and Red Sea water, achieving removal efficiencies exceeding 80%, even at low concentrations. The highest adsorption capacity varied between 20.4 and 30.5 mg/g [43].

2.1.3. Organoclays

The term "organoclay materials" refers to hybrid substances formed when clay minerals, including swelling varieties such as saponite, vermiculite, and montmorillonite (Mt), interact with surfactants and/or other organic chemicals [44]. Through various chemical and physical processes, surfactants are incorporated into the clay's internal structure, resulting in materials that exhibit hydrophobic behavior and possess a large specific surface area. This modification broadens the applications of clay minerals across several sectors. The final properties of organoclays are primarily influenced by the nature of the inorganic layered materials selected and the chemical composition of the surfactant employed for surface modification [45]. Depending on how they behave in water, they are divided into cationic, anionic, and nonionic surfactants. Nonionic surfactants exhibit superior chemical stability compared to cationic surfactants. Anionic surfactants offer a more cost-effective alternative to traditional surfactants. Nevertheless, anionic surfactants have limited application in clay modification processes, according to Sinha Ray & Okamoto [46].

In clay mineral modification, cationic surfactants were primarily employed. The adsorption mechanism involves the replacement of inorganic hydrated cations in the interlayer space by surfactant cations, resulting in the incorporation of surfactant aggregates. These aggregates' configuration depends on the amphiphilic molecules'

concentration and the length of their alkyl chains [44]. In recent years, ongoing exploration of new modification techniques has led to the proposal of alternatives, such as zwitterionic surfactants and unconventional nonionic surfactants [47]. The effective incorporation of surfactant aggregates, with arrangements resembling their cationic counterparts but exhibiting distinct adsorption characteristics, allows for potential water remediation applications, even if they involve different interaction mechanisms. The most commonly utilized cationic surfactants include CTAB [48], ODTMA [49], TMAB [50], DTAB [51], HDTMA [52], BTMA [53], HTBPB, HTPB, TPB [54], and DMHDA, have been extensively employed as modifying agents for clay [55]. Table 1 summarizes the adsorption efficiency of organoclays towards pharmaceutical pollutants.

Rahardjo *et al.* employed both unmodified bentonite (BENT) and cetyltrimethylammonium bromide (CTAB)-modified bentonite (CTAB-BENT) to adsorb ampicillin from wastewater [56]. While both adsorbents exhibited high ampicillin removal efficiency in synthetic wastewater (89.9% for BENT and 100% for CTAB-BENT), efficiency decreased when real wastewater was used (59.3% for BENT and 90.6% for CTAB-BENT). This reduction in efficiency is likely due to the complex matrix of real wastewater, which may interfere with the adsorption process. The enhanced adsorption capacity of CTAB-BENT is attributed to the electrostatic attraction between the negatively charged ampicillin molecules and the positively charged surface of the organo-bentonite [56].

Obradović *et al.* reported the results of the ibuprofen (IBU) adsorption achieved with organokaolins, which were produced by mixing natural kaolin (KR) with hexadecyltrimethyl ammonium bromide (H) as a surfactant [57]. Two different surfactant concentrations (50 and 90% of kaolin's cation exchange capacity) were used for KR modification. IBU adsorption on organokaolins in phosphate buffer at pH 7 was investigated using varying initial drug concentrations (2–20 mg/L). Alteration of KR with H improved IBU's adsorption compared to KR, which has no affinity for adsorbing this drug. The adsorption of IBU was observed to increase with the surfactant content in organokaolins and the initial drug concentration in the solution. The Langmuir model indicated that the maximal sorption capacities for HKR-50 and HKR-90, which followed nonlinear isotherms, were 2.05 and 3.12 mg/g, respectively, for the adsorption of IBU by both adsorbents [57].

Kryuchkova *et al.* evaluated the adsorption capacities of pristine montmorillonite (MMT) and stearyl trimethyl ammonium-modified montmorillonite (hydrophobic MMT-STA) for the pharmaceuticals carbamazepine, ibuprofen, and paracetamol [58]. Hydrophobic MMT-STA exhibited superior adsorption capabilities for all three pharmaceuticals compared to pristine MMT. The adsorption capacity of hydrophobic MMT-STA followed the order: ibuprofen > paracetamol > carbamazepine. Optimal adsorption conditions were identified as a 1:300 adsorbate-to-adsorbent mass ratio, pH 6, and a temperature of 25°C,

within a drug concentration range of 10-50 mg/L. These results demonstrate that MMT-STA has significant potential as an adsorbent for removing paracetamol, ibuprofen, and carbamazepine from water [58]. Shamsudin *et al.* examined the possibility that cetylpyridinium chloride surface functionalization enhanced kaolin's diclofenac (DCF) adsorption characteristics [59]. Based on the findings from the characterization, it was determined that the modified kaolin removed DCF more effectively after adding new surface characteristics. The pH of the solution influenced the removal of DCF using modified kaolin, the amount of adsorbent used, the initial concentration of DCF, and the temperature. The DCF adsorption capacity was 392 µg/g, and the removal rate was 93.5% when the adsorbent was used at an optimal dosage of 0.5 g/L at 303 K and pH 5.86 [59].

Allaoui *et al.* utilized HDTMA to modify raw clay to remove the paracetamol from wastewater [60]. Paracetamol uptake-related factors were investigated, including pH, equilibrium time, adsorbent dose, and initial paracetamol concentration. Based on the new hydrophobic interaction, the data obtained demonstrated that HDTMA successfully modified the raw clay, increasing its adsorption capability. After 120 minutes of contact, the paracetamol adsorption on the modified clay reached equilibrium. The adsorption kinetics and isotherm data were most accurately represented by the pseudo-second-order kinetic model and the Langmuir isotherm model, respectively. The maximum experimental adsorption capacity, as estimated by the Langmuir model, was significantly higher (112.63 mg/g) than that of the unaltered sample (62.11 mg/g) [60].

2.2. Physical Treatment

The study of thermal treatment began in 1951, according to Sarikaya [61]. Two physical methods for modifying clay are microwave heating and calcination. These techniques aim to alter the chemical composition of the clay material. The clay is usually heated to very high temperatures, which can break specific chemical bonds and change the molecular arrangement within the clay's lattice structure [62]. Thermal modification alters clay minerals' physicochemical and structural properties, enhancing their adsorption capacity. Heating clay may change its size, shape, porosity, amorphization, and crystallization. Three primary temperature ranges govern this process: dehydration, dehydroxylation, and crystallization. Dehydration removes adsorbed water, while dehydroxylation modifies the macro- and microporosity of the clay mineral structure and eliminates structural water. Above the point of dehydration lies the temperature at which crystalline phases occur. At this temperature, many clay minerals, such as those in the kaolinite group, often transition to an amorphous form, although certain structural frameworks are retained. Consequently, montmorillonites in the smectite clay group lose their CEC properties and essentially cease to develop at 300 °C following thermal treatment. Thermally treated smectite clay showed a significant increase in its surface area and porous structure, according to *Mathers et al.* [63].

Table 1: The adsorption efficiency of organoclays towards pharmaceutical pollutants.

Antibiotics	Clay	Modifier	Dosage	pH	Initial concentration	Time	Temperature	Adsorption capacity / %removal
Tetracyclines	Na-montmorillonite [98]	BDMHDA	----	7	5 - 50 mg/L	----	----	98%
Oxytetracycline								94%
Chlorotetracycline								94%
Sulfamethoxazole								98%
Sulfisoxazole								97%
Sulphamethizole								99.9%
Ampicillin	Bentonite [56]	CTAB	4.5 g	7.8	126.4 mg/L	35 min	30 – 50 °C	90.6%
Amoxicillin	Montmorillonite [50]	myristyltrimethyl ammonium (MTA)	0.1–1 g	7	0.80 mmol/L	24 h	303.15 K, 313.15 K and 323.15 K	0.124–0.133 mmol/g
Ampicillin					0.82 mmol/L			0.143–0.157 mmol/g
Sulfamethoxazole	Montmorillonites [99]	cetyltrimethyl ammonium bromide (CTMAB)	0.05 g	3-11	100 mg/L	6h	25°C	235.29 mg/g
		3-(N,N-dimethylhexadecylammonio) propane sulfonate (HDAPS)		3				155.28 mg/g
		1,3-bis(hexadecyltrimethylammonio)propane dibromide (BHDAP)		3-11				242.72 mg/g
Penicillin G,	Montmorillonite [100]	didodecyltrimethyl ammonium bromide (DDAB)-	40 mg	7	10 mg/ L	2 h	25 °C	>98%
Diclofenac	Montmorillonite [101]	BDTA	100 mg	> 4	10 mg/L - 2 g/L	24 h	< 35°C	90.62%
		HDTMA						93.58%
Diclofenac	Kaolin [102]	HDTMA bromide	0.5 g	7	0.5 - 5 mmol/L	24 h	25 °C	0.88 mg/g
Chloramphenicol				3.5	0.2 - 2 mmol/L			8.1 mg/g
Carbamazepine	Sepiolite [103]	OTES	24 mg	6.7-8.5	0-50 mg/L	24 h	25°C	16.66 mg/g
		CPTES						20.12 mg/g
Ibuprofen	Kaolin [57]	hexadecyltrimethyl ammonium bromide (H)	5 mg	7	2 – 20 mg/L	30 min	Room temperature	3.12 mg/g
Chloroquine	Kaolinite [104]	citric acid	0.05 g	2	20 mg/L	5–120 min	293 K	84.03 mg/g
Aspirin								80.00 mg/g
Carbamazepine	Montmorillonite [58]	stearyl trimethyl ammonium (MMT-STA)	0.15 g	6	50 µg/mL	6 h	25°C	97%
Ibuprofen						24 h		95%
Paracetamol								63-67%
Diclofenac	Kaolin [59]	cetylpyridinium chloride (CPC)	0.5 g	5.86	200 mg/L		303 K	392 mg/g
Diclofenac	Bentonite [105]	Hexadecyl trimethyl ammonium bromide (HTAB)	0.3 g	7	30 ppm	100 min	-----	98%
Amoxicillin	Bentonite [106]	Hexadecyl trimethyl ammonium bromide (HTAB)	3 g	10	30 ppm	240 min	-----	93%
Paracetamol	Oriental clay [60]	Hexadecyl trimethyl ammonium bromide (HDTMA)	0.02 g	7.6	500 mg/L	60 min	298 K	112.36 mg/g

Other authors [64,65] utilized calcined Verde-Lodo (CVL) bentonite clay to remove the pharmaceutical components of ofloxacin and ciprofloxacin from

wastewater. The clay's stability for use in fixed-bed testing was enhanced by calcining it for 24 hours at 500 °C in a muffle furnace. Based on the analyses, the CVL clay exhibits a rough lamellar morphology with pore sizes

reaching 80,000 nm, significantly exceeding the threshold for macropores ($N > 50$ nm). The maximal Langmuir adsorption capacity for ciprofloxacin and ofloxacin was found to be 114.4 mg/g [64] and 116.72 mg/g [65] using CVL-BENT, with starting concentrations varied between 0.01 and 4 mM. Heat treatment is used on clay to eliminate impurities and lose hydroxyl, increasing stability and reducing swelling in water [64,65]. Maged et al. used thermal activation to modify bentonite clay (BC) and applied it to the study of tetracycline (TC) adsorptive removal from aqueous solutions [33]. The BC sample was thermally treated at $500 \pm 1^\circ\text{C}$ for four hours in a muffle furnace to enhance its structural stability and ion exchange capacity [66]. Comparing thermally activated bentonite (TB) to bentonite (BC), the BET analysis showed that TB has superior properties. TB was found to have a surface area that was more than twice as large as BC. It was confirmed that hydrated aluminosilicate was present in the clay by the FT-IR spectra, which showed the presence of Al—OH, Si—O, and Si—O—Si functional groups in the sample. Through optimization studies, the impacts of different operating parameters were evaluated. The Langmuir model assessed BC and TB's maximum monolayer adsorption ability to be 156.7 and 388.1 mg/g for each, respectively [33].

3. clays and clay minerals composites

Recent advancements in materials science have led to the development of clay-based composite materials by incorporating two or more components with clay minerals. These composites, particularly those combining clay minerals with metals, metal oxides, chitosan, polymers, and carbonaceous materials, have exhibited considerable potential for the adsorption of pharmaceutical residues from aqueous environments (Figure 3). Among the various clay minerals, bentonite, montmorillonite, and kaolinite are commonly employed as adsorbents in wastewater treatment due to their abundance and effective adsorption capabilities [67]. Researchers have created specially designed adsorbents in response to the demand for better adsorbent performance. The adsorbent materials' specific surface area and pore diameters can be adjusted, and various surface functional groups can be introduced through these modifications. The development of novel clay-based nanocomposites has significantly enhanced maximum adsorption capacity by providing additional binding sites for antibiotics. The adsorption performance of both pristine and modified clay minerals is influenced by intrinsic material properties, as well as the physicochemical characteristics of the target contaminants and operational conditions [68]. Table 2 provides an overview of the adsorption efficiency of clay composites for pharmaceutical contaminants. In this section, we examine the various forms of clay mineral composites, their manufacturing processes, and their adsorptive performance for antibiotic pollutants, with all aspects critically analyzed and summarized.

3.1. Clay-metals/metal oxide composites

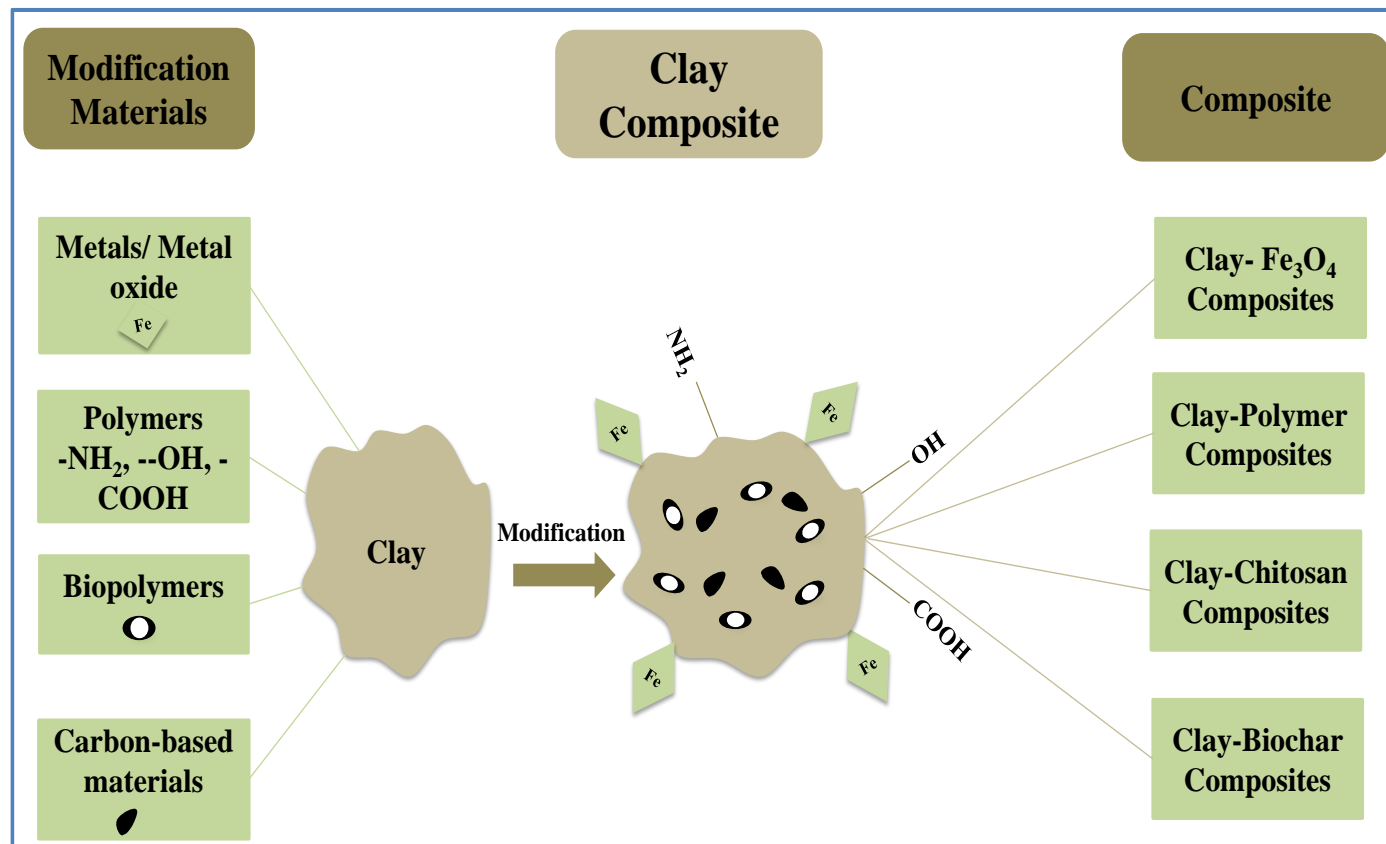
Metals and metal oxides have various applications, such as environmental cleanup, gas sensors, and catalysis [69–72]. Due to their unique surface features, high specific surface area, strong mechanical and chemical durability, and non-toxicity have been widely used as adsorbents in environmental cleanup [73]. Centrifugation and filtration techniques are typically used to extract non-magnetic waste adsorbents from aqueous solutions; however, these processes are costly and time-consuming [74]. As an alternative, magnetic metal oxides, such as iron oxide nanoparticles, are often used as adsorbents in wastewater purification because of their magnetic properties, allowing easier extraction from aqueous solutions using an applied magnetic field. In the last 10 years, composite materials made of clay minerals and metal oxides have demonstrated great promise as highly selective adsorbents for efficiently removing organic contaminants. The primary clay mineral combinations used with metal oxides to effectively remove organic pollutants include bentonite, montmorillonite, and kaolinite [75].

A magnetic montmorillonite ($\text{Fe}_3\text{O}_4/\text{MMT}$) composite was created that effectively adsorbs enrofloxacin (ENR) from water [76]. A straightforward process was used to produce the $\text{Fe}_3\text{O}_4/\text{MMT}$ composite. The $\text{Fe}_3\text{O}_4/\text{MMT}$ composite demonstrated superior adsorption and catalytic capability, effectively adsorbing ENR onto its surface. The adsorbed ENR was then rapidly degraded on-site by reactive radicals generated on the material surfaces in the presence of persulfate (PS). The ENR degradation efficiencies remained above 90% within 60 minutes at an initial ENR concentration of 30 mg/L by catalyzing PS (5 mM) with 0.1 g/L $\text{Fe}_3\text{O}_4/\text{MMT}$ [76]. Moreover, tetracycline antibiotics were effectively removed from an aqueous system using green-produced bentonite-supported Fe/Pd. The clay-supported Fe/Pd nanocomposite was synthesized through an in-situ coating method [77], where a 15 mM Pd solution and 0.1 M Fe precursor were combined with 0.1 g of bentonite clay. Under optimal conditions, the Fe/Pd nanocomposite and B-Fe/Pd nanocomposite removed 81 and 97% of tetracycline from aqueous samples, respectively. The higher removal efficiency, longer shelf life, and larger surface area of B-Fe/Pd enhance its performance as a superior and highly efficient material for TC removal. The reduced toxicity of the residual B-Fe/Pd-treated TC solution on freshwater *Chlorella sp.* indicates that B-Fe/Pd is a safe and environmentally friendly substance [78].

Olusegun & Mohallem synthesized kaolinite-supported CoFe_2O_3 (KCF) for the adsorption of doxycycline (DOX) from an aqueous solution [79]. DOX adsorption was governed by hydrogen bonding and π - π interactions, with the highest adsorption capacity of 400 mg/g at 333 K, as explained by the Langmuir isotherm model. Thermodynamic analysis confirmed that DOX adsorption was feasible, spontaneous, and endothermic, indicating increased adsorption capacity with rising temperature [79].

Table 2: The adsorption efficiency of clay composites towards pharmaceutical pollutants.

Antibiotics	Clay composite	Dosage (g/L)	pH	Initial concentration (mg/L)	Time (min)	Temperature (°C)	Adsorption capacity q_{max} (mg/g)
Bentonite-Fe/Pd [78]	Tetracycline	0.009	7	20	90	–	98%
Iron-pillared montmorillonite [107]	Levofloxacin	0.025	7	20–100	2880	35	65.0
Iron oxide-montmorillonite [76]	Enrofloxacin	100 mg/L	6.85	–	720	25	162.9
Ti-pillared montmorillonite [108]	Diclofenac-sodium	0.005	7	0–100	60	45	23.8
	Paracetamol	0.005	7	0–100	60	25	22.1
Kaolinite supported $CoFe_2O_4$ nanoparticles [79]	Deoxycycline	0.016	6	0–600	720	25	547
Nano-titanium oxide/chitosan/nano-bentonite [82]	Levofloxacin	0.03	4	5–100	10	–	90.9
	Ceftriaxone	0.2	5	5–100	10	–	90.9
Carboxymethyl-chitosan reformed montmorillonite [109]	Tetracycline	0.0008	3	5–400	120	25	95.2%
	Chlortetracycline	0.0008	3	5–400	120	25	96.4%
Lignin xanthateresin-bentonite [110]	Doxycycline hydrochloride	0.1	6	0–1000	60	25	438.8
Biochar-bentonite [12]	Ciprofloxacin	1	7–8	10–250	720	25	190
wheat straw-biochar-MMT [91]	Norfloxacin	2.5	3-11	0.4–15	48 h	25	25.53

**Figure 3.** Schematic diagram of clay composites based on various modification techniques.

3.2. Clay bio-nanocomposites

The utilization of clay minerals and biopolymers in bio-nanocomposites has shown great promise in removing contaminants from polluted water due to the enhanced biological compatibility and environmental degradability of the biopolymers and the superior adsorption ability of the clay minerals. The most investigated bio-nanocomposites for environmental applications are those made of natural polysaccharides (chitosan, cellulose, or alginate) integrated with layered silicates of the smectite group. The modification technique and the agent employed for clay functionalization define the final properties of bio-nanocomposites. Clay is typically incorporated into the polymer matrix using three main methods: direct polymerization, solution blending, and polymer melt blending. Mixing the solutions appears to improve the clay's dispersion in the matrix. Chitosan is a bioactive polysaccharide found in living organisms, valued for its antibacterial properties, cost-effectiveness, natural abundance, biodegradability, biocompatibility, and environmental friendliness [80]. Due to these qualities, chitosan is regularly employed as an adsorbent in effluent purification. Chitosan is often blended with other adsorbent materials, including clay minerals, to improve its physicochemical characteristics and durability. Bentonite and montmorillonite are among the most widely utilized clay minerals in combination with chitosan [81].

Nano-titanium oxide-bentonite (NTiO₂-Bent) and nano-titanium oxide-chitosan (NTiO₂-Chit) were crosslinked with formaldehyde to form the novel nanocomposite NBent-NTiO₂-Chit. This composite demonstrated enhanced removal efficiencies for two key antibiotics: Levofloxacin (LEVO), a fluoroquinolone, and Ceftriaxone (CFT), a cephalosporin. Maximum extraction efficiencies for LEVO and CFT were obtained within 10 minutes, achieving 90.2% at pH 4 and 93.5% at pH 5, respectively. Increasing the NBent-NTiO₂-Chit dosage to 60.0 mg enhanced LEVO removal to 92.4%. The thermodynamic evaluation revealed that the reaction was endothermic and spontaneous. Kinetic investigations demonstrated that the pseudo-second-order model most accurately described the interactions between NBent-NTiO₂-Chit and the antibiotics, with R² values of 0.999 for LEVO and 0.997 for CFT. The findings revealed that NBent-NTiO₂-Chit effectively removed LEVO and CFT from industrial wastewater, achieving extraction rates of 83.2% with 10.0 mg and 79.0% with 150.0 ± 1.0 mg of NBent-NTiO₂-Chit, respectively [82].

Maged et al. (2024) developed a novel three-dimensional (3D) network composite film composed of bacterial nanocellulose (BNC) combined with nano-kaolinite clay particles (KC) for the removal of norfloxacin (NFX) from water [20]. The BNC was produced by cultivating the *Komagataeibacter hansenii* KO28-05D strain, which was exposed to a low dose of gamma radiation (0.5 kGy) before being cultured for seven days at 30°C. The negative surface charge of BNC, along with the additional oxygen-containing functional groups from KC, enhances its ability to interact electrostatically with NFX

cationic species. Furthermore, the NFX sorption process is significantly influenced by electrostatic interactions, multi-layered sorption, and the composite's three-dimensional structure. The intricate structure of BNC-KC greatly improves sorption efficiency by effectively trapping molecules in the interlayer gaps. The synthesized composite exhibited the highest sorption capacity of 101.68 mg/g for NFX [20].

3.3. Clay/minerals-polymer composites

The adsorption capacity of clays can be enhanced by inserting polymers with ion exchange, chemical grafting, or physical adsorption into the interlayer spaces between clay mineral layers. Polyacrylamide is a common ingredient in polymer-modified clay [36]. Recently, various polymers, such as polyesters, epoxies, polyvinyl chloride, polypropylene, and polystyrene, have been used to produce polymer-clay nanocomposite. The polymer component of clay-polymer nanocomposites doesn't chemically degrade the crystalline structure of the clay minerals. However, combining polymer and clay at the nanoscale enhanced physical and chemical properties compared to the individual components [83]. Table 3 summarizes the recent research on removing antibiotics using polymer and biopolymer nanocomposites.

According to Hasan et al., polymeric adsorbents are widely used in wastewater purification because of their excellent durability, flexibility, and economic viability [84]. Regeneration techniques that rely on the physicochemical properties of the adsorbate are also feasible, as certain polymeric adsorbents exhibit relatively weak binding forces with water contaminants [85]. Several studies have examined clay minerals' adsorptive capacity and physicochemical properties, primarily bentonite and montmorillonite, when embedded in extracellular [86], synthetic [87], and cellulose-based polymeric materials. The adsorptive uptake and cumulative discharge of ampicillin (AMP) in various solutions were investigated using a hydrogel nanocomposite made of xanthan gum-graft-poly(itaconic acid)/bentonite (XG-cl-poly(IA)/BN) by Thakur et al., (2020). To create the composite, xanthan gum solution, itaconic acid, and bentonite clay solution were mixed. After blending for an hour at room temperature, the resulting mixture was subjected to microwave heating at 40 W, then cleaned and dried at 40°C. The addition of bentonite clay to the nano-hydrogel enhanced its swelling capacity (145%) without causing leaching. The maximal adsorption capacity, determined using the Langmuir model at 318 K and pH 7, was 245.09 mg/g. The study also demonstrated that ampicillin could be effectively eliminated from aqueous media using the XG-cl-poly(IA)/BN nano-hydrogel in several cycles [88].

3.4. Clay -carbonaceous composites

According to Duan et al. and Gusain et al., Carbon-based adsorbents, including activated carbon, carbon nanotubes, biochar, and graphene, exhibit remarkable properties such as high specific surface area, robust mechanical and thermal stability, customizable shape, abundant availability, and exceptional adsorption capacity. They are, therefore, widely used in wastewater treatment

[89,90]. Despite the relatively high adsorption capacities of carbonaceous adsorbents, combining these materials with clay minerals may enhance composite adsorption performance against specific pharmaceutical pollutants and improve adsorption behavior over multiple regeneration cycles [75].

Zhang *et al.* developed a composite of montmorillonite and biochar (MMT-BC) derived from wheat straw for the removal of norfloxacin from water [91]. Ten grams of wheat straw were soaked in montmorillonite suspensions and

stirred for two hours, after which the mixture was heated in a muffle furnace at 400 °C for six hours. The results indicated that, for norfloxacin with an initial concentration ranging from 0.4 to 15 mg/L, the maximal Langmuir adsorption capacity of biochar was 10.58 mg/g, while that of the MMT-BC composite reached 25.53 mg/g. The increase in oxygen-containing functional groups on the biochar with the addition of MMT accounted for the enhanced adsorption [91].

Table 3: Recent research on the removal of antibiotics using polymer and biopolymer nanocomposites.

Antibiotics	Clay composite	Dosage (g/L)	pH	Initial concentration (mg/L)	Time	Temperature	Adsorption capacity / %removal
Doxycycline hydrochloride	Lignin xanthate resin (LXR) intercalated bentonite clay composite [110]	0.1	6	0-1000	60 min	25°C	438.8
5-fluorouracil	Bentonite/Co-Poly 2-hydroxyethyl methacrylate/methyl methacrylate [111]	0.02	8	100-700	1440 min	50 °C	369
Levofloxacin	Nanotitanium oxide-chitosan-nano-bentonite [82]	60 mg	4	25	30 min	-----	92.4 %
Ceftriaxone		200 mg	5				74.2%
Levofloxacin	Carboxylated cellulose nanofiber/MMT [112]	0.45	4.33	6.40	92 min	313 K	65.90 mg/g
Ampicillin	Xanthan gum-cl-poly (itaconic acid)/bentonite (XG-cl-poly(IA)/BN) nanocomposite hydrogel [88]	30 mg	7	50	110 min	318 K	245.09 mg/g
Ciprofloxacin	Fe clay cellulose-acrylamide beads [113]	15	5	10	3 h	25°C	57.84 mg/g
Levofloxacin							38.01 mg/g
Ciprofloxacin	Chitosan–smectite nanocomposite with cobalt [114]	0.2	5.5	5-80	1440 min	25°C	72.3 mg/g
Doripenem	Bentonite-chitosan composite [115]	0.4–5	6	250	303.15 - 323.15 K	30–50 °C	70.4–88.0 mg/g
Ampicillin							57.8–79.2 mg/g
Amoxicillin							38.6–67.5 mg/g
Tetracycline	Chitosan (CS) and sodium alginate (SA) - sodium bentonite [116]	25 mg	5.5	10	30 min	-----	97.7%
Ciprofloxacin	Montmorillonite -chitosan (CS) hydrogel [117]	0.03	7	30	120 min	298 K	30.86 mg/g
Norfloxacin	Bacterial nanocellulose incorporated nano-kaolinite clay particles [20]	400 mg	6	up to 200	150 min	-----	101.68 mg/g

Ashiq *et al.* examined the adsorption of ciprofloxacin (CPX) onto biochar derived from municipal solid waste (MSW-BC) and a composite material created by blending this biochar with bentonite clay [12]. A bentonite-MSW slurry was prepared in a 1:5 (w/w) ratio and then pyrolyzed at 450 °C for 30 minutes. The fabrication of the biochar with bentonite was validated through SEM images, which showed plate-like structures. FTIR spectra demonstrated the convergence and broadening of specific bands following CPX adsorption. At the same time, PXRD patterns revealed alterations in the crystalline lattice of both MSW-BC and the composite pre- and post-CPX adsorption. As determined by isotherm modeling, the composite achieved the highest adsorption capacity of 190 mg/g, around 40% greater than the unmodified MSW-BC. Optimal CPX adsorption was observed at pH 6. This increased adsorption capacity is likely due to enhanced electrostatic interactions between the functional groups on the composite and CPX molecules, resulting in more active adsorption sites. Compared to pristine biochar, the biochar-bentonite composite exhibited improved CPX adsorption owing to additional reactive surfaces provided by bentonite and incorporating CPX within the clay layers [12].

Maged, *et al.* investigated the effective production of a functionalized algae biochar-clay composite (FBKC) for the adsorption of the antibiotic norfloxacin (NFX) from water [21]. The dried marine green alga powder underwent pyrolysis at a 5°C/min heating rate under a nitrogen flow of 0.1 L/min. The resulting biochar (BC) was then dried for six hours at 105°C. KC and BC were combined and placed in a ball-milling container for processing. The study revealed that the surface area of FBKC was thirty times greater than that of the original components and exhibited a well-developed pore structure. Mechanistic analyses of NFX/CVD adsorption onto FBKC identified several mechanisms, such as π - π interactions, hydrogen bonding, surface/pore occupation effects, and electrostatic attraction. The highest adsorption capacity of FBKC for NFX was 192.80 mg/g [21].

4. Geopolymers

One approach to enhancing the properties of clays for environmental and industrial applications is their modification into geopolymers. Geopolymers are synthetic materials that exhibit unique properties such as high strength, durability, and resistance to heat and chemicals. They are formed through a process known as geopolymerization, in which aluminosilicate materials, such as clays, are activated by alkaline solutions, typically containing sodium or potassium hydroxide. This process produces a three-dimensional network structure, providing the geopolymer with distinctive characteristics [5].

The conversion of clays into geopolymers significantly improves their performance in applications such as wastewater treatment, where geopolymers demonstrate superior adsorption capacity for a broad range of pollutants, including heavy metals, dyes, and antibiotics. Additionally, geopolymers are valued for their eco-friendliness, as they can be produced using industrial

byproducts and require relatively low energy input, aligning with circular economy principles. This modification not only enhances the functional properties of clays but also broadens their applicability in areas such as construction, environmental remediation, and sustainable material development [19].

5. Future recommendation

Future research on clay modification should focus on developing innovative, sustainable, and cost-effective approaches to enhance their performance for environmental applications. Expanding the use of natural minerals and resources, such as kaolinite, montmorillonite, and zeolites, in clay-based composites can offer eco-friendly alternatives for water treatment. Additionally, incorporating recycled industrial waste materials, such as fly ash, slag/sludge [92], E-waste [93], biochar [94], or discarded membranes [25], into modified clays can improve their adsorption efficiency while promoting resource recovery and waste minimization. Exploring other natural minerals, such as diatomite, fluorite [95], Rare earth elements [96], and feldspar, in water treatment can further enhance pollutant removal while minimizing the reliance on synthetic materials. These advancements align with circular economy principles and contribute to mitigating climate change-related challenges by reducing energy-intensive processes, lowering carbon emissions, and enhancing water security [97]. Future efforts should also explore integrating clay-based materials with emerging technologies, such as nanotechnology and IoT-based monitoring systems, to optimize pollutant removal efficiency and ensure real-time water quality management.

6. Conclusion

The increasing presence of pharmaceutical contaminants, particularly antibiotics, in water sources due to industrial, agricultural, and hospital waste discharge poses significant risks to human health and ecosystems. Conventional wastewater treatment plants struggle to remove these pollutants, necessitating advanced solutions effectively. Modified clay minerals have shown promise as affordable, efficient, and environmentally friendly adsorbents. Their high adsorption capacity is due to their unique physicochemical properties, which can be enhanced through various modification techniques, such as acid activation, pillaring, thermal treatments, and adding organic or inorganic compounds. These modifications increase surface area, porosity, and functional group availability, making clays highly effective for adsorbing contaminants from wastewater. The development of clay-based nanocomposites has further improved the performance of these materials by introducing specific binding sites tailored for pollutant molecules, enhancing adsorption capacity and selectivity. Future research should focus on optimizing clay modification techniques, combining different modification methods, and scaling up processes for industrial applications. Addressing these challenges will enable the deployment of clay minerals as viable, cost-effective solutions for pharmaceutical pollution

in water systems, aiding in the protection and sustainable management of water resources.

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