

Review Article

A Review on Natural Clay Application for Removal of Pharmaceutical Residue in Wastewater

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- Clay-based nanocomposite can be utilized as a cost-effective adsorbent for the adsorption of pharmaceutical residues from wastewater.
- The adsorption sites of clay minerals can be improved by acid activation or incorporation of functional groups with an affinity for the contaminant.
- Modified clays are better adsorbents for the remediation of pharmaceutical residues in waste water compared to natural clays.

ABSTRACT

Clay minerals are eco-friendly adsorbent materials that are abundant in nature. The usage of nano-clay for the cleanup of contaminated water has grown recently due to its distinctive physicochemical properties and characteristics. Emerging contaminants, such as pharmaceutical residue, are not typically monitored in the environment and are not controlled in our wastewater. However, due to environmental dangers and their influence on human and aquatic life, removing pharmaceutical residues and their metabolites from wastewater has piqued attention. Several researchers have investigated the application of natural clay, clay-carbon, and clay-polymer composites, among others, to remove this specific pollutant. In addition, to enhance the adsorption efficiency of natural clay minerals, the adsorption sites can be improved by acid activation, thermal treatment, or incorporation of functional groups into the clay mineral layers, which have a strong affinity for the adsorption of pharmaceutical residues. The literature review findings show that modified clays are better adsorbents for the remediation of pharmaceutical residues in wastewater than natural clays and represent an economically viable and efficient option for the cleanup of wastewater containing this contaminant. Consequently, this review gives an inclusive overview of current trends in employing clay minerals for the remediation of pharmaceutical residues in wastewater and outlines the research gaps for future research.

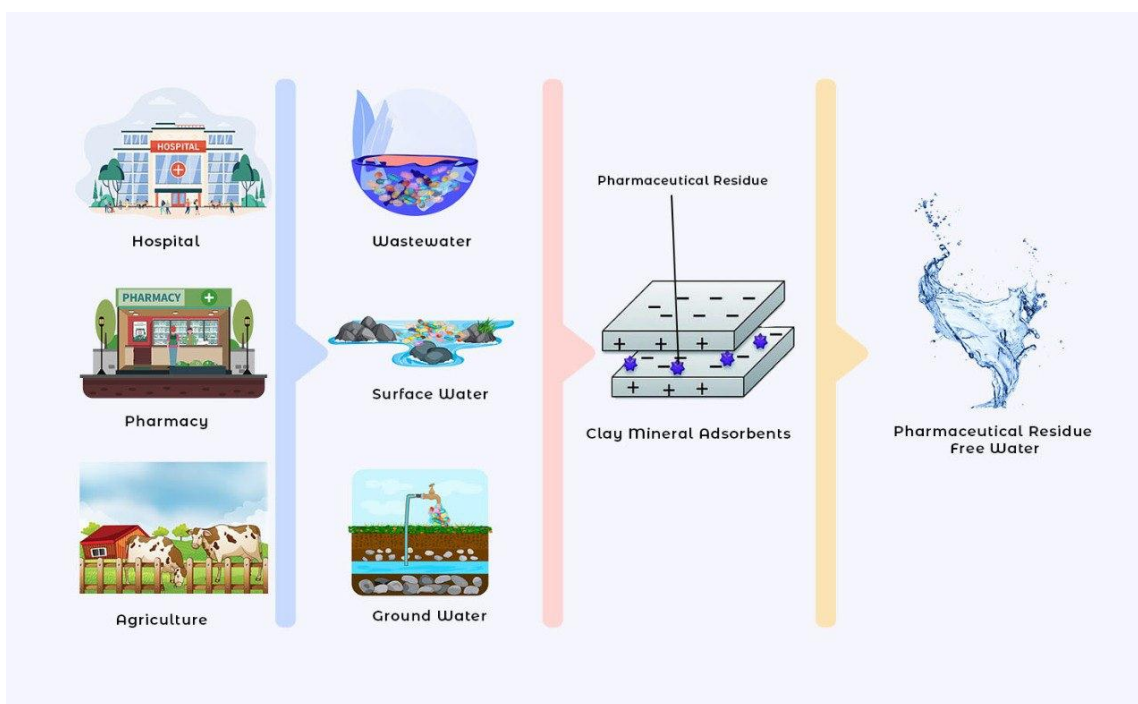
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GRAPHICAL ABSTRACT



1- Introduction

Pesticides, polyaromatic hydrocarbons (PAHs), and metals have been considerably reduced by implementing apt legal measures and deleting numerous prevailing pollution sources [1]. Eliminating developing pollutants from aquatic ecosystems has sparked considerable attention due to their environmental dangers and resulting impacts on flora, fauna, and humans [2]. Emerging contaminants (ECs) are pollutants at extremely minute environmental concentrations and are not continuously monitored [3]. Despite their minute concentration, ECs harm human and animal health [4]. Pharmaceutical chemicals, insecticides, dyes, surfactants, detergents, and personal care items are the only common types of ECs [5].

The incidence of pharmaceutical chemicals in natural water resources as new developing contaminants is becoming a worldwide concern [6-8]. Until recently, these residues have been unregulated, and their impacts on the ecosystem are still unknown [9,10]. Pharmaceuticals are essential elements in contemporary living, with

indisputable advantages [9,11]. However, the beneficial role might not be accomplished if the non-target species are exposed. In contrast, its bioactivity may generate chronic and severe consequences that may severely alter the ecosystem [9,12]. The mode of action of pharmaceuticals is the basis for its classification into eight key classes, which are central nervous system (CNS) stimulants, antibiotics, analgesics and antipyretics, antidepressants, beta-blockers, hormone/steroid, X-ray iodinated media, and lipid regulators [13,14].

Pharmaceuticals may enter aquatic habitats through various routes [10]. Essentially, four primary sources are put into the presence of medicines in the aquatic environment: man, agricultural and veterinary use as well as industrial production [15]. Hospitals are the principal source of pharmaceuticals emitted into the ecosystem, mainly via patient excretions [16]. In addition, human ingestion and expelled residue (feces and urine) may reach the septic tank as a metabolite or the parent compound [17]. Furthermore, incorrect disposal of

unwanted expired or excess medications into drains or toilets is a significant source of environmental and pharmaceutical residue pollution [1,18]. Depending on the hydrological system, these residues are most likely absorbed into groundwater [10]. Also, veterinary usage is an essential source of the ecosystem's residues and metabolites [19]. Many of them are used as growth promoters and breeding aids [20]. In the ingestion of a pharmaceutical by cattle, a portion of the drug is excreted in metabolized or the main form via the urine and feces. Without treatment, medications enter the land and groundwater [21]. In addition, drugs used to combat bacterial infections in the agricultural sectors may build up on cropland and ultimately reach the ground and surface water by leaching and runoff [7,12,22,23]. Furthermore, pharmaceutical industries add to the incidence of pharmaceutical residues in the environment through inappropriate disposal, unintentional spillage during the manufacturing and circulation processes, and express discharge into wastewater [1,24,25].

The concentrations of residual pharmaceutical compounds in the environment have been found to range from ng/L to mg/L [26]. Nonetheless, it is crucial to note that even at low concentrations, these contaminants may endanger aquatic life via various methods [2,11]. Pharmaceutical pollution has been shown to cause an endocrine disturbance, resulting in aberrant fish reproduction [27]. Sangion and Gramatica [9] recently found that they cause EE2 feminization even as little as a few ng/l in male fish. Nonetheless, compared with other growing pollutants, numerous researches have reported the elimination of pharmaceutical residue from the water. This includes a range of means such as Photocatalytic degradation [28], microextraction [29], oxidation [30,31], biodegradation [32,33], chlorination [33,34], biofiltration [35,36], reverse osmosis and nanofiltration [37-39], electrochemical oxidation [40,41], and

adsorption [42,43]. Except for adsorption, these procedures are recognized for high execution costs or a limited capacity to provide acceptable water quality. The adsorption technique has shown excellent efficacy in water decontamination against various contaminants, including pharmaceutical residues and heavy metals [44,45].

The clay minerals (Illite, kaolinite, montmorillonite, and bentonite) are abundant adsorbent materials on the planet, with critical historical implications for developing human civilization [45]. Because of their cation exchange capacity (CEC), clay minerals participate in environmental protection when used for hazardous chemical transport and storage [46]. Several studies on using natural, commercial, and composite clay materials for the removal of residues in wastewater have been accounted for; this includes kaolinite [47], synthesized nanoceria [48], schorl [49], halloysite, graphene oxide/calcium and alginate activated carbon by Duan *et al.* [50] and Wu *et al.* [51], respectively. Hence, the ability to alter clay minerals using various modifiers such as organic/inorganic compounds and alkaline/acid solutions might increase the sorption capacity for many contaminants. This review is designed to give an overview of using clay minerals to clean up pharmaceutical residue in wastewater.

2. Remediation of wastewater

Adsorption is a renowned equilibrium separation method that is functional for water purification [52]. In terms of simple design, preliminary cost, user friendly, and sensitivity to hazardous contaminants, adsorption is known to be better quality than alternative methods for water remediation [53]. The adsorption of organic pollutants like pharmaceuticals in water have been described using various adsorbent, including carbon nanomaterials (carbon nanotube graphene and graphene oxide), activated carbons, zeolites, metal-organic

frameworks (MOFs), among other [14,54]. In addition, numerous studies have reported on using clay as an adsorbent for the remediation of pharmaceuticals in water, on which this publication provides a review.

2.1. Clay minerals

Clay mineral is an ancient substance used by various ceramists from the primeval era to this contemporary age to create many products [55]. Numerous uses of clay minerals have been documented in various areas of science and technology. Hence, they are gaining much attention in the present adsorption nanotechnology [56,57]. This can be attributed to their contribution to product quality and efficiency while lowering costs, eventually preserving the environment [58].

Clays are naturally occurring finely fragmented mineral particles; with most minerals being silicates layered coated [59]. They are two-dimensional "stacks" of single or multilayer tetrahedrons corner-linked silicate (SiO_4) [60]. The geometry of these silicates is organized on each other like the page of a book, with the same space of Van der Waals forces existing between each layer, known as the "interlayer" [61]. Each interlayer comprises negative charges counteracted by the cations in the clay structure's inter-lamellar gaps [62]. The cations (Na^+ , Mg^{2+} , and Ca^{2+}), or exchangeable cations, may be readily replaced to modify the clay mineral's chemistry for the desired usage by introducing new molecules and sometimes anions to the surface [62].

2.1.1. Some of the main clay minerals with their structural characteristics

The main constituent of clay minerals is alike, typically consisting of two foremost geometries sheets (tetrahedral and octahedral) organized jointly in a different structure [63]. Differences in the fundamental structure of clay minerals resulted in a novel type of clay mineral development.

2.1.1.1. Kaolin

The kaolinite group is a vast collection of clay minerals, including kaolinite, dickite, halloysite, and nacrite; the breakdown of orthoclase forms it. Nacrite Dickite and clays are formed from a kaolinite combination hydrothermally [64]. The kaolinite group is mainly composed of alumina (octahedrons and tetrahedrons) and silica, which are in a ratio 1:1. The kaolinite group has a formula of the $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, with the central part enclosed by SiO_2 , Al_2O_3 , H_2O , and the small segment covered by Mg magnesium, potassium (K), Iron (Fe), and others [65]. Kaolin clay, also known as China clay, has a variety of industrial uses; it is one of the most crucial clay minerals in the kaolinite group. The inert chemical structure and white tint of its fine particle size make it an excellent feedstock for ceramics, catalysts, adhesives, and adsorbents [59].

2.1.1.2. Smectite and montmorillonite

Smectite is the most common and vital phyllosilicate clay mineral [66]. Smectite is known to be chemically distinct from the kaolinite group with the group's typical structural formula $(\text{Ca}, \text{Na}, \text{H})(\text{Al}, \text{Mg}, \text{Fe}, \text{Zn})_2 (\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2\text{-XH}_2\text{O}$ [59]. Smectite clay mineral has equidimensional and lengthened symmetry. The elongate structure consists of saponite (magnesium montmorillonite), hectorite (lithium montmorillonite), and nontronite (iron montmorillonite) [67]. The substitution of the octahedral and tetrahedral sheets is a unique feature of smectite group. Mg and Fe are substituted for aluminum in the octahedral sheet, while silicates and alumina are substituted on the tetrahedral sheet [68]. Ca and Na montmorillonite are essential clay minerals of the smectite group, with slight geometrical differences [64]. Na montmorillonite has a monolayer of water at the structure, while Ca montmorillonite has di-layers of water in the interlayer position [64]. Due to two water layers in the interior position, Na-montmorillonite has a

higher viscosity and swelling capacity than Ca-montmorillonite [65].

2.1.1.3. Bentonite clay

Bentonite primarily comprises the mineral montmorillonite and aluminum phyllosilicates [69]. Bentonite clay is formed through the combination of glassy minerals (volcanoes). Feldspar Kaolin and quartz mica, among others, are minerals found in bentonite. Bentonite clay has the typical molecular formula $Al_2H_2Na_2O_{13}Si_4$ [59]. Bentonite clay is two kinds: sodium bentonite with a water layer particle and swelling characteristic and one Na^+ ion as an exchangeable cation [70]. In contrast, calcium bentonite is a non-swelling with a double layer of water clay and Ca^{2+} as an exchangeable cation.

2.2. Modification of clay minerals

Clay minerals are distinguished by their large surface area and strong cation exchange capabilities. Clay minerals, except for kaolinites, contain OH groups that are singly coordinated, thereby limiting their use for adsorbent productions [71].

2.2.1. Acid activation of clay minerals

The activation of clay minerals via acid resulted in the leaching of the inorganic cations, thereby enhancing the surface area for the adsorbent's design [72]. The effect of acid activation is determined by many variables, including the acid's relative quantity and type [73]. The acid's nature has only a little consequence on the characteristics of the resultant activated adsorbent [74]. In contrast, the acid quantity employed during activation significantly affects the final characteristics [75].

2.2.2. The thermal treatment of clay minerals

The dehydration temperature is affected by clay and compensatory cation [76]. Depending on the maximum temperature, the thermal treatment of clay minerals may cause various changes. Two kinds of mass losses are anticipated throughout the slow heating of clay minerals. Firstly

dehydration occurs between 50 and 200 °C and is not irreversible [76]. Dehydroxylation happens between 500 and 750 °C, which is a factor in the type of clay and occupancy of the octahedral sheet [77].

In contrast, the effect on adsorbent is not reversible above this temperature. Likewise, the values of SSA (Specific Surface Area) and CEC are unaffected by the dehydration temperature with a slight reduction [78]. Beyond 2000 °C, the values of SSA and CEC continue to drop somewhat, and beyond the dehydroxylation temperature, both CEC and SSA values decrease dramatically [79]. Many heat-activated commercially accessible clays are advertised as 'expanded clays,' Light Expanded Clay Aggregates (LECA), and Filtralite VR. They are widely used as adsorbents in various applications, including construction materials, aquaculture, and water filtering [80,81].

2.2.3. Expanded clay minerals

Expanded clay minerals are often generated by dehydroxylation temperature (1000 °C) or flash heating, significantly impacting their CEC and SSA [82]. Consequently, their characteristics vary significantly from those of raw clay minerals, raising concerns about their ability to absorb organic pollutants effectively.

Anionic and neutral pharmaceutical residues

Dordio *et al.* [83] used lab-scale batch tests to compare the ability of two clay materials (exfoliated Vermiculite and LECA to adsorb, Naproxen (NA) Mefenamic acid (MA) and Gemfibrozil (GB). LECA produced complete superior remediation of all the residues. In contrast, Vermiculite demonstrated more excellent adsorption capabilities per unit mass of adsorbent and a quicker adsorption rate of at least >70% during the first 2 hours, reaching equilibrium within the first 24-48 hours of contact. However, for the LECA this is only possible after 72-96 hours of interaction time. The removal efficiencies achieved in this study

using Vermiculite for three residues (GB, MA, and NA) are 37%, 35%, and 80%, respectively. This was consistent with previous adsorption studies for the removal efficiencies of GB and MA employing clay material, which are 10-40% [84,85]. However, a reasonably high efficiency of 95-97% is achieved using LECA for all three medicines, which is consistent with earlier investigations of other substances [86,87]

Rafati *et al.* [88] employed a nano-composite adsorbent CCP (Clay/-CD/PVP) to clean up an aqueous solution containing Ibuprofen and tested its effectiveness using fixed-bed column experiments. The functionalized nano-clay composite allows for 94.5% ibuprofen elimination efficiency. This adsorbent has excellent adsorption affinity for this residue when compared with the adsorbent capacity reported for the same pharmaceutical residue using natural clay 7.04% [89], olive waste cakes 70.07% [90], and molecularly imprinted polymer (MIP), 69%.

Khatem *et al.* [91] used sorption on a synthetic calcined hydrotalcite to remove diclofenac. The [Mg-Al-CO₃] solid was produced by coprecipitation at unvarying pH, and its mixed calcined oxide was studied by XRD (X-ray diffraction) and FTIR (infrared spectroscopy). The interaction with diclofenac demonstrated rapid sorption kinetics and obeyed the second-order model. The calcined hydrotalcite sorbed 95% of diclofenac, which is approximately 1.9 mmol/g-1 indicating HT-C hydrotalcite calcined (HT-C) may be an attractive adsorbent for diclofenac elimination.

Ghemit *et al.* [92] created organobentonite adsorbents for the sorption of Diclofenac (DIC) and Ibuprofen (IB). Three concentrations of cetyltrimethylammonium bromide (0.5, 1, and 2 CEC) (IBU) were employed for the activation of raw bentonite (RB). The best efficiency was achieved with 2CEC, which had 99.4% and 94% adsorption efficiencies for IBU and DIC, respectively. The adsorption capacity of 600.6

mg/g achieved in this research was lower than the 925.0 mg/g reported by Barczak *et al.* [93] for a comparable investigation on DIC utilizing amine groups' functionalized mesoporous silica. In contrast, this was higher than 320 mg/g and 596.7 mg/g reported by Bhadra *et al.* [94] and Hiew *et al.* [95], respectively, using porous carbon frame with metal-organic and decreased Graphene oxide Aerogel in their separate studies (GAO). The IBU adsorption capacity was 194.9 mg/g, which was higher than the 12.60 mg/g obtained by Baccar *et al.* [90] with agricultural by-products, 16.84 mg/g was reported by Essandoh *et al.* [96] using Activated Carbon from Pinewood, and 96.15 mg/g was obtained by Nourmoradi *et al.* [97] using Activated Carbon from an oak acorn.

An anti-inflammatory nonsteroidal (Ibuprofen) was examined by Behera *et al.* [98] on different minerals; including montmorillonite, kaolinite, and goethite using batch tests. The sorption of Ibuprofen on the clay mineral was discovered to be relative to the concentration of Humic Acid. Less Ibuprofen was absorbed by goethite and kaolinite (2.2 mg/g and 3.1 mg/g, respectively) compared with 6.1 mg/g achieved with montmorillonite when 100 mg/L Humic Acid (HA) was used. In contrast, HA-complexed ibuprofen rose to 1000 mg/L at 10.5 mg/g (goethite), 64 mg/g (kaolinite), and 59.5 mg/g (montmorillonite). Similarly, the adsorption of neutral and anionic PPs in wastewater effluents on montmorillonite is studied by Thiebault *et al.* [99]. The adsorption of the anionic pharmaceutical residues was found to depend on the organic moieties' adsorption on clay and compensating inorganic cations. 100% sulfamethoxazole (SUL) adsorption was observed among all the anionic drugs. In contrast, the adsorption efficiency obtained for the other drugs was Diclofenac (DCF) at 38%, gemfibrozil (GEM) at 47%, naproxen (NAP) at 57%, and ketoprofen (KET) at 68%.

Kryuchkova *et al.* [100] investigated the adsorption characteristics of unmodified montmorillonite (MMT) and MMT-STA (stearyl trimethyl ammonium) towards Paracetamol (PAR), Ibuprofen (IBP), and carbamazepine (CBZ) pharmaceuticals at 10-50 g/mL concentrations. The best mass ratio of adsorbents to adsorbates was 300:1 at a pH of 6 and 250°C. MMT-STA outperformed pure MMT in eliminating all of the residues tested. The adsorption capability of non-hydrophilic montmorillonite to medicines increased in the subsequent order: paracetamol (63–67%), Ibuprofen (95%), and carbamazepine (97%). Under the same circumstances, pure montmorillonite efficiently adsorbed only CBZ (75–80%), to a lesser degree IBP (16–23%), and did not adsorb PAR. As a result, MMT-STA may be utilized as an effective adsorbent to remove carbamazepine, Ibuprofen, paracetamol, and other hydrophobic organic pollutants from wastewater. Khazri *et al.* [101] describe the adsorption of three pharmaceutical compounds (Ibuprofen, naproxen, and carbamazepine) onto the natural clay, which contains a mixture of quartz and kaolinite-smectite. The amount of adsorbed naproxen and ibuprofen onto clay is higher than that of carbamazepine (carbamazepine 32 mg.g⁻¹ < ibuprofen 36 mg.g⁻¹ < naproxen 37 mg.g⁻¹). This might be due to the protonation of Ibuprofen and naproxen, which renders them more easily adsorbed than carbamazepine at a pH of 6.

Hadi *et al.* [102] employed a batch system to remove Diclofenac sodium (DF). The number of active sites and specific surface area of the pumice was modified by doping with Trimethylamine (TMAP) from 0.1 g/L to 1.5 g/L. The study observed that removal efficiency increased from 18.12% to 88.46% due to the availability of more active sites for the adsorbed molecules. As the initial concentration increased from 100 to 1000 mg/L, the adsorption capacity increased from 64.71 mg/g to 373.33 mg/g. In

contrast, at C₀ > 1500 mg/L, no significant increase was observed in the study. In addition, the DF adsorption was found to be pH-dependent. The negative charge on the surface of adsorbent increased as the pH increased from 3–11, resulting in a robust repulsive interaction between the opposing charge surface and DF, which lowered the adsorption capacity to 55.19 mg/g from 64.71 to mg/g.

Cationic pharmaceutical residue

Maged *et al.* [103] investigate Tetracycline elimination using bentonite and modified bentonite. Tetracycline (TC) adsorption onto bentonite depends on medium pH, owing to the interactions involving the TCH₃⁺ of TC and the rate of functional group ionization on clay mineral surface. At optimal pH 3, the removal effectiveness of modified bentonite was greater than that of natural bentonite, with 98.39% and 51.90%, respectively. The adsorption capacity reported in this study was 156.7 for Bentonite (BC) and 388.1 for Thermally activated bentonite (TB), which was greater than the 32.0 for Illite reported by Chang *et al.* [104], 127.0 for Stevensite reported by Antón-Herrero *et al.* [105], and 250.0 for Montmorillonite for a similar study on TC. In addition, Genc *et al.* [106] utilize batch tests to investigate bentonite as a possible sorbent for removing CIP from aqueous solutions. The removal efficiencies were found to depend on the agitation speed. Hence, optimum agitation was observed between 100 to 150 rpm with CIP adsorbs up to 99 %, and adsorption capacity (QE) rose from 84.64 to 147.06 mg/g.

Thiebault *et al.* [99] designed an adsorbent to remove pools of cationic pharmaceutical residues. Due to the electrostatic interaction between montmorillonite cations, the cation exchange was the driving force for the adsorption process. With 200 mg of Montmorillonite, the removal rate ranges from 58 to 95 %.

Table 1. Remediation of some Anionic Pharmaceutical Residue employing clay minerals

Clay Mineral	Pharmaceutical Residue	pH	Adsorption Capacity(mg/g)	Adsorption efficiency%	Reference
Functionalized Nano-Clay Composite	Ibuprofen			94.8	[88]
Exfoliated Vermiculite	Gemfibrozil	7.47	0.058	37	[83]
Light Expanded Clay Aggregates	Mefenamic Acid	9.04	0.068	35	
	Naproxen		0.062	80	
	Gemfibrozil		0.0125	95-97	
	Mefenamic Acid		0.014	95-97	
Montmorillonite Modified with Stearyl Trimethyl Ammonium	Naproxen	6	0.009	95-97	
	Carbamazepine		61.99	97	
Pristine Montmorillonite	Ibuprofen	6.5	63.66	95	
	Paracetamol		63.39	65-67	
	Carbamazepine		66.47	75-80	
Organobentonite	Ibuprofen	6.5	65.07	16-23	
	Paracetamol		N/A	N/A	
Montmorillonite Goethite	Diclofenac	2-7.5	600.6	99.4	[92]
	Ibuprofen		194.9	94	
	Marbofloxacin		117-225	>85-99	
Montmorillonite	Ibuprofen	7	64.4	60	[98]
			59.5	20	
Montmorillonite	sulfamethoxazole	6.4	10.5	20	[99]
			100	100	
			37	37	
			48	48	
			57	57	
	Ketoprofen		68	68	

The high relative removal of the PHAC can be attributed to the high affinity between the PPs and clay. The trends observed in the study were atenolol (ATE) 58%, tramadol (TRA) 72% > metoprolol (MET) 63% > doxepin (DOX) 92%, > and codeine (COD) 94%.

Arya and Philip [107] examined the adsorption of gemfibrozil, atenolol, and ciprofloxacin using a manufactured composite (magnetic-polymer-clay). The optimal composite adsorbent ratio was 0.3:0.5:0.3:1 for magnetic nanoparticles (MNP) chitosan, powdered activated carbon (PAC), and clay. Electrostatic contact was the primary driving factor for adsorption. The maximal adsorption capabilities of gemfibrozil, atenolol,

and ciprofloxacin were calculated to be 24.8, 15.6, and 39.1mg/g, respectively. The magnetically distinguishable clay composite was discovered to be an effective adsorbent for removing pharmaceuticals from water. When 1.5 g/L of adsorbent was employed to extract one mg/L of chemicals in solution, gemfibrozil, atenolol, and ciprofloxacin were removed up to 90, 85, and 95 %, respectively. In contrast to Arya and Philip [107], Wang *et al.* [108] reported more than 90% ciprofloxacin sorption; Bui *et al.* [109] reported greater than 90% ciprofloxacin sorption utilizing trimethylsilylated silica SBA 15 and magnetic zeolite adsorbent respectively. Similarly, Chang *et al.* [110] examined the

remediation of atenolol (AT) by employing Ca-montmorillonite in an aqueous solution by batch experiments under various physicochemical circumstances. At pH 10, the AT was found in its un-dissociated neutral form. After 1 hour, the adsorption capacity was 75 mmol/kg (54 % adsorption capacity), with 330 mmol/kg as the maximum capacity of adsorption achieved after the sorption was completed. As a result of the relatively high starting rate and rate constant, Ca-montmorillonite may be an excellent adsorbent for AT.

In contrast to their starting material (a natural clay mineral), Mabrouki and Akretche [111] investigated the removal of diclofenac potassium

using iron-pillared clays as adsorbents. The batch experiment yielded adsorption capacities of 62.50 for natural bentonite, 40.00 for Na-bentonite, and 100 mg/g for iron-pillared bentonite. Iron-pillared bentonite has a high adsorption capacity in acidic solutions owing to synergistic electrostatic interactions of the anionic diclofenac and the adsorption sites. The pillaring process resulted in the changes observed in the texture and the structure. In addition, as pH tends to be more basic, lower adsorption was obtained due to the ionic repulsion caused by more OH⁻ and the diclofenac potassium surface negative charges adsorbents outer have more exchangeable anions [112].

Table 2. Remediation of some cationic pharmaceutical residue employing clay minerals

Clay Mineral	Pharmaceutical Residue	pH	Adsorption Capacity(mg/g)	Adsorption efficiency%	Reference
Bentonite	Ciprofloxacin		147	99	[106]
Ca-Montmorillonite	Atenolol	10	330 mmol/kg	57	[110]
Bentonite (BC)	Tetracycline	3	156.7	51.90	[103]
Thermal Activated Bentonite (Tb)	Tetracycline	3	388.1	98.39	[107]
Magnetic Polymer Clay Composite	Atenolol	10	15.6	85	
	Ciprofloxacin	7	39.1	95	
	Gemfibrozil	4	24.8	90	
Natural Bentonite	Diclofenac potassium	2	62.5		
Na-Bentonite	Diclofenac potassium	2	40		[111]
Iron-Pillared Bentonite	Diclofenac potassium	2	100		
Kaolinite	Enrofloxacin	2-7.5	9-25	>85-99	[97]
	Marbofloxacin	2-7.5	117-225	>85-99	
	Atenolol	6.4		58	
Montmorillonite	Tramadol			72	[99]
	Metoprolol			63	
	Doxepin			92	
	Codeine			94	

3- Conclusion

Persistent pharmaceutical residue in wastewater is a growing environmental concern worldwide, and clay mineral application has proven to be a dependable, long-lasting, environmentally friendly, and cost-effective treatment option. The change in surface geometry and surface area increases the adsorptive efficiency of clay

minerals towards pharmaceutical residues, making them a suitable material for remediation. Compared with the natural clay minerals, the review shows that modified clay minerals are better adsorbents for the cleanup of cationic, anionic, and neutral pharmaceutical residues. The PPs adsorption from aqueous solutions using clay mineral and its composite in batch

experiments and simulated solutions has been extensively reported by researchers. However, future research should extensively explore the application in real environmental media. In addition, its potential application in dynamic experiments should be considered with utmost concern regarding the challenges of swelling capacity. Furthermore, exploring the advancing nanotechnology to generate novel materials and composites (such as polymer-clay, Biochar-clay nanocomposites) will provide a high surface-to-volume ratio with active sites for residue removal. Therefore, more research is needed to properly understand the property, structure, and interaction formulation in clay-nano composites and their sorption of the pharmaceutical residues for a higher water quality output.

Authorship contribution statement

OOA: Conceptualization, writing-original draft, writing- review, editing, and supervision. OMB: Writing-original draft, writing-review, editing, and supervision. ABO: Writing-review and editing. BBO: Writing- review and editing. IEA: Writing-original draft. SSO: Writing-original draft, OOA: Writing- original draft. BTD: Writing-original draft, writing-review, and editing

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Ethical approval

This study does not involve experimentation on animals or humans.

Consent to Publish

All authors gave their approval for the manuscript publication.

Conflict of Interest

The authors declare no competing interests.

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