Canadian Scientific Researchers
Discovering Science

Canadian Journal of Scientific Research

Clay Composites for Wastewater Treatment

Naeema Amjad*, Mohammad Nouman Amjad*

Northwestern Polytechnical University, Xi'an, China

Abstract

Wastewater treatment is vital for providing clean and safe drinking water. Clay-based materials have received a lot of interest in recent years for their potential use in wastewater treatment applications. Various clay kinds are utilized to create clay composites for wastewater treatment. Common clays used in wastewater treatment comprise kaolin, montmorillonite, bentonite, and others. Each clay type is investigated for its distinct mineral composition, structural features, and surface qualities. Clay composites have received a lot of interest in recent years because of their increased adsorption capacity, ease of recovery from water solutions, and superior physiochemical characteristics when compared to raw and modified clay composites. Several types of clay composites are used to remove various impurities from wastewater. These contaminants include heavy metals, dyes, organic and inorganic contaminants, and emerging contaminants. Clay composite advancements, such as chemical and physical modifications, can improve their adsorption capacity, selectivity, and stability. pH, temperature, and ionic strength all have an impact on adsorption efficiency. There are certain challenges and potential research prospects for improving clay composites in environmental applications.

Keywords: Clays, Composites, Wastewater, Treatment, Dyes, Contaminants

Submitted: 27-02-2025; Accepted: 11-06-2025; Published: 15-07-2025; https://doi.org/10.66487/2-25-CJSR-2-2-2

Review article
**Corresponding Author*, e-mail: *naeemaamjad52@gmail.com*; *noumanrandhawa52@gmail.com*

1. Introduction

In recent years, the rapid development of innovative technology has been driven by one of the world's significant worries about environmental deterioration. One of the primary sources of contamination in water bodies is wastewater, which originates in a variety of ways. A purified water source is an absolute necessity for each human community. The discharge of hazardous elements into water bodies is increasing dramatically. However, the rising usage of toxic materials has significantly increased the level of unwanted compounds in freshwater and the biosphere [1]. Scientists discovered over seven hundred carcinogenic and highly hazardous inorganic and organic micro contaminants as a result of rapid industrialization. These are classified as persistent ecological pollutants that are not able to degrade. Poisonous inorganic elements include As (V), Cr (VI), Pb (II), Cd (II), Hg, and others, whereas organic pollutants include dyes and pigments. The pollution of fresh water with hazardous and heavy metals like fluorine, arsenic, and a high concentration of dissolved matter is a big public concern [2].

Pathogenic organisms are the primary source of waterborne illness in children. It is just not possible to eliminate these harmful poisonous contaminants. The simplest way to address this inclusive issue is to expand low-cost and competent water and wastewater treatment techniques, which require environmentally benign and non-contaminating components. Numerous materials for treatment of wastewater have been produced using graphene, diatomite, zeolites, hydrated layered polysilicates, mesoporous materials, and double-layered hydroxides. As a result, the composites provide a synergistic effect and have the potential to eliminate a range of contaminants. However, these materials have some problems, such as not being readily available, easily prepared, stable, cheap, biodegradable, or toxic. For example, graphene and its modified forms are effective at removing several contaminants from water, but they are very expensive to make. To solve these issues, scientists began searching for a solution [3].

Clay composites are the most preferred wastewater treatment and water purification technology. Also, using clay-based composites to treat water and wastewater is helpful because the materials have excellent qualities and can be recycled, which makes them more desirable than regular treatment methods. The use of clays in pollution removal could provide significant economic and environmental benefits to the wastewater industry [4]. Clay minerals are very common in nature, low in toxicity, affordable, environmentally acceptable, and have excellent physical and chemical stability. Solids of this type have been used a lot in medicine and the environment throughout history because they can absorb and hold onto contaminants, micro pollutants, and other harmful chemicals. They have been used to get rid of germs and both organic and inorganic pollutants because they are stable, don't harm living things, have a lot of surface area, can swell, and don't react with water [5].

In the past, researchers used different types of adsorbent materials to clean water and wastewater of harmful contaminants. These included chemical oxidation, electrolysis, electro dialysis, adsorption, reverse osmosis, chemical precipitation, membrane filtration, and conventional coagulation. Many of these approaches are costly and cannot be implemented in developing countries. Coagulation methods and chemical precipitation require additional treatment for secondary contaminants, increasing treatment costs. Surprisingly, adsorption accounts for the majority of the pollutant elimination method since it is low-cost, simple to use, and has the highest elimination capacity for a variety of contaminants. The chosen adsorbent material must be readily available, inexpensive, and easily produced, as well as have a greater selectivity for the contaminants being targeted. Excellent biological, organic, and mineral adsorbents have been created for water purification. However, natural clays alone can be utilized only in limited ways due to their low specific surface area, complex regeneration and recovery protocols in water systems, limited ability to remove micropollutants [6].

To solve the mentioned issues, clay-based composites have been created. These resultant polymers have recently received increased interest in wastewater treatment. Clay minerals have been improved, creating a new group of materials called clay composites. These materials have clay minerals that are well dispersed, adsorbed on the surface, immobilized, or interposed. The composites that are made have big improvements in a lot of important factors, such as their physical and chemical properties, their mechanical strength, their resistance to heat, and their ability to keep gases from escaping. As a result, clay composites are incredibly promising, not only because they are inexpensive, but also because they are very effective at eliminating a wide range of contaminants from water media. Furthermore, some of these clay composites are long-lasting materials because they are made from abundant resources [7].

2. Role of Clay Materials

Clay is an adaptable adsorbent that may be utilized in a variety of applications to eliminate pollutants and impurities from liquids and gases. Adsorption is process of attracting and keeping adsorbate (pollutant) molecules to surface of adsorbent (clay). Clay is a hydrous aluminosilicate material made up of two repeating units: a tetrahedron of silicon and oxygen $(Si_2O_5)_2^-$ and an octahedron of aluminum, also known as a gibbsite sheet. Tetrahedral sheets share three of the 4 oxygen atoms. These tetrahedrons are arranged in a hexagonal arrangement, with the basal oxygens connected and the apical oxygens pointing upward and downward. In octahedral sheets, each octahedron shares edges with a neighboring octahedron. These edges are made up of oxygen atoms and hydroxyl anions, as well as coordinating cations such as Mg^{2+}, Fe^{2+}, and Al^{3+}. These octahedrons form a hexagonal configuration. Both natural and modified clay materials can be utilized as adsorbents. In Figure 1: a general chemical composition of a raw clay is described [8].

3. Properties of Clays

Clay minerals exhibit various properties, including shrinkage, air-drying in fire, plasticity, hardness, porosity, and adsorption ability. Clay mineral's very small molecule size, high porosity quality, and huge surface area resulted in favorable physical and chemical interactions on their surfaces. These reactions happened on the surface of clay under favorable conditions, for example high electrostatic revulsion and selective cation exchange with crystallinity as a result of adsorption. The effective porous surface of nano-clay increases bonding power on the surface with confinement. Clay's hydrous aluminosilicate structure is made up of metal and mineral oxides that have a greater stability range. Clay minerals were categorized into different classes based on these properties [9].

4. Types of clays

Clay is classified into various kinds, each with its own set of adsorption characteristics. Clay is classified into four to five main groups: kaolinite, illite, montmorillonite, chlorite, and smectite. Some of the most common clays that serve as adsorbents include: Kaolin clay, commonly referred to as china clay, which is a white or light-colored clay with a high adsorption capacity for organic molecules. It is widely used in the treatment of wastewater to get rid of contaminants like organic dyes, oils, and heavy metals [10]. Bentonite is a clay comprised primarily of montmorillonite. It has a large surface area and a great affinity for organic molecules and several heavy metals. Bentonite clay is commonly used to remove pollutants from water and purify culinary oils and wines. Montmorillonite is a clay with high swelling capabilities and a wide surface area. It functions as an adsorbent in a variety of applications, including the removal of radioactive elements, heavy metals, and organic compounds from water and soil. These are only a few examples of the various kinds of clay that can act as excellent adsorbents. In Figure 2: major forms of clay are shown [11].

The type of clay used depends on its use and the pollutants that need to be eliminated. Each variety of clay has distinct adsorption characteristics that may necessitate various preparation and activation methods to maximize its adsorption capacity. Illite is the sole common mineral, and chlorites are sometimes thought to be a separate group of phyllosilicate minerals. These categories contain about thirty different forms of clays; however, natural clay is combination of these clay types along with weathered minerals. Adsorption capability of clay minerals determined by their negatively charged silicate groups. Montmorillonite clay has highest adsorption capability. The clay can be modified to increase its adsorption efficiency. The 1:1-layer structure is composed of one tetrahedral and one octahedral sheet, with each octahedral sheet coupled to tetrahedral sheets via apical O_2^- ions. The 2:1-layer structure consists of 2 tetrahedral sheets and one octahedral sheet, with one of tetrahedral sheets bonded to octahedral sheet on each side [12].

5. Structure and Composition of Clays

Each variety of clay mineral has distinct and captivating chemical and physical qualities resulting from its structure. The majority of clays comprise only 2 basic components, which appear in various arrangements: the silica tetrahedron and the aluminium octahedron. They are classified into 2 categories: 1:1 and 2:1. Class 1:1 clay is made up mostly of a tetrahedral silica sheet stacked over an octahedral gibbsite or brucite layer. For instance, kaolinite is mostly made up of tetrahedral silica and an octahedral gibbsite sheet. The most common example of class 2:1 is montmorillonite, which consists of two sheets of tetrahedral silica and one sheet of octahedral gibbsite. Take montmorillonite as an example; this structure has been widely used in a range of applications, including adsorption, catalysis, and ion exchange. Due to its industrial applications, montmorillonite is regarded as an important clay mineral. The crystalline structure is made up of an octahedral aluminium layer sandwiched between 2 tetrahedral silicon sheets [13].

Montmorillonite is made up of 3 layers joined by oxygen bridges. Metal ions, like iron (II) and magnesium (II), can substitute isomorphically for octahedral aluminium (III) ions. Therefore, silicon (IV) and aluminium ions (III) can be substituted isomorphically. One feature of this structure is that the substitution renders the surface negatively charged. Polar molecules or cationic surfactants can also be contained within the galleries, resulting in unique surface characteristics [14]. Different types of clay structures have made it possible to combine them with many other materials to make a wide range of composites. The goal is to make unique, useful hybrid materials with a range of properties for treating wastewater. In Figure 3: chemical composition of kaolinite, illite, and chlorite clays is represented [15].

6. Clay Composites

Composite materials are described as a combination of two or more physically separate materials that are easily recognized by microscopy, disseminated in a controlled manner to attain optimal characteristics, and whose characteristics outperform those of the individual elements. The International Union of Pure and Applied Chemistry (IUPAC) specification 10 defines a composite as: ‘‘A multicomponent material comprising multiple different (non-gaseous) phase domains in which at least one type of phase domain is a continuous phase’’. Thus, the clay composites are the materials which are made from the combination of clay with other materials [16].

7. Fabrication of functional clay composites

Clays and minerals are commonly used to create useful clay composites at a low cost. These minerals, along with other components, are intercalated in the clays' structural lattice. This results in significantly improved functional qualities for the composite as compared to the pure materials, making them appealing materials for adsorbent-adsorbate interactions. Pyrolysis and sol-gel chemistry are both safe and simple ways to make composites, depending on the desired qualities and available energy and temperature. Before being washed, dried, ground, and sieved to make clean clay material of the same size, raw clay material is usually processed to get rid of debris, organic matter, and other outside contaminants [17]. Depending on the functional qualities to be improved, the mass ratio of pure clay to processed minerals (or additional beginning materials, if necessary) can be adjusted.

During the fabrication process, the weighted components are dispersed in a chemical solution (depending on the kind of clay composite), left to stand for a few hours to days (depending on the aim), subsequently moved to a crucible, and heated until dry. The pyrolytic process requires elevated temperatures, which are maintained. The temperature and time depend on desired outcome. This is followed by cooling to room temperature, grounding, and washing repeatedly until the filtrate is colorless and has a neutral pH, indicating that there is no additional leaching from leftover, unconnected components. The composite is then dried to a fixed weight and sieved through a particular mesh-size sieve. This is a general functionalization of the clay composites method, but the method varies according to the type of clay composite, raw material, and the carrying process conditions [18].

8. Characterizations of Clay Composites

Characterizations of clay composites are performed to determine their chemical and physical characteristics, which improve their functionality. Some of the chemical properties are the attached functional groups, how they act in different conditions like pH, the type of interactions between atoms, and maybe even how the atoms or groups of atoms are arranged. The physical properties include shape, structure, and texture. Using the gas physic-sorption method, the physical properties are (i) the specific surface areas, pore volume, and diameter; (ii) the surface and internal morphology of the composite using electron (both scanning and transmission) microscopic techniques; and (iii) the lattice structure of the composite using diffraction (X-ray and electron) techniques. Chemical characteristics include: (i) Spectroscopic techniques include infrared, Raman, and ultraviolet-visible spectroscopy [19]. These techniques may give insight into the form and nature of the chemical components in addition to the efficiency of functionalization.

(ii) Thermogravimetric analysis; the percentage quantity of functional and labile groups within the composite structure and their stability can be determined; (iii) Elemental chemical analysis; the number of basic elements in the composite can be determined; and (iv) Nuclear magnetic resonance can be used to determine notable covalent bonds in the framework of the composite. Clay materials feature well-defined crystal structures and distinctive X-ray diffraction (XRD) patterns. During composite production, the XRD spectra of the composite hybrids become noisier than those of pure clay, but there are usually no major problems with the structure of the clay lattice. XRF spectroscopy showed that the mixture had a higher silica-to-alumina ratio than pure clay materials. This might be because silicon and aluminium leaked out during the building process [20].

9. Advantages of Clay Composites for Wastewater Treatment

An economic analysis indicates that benefit-cost ratios represent one of the most significant areas of research for the use of clay composites in wastewater treatment systems. The feasibility as well as the sustainability of this kind of unique adsorbent depends significantly on the cost of adsorbent synthesis, energy inputs, and environmental safety. An economic analysis would be extremely useful in assessing if these items are appropriate for long-term use at ground level. However, just a few have looked into the economics of clay composites for sustainable water treatment. The cost of raw materials, such as clay, can help reduce the cost of producing composites, such as nanocomposites with high pollutant removal capacity. Costs for clay minerals such as normal palygorskite, kaolin, and bentonite vary greatly. Researchers have found that mixing clay minerals with materials like biopolymers or activated carbon improves the clay composite's ability to attract and hold different pollutants. Furthermore, incorporating naturally occurring clay minerals into a suitable material may reduce the product's cost. Although only a few research studies have focused on regeneration capacity, these low-cost minerals can be efficiently used in adsorbent regeneration research. In Figure 4: advantages of clay composites are shown [21].

Clay composite adsorbents can be reused effectively, creating less waste and removing many pollutants during their use. Some clay-polymer nanocomposite (CPN) adsorbents have been employed as catalytic agents to investigate pollutant degradation. A montmorillonite clay/TiO_2 nanocomposite was used to remove methylene blue from wastewater. It was created using a simple sol-gel technique that was both cost-effective and had a high degradation capacity. However, green leaf extract has been employed with clays to reduce production costs while maintaining environmental sustainability. Similarly, metal-doped clay composites should be created using metals that are less hazardous than elements like Ag and Ti. In general, the utilization of low-cost, suitable clay minerals, green leaf extract, and low-cost raw materials can be used to economically prepare low-cost, efficient clay composites that promote environmental sustainability [22].

10. Synthesis and properties of clay composites, as well as their classification based on different modifications

Clay composites have gained special attention since their characteristics and structural performance excel those of their components. Such composites are created by mixing two or more chemically different, insoluble components. As previously said, they are classified into four major categories: carbon material, organoclay composites, hybrid silicate-clay composites, and nanocomposites. Following are the preparation and properties of clay composites prepared using numerous modifications, are discussed [23].

10.1. Modification of clay composites with organic compounds

10.1.1. Clay composites with anionic or cationic surfactants

Anionic surfactants, unlike cationic surfactants, are not easy to inject into the interlayer region of clay minerals without ion pairs (H_3O^+) or counter ions (sodium and calcium ions). Co-modification with anionic and cationic surfactants efficiently addresses this problem. It involved adding a predefined quantity of cationic surfactant to clay solutions and mechanically stirring them for one hour. The mixture was agitated for four hours at 70°C, after adding the anionic surfactant. This method results in clay particles with 4 times the basal spacing of raw clay (1.55 nm). Furthermore, the mixed micelles found in this form of composite demonstrated synergistic effects in the elimination of organic pollutants. It is important to think about the environmental risks of releasing surfactants into the water, but anionic or cationic surfactant-modified clays may be very helpful in removing cationic dyes [24].

10.1.2. Surfactant/polymer-clay composites

Surfactant-modified clays have a significantly higher affinity for humic acid than raw clays. Several investigations struggled to co-modify clays with surfactants and polymers. Such composites were developed in 2 stages, using surfactant-modified CSZ (SCMZ) and chitosan-modified zeolite (CSZ). A chitosan solution was mixed with zeolite for 1.5 hours, and the pH of the reaction was adjusted with a 2 mol/L NaOH solution. The resultant CSZ was shaken with a CPB solution containing 25 mmol/L for 48 hours at 40°C. Centrifuge the supernatant mixture and wash the final SCMZ with distilled water until no Br^- residue is identified by $AgNO_3$. The combination showed two different adsorption bands. Before using clay, minerals treated with surfactants, it's important to do an $AgNO_3$ test to monitor the residue in real-time. Furthermore, heavy metals and phenolic compounds can be removed by using the surfactant/polymer clay composites [25].

10.1.3. Acid /surfactant-clay composites:

Acid activation (using sulfuric acid, nitric acid, and hydrochloric acid) permits the partial dissolution of Al_2O_3 and MgO from the crystal lattice, increasing internal surface area. But, acid-activated clays have a limited affinity for organic compounds. One common example of combined modification is H_2SO_4/surfactant-activated Bent, which has been changed with four alkyltrimethylammonium bromides. The preparation of such material proceeded as in this order: raw Bent was processed by a low-concentration acid (1 M H_2SO_4) at 90°C for four hours, and the activated solid, free of SO_4^{2-} ions dried at 80°C. A 1 L solution of different surfactants mixed with 10 grams of acid-activated Bent (AB) to make 4 different compounds. The acquired samples rinsed many times with distilled water to eliminate any remaining bromide ions. As a result of this change, clay's basal spacing (d001) increases, indicating a positive link between d001 and alkyl chain length. The structure of AB was more porous than that of raw bentonite (RB), but adding a large molecular surfactant filled up some of the interlayer space in organo-bentonites, making them less permeable. This composite's properties make it a good choice for removing dyes and aromatic substances from wastewater [26].

10.1.4. Magnetic and polymer-clay composites

The primary impediment to adsorbents' extensive industrial use is their separation from aqueous solutions. Magnetic treatment, in addition to flotation as a fine particle separation approach, offers another remedy to this problem. To create magnetic composites, clay is typically treated with iron or chemically precipitated iron oxides (Fe_3O_4 or γ-Fe_2O_0). To make beads, a certain quantity of ferrofluid is dissolved with an acetic acid solution that contains chitosan. The combination is then added to an alkaline epichlorohydrin solution. The beads were then rinsed in ethanol to eliminate any remaining chloride ions. Magnetic adsorbents can offer active sites with a great affinity for inorganic or organic substances. The unlike charges of the composite's components, magnetic nanoparticles (whose charge varies with pH), clay (which has a permanent negative charge), and chitosan (which has a positive charge in acidic environments), ensured that they were very effective at removing things over a wide pH range (3 to 12). When the contaminants were adsorbed onto the surface of the magnetic clay components, a magnetic field easily separated the composite without changing the water's turbidity. Magnetic clay composites are very stable and can be used again and again. They can be used as multifunctional adsorbents to eliminate cationic and anionic contaminants [16].

10.2. Clay composites modified with hybrid silicates

Making inorganic-inorganic hybrids, especially hybrid silicate-clay composites, is seen as a possible way to form new materials because they are very stable, don't contain any harmful chemicals, and work well with other materials. These clay composites created by a one-step hydrothermal process. A uniform mixture of Na_2SiO_3 and palygorskite (PAL) is mixed with zinc sulfate or magnesium sulfate solution to make a white solid. This solid is then heated to 180°C and reacted in a Teflon tank for 8 or 24 hours. By adding monochloroacetic acid to hybrid silicate-clay composites, PAL nanorods were made easier, and −Si(M)O- groups were created. The total pore volume increased as the silicon/magnesium ratio increased, reaching its peak at a Si/Mg ratio of 1:2. These non-hazardous hybrid adsorbent composites made from environmentally friendly elements (such as magnesium, silicon, sodium) and natural clay minerals, could be ideal for the elimination of heavy metal ions and dyes [27].

10.3. Modification of clay composites using carbon components

10.3.1. Activated Carbon Clay Composites

Activated carbon is widely used as an adsorbent for pollutant removal. Because activated carbon (AC) is pricey, mixing it with clay minerals may allow you to benefit from their particular adsorption properties. The most commonly used AC-clay composite is activated carbon-zeolite, which is made from elutrilithe and pitch. Elutrilithe's carbon, SiO_2, and Al_2O_3 components were ion-exchanged in $CaCl_2$ solution to create an activated carbon-zeolite composite. The material had a hierarchical porosity of micropores to mesopores (zeolite), a 29.9% increase in carbon. A researcher devised simple ways for producing AC-zeolite composites by combining limestone (15.2%), ordinary Portland cement (OPC) (29.9%), activated carbon (4.39%), zeolite (4%), and rice husk carbon (4.39%). These activated carbon-clay composites have potential uses in treating NH_3, heavy metals, phenolic chemicals, and dyes [19].

10.3.2. Clay-Biochar Composites

Biochar is a carbon-rich material produced by pyrolysis of plant or animal biomass in an oxygen-deficient system. Because it is porous, doesn't rust, and has many functional groups, modified biochar can do more than just store carbon and soil remediation. It can also act as a green adsorbent for various kinds of contaminants. However, for the formation of clay-biochar composites, there has been little systematic research on it. According to research, six clay-biochar composites were created in 2014 using a straightforward approach. 3 biomass feedstocks, comprising bamboo (BB), bagasse, and hickory chips, were treated with methylcyclopentadienyl manganese tricarbonyl (MMT) solution and subsequently pyrolyzed at 600°C in a nitrogen dioxide atmosphere. When biochar was added to the clay composites, the average pore width and pore volume increased by 1.59 and 1.8 times, respectively, compared to using biochar alone. Clay-biochar composites have been studied for their effectiveness in immobilizing NH_4^+, PO_4^-, norfloxacin (NOR), and heavy metals. In conclusion, clay-biochar composites provide a safer and more cost-effective technique of treating wastewater. In Table. 1 various top discipline are described that were involved in developing clay-biochar composites in previous years [28].

10.4. Nanocomposites

A nanocomposite is a multiphase matrix made up of a standard material and nanoparticles. Nanoparticles have a large surface area compared to their volume, which makes the properties of the matrix (metal, polymer, or ceramic) much better when they are mixed in to make a composite. Recently, environmentalists and researchers have become very interested in nanocomposites as a way to clean water because they have a large surface area, good binding properties, thermal stability, great mechanical characteristics, the ability to remove micropollutants, antifouling properties, and are cheap. To solve the problem of wastewater treatment, a ceria nanocomposite structure was devised with the ability to eradicate both water contaminants and carbon monoxide. Researchers made great progress by making a hetero-agglomerate of anatase and maghemite nanoparticles at a pH of neutral. This effectively removed pollutants from wastewater using photocatalysis. Currently, membrane separation methods are gaining popularity for water purification. The polymerization method was utilized to create MCM-41 silica nanoparticle membranes. Porous MCM-41 silica nanoparticles have been shown to have high water permeability and salt rejection effectiveness [29].

Adding multi-walled carbon nanotubes to nano-silver particles also made the nanocomposite more permeable and showed that it was very good at keeping things from sticking and fouling up. The latest scientific innovation is carbon nanotubes, which are useful in the field of water filtration, particularly for brackish water. Researchers have demonstrated the usefulness of carbon nanotubes in an approach to the water crisis. Molecular dynamics simulation helps us better understand nanoscale systems. The theoretical aspects help in creating a link between the flow of water, the rejection of ions, and the structure of the nanocomposite, especially for uses in desalination. A $Cu/TiO_2/SiO_2$ nanocomposite was used for the removal of Rhodamine B, which is one of the most well-known dyes. The ability of nanocomposites and carbon nanotubes to remove dye has been established. Carbon nanotubes have a larger specific area, which accounts for their increased extraction ability. Heavy metal ions in water have also been eliminated using nanoscale composites [30]. Nanocomposite designed with iron carbide nanoparticles selectively adsorbed metal ions such as Zn, Pb, Cr, Ni, and Cu. Another strategy for using carbon nanotubes, both single- and multi-walled, was proposed for the elimination of dissolved organic matter from polluted water, as well as medicines and personal care products. One important way to use nanocomposites is to magnetize carbon nanotubes with iron (zero valent) and then find the best way for them to absorb nitrate, metal, and chlorinated organic pollutants from wastewater [31].

11. Applications of modified clay composites in Wastewater Treatment

Water contamination is one of the most important environmental hazards affecting living organisms: roughly two billion individuals worldwide suffer from water pollution-related illnesses, with over ninety-five percent living in developing nations (such as Pakistan and India). The widespread use of numerous pollutants caused an increase in microorganism resistance, raising the threat to human health posed by proactive diseases. Raw or modified clay materials are highly effective at removing or immobilizing inorganic (such as ammonia, heavy metals,) and organic (such as dyes, aromatic compounds) contaminants, along with cytotoxins. But mixing an adsorbent with other results in better adsorption characteristics than each of its constituents. Following are the performance and adsorption mechanisms of raw clays, single-modified clays, and combined-modification clay composites [32].

11.1. Antibiotics elimination from wastewater

The usage of antibiotics in stock breeding and seafood is a major issue since synthetic compounds (like fluoroquinolone antibiotics) are difficult to biodegrade. Their prevalence in marine habitats has harmful effects on living things and affects antibiotic-resistant microbe species. The ideal adsorbent for norfloxacin elimination is biomass-based activated carbon. A researcher looked into using a mix of clay and biochar (called APB) made from burning potato stems and natural attapulgite. This combination effectively removed more norfloxacin (NOR) from water, potentially lowering the cost of activated carbon or biochar. APB composites may be more successful than pure biochar in eliminating NOR from 3 kinds of water (tap, river, and distilled) [33]. Biochar's high norfloxacin adsorption ability can be attributed to silicon dioxide particles and its functional groups. NOR-Cu^{2+} complexes are proposed to minimize the adverse effect. In general, these 2 forms of clay-biochar composites retained eighty-five percent of their norfloxacin removal efficiency. Biochar-clay composites can adsorb NOR through several methods, including hydrogen bonds, hydrophobic effects, interactions between π-π electrons, filling pores, and electrical attraction among others. Antibiotics are widely utilized in human medicine and agriculture. Furthermore, the colloidal characteristics of hybrid silicate-clay must be enhanced by modifying them with natural polymers (such as chitosan) to promote regeneration and reuse [34].

11.2. Dyes elimination from wastewater

Dye contaminants are one of the most serious water contamination concerns in various industries. Dyes, especially methylene orange (MO) and methylene blue (MB), are classified as common contaminants because of their mutagenic, cancer-causing, and highly colorful environmental impacts. Although commercial activated carbon (CAC) has the maximum elimination rate, the cost of available clays (for example, vermiculite) is around twenty times lower than activated carbon. A study looked at how well different types of activated carbon and raw clay can absorb methylene blue. It found that coal-based activated carbon (400-590 mg/g) absorbed much more methylene blue than raw clay (6.29-290 mg/g). This big difference happens because virgin clays have a layered structure, leading to different ways they can absorb substances. Adsorption is a complex procedure that is affected by the size of particle as well as electrostatic or hydrophobic interactions. Several researches have been conducted to increase the methylene blue elimination capacities of single modified clays using polymer, heat, surfactant, and acid activation [35].

Low acid concentrations (≤1 M) decarbonized the material, increasing its surface area and pore volume while maintaining its crystal structure. Currently, there has been rising interest in using mixed-modified clay composites to absorb multiple dyes at the same time. When H_2SO_4/CTAB-activated bentonite (AOBent) was mixed with salicylic acid (SA), it had a small impact on the clay's spacing. As the pH increases, the carboxyl and hydroxyl groups in the beads lose protons, which boosts the electrostatic attraction between methylene blue and H_2SO_4/CTAB-activated bentonite/ salicylic acid (AOBent/SA). The coating of AOBent greatly reduced the removal of methylene orange. To increase the rate of methylene orange elimination, anion-cationic composites were created by combining the anionic surfactants sodium stearate (SSTA) and cationic surfactants cetyltrimethylammonium bromide (CTMAB) with methylcyclopentadienyl manganese tricarbonyl (MMT), which contains more organic carbon and is an efficient partition medium. Anionic/cationic-clay composites outperform acid/surfactant-clay composites like AOBent/SA when it comes to methylene orange sorption. Novel activated carbon bentonite alginate beads (ABA) can absorb the most methylene blue, with a capacity of 995 mg/g at 50 °C [36].

11.3. Heavy metals removal from wastewater

A large number heavy metals have drawn widespread interest because of threats they pose to environments and human well-being, resulting in a significant need for effective elimination methods. Batch adsorption studies show how sodium montmorillonite (Na-MMT) and calcium montmorillonite (Ca-MMT) can remove metals like copper (Cu^{2+}), zinc (Zn^{2+}), cobalt (Co^{2+}), lead (Pb^{2+}), and cadmium (Cd^{2+}) through a process called ion exchange. A single modified clay, created by treating silicon dioxide or Fe_2O_3 and adding a chelating agent, showed great effectiveness in cleaning wastewater that contained either one type or a mix of heavy metal ions, based on a study. Since 2006, activated carbon-clay composites have been utilized to remove $Cr_2O_7^{2-}$, Cu^{2+}, Pb^{2+}, Ni^{2+}, and Cd^{2+}. A new chitosan/clay/biochar (MTCB) nanocomposite is as effective as others at removing Zn, Pb, and Cu metal ions at same time. Among these ions, MTCB has strongest affinity for Pb^{2+} [37]. Some components of this combination, such as -NH_2 groups, serve to hold metals in place. However, it performs better than the Bent modified with epichlorohydrin and chitosan.

Si/Mg-modified palygorskite (PAL) is an in-expensive and efficient material, capable of adsorbing 210.7 mg of Cu^{2+} per gram. A 2:1 Si/Mg ratio and an alkaline atmosphere aid the overall adsorption procedure. Such silicate materials have greater surface areas and perfect surface charge distribution, allowing them to remove certain dyes and heavy metals from polluted water. Hybrid silicate-clay composites excelled over organoclay and biochar-clay composites in terms of Cu^{2+} adsorption [38]. One probable cause is that the -Si(M)O—groups in hybrid silicate-clay composites significantly contribute to pollutant adsorption through chemical adsorption, electrostatic attraction, and ion exchange. Hexavalent chromium (CrO_4^{2-}, $Cr_2O_7^{2-}$) is one of the most dangerous metallic species due to its carcinogenic nature. Cellulose's OH groups promote metal ion adsorption, making cellulose/CTAB-activated MMT composites efficient $Cr_2O_7^{2-}$ adsorbents. Organo-clays can help eliminate extra impurities like molybdate, selenate, anionic dyes, nitrate, antimonate, phosphate, and arsenate. Different methods have been used to remove cesium from contaminated clay, including using special cation-exchange polymers and flotation techniques [39].

11.4. Elimination of aromatic compounds from wastewater

Aromatic contaminants are made up of one or more fused benzene rings, either natural or synthetic. The phenolic compounds are one of the most common aromatic contaminants because of their less solubility and durability. Adding 1,2-dioleyloxy-3-dimethylaminopropane (DODMA) to palygorskite made the surface positively charged. This made it possible for the modified composite to attract 42 mg/g of the negatively charged pollutant p-nitrophenol (PNP) through electrostatic forces. Adding Cu^{2+} significantly improved the elimination of p-nitrophenol from all clay beads [40]. This likely happened because Cu^{2+} changes how the clay interacts with substances or increases the acidity of phenol, making it harder for PNP to stick to the clay. Electron donor-acceptor interactions, π-π interactions, and solvent effects all have a significant impact on how phenol adheres to activated carbons. In general, acid/surfactant- and anionic/cationic surfactant-clay composites are excellent at removing aromatic pollutants. However, several surfactants employed in clay composites may offer health hazards. Therefore, an extra silver nitrate test to determine residual surfactants is needed before employing these clay composites [41].

11.5. Other contaminants removal from wastewater

Humic acid (HA) in freshwater may impart color, smell, and taste issues. In 2004, researchers found that H_2SO_4-activated natural clay and chitosan composites were much better at absorbing humic acid (HA) and tannic acid than regular clay. The composites could absorb 231.9 mg of HA and 1394.9 mg of tannic acid per gram, while raw clay could only absorb 137.9 mg of HA and 27 mg of tannic acid per gram. At first, clay composites were found to have equivalent adsorption capabilities for tannic acid (TA), RR222 dye, and the humic acid to chitosan beads. A surfactant and chitosan-modified zeolite (SMCSZ) was the best at adsorbing monolayer HA, but it worked less effectively than acid/polymer-clay mixtures and single-modified clays [42]. The way SMCSZ sticks to HA involves three processes: hydrogen bonding, organic partitioning, and electrostatic interaction. In contrast, CSZ only sticks to humic acid. The various adsorption methods demonstrate the benefits of these surfactant/polymer-clay composites. Recent research highlights the benefits of chitosan/alginate-clay composites for removing pollutants. Additionally, there is growing interest in using natural materials like wheat bran to make environmentally friendly superabsorbent composites with wheat bran, poly (acrylic acid), and clay. Activated carbon/zeolite composites have been utilized to adsorb ammonia, chemical oxygen demand, and N-nitrosamines. NH_3 (ammonia) adsorbed better on activated carbon/zeolite composites compared to activated carbon and zeolite [43].

12. A comparative study of clay composites, raw clays, and activated carbon

Besides natural biomass, coal is the most important precursor in the production of calcium aluminate cement (CAC). This type of carbonaceous material exhibits mechanical strength, physicochemical stability, significant porosity, adsorption capacity, and surface area. Activated carbon's surface contains ionized (CO^-), neutral (COH), and protonated ($C{-}OH_2^+$) groups, making it a potent target for organic pollutants. Depending upon the forms of the precursor and activation procedures, coal-derived activated carbon has a methylene blue elimination capability ranging from 229 to 589 mg/g. Similarly, activated carbon more frequently adsorbs p-nitrophenol (PNP), with adsorption capacity decreasing in the following order: activated carbon > activated carbon/salicylic acid > sodium montmorillonite > sodium montmorillonite/salicylic acid. Clays are types of minerals that contain water and aluminium silicate. They can exchange certain ions, which makes them useful for removing contaminants. These ions include sodium (Na^+), chloride (Cl^-), calcium (Ca^{2+}), hydrogen (H^+), potassium (K^+), magnesium (Mg^{2+}), ammonium (NH_4^+), nitrate (NO_3^-), sulphate (SO_4^{2-}), and phosphate (PO_4^{3-}), among others [44]. Heavy metals like Cu^{2+}, when used as model contaminants, adsorption efficiency of Cu^{2+} changed in this order: Salicylic acid > composite microbeads > clays, activated carbon. Clays and activated carbon have various adsorption mechanisms, which explains why their adsorption effectiveness differs.

Adsorption on activated carbon involves interactions between hydrophobic substances and their electrons, as well as surface bonding. In contrast, adsorption on clay happens through electrostatic attraction, hydrogen bonding, exchanging ions, and partitioning. Additionally, several factors influence cost of various adsorbents, including availability, stability, source, recycling, and synthesis process. In general, biochar costs less than activated carbon. Natural clays are cheaper, which is a clear advantage over activated carbon [45]. Other adsorbents (for example, chitin and chitosan) cost about twelve times as much as natural adsorbents like peat, ash, and clay. Thus, clay composites treated with natural polymers or biochar can be called affordable adsorbents. Renewal is another critical objective for allowing quick recycling or recovery of adsorbents using low-cost approaches. A study showed different methods for regeneration, such as chemical, steam, vacuum, pressure, and thermal. Choice of method depends on the kind of adsorbates and adsorbents used. Efficiency of activated carbon, when restored using heat or electricity, depends on temperature and current. Regeneration rates are b/w 70% and 80%. In most circumstances, combined regeneration procedures can be an effective alternative to recovering tested adsorbents [46].

13. Mechanisms of Wastewater Treatment using Clay composites

13.1. Adsorption mechanism

The adsorption mechanism is directly related to the adsorbent surface characteristics and the nature of the adsorbate. The addition of other materials to an adsorbent alters the surface characteristics and impacts the interaction, ultimately influencing the adsorption mechanism. Clay and minerals mainly absorb organic water pollutants through several methods: ion exchange, π-π interaction, electrostatic interaction, hydrophobic interactions, van der Waals forces, hydrogen bonding, surface complexation, and chemical adsorption like covalent bonding [47]. Dominant adsorption mechanism is determined by chemical characteristics of the organic contaminants, as well as functional groups, structure, and surface qualities of clay mineral composites. Moreover, adsorption conditions such as ionic strength and pH have an impact on the adsorption mechanism since they can modify adsorbent's surface characteristics. Electrostatic interaction is most commonly used adsorption process. Ionic bond formation comprises electrical attraction and repulsion. Anions and cations exchange electrons to generate ionic bonds. It is important to investigate effect of solution pH on clay absorption capability.

This is due to solution pH changing the charges on clay composite, which influences electrostatic interaction [48]. The key components of clay and mineral combinations that aid in electrostatic contact include Si-O and Al-O, which are found in clays. Despite the existence of surface functional groups, electrostatic interaction is reduced in some situations. This is owing to the composite's extra contacts, which weaken the electrostatic interaction. Other interactions, such as the π-π interaction, were attributed for the adsorption process because graphene oxide contains a benzene ring. Ion exchange refers to the transfer of ions with the same charge that occur between an adsorbent and an adsorbate [49]. It takes place when the adsorbent removes ions from solution while adding equivalent ions to keep it electrically neutral. Ion exchange is a common adsorption mechanism in clay/minerals, chitosan and clay/minerals-polymeric composites, which might involve the exchange of Na^+ or ligands. In the π-π interaction, unsaturated bonds on both aromatic rings in the adsorbent and adsorbate form a weak link. It is a basic adsorption mechanism found in clay mineral carbonaceous and clay mineral polymer composites. π-π interaction is affected by pH of the solution.

Hydrogen bonding is a form of dipole-dipole attraction when a hydrogen (H) atom connects with an electronegative atom (such as oxygen (O), fluoride (F), or nitrogen (N)). Most clay composites form hydrogen bonds with organic contaminants, which is an influential form of interaction. Different methods of adsorption of contaminants from wastewater are described in Figure 5: [50]. The hydrophobic interaction means the interaction of a non-polar compounds in an aqueous environment. Clays and minerals are naturally hydrophobic, and they retain some hydrophobicity when mixed with other materials, particularly metal oxides. Several researches have combined metal oxides with clay/minerals to increase hydrophobicity, which boosts adsorptive capacity. Furthermore, most organic contaminants have a less solubility in water, making them easily adsorbed on the clay composite surface. Surface complexation may play a role in interaction of clay with organic contaminants. The surface complexation happens when adsorbent interacts with the adsorbate via electrical forces, while the adsorbate ions maintain their water layer around them. This occurs because clay composites include metal ions with vacant gaps in their electron structure. These ions can attach to organic contaminants by interacting with their ligands [51].

13.2. Catalysis Mechanism of Clay Composites for Wastewater Treatment

A simple, quick, and effective way to treat colorant-polluted wastewater is to use metallic species as nanoparticles or oxides to break it down or reduce its amount. Such species work well as catalysts because they have excellent thermal, optical, and electrical characteristics. They also have a large surface area and are easy to produce because they are selective and specific. The use of noble metals (Au, Pd, Pt, and Ag) for catalytic reduction is widely used and extensively studied for wastewater treatment. Usage of these species alone is unsatisfactory because of agglomeration/aggregation, reduced performance, and the difficulties of reuse in water solutions [52]. To reduce the inconvenience, numerous researchers developed low-cost, widespread, and environmentally friendly materials to immobilize or disperse these metals on their surfaces. Clays possess a large specific surface area, a sheet-like structure, and surface negative charges, which makes them an ideal support for immobilizing or dispersing metallic species through a simple technique like ion exchange. In Figure 6: a general scheme of wastewater treatment by using clay composites as catalyst is represented [53].

The nanoparticle species can be generated on the clay's surface through chemical, biological, or thermal treatments. To reduce environmental contamination, effective and eco-friendly treatment solutions have been created. Among these options is the use of sophisticated oxidation technologies. These are oxidative treatment methods that necessitate the use of metallic catalytic support. Following pollutant distribution across the nanocomposite surface, metallic nanoparticles supported by the nanocomposite (clay) aid in dye elimination or degradation reactions. Catalytic reductions need a reducing agent like NaOH, $LiBH_4$, or $NaBH_4$. On the other hand, photocatalytic reactions need UV light. Clay-based nanocomposites are better for removing contaminants than other methods. They work faster, produce less harmful byproducts, and create interesting raw materials. They are also affordable, simple to design, and easy to use [54].

14. Advancements in Clay Composites for Wastewater Treatment

New adsorbents that are efficient and selective in moderate conditions (low usage of energy and non-toxic oxidants) are rapidly being produced. Modification and hybridization have advanced significantly over the last two decades, ranging from simple contact and surface engineering to the production of nanocomposites and hierarchical assemblies. Numerous researchers have devised a wide range of techniques for introducing functional inorganic, organic, and organic-inorganic hosts between layers of lamellar clay minerals. In addition to acid activation, inorganic cation exchange, intercalation, and pillarization processes, as well as their use as catalytic supports, functionalization has given clay-based materials new applications, allowing for the creation of a nanoscale space. Changing clay mineral surfaces with organic substances is an important step for their use in industry. Clay's naturally hydrophilic surface is transformed into an organophilic surface, allowing mineral clays to be dispersed in low-polarity chemicals or solvents. Clay minerals can be modified in a variety of ways, including by exchanging their intrinsic interlayer cations with cationic surfactants, grafting clay mineral surfaces with silanes, and using silanes as a silicon source in clay mineral synthesis. Cationic surfactants are commonly used as modifying agents.

Recently, dimeric or gemini surfactants have gained a lot of attention because of their flexible molecular structure [55]. Nanotechnology has recently emerged as a rising field, bringing with it a range of methods that are currently being advanced at the nanoscale. It contributes significantly to the advancement of novel techniques to reduce water pollution and enhance environmental protection.

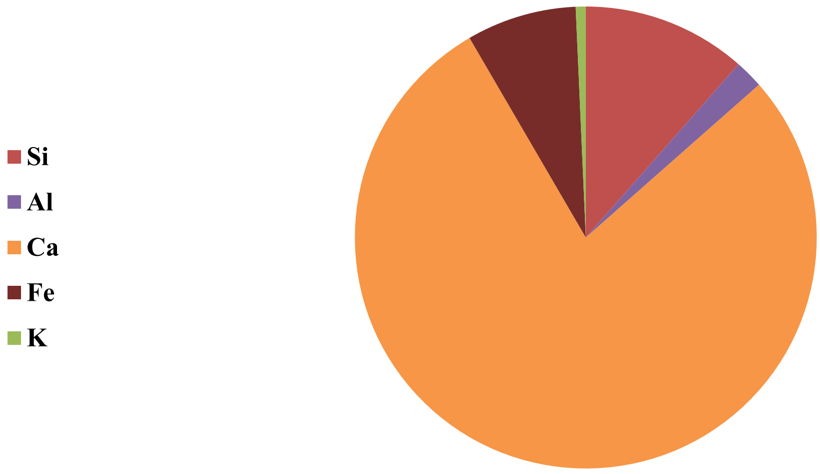

Figure 1: General chemical composition of a raw clay

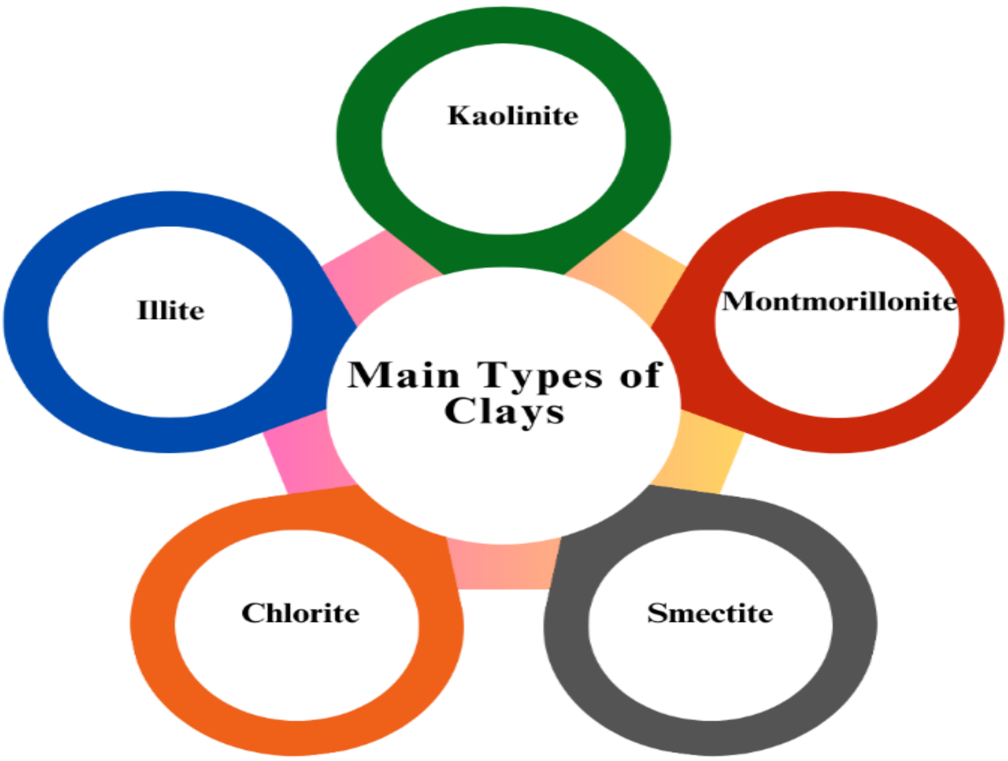

Figure 2: Major Forms of Clays

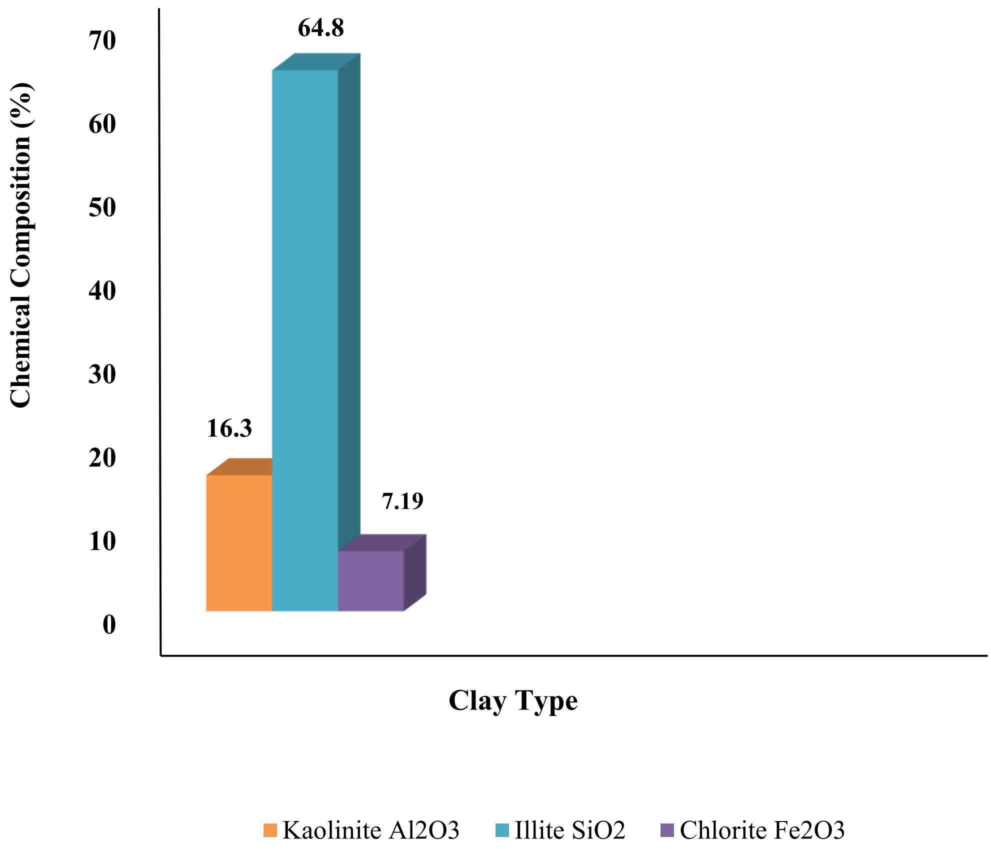

Figure 3: Chemical Composition of Kaolinite, Illite, and Chlorite Clays

Figure 4: Advantages of Clay Composites

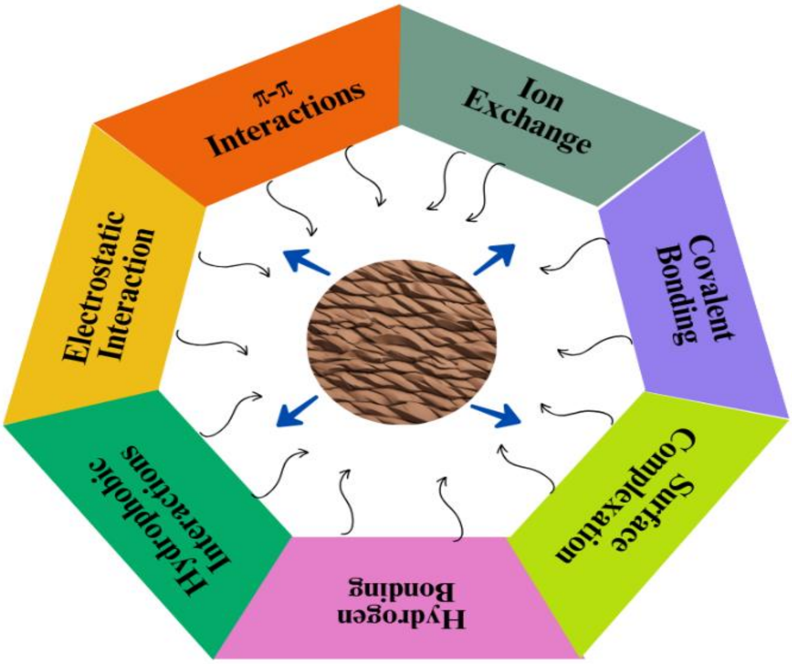

Figure 5: Different methods of adsorption of contaminants from wastewater

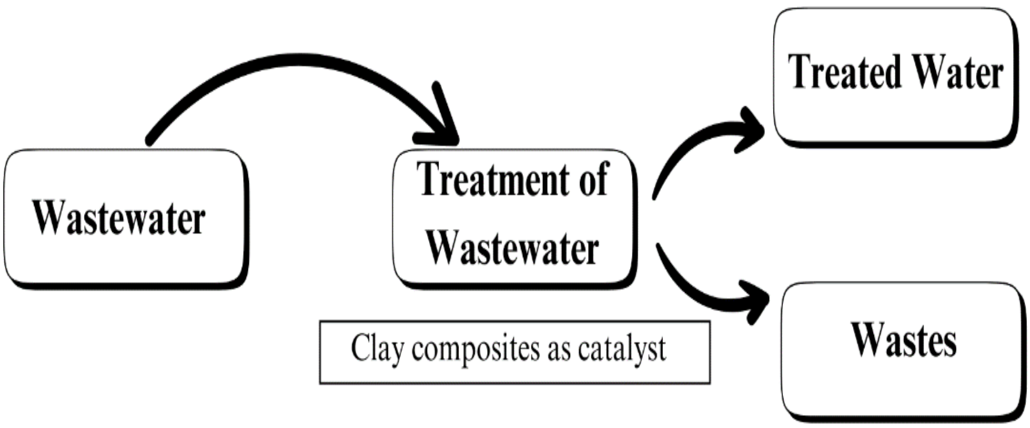

Figure 6: A general representation of wastewater treatment by using clay composites as catalyst

Table. 1: Various top discipline that were involved in developing clay-biochar composites in previous years

Discipline	Percentage (%)
Chemistry	19
Materials Science	8.01
Environmental Science	27.5
Engineering	26.3
Energy	4.63
Agriculture and Biological Sciences	8.69
Earth and Planetary Sciences	0.64
Health Professions	0.12
Multidisciplinary	0.67
Mathematics or Computer Science	0.44

Nanotechnological approaches are frequently investigated to improve traditional water treatment systems. This is less costly and more effective than conventional approaches for removing contaminants from water sources. Nanoparticles employed as effective adsorbents in clay-based nanocomposites to adsorb pollutants from wastewater. Nanoparticles can be very useful in cleaning water because they have special properties. They are more porous and have good stability in heat and strength, making them effective at removing harmful microbes, inorganic materials, and organic pollutants from water. Clay-based nanocomposites and their application in wastewater treatment have been extensively studied, and they have been utilized in a variety of methods to compact contaminate-containing water [56].

15. Limitations of Clay Composites

Clay composites, including nano-clay composites, clay hybrids, clay-surfactant composites, and organo-clay composites, can be very useful for cleaning water. They also have various disadvantages, such as difficulty recovering from aqueous solutions, poor selectivity for specific contaminants, low reusability, and an ability to aggregate in water. One of the major drawbacks is their high cost, especially in large-scale applications. Clay composite regeneration might be expensive in some situations. Some clay composites, for example, clay-biochar composites, have low adsorption capacity. The majority of clay composites were developed to remove dyes from the textile industry, particularly ionic dyes. However, no studies have investigated the removal of non-ionic dyes like dispersion dyes, which are frequently used in the textile sector. Environmental sustainability necessitates careful consideration of clay composite regeneration, use of adsorbent disposal, increased clay composite stability, and reusability for long-term performance. These disadvantages limit its wider applicability in practical wastewater treatment systems. In conclusion, while clay composites have shown enormous potential in wastewater treatment, further development is required to solve the present challenges [57].

16. Future Perspectives

There has been a significant rise in the need for environmentally friendly and less expensive clay composites for removing different kinds of contaminants from wastewater. As previously discussed, clay composites are an effective pollution removal method. However, this unique technology faces limitations and issues that limit its potential for large-scale applications. Scientists have suggested various research methods to make clay composites for water treatment affordable and to enhance their environmental safety and sustainability. The previously mentioned studies concerned contaminant removal from standard solutions. Recent investigations focused directly on sewage effluent. Furthermore, the majority of research focused solely on specific contaminants. In contrast, many effluents from different sources contain several contaminants, such as dyes, heavy metals, and electrolytes. There is a requirement to examine the simultaneous removal of many contaminants by producing a multipurpose adsorbent capable of removing various types of contaminants. Although implementation is complicated, this represents a more realistic approach to design [58].

Many industrial and other wastewater have extremely low pH values, which may lead to the dissolution of raw materials from the composite. Also, a very high pH lowers the ability of the composites to adsorb because it removes the cationic amine group. As a result, maintaining optimal pH during adsorption is a critical problem for maximizing composite efficiency. Many industrial effluent streams are emitted at temperatures above 100°C even after heat recovery, and they may enter the adsorption portion at higher temperatures. As a result, consideration should be exercised when developing such a system, taking into account the thermal stability of the composite materials. As a result, for various applications, effort should be directed to developing clay composites with increased mechanical, chemical, and thermal stability while maintaining the composites' adsorption capacity. Furthermore, the situation becomes more challenging when different types of contaminants are present in the same effluents. There should be substantial research into the potential design of clay composites for multicomponent systems [59].

It is critical to investigate how the composites affect the group's indigenous microbial population. The reusability of clay composites is critical in deciding the overall cost of the system. Attention might be devoted to the production of clay composites with improved regeneration capability without affecting the composite structure. More alternatives for employing modified clay derivatives should be explored to create new composites with higher efficiency and selectivity for contaminant removal. There are opportunities for innovation through research and development, which will lead to advanced clay composite materials and a more efficient synthesis procedure. Combining versatile and adaptable clay materials with current water treatment methods can create energy-saving and responsive ways to purify water when needed. Collaboration between researchers and industry stakeholders is critical for progressing these solutions and providing long-term, cost-effective water treatment. Further research into additional technologies and real-world industrial effluent testing will improve water treatment [60].

17. Conclusions

Large quantities of industrial, agricultural, and home wastewater must be purified before it is released into the water environment. The clay composites are the best for wastewater treatment since they are low-cost, environmentally beneficial, and readily available. A variety of clay composites are used to remove contaminants from wastewater. Modified clay composites performed better than single-modified clays because of their excellent adsorption capacity and inexpensive cost. The continued development of clay composites to eliminate different pollutants has considerable potential. There is an immediate need to create novel, multifunctional composites that may successfully target a broader spectrum of contaminants found in the same wastewater. Using clay composites presents several challenges, including the need to recover the composites from water solutions after use, the formation of by-products, a decrease in adsorption efficiency after repeated cycles, low selectivity for certain types of pollutants, and challenges with desorbing the adsorbed pollutants from the composite matrix. One of the most difficult issues in progressing this field is the development of composites that can address a wider range of contaminants while remaining economically and practically viable for large-scale use. Future research should focus on developing clay composites for wastewater treatment that have not only improved adsorption and catalytic abilities but are also inexpensive, easily recoverable, and have the ability to maintain high performance over multiple times of use.

References

[1] Z. Wang, P. Luo, X. Zha, C. Xu, S. Kang, M. Zhou, D. Nover, Y. Wang. (2022). Overview assessment of risk evaluation and treatment technologies for heavy metal pollution of water and soil. Journal of Cleaner Production. 379: 134043.

[2] E.W. Gabisa, C. Ratanatamskul. (2024). Effects of operating conditions on removal of microplastics (PET, PP, PS) from wastewater by electrocoagulation systems and kinetics of chromium removal in the presence of microplastics. Journal of Water Process Engineering. 61: 105313.

[3] Z. Yin, C. Cui, H. Chen, Duoni, X. Yu, W. Qian. (2020). The application of carbon nanotube/graphene-based nanomaterials in wastewater treatment. Small. 16(15): 1902301.

[4] G. Costamagna. (2022). Study of micro and nano-structured materials aimed to anions, heavy metals and herbicides abatement in water treatment.

[5] D.V. Bhalani, B. Nutan, A.K. Singh Chandel, Wastewater Treatment and Remediation of Harmful Substances Using Green Materials. In *Encyclopedia of Green Materials*, Springer: 2024; pp 1904-1914.

[6] A. Mokhtar, B. Asli, S. Abdelkrim, M. Hachemaoui, B. Boukoussa, M. Sassi, G. Viscusi, M. Abboud. (2024). Polymer/Clay Nanocomposites as Advanced Adsorbents for Textile Wastewater Treatment. Minerals. 14(12): 1216.

[7] M.M. Wijesooriya, H. Wijesekara, N. Bolan, A.U. Rajapaksha, M. Vithanage, Clays and clay minerals: Long-lasting applications in environmental remediation. In *Clay composites: Environmental applications*, Springer: 2023; pp 3-28.

[8] T. Zhang, W. Wang, Y. Zhao, H. Bai, T. Wen, S. Kang, G. Song, S. Song, S. Komarneni. (2021). Removal of heavy metals and dyes by clay-based adsorbents: From natural clays to 1D and 2D nano-composites. Chemical Engineering Journal. 420: 127574.

[9] S. Gu, X. Kang, L. Wang, E. Lichtfouse, C. Wang. (2019). Clay mineral adsorbents for heavy metal removal from wastewater: a review. Environmental Chemistry Letters. 17: 629-654.

[10] M. Hnamte, A.K. Pulikkal. (2022). Clay-polymer nanocomposites for water and wastewater treatment: A comprehensive review. Chemosphere. 307: 135869.

[11] M. Belghazdis, E.-K. Hachem. (2022). Clay and clay minerals: a detailed review. International Journal of Recent Technology and Applied Science (IJORTAS). 4(2): 54-75.

[12] S. Yaqoob, A. Mushtaq. (2023). Clay and other natural Inorganic materials effectiveness in wastewater treatment: A review. Int J Chem Biochem Sci. 23(4): 198-207.

[13] N. Worasith, B.A. Goodman. (2023). Clay mineral products for improving environmental quality. Applied Clay Science. 242: 106980.

[14] H. Abd-ElFattah, R.M. Kamel, A. Maged. (2025). Harnessing clays and clay composites for efficient removal of pharmaceutical contaminants from water: A review. Frontiers in Scientific Research and Technology.

[15] K.K. Kennedy, K.J. Maseka, M. Mbulo. (2018). Selected adsorbents for removal of contaminants from wastewater: towards engineering clay minerals. Open Journal of Applied Sciences. 8(8): 355-369.

[16] A. Sharma, D. Mangla, S.A. Chaudhry. (2022). Recent advances in magnetic composites as adsorbents for wastewater remediation. Journal of Environmental Management. 306: 114483.

[17] C. Chuaicham, J. Trakulmututa, K. Shu, S. Shenoy, A. Srikhaow, L. Zhang, S. Mohan, K. Sekar, K. Sasaki. (2023). Recent clay-based photocatalysts for wastewater treatment. Separations. 10(2): 77.

[18] A. Naseer, F. Younas, R. Munir, M.F. Sardar, S. Noreen, Z. Cui. (2024). Clay-Based Nanocomposite Materials Used in Treatment of Wastewater: Recent Advancements, Cost Investigation and Future Perspectives. Separation & Purification Reviews. 1-18.

[19] L. Huang, G. Chen, X. Luo, D. Xie, W. Zeng, S. Li, Z. Tang. (2025). Dynamic experimental study on the radon adsorption performance of clay mineral-based walnut shell activated carbon composites. Journal of Radioanalytical and Nuclear Chemistry. 1-12.

[20] A. Hamd, D. Rady, M. Shaban, K.N. Elsayed, H. Al Mohamadi, A.M. Elzanaty, S.A. Ahmed, R. El-Sayed, N.K. Soliman. (2021). Application of nano bio-clay composite in a scaling-up study for wastewater treatment. Biointerface Res. Appl. Chem. 12: 6393-6414.

[21] E. E. ElSayed, L.A. Ibrahim, A. Ghandour, M. Zelenakova, Z. Vranayova, M. Abu-Hashim. (2021). Efficiency of natural clay mineral adsorbent filtration systems in wastewater treatment for potential irrigation purposes. Sustainability. 13(10): 5738.

[22] J.O. Eniola, B. Sizirici, Y. Fseha, J.F. Shaheen, A.M. Aboulella. (2023). Application of conventional and emerging low-cost adsorbents as sustainable materials for removal of contaminants from water. Environmental Science and Pollution Research. 30(38): 88245-88271.

[23] M. Ahmad, U. Riaz, S. Iqbal, H. Rasheed, M.A. Mousa Mousa, A.S. Al-Farraj, M.I. Al-Wabel, Advances in the Development and Applications of Clay-Based Composites. In *Clay Composites: Environmental Applications*, Springer: 2023; pp 75-88.

[24] D. Ewis, M.M. Ba-Abbad, A. Benamor, M.H. El-Naas. (2022). Adsorption of organic water pollutants by clays and clay minerals composites: A comprehensive review. Applied Clay Science. 229: 106686.

[25] H. Han, M.K. Rafiq, T. Zhou, R. Xu, O. Mašek, X. Li. (2019). A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants. Journal of hazardous materials. 369: 780-796.

[26] L. Sciascia, S. Casella, G. Cavallaro, G. Lazzara, S. Milioto, F. Princivalle, F. Parisi. (2019). Olive mill wastewaters decontamination based on organo-nano-clay composites. Ceramics International. 45(2): 2751-2759.

[27] L. Wang, F. Wang, B. Huang, Q. Tang. (2020). Recent advances in superhydrophobic composites based on clay minerals. Applied Clay Science. 198: 105793.

[28] K. Niththiyaraja, O. Hettithanthri, M. Vithanage, Modified Biochars and the Applications in Water and Wastewater Treatment. In *Biochar Amendments for Environmental Remediation*, CRC Press: 2025; pp 201-212.

[29] H.K. Mezerji. (2025). Removal of Heavy Metals from Water using Nanocomposites Materials.

[30] F. Mohamed, F. Hashem, M. El-Aassar, M. Mekewi, R. Khalifa, O. Ibrahim, M.A. Rafea, M.E. Gamal. (2025). Carbon nanotube/bentonite@ polyvinylidene fluoride tri-flouro ethylene nanocomposite matrix for surpior elimination of carcinogenic dye from wastewater. International Journal of Environmental Science and Technology. 1-20.

[31] G. Fadillah, S.P. Yudha, S. Sagadevan, I. Fatimah, O. Muraza. (2020). Magnetic iron oxide/clay nanocomposites for adsorption and catalytic oxidation in water treatment applications. Open Chemistry. 18(1): 1148-1166.

[32] N.M. Azzam, S.S. Ali, G.G. Mohamed, M.M. Omar, S.K. Amin. (2025). Fabrication of composite ceramic polymeric membranes for agricultural wastewater treatment. Scientific Reports. 15(1): 2330.

[33] M. Arif, G. Liu, M.Z. ur Rehman, B. Yousaf, R. Ahmed, M.M. Mian, A. Ashraf, M.A.M. Munir, M.S. Rashid, A. Naeem. (2022). Carbon dioxide activated biochar-clay mineral composite efficiently removes ciprofloxacin from contaminated water-Reveals an incubation study. Journal of Cleaner Production. 332: 130079.

[34] G. Gopal, C. Natarajan, A. Mukherjee. (2022). Adsorptive removal of fluoroquinolone antibiotics using green synthesized and highly efficient Fe clay cellulose-acrylamide beads. Environmental Technology & Innovation. 28: 102783.

[35] S. Sultana, A. Hore, K. Shams, T. Ur Rashid, M.M. Rahman, M. Shahruzzaman. (2025). Removal of organic dyes from wastewater by kaolinite/poly (HEAA-co-MAPTS) composite as an adsorbent. Water Practice & Technology. wpt2025006.

[36] Y. Fu, S. Wang, H. Liu, K. Zhang, L. Zhang, Y. Song, Z. Ling. (2025). Large-Area Clay Composite Membranes with Enhanced Permeability for Efficient Dye/Salt Separation. Membranes. 15(1): 25.

[37] A.K. Dhar, H.A. Himu, M. Bhattacharjee, M.G. Mostufa, F. Parvin. (2023). Insights on applications of bentonite clays for the removal of dyes and heavy metals from wastewater: a review. Environmental Science and Pollution Research. 30(3): 5440-5474.

[38] H.G. Castellanos, Y. Aryanfar, S. Mohtaram, A. Keçebaş, G. Karaca-Dolgun, S. Ahmad, A.N.M. Asiri, S. Islam. (2025). The efficacy of nano-cellulose-based composites in heavy metal removal from wastewater: a comprehensive review. Journal of Chemical Technology & Biotechnology. 100(2): 291-312.

[39] J. Hızal, M. Yılmazoğlu. (2021). Montmorillonite clay composite for heavy metal removal from water. Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water. 93-112.

[40] Y. Dehmani, S. Arif, D.S. Franco, J. Georgin, T. Lamhasni, H. Hajjaj, A. Dehbi, S. Abouarnadasse, H. Gallard, E.C. Lima. (2024). Copper and nickel composite carbon catalysts prepared from olive husks on the adsorption process of phenol and p-

nitrophenol: Comparative theoretical study via an analytical model. Journal of Molecular Liquids. 409: 125346.

[41] Z.U. Zango, N.S. Sambudi, K. Jumbri, A. Ramli, N.H.H. Abu Bakar, B. Saad, M.N.H. Rozaini, H.A. Isiyaka, A.M. Osman, A. Sulieman. (2020). An overview and evaluation of highly porous adsorbent materials for polycyclic aromatic hydrocarbons and phenols removal from wastewater. Water. 12(10): 2921.

[42] D. Yadav, Priyanka, J. Dutta. (2021). Green Approaches to Prepare Polymeric Composites for Wastewater Treatment. Green Composites. 531-570.

[43] C. Genethliou, I. Triantaphyllidou, D. Giannakis, M. Papayianni, L. Sygellou, A. Tekerlekopoulou, P. Koutsoukos, D. Vayenas. (2021). Simultaneous removal of ammonium nitrogen, dissolved chemical oxygen demand and color from sanitary landfill leachate using natural zeolite. Journal of hazardous materials. 406: 124679.

[44] E. Behrami, K. Xhaxhiu, B. Dragusha, A. Berisha, Z. Hajrulai-Musliu, A. Reka, A. Andoni, X. Hamiti, S. Drushku. (2021). Theoretical and practical comparative study on the use of clays for the treatment of wastewater contaminated with pesticides. International Journal of Ecosystems & Ecology Sciences. 11(3).

[45] A. Heidari, M. Sayadi, Z. Biglari Quchan Atigh. (2021). A comparative study of different materials (drinking water treatment sludge, nanoclay, and modified nanoclay) for simultaneous removal of hexavalent chromium and lead. International Journal of Environmental Science and Technology. 18(11): 3553-3570.

[46] T. Jamil, S. Yasin, N. Ramzan, H.M.Z. Aslam, A. Ikhlaq, A.M. Zafar, A. Aly Hassan. (2023). Bentonite-Clay/CNT-based nano adsorbent for textile wastewater treatment: optimization of process parameters. Water. 15(18): 3197.

[47] J. Su. (2021). Adsorption of organic compounds on minerals. Adsorption at natural minerals/water interfaces. 225-261.

[48] H.N. Tran, Adsorption technology for water and wastewater treatments. In MDPI: 2023; Vol. 15, p 2857.

[49] F. Kalitsilo, H. Hashemi, E. Mombeshora. (2025). Pristine graphene oxide treatment of wastewater from a typical sub-tropical mine in Chegutu, Zimbabwe. International Journal of Environmental Science and Technology. 1-13.

[50] S. Khan, S. Ajmal, T. Hussain, M.U. Rahman. (2023). Clay-based materials for enhanced water treatment: adsorption mechanisms, challenges, and future directions. Journal of Umm Al-Qura University for Applied Sciences. 1-16.

[51] B. Sarkar, R. Rusmin, U.C. Ugochukwu, R. Mukhopadhyay, K.M. Manjaiah, Modified clay minerals for environmental applications. In *Modified clay and zeolite nanocomposite materials*, Elsevier: 2019; pp 113-127.

[52] K. Lebelo, M. Mochane, S. Magagula, M. Mohapi, J. Sefadi. (2020). Effect of LDHs and Other Clays on Polymer Composite in Adsorptive Removal of Contaminants: A Review.

[53] C. Sivodia, A. Sinha. (2022). Clay supported zero valent iron nanocomposites: advancement in the field of green catalyst for abatement of persistent pollutant. New Trends in Emerging Environmental Contaminants. 311-331.

[54] L. Liu, Y. Li, B.A. Yoza, K. Hao, Q.X. Li, Y. Li, Q. Wang, S. Guo, C. Chen. (2020). A char-clay composite catalyst derived from spent bleaching earth for efficient ozonation of recalcitrants in water. Science of the Total Environment. 699: 134395.

[55] Z.U. Zango, M.N.H. Rozaini, N.H.H.A. Bakar, M.U. Zango, M.A. Haruna, J.O. Dennis, A. Alsadig, K.H. Ibnaouf, O.A. Aldaghri, I.A. Wadi. (2023). Advancements in clay materials for trace level determination and remediation of phenols from wastewater: a review. Separations. 10(2): 125.

[56] A. Alhanish, G.A. Ali. (2022). Recent developments in wastewater treatment using polymer/clay nanocomposites. Advances in Nanocomposite Materials for Environmental and Energy Harvesting Applications. 419-451.

[57] A. Anjum, D. Gupta, B. Singh, R. Garg, B. Pani, M. Kashif, S. Jain. (2024). Clay–polymer nanocomposites for effective water treatment: opportunities, challenges, and future prospects. Environmental Monitoring and Assessment. 196(7): 666.

[58] A. Maged, H.A. El-Fattah, R.M. Kamel, S. Kharbish, A.M. Elgarahy. (2023). A comprehensive review on sustainable clay-based geopolymers for wastewater treatment: circular economy and future outlook. Environmental Monitoring and Assessment. 195(6): 693.

[59] I. Liaquat, R. Munir, N.A. Abbasi, B. Sadia, A. Muneer, F. Younas, M.F. Sardar, M. Zahid, S. Noreen. (2024). Exploring zeolite-based composites in adsorption and photocatalysis for toxic wastewater treatment: Preparation, mechanisms, and future perspectives. Environmental Pollution. 123922.

[60] C.L. Recio-Colmenares, J. Flores-Gómez, J.P. Morales Rivera, H. Palacios Hinestroza, B. Sulbarán-Rangel. (2025). Green Materials for Water and Wastewater Treatment: Mechanisms and Artificial Intelligence. Processes. 13(2): 566.