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## Local and Industrial Applications of Clay

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**Abstract** Modern research aims to use eco-friendly and naturally-occurring materials as a sustainable pathway to scientific development. In this context, clay has gained significant relevance and applied as a bio- and eco-compatible, and low-cost resource. Clay minerals occur in different morphological and physicochemical properties based on their constituents and layer arrangements. The applications of clay in construction, petroleum refining, water treatment, development of adsorbent have been established with other interesting applications on the horizon. The most representative clay minerals are kaolinite, montmorillonite, sepiolites, and halloysite. This review provides insights into some clay minerals and applications and suggests the need for further research to tap into the inexhaustible potentials of one of the world's most abundant geological materials.

**Keywords** Clay, Morphology, Naturally-occurring materials, Applications

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### 1. Introduction

Found naturally on the earth's surface, clay is a small, fine particle, mainly composed of silica, alumina, water as well as a weathered rock [1]. The name of the clay minerals described a group of minerals that are indispensable fragments of loam rocks like kaolins, clays, soils, shales, and bentonite and control the specific characteristics of these rocks. As they occur naturally, clays comprise a heterogeneous mixture of finely disunited minerals like quartz, feldspars, calcite as well as pyrites [2]. Clay minerals comprise some of the most vital, if not the most important, minerals utilized in the industries [3]. Clay is the product of geological weathering of the earth's surface. Clay is composed of microscopically fine particles. Pure clay contains aluminum ( $\text{Al}_2\text{O}_3$ ) silica ( $\text{SiO}_2$ ) and water ( $\text{H}_2\text{O}$ ) hence the pure clay is chemically referred to as Hydrous Aluminum Silicate with the chemical formula of  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . China clay is a good example of pure clay [4]. Clay is the essential ingredient of all pottery or ceramics bodies. It is the hydrated silicate of aluminum [ $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ]. Clay is a common mineral, cheap and abundant in nature. It can be crumbled, mixed with water, and made into different shapes and forms. As a material, clay is soft, plastic, and impressionable, and has a cold feel. It can be pounded, molded, flattened, rolled, pitched, coiled, pressed, pulled, pushed, squeezed, and thrown on the potter's wheel. Large as well as small delicate objects which are either sculptural or architectural can be molded from clay. Clay is regarded as fine-grain mixtures of several minerals which form a plastic mass with water. They may be classified according to the mineralogical composition or properties [5]. They are hydrous aluminosilicates and are abundant in soils and sedimentary rocks, colored by iron oxides or hydroxides. Its major constituent is kaolinite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) [6]. Clay minerals are a well-known class of natural inorganic materials with well-known structural adsorption, rheological and thermal properties. These materials originally have a hydrophilic character due to the presence of the surface hydroxyl ( $-\text{OH}$ ) groups, which can link very easily water molecules [7]. Owing to specific feature like plasticity, hydration, and



catalytic properties, clay minerals belong to the enormously vital group of minerals. Owing to its detailed characteristics like plasticity, hydration, and catalytic properties, clay minerals are utilized in numerous industries. The fields in which clay minerals found applications include agriculture, chemistry, pharmacy, refractory technology, and ceramics [8]. For many years, clay materials have been used for the adsorption of heavy metals, dye molecules, herbicides, anions such as nitrates, phosphates and sulphates, or gas adsorption, like  $\text{SO}_2$  [9]. Clay also responds to blending, combining, shaping, drying, and firing. When fired, clay becomes hard, dense, rock-like, durable, and permanent. In shaping objects from this humble material, the need for great skill in handling and the avoidance of mal-handling is of paramount importance [4]. Clays or clay-modified catalysts are commercially used catalysts. Due to their surface properties, they are very important minerals, their reactive nature accounts for their importance in industrial applications and environmental control. The properties of clay minerals such as acidity, high surface area, and cation exchange capacity (CEC) make them play important roles such as catalysts, supports, and adsorbents for toxic substances. They are mainly composed of layers (sheet-like structures) and are therefore referred to as phyllosilicate minerals [10]. Clays possess different kinds of physical features such as fineness of particles, hardness, good plasticity, associativity, appropriate shrinkage, excessive refractoriness, and the ability for surface decoration [11]. Clays have extensive applications due to their swelling, adsorption, and ion exchange properties, and high surface areas. Starting from the beginning of petroleum refining and petrochemical industries, clays have been used as catalysts. The first hydrocracking process developed over 80 years ago was based on acid-modified clays, but later and still now, zeolites and aluminosilicates are used [12]. These clay minerals possess a huge area of surface and can absorb heavy metals from aqueous as well as natural environments. Clay minerals such as bentonite, sepiolite, and palygorskite have been utilized to a large extent in the removal of heavy metals from wastewater and agricultural soil and the mechanisms of remediation are sorption, precipitation, and liming [13]. Clays possess minute particle sizes and swift specific surface areas owing to their complex porous frameworks which facilitate physical and chemical interactions with dissolved species. These interactions are a consequence of crystallinity, electrostatic repulsion, adsorption, and some cation exchange reactions. The swift porous surface area specifies a huge bonding force on the surface of the clays [14].

This review examines the development in the use of clay minerals in the various fields, with particular attention directed to kaolinite, montmorillonite, sepiolite, and halloysite. The clay mineral properties, their application and modifications are discussed.

## 2. Clay Structure

The composition, as well as the structure of a particular clay mineral, is a deciding factor of its properties, (both physical and chemical properties). A study was conducted on the behavior of both the physical and chemical properties of clays due to their relations to the adsorbent and/or catalytic properties in the process industries. This behavior is governed by the extent and nature of their external surface, which can be modified by suitable methods such as acid and thermal modifications. The catalytic and adsorbent activity of some clays increases through acid and thermal modification. But the activity decreases when the clays are modified further and stronger. They have significant potential in chemical processing. The chemical composition of distinct natural clays is presented in Table 1.

**Table 1:** Chemical constituents of distinct natural clay [14]

Natural clays	Elemental composition (wt%)								
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{TiO}_2$	Loss on ignition	$\text{N}_2\text{O}$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{MgO}$
Kaolinite	53.70	43.60	2.00	0.10	-	-	0.50	-	-
Halloysite	46.86	34.10	2.27	2.72	12.60	0.05	0.80	0.13	0.08
Bentonite	50.08	17.40	6.00	-	20.32	1.39	0.84	0.28	3.95
Montmorillonite	65.34	12.89	2.38	0.52	8.06	0.53	1.54	0.24	0.95
Vermiculite	39.00	12.00	8.00	-	-	-	4.00	3.00	20.00
Attapulgite	58.38	9.50	-	0.56	-	-	-	0.40	12.10
Sepiolite	55.21	0.43	0.15	0.05	19.21	0.10	0.15	0.20	24.26



### 3. Kaolin

Kaolin is one of the most vital industrial clay minerals, chemically described as  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , has the theoretical constituents of  $\text{Al}_2\text{O}_3$  (39.53%),  $\text{SiO}_2$  (46.53%), as well as  $\text{H}_2\text{O}$  (13.94%) in the case of the oxides [14]. Kaolin is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral. Kaolin has a relatively low surface area and a low surface charge because of the limited substitution in the kaolin layer compared to smectites and palygorskite and sepiolite [15]. The chemical formula shows that there is no substitution involving  $\text{Si}^{4+}$ , replaced by  $\text{Al}^{3+}$  in the tetrahedron layers, and  $\text{Al}^{3+}$  substituted by other ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , etc.) in the layer of an octahedron [14]. Kaolinite being the most common kaolin mineral is also a common clay mineral, but the relatively pure and commercially useable deposits are few. Kaolinite has physical-chemical properties which make it useful in a great number of applications. Due to its less reactive nature, this accounts for many of its more important applications when incorporated into most industrial formulations. Other kaolin minerals are dickite, nacrite, and halloysite. Dickite and nacrite are rather rare and usually are found mixed with kaolinite in deposits of hydrothermal origin. Relatively pure halloysite deposits are rare; one of the only commercial halloysite deposits now operating is located on the North Island of New Zealand [16]. Kaolinite possesses a 1:1 layered framework made up of a tetrahedral  $\text{SiO}_4$  sheet having  $\text{Al}^{3+}$  as the octahedral cation. The hydroxyl groups located below and above the two atoms of Al make a central hexagonal distribution in a single plane in the range of the octahedral sheet. Additionally, there is a little net negative charge at the broken edges on the kaolinitic crystals despite the neutral surface charge of kaolinite [14]. Figure 1 reveals the relative abundance of articles published on the different types of natural clays as of 2021.

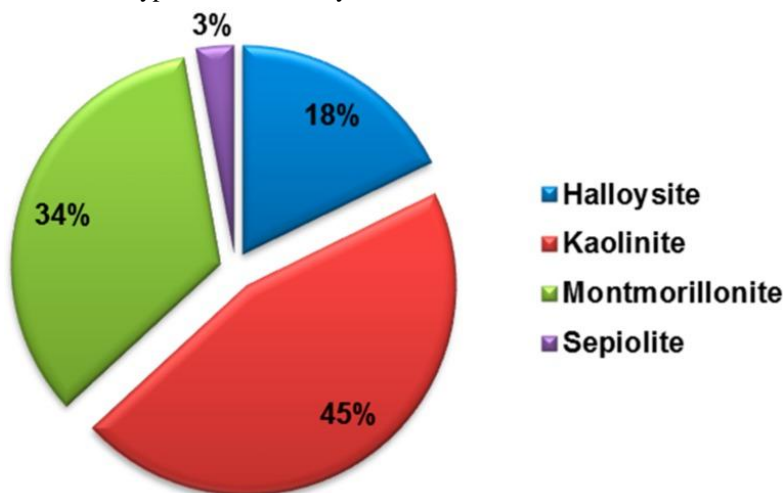


Figure 1: Comparison of the number of scientific publications on “Halloysite”, “Kaolinite”, “Montmorillonite” and “Sepiolite”. Data analysis of publications, as of February 2021, was done using the SciFinder Scholar search system

### 4. Smectite

Smectite minerals are made up of a central octahedral sheet possessing two tetrahedral silica sheets and are designated as a 2:1 layer mineral (Table 1) [12]. Montmorillonite (Figure 2), a member of the smectite clay mineral group is the most popular kind of clay used in pillaring procedures. The fundamental unit framework of this group of clay comprises two tetrahedral Silica sheets disentangled by one octahedral sheet of Al or Mg [17] as described in Figure 3 & 4 below. Ca-montmorillonite, saponite (Mg), montmorillonite, nontronite (Fe), beidellite (Al) as well as hectorite (Li) are the constantly utilized smectite minerals. Na-montmorillonite is somewhat rare in co-occurrence as compared with Ca-montmorillonite which is the most preeminent of the smectite minerals, found in numerous spheres of the world [12]. The smectite is found as fine particles of the size  $0.5\ \mu\text{m}$  or less. Smectite is the chief component in bentonite, which is a term used in rock. Bentonite was described as clay refashioned from limpid rock. Clay minerals of smectite and vermiculite groups have Fe in octahedral sites, and oftentimes other transition



elements may also engross this site replacing other cations. This bestows the minerals green, yellow or brown tints, thus making them unacceptable in the manufacture of high-quality porcelain. Illites can also demonstrate numerous pale shades [18]. In accordance with Grim and Guven [19], bentonite was again described to mean any of the smectite clay in which the mode of extraction is not included. Na-montmorillonite or Ca-montmorillonite and to a much smaller ambit saponite and hectorite are the foremost used bentonite in the industries [12].

### 5. Palygorskite

Palygorskite is used to mean a hydrated Mg-Al silicate material with the chemical composition;  $(\text{Mg}, \text{Al})_5\text{Si}_8\text{O}_{20}(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$  (Melo *et al.*, 2002). This mineral consists of double silica tetrahedral chains linked together by octahedral oxygen and hydroxyl groups containing Al and Mg ions in a chainlike inverted structure. This inverted tetrahedral structure is elongated, occurs regularly, and causes channels through the structure [12]. The unique colloidal properties, most importantly, high concentrations resistance of electrolytes resulted from the elongated shape/structure of this mineral (palygorskite). The variations in the elongated particles' length are in the range of 1 to 10  $\mu\text{m}$  and the diameter is 0.01  $\mu\text{m}$  approximately. The high porosity when thermally activated and the high surface area are both due to the shape and size [12]. Table 2 reveals the characteristics of selected naturally occurring clays.

**Table 2:** Physicochemical and morphological characteristics of clays

Kaolin	Smectite	Palygorskite
1:1 layer	2:1 layer	2:1 layer inverted
White or near white	Tan, olive green, white	Light tan
Little substitution	Octahedral and tetrahedral substitution	Octahedral substitution
Minimal layer charge	High layer charge	Moderate layer charge
Low base exchange capacity	High BEC	Moderate BEC
Pseudo hexagonal flakes	Thin flakes and laths	Elongate
Low surface area	Very high surface area	High surface area
Very low absorption capacity	High absorption capacity	High absorption capacity
Low viscosity	Very high viscosity	High viscosity

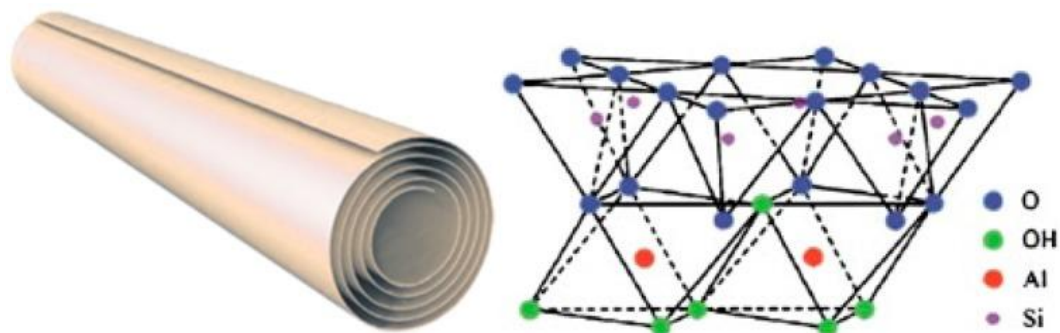


Figure 2: Structure of a Montmorillonite clay mineral revealing the (●) oxygen atoms and (○) hydroxyl groups. Silicon as well as aluminum sometimes engrosses the tetrahedral status in the oxygen framework. Either Aluminium, magnesium, iron, or lithium may occupy octahedral sites.  $\text{Mn}^{+} \cdot x\text{H}_2\text{O}$  is a representation of the interlayer exchangeable cation (Reproduced with permission from Massaro *et al.* 2018.).

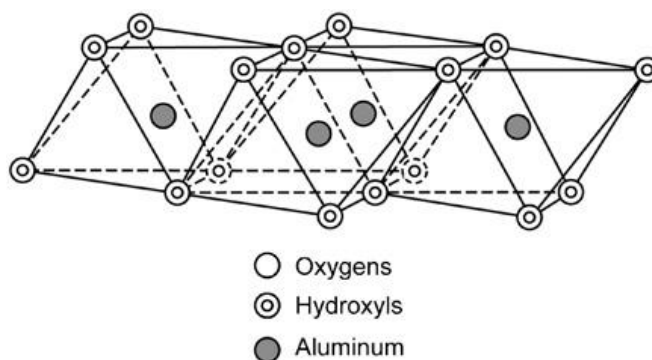


Figure 3: Structure of clay; octahedral sheet.

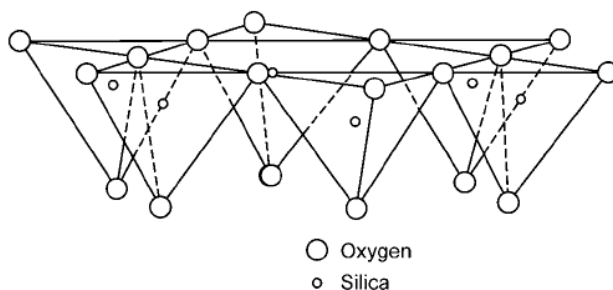


Figure 4: Structure of clay; tetrahedral sheet.

## 6. Applications of clay

The ease with which clays are available in almost every inhabitable place on the earth and their unquestionable characteristic features ease its heterogeneous use in the human civilization since prehistoric time. The clay materials were universally utilized in building (muddy) huts as well as in the production of bricks, potteries. In recent times, there is an increase in the use of clay and clay minerals daily and they are moderately replacing metals in different fields as low-cost, better, and environment-friendly substitutes [18]. Clays or refined clay catalysts are economically utilized catalysts [20]. Clays possess extensive uses because of their adsorption, swelling, and ion exchange features as well as the enhanced surface areas. Since the commencement of petroleum refining and petrochemical industries, clays have been utilized as catalysts [12]. Tons of clay up to millions of tons are annually used in various applications in large quantities [3]. Kaolinite is a clay mineral with the chemical formula  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  having a 1:1 uncharged dioctahedral layer framework where each of the layers contains single silica tetrahedral sheet and single alumina octahedral sheet. It is conveniently utilized as a nascent material for the synthesis of Zeolite A due to its Si/Al ratio which is closed to unity [21]. Kaolinitic clay has been refined for the manufacture of an alternative mineral to bauxite; alumina. Kaolin is widely utilized in paper production, and in the manufacture of functional filler, fiberglass as well as ceramics. Kaolin is a common outcome of weathering of many tropical and sub-tropical soils and it is made up of kaolinite mineral of chemical formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , in addition to other numerous accessory minerals like carbonates, feldspars, and hematite. Kaolinite belongs to the group of the two-layered planar hydrous phyllosilicate minerals known as kaolin [22]. The clay minerals are found useful in geology, the process industries, agriculture, and remediation of the environment as well as construction [3]. The numerous applications of clays, as well as their derivatives in the industries, are numerous and differing. The sustainability of clay in a particular industry depended on the properties of the clay minerals present in it which are in turn determined by the characteristics of the internal frameworks and chemical compositions of those clay minerals. The scarcity or non-existence of transition elements that possesses strong pigmentation properties to aid the use of clays rich in kaolinite in producing top-quality porcelain. As a result of their characteristics structures, clay minerals exist with very fine grain size and have huge surface activity and are therefore acceptable as fillers in rubber-producing industries [18].





The various prominent applications of claysite, as well as argillites in the industries, are painstakingly described in the following sections.

### 6.1 Water Treatment

Water is an important necessity for the sustainability of humans. Heavy metals are part of the toxic and harmful pollutants because it is not degraded in nature. Cadmium (Cd) is a heavy metal resulting from the erosion of rocks and soil, volcanic eruptions, mining activities as well as industrial waste like leather, textiles, batteries, paints, and pesticides. Heavy metals can pose health risks for humans and ecosystems in the long term and at high concentrations [23]. The application of kaolinite in the treatment of water is gaining much attention in concurrence with other clay ore, and hydrogen ions ( $H^+$ ) discharged from the edge of the layer framework in acidic surroundings encourage the adsorption of heavy metals ions like Pb(II), Cu(II), Hg(II) and Cd(II), from aqueous matrices [24]. Pollution of water is a representation of swift challenge activated carbon is a common adsorbent utilized in removing hazardous contaminants from wastewater [25]. Nonetheless, activated carbon is relatively expensive despite its effectiveness [26]. Globally, water treatment has become a major industry. The industry is classified as wastewater treatment, industrial process water treatment as well as potable water treatment [27]. One of the notable efficient procedures to make contaminated water clean is the adsorption process [14]. The quagmire of pollutants removal from water is a vital procedure and is becoming more meaningful owing to the rise of industrial activities. Consequently, the decimation of heavy metals like cadmium, lead, nickel, chromium, iron, zinc, and copper from aqueous solutions is imperative due to the frequent appearance of these metals in waste streams from numerous industries [28]. The rapid increase witnessed in the world population has an increasing effect on the demand for water as well as the urgent need for enhanced water quality [14]. The heavy metals in the waste streams can be desirably adsorbed by marine animals and bluntly get in the human food chains, thus putting forward a huge risk to the end-users [28]. Researchers have developed numerous procedures aimed at improving the quality of water. The adsorption method has evolved as a process of reducing heavy metals because it is more effective, simpler, and inexpensive than the other methods. Sorption is the procedure of centralization of adsorbate molecules or ions on the adsorbent surfaces [23]. Adsorption is an efficient way of removing pollutants from wastewater. Activated carbon is broadly utilized in water treatment techniques especially in the removal of pharmaceuticals during drinking water treatment, landfill leachate treatment, and colour removal treatment [26]. Distinct procedures for the removal of metal ions from aqueous solutions have been fashioned as chemical precipitation, filtration, ion-exchange, reverse osmosis, and membrane systems. Notwithstanding, all these procedures have their characteristic advantages as well as limits in their usage. In the past years, adsorption has proven to be an alternative procedure for the removal of dissolved metal ions from liquid wastes [28]. Awasthi et al, [29] reviewed the structures, uses, and mechanisms of clay nano-adsorbent for water treatment. The main sources of contamination in natural water bodies are wastewater coming from various industrial processes. The basic need of a healthy human community is fresh drinking. The release of hazardous substances into the water bodies is substantially increasing daily. Howbeit, the rapid rise in the use of bane substances for distinct concerns has consequentially accelerated the abundance of undesired pollutants in clean water across the globe. They believed that nanotechnology plays a vital duty in the present environmental exercises for the redressing of contaminants in the environment. Nanoparticles possess a huge ability to be employed in wastewater treatment. Its distinctive features of possessing enhanced surface area can be utilized efficiently in removing toxic metal ions, disease-causing microbes, and organic as well as inorganic solutes from water. The properties associated with nanoclays found to be highly effective and efficient are an enhancer for water purification. The utilization of clay minerals as adsorbents for the adsorption of numerous hazardous materials such as heavy metals, dyes, antibiotics, biocide compounds, and other organic chemicals has been greatly investigated by a great number of researchers [29]. Organo-clays have been used prosperously in wastewater treatment applications. Organo-clays have proven to be better than any of the water treatment technology in various applications where the water to be treated consists of significant amounts of oil and grease or humic acid. The commercial applications of organo-clay globally on offshore platforms in cleaning acid and water produced and other process water. Owing to



the growing carcinogenic effects of trihalomethane previously utilized in wastewater treatment, the commercialization of the applications of organo-clay in the treatment of wastewater is a new effective technology [27]. Andisol soil is the soil that results from the weathering of volcanic rocks; scattered throughout Indonesia. Allophone adsorbent possesses good characteristic properties such as porosity, absorption, as well as high cation exchange. Many studies have used allophone as an adsorbent with relatively high efficiencies. Allophone and clays can be combined owing to their similar adsorbent properties. Clay is an aggregate of minerals that contains chiefly hydrous aluminum silicates, with active sites on the surface, hard and stiff when dried and stable at excessive temperatures [23]. Figure 5 reveal the adsorption of biological agents (quercetin) and the delivery in human body for therapeutic treatment of cancer due to the biocompatibility of clay materials [30].

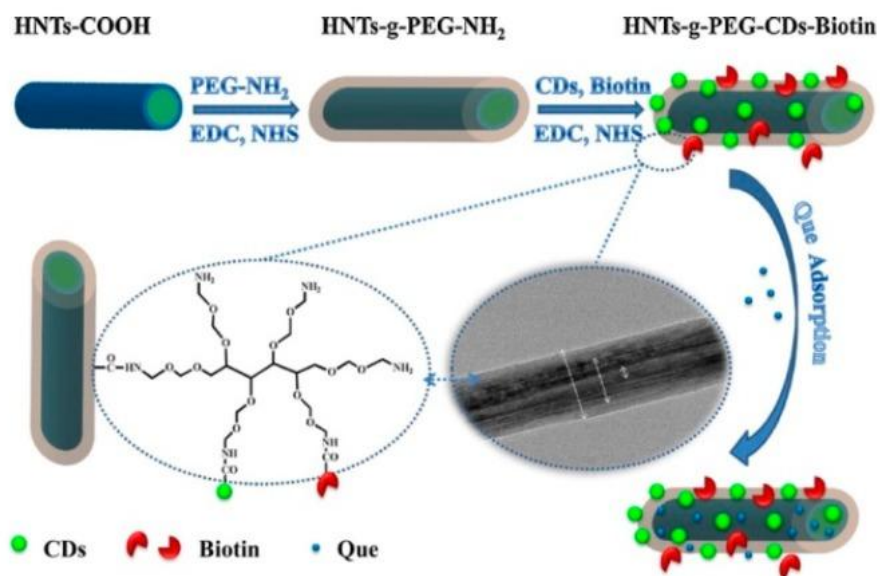


Figure 5: Schematic representation of structure and synthesis of HNTs-g-PEG-CDs-Biotin, followed by adsorption.

Reproduced with permission from Yamina et al, [30]

The application of clay ceramics and nanotechnology in water treatment was reviewed by Annan et al [31]. Their work highlighted water contaminants, and the numerous technologies used in their treatment. Elaboration on the kinds of clays that are common and their associated advantages regarding filtration of water and nanotechnology. The efficacy of purification systems for water can be improved using nanotechnology. These nanomaterials have enhanced surface-to-volume ratios and huge aspect ratios and hence possess many active sites to enhance the removal of pollutants via adsorption, microbial disinfection, and photocatalysis. Nanomaterials can be utilized in evolving water systems or besides to other macromaterials. Nevertheless, the nanomaterial's pollutant removal efficiency can be greatly reduced during macro assembly. Nonetheless, studies should be conducted to establish techniques that can be utilized to assemble nanomaterials without altering their efficiency [31]. Pranoto et al, [23] reported the treatment of drinking water with clays/andisol adsorbent in Lariat heavy metal cadmium (Cd) and bacterial pathogens. The composition of clay and andisol, the temperature of calcination, and contact time affect the adsorption ability of Cd metal ions in solution models are the composition of Andisol: Clay (60:40), the 100°C calcination temperature as well as the 60 minutes contact time. The ceramic filter of the mixture of Andisol/Clay was efficient in the reduction of the cadmium metal ion content in water by 98.9% and the bacterial pathogens that produce potable water [23].

## 6.2. Petroleum

The choice of the catalysts used in catalysis applications depended solely on the regenerative ability, distinct microporous framework, cost as well as thermal stability. The present-day refinery commonly makes use of zeolite



catalyst during the catalytic cracking procedure. Along with all other single catalyst utilized in the petroleum industry, it is tedious or nearly not possible for a catalyst to do all required reactions in cracking. However, based on this limitation, the doping of existing materials with other materials utilized as the catalyst to form a new material with entirely different features for added functionality is a technology that is evolving in the refinery [32].

Crude oil is the liquid phase of petroleum occurring naturally, consisting of hydrocarbons found under the ground. It is mainly found along with natural gases. Other materials include solid hydrocarbon substances such as waxes and asphalt, as well as saltwater [33]. Crude oil refineries are chiefly designed to produce transportation fuels (mainly gasoline, diesel as well as kerosene), with lower but economically vital side manufacture of starting materials for the petrochemical industry, notably light olefins (such as ethylene, propylene, butenes, etc) and BTX. The aforementioned are the feedstock commonly used in petrochemical industries [34]. At present, the application of new materials as catalysts' support is one of the many efforts directed at enhancing the activity of catalysts. The most applicable advances in the history of catalytic cracking were the commencement of porous materials as fillers and supports, especially zeolites and clay, in commercial Fluid Catalytic Cracking (FCC) catalysts in the early 1960s for numerous industrial procedures. Through little capital investment, zeolite catalysts offered a huge profit, cost-effective, and environmental benefits like the replacement of low-selective dangerous mineral acids and catalysts containing chloro, enhanced selectivity and yields of reactions, products' quality, as well as the catalytic system' overall life, and the diminution of consumption of energy at the same time [32].

### 6.3. Adsorbent

Adsorption is a principal industrial separation procedure for the purification of effluent media. It involved the mass transfer operation via a solid material that can choosily eliminate dissolved constituents from an aqueous solution through the attraction of the dissolved solute to its surface. Therefore, entails the interphase accumulation of concentrated substances at a surface or the interphase. This detachment technique finds broad application in the removal of dye from aqueous media. Uniquely, adsorption finds application in textile, leather, dyeing, cosmetics, plastics, food as well as paper industries where water recovery is very crucial. To obtain and sustain the efficient recovery of the appropriate water quality, a meticulous discretion of the adsorbent is of supreme importance [35]. The application of kaolinite in the treatment of water is gaining much attention in concurrence with other clay ore, and hydrogen ions ( $H^+$ ) discharged from the edge of the layer framework in acidic surroundings encourage the adsorption of heavy metals ions like Pb(II), Cu(II), Hg(II) and Cd(II), form aqueous matrices [24]. The severity of the environmental problem is a sole result of the abundance and toxicity of heavy metals in the environment. The prolongation of heavy metals, such as Cu (II), Hg (II), Pb (II), Cd (II), and Cr (VI) in water environments has led to different health complications in humans and animals. Heavy metals are the main components of inorganic pollutants, like pesticides, fertilizers, sludge, as well as municipal waste, which have contaminated large areas of water and land. Heavy metals are carcinogens and may present a critical health threat to every living being [14]. Clay, which is a fine-fragmented naturally occurring raw material, has gained much attention as a result of its uses as a potent adsorbent to the existence of trace heavy metal ions in aqueous solution for over a decade [1]. Both natural, as well as synthetic clay minerals, maybe the needed alternative adsorbents for removing dye owing to their inexpensive and available in nature. Among the clay mineral, sepiolite, kaolin, and synthetic talc has been successfully demonstrated for removal of dye. Sepiolite was studied for removal of Reactive Blue 221 and Acid Blue 62, kaolinite for removing Brilliant Green dye as well as synthetic talc for removal of acid orange 7 and Reactive Red 3 [26]. Heavy metals in solution can exist either as free-ions or complexes along with organic as well as inorganic ligands. To reduce the costs of production, numerous attempts are directed on the application of low-cost adsorbents such as agricultural by-products, biosorbents, slag, and clay-based materials. Generally, clay-based adsorbents majorly are inexpensive materials that are readily available and provide a cost-effective alternative to traditional treatment. Clay porous framework and huge surface area offer value in liquids absorption as well as in heavy metals adsorption [28].





El-Maghrabi and Mikhail [28] reported the use of clay material as an adsorbent as an alternative to the existing commercial adsorbents for the removal of Fe(II), Ni(II), and Zn(II). The impact of numerous parameters such as contact time, initial metal ion concentration, and adsorbent amount, and pH of the solution was studied. The study demonstrated that the heavy metals Ni(II), Zn(II) as well as Fe(II) can be absorbed and removed in notable quantities making use of the inexpensive clay material (adsorbent) originating from aqueous solutions. The removal of the metal ions rose with a corresponding increase in the quantity of the adsorbent used. The increase in the initial concentration of metal ion impacted a corresponding increase in the quantity of the metal uptake per unit weight of the adsorbent, whereas the degree of adsorption percentage was reduced. The order of adsorption of heavy metals from the single-metal solutions is  $\text{Fe} > \text{Zn} > \text{Ni}$  [28].

Gu et al, [14] reviewed the structure, composition, and synthesis, and use of clay minerals and modified clays as adsorbents for removing heavy metals from wastewater. Heavy water pollution such as contamination of water by ions of lead (Pb), mercury (Hg), copper (Cu), cadmium (Cd), and chromium (Cr) induced by the swift urbanization as well as industrialization and it the principal threat to the health of humans. Processes that make use of adsorbents such as clay minerals and modified clays possess high efficiency in the removal of metal ions from wastewater are one of the most suitable processes of water treatment [14].

Adeyemo et al, [35], reviewed the application of different types of clay in the adsorption of dyes. The different clay types demonstrated high efficiencies of dye removal with activated clays showing higher adsorption abilities than the raw clays. The sorption characteristics of the clays as adsorbent for removing multiple types of dyes from water and wastewater have been reviewed based on a considerable number of relevant published articles considering numerous procedure parameters. The adsorption behavior of basic dyes such as basic red 18 (BR 18), basic red 46 (BR 46), basic yellow 28 (BY 28) on activated clay. The rate of adsorption was about the same regardless of the alterations in the speed of agitation above 200rpm, which was in line with a study previously reported. This implies that solute transfer on the surface of the particle was not affected by the thickness of the film [35].

The adsorption characteristics of clay adsorbents and synthetic talc in removing an anionic reactive dye (Yellow 138:1) as well as their application in dye removal from stream water were reported by Rahman et al, [26]. Their study revealed that the equilibrium curve for the synthetic talc pointed out that an adsorption capacity higher than those of sepiolite and kaolin. Kaolin demonstrated an exceptional ability in the lower concentration range, the capacity saturation having increasing dye concentration seems to be faster than that seen in sepiolite and synthetic talc. The Langmuir adsorption isotherm model demonstrated that synthetic talc possessed the highest maximum monolayer adsorption ability ( $q_{\text{max}}$ ) of 10.07mg/g followed by kaolin with 3.73mg/g and sepiolite (3.23 mg/g), for decolourizing Reactive Yellow 138:1 solution. The results further indicated that numerous important influenced the adsorption capacity of different clays in the removal of Reactive Yellow 138:1, such as specific surface area, ion exchange capacity, and surface charge. Physical adsorption depended on the specific surface area, electrostatic interactions related to the surface charge and AEC were seen to be the prominent factors affecting the elimination of Reactive Yellow 138:1 from the solution. The clay adsorbent's adsorption ability was higher under acidic conditions than under neutral and alkaline conditions since the more positive charge of the adsorbent surface is the consequence of the protonation effect. Although the clay adsorbents' adsorption capacities were lower than those of activated carbon, clay adsorbents are an alternative material that can be used in place of the expensive activated carbon for adsorption treatment. Because of its huge volumetric adsorption capacity and ability to be reused, synthetic talc possesses the promising adsorbent potential for removing reactive anionic dyes [26].

## 7. Conclusion

Clay minerals have attracted great scientific attention due to their biocompatible nature, relative abundance and interesting properties. The dominant examples of clay minerals are kaolinite, montmorillonite, sepiolites, and halloysite. Future research in application of clay minerals should focus on the development of suitable clay-based composites and application as carrier for the drug delivery and sustained release of biological active species, better adsorbents for water purification, and efficient catalyst. The modification of clays surfaces, employing



supramolecular interactions or covalent modifications, suggests remarkable potentials and sustainable ways to obtain efficient and unique nanomaterials with improved biological, morphological and physicochemical properties.

### Conflict of interest

Author declare that there is no conflict of interest regarding the publishing of this article.

### References

- [1]. Uddin Mohammad Kashif, (2017). "A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade". *Chemical Engineering Journal*, 308, 438–462, <http://dx.doi.org/10.1016/j.cej.2016.09.029>.
- [2]. Karpiński B., and Szkodo M., (2015). "Clay Minerals – Mineralogy and Phenomenon of Clay Swelling in Oil & Gas Industry". *Advances in Materials Science*, vol. 15, no. 1 (43), 37-55. DOI: 10.1515/adms-2015-0006.
- [3]. Murray H. H., (1999). "Applied clay mineralogy today and tomorrow". *Clay Minerals* (1999) 34, 39-49.
- [4]. Gadzama Mataba Ruth, (2015). "Utilization of kaolin (kankara clay) and grey cast iron for the production of composite refractory". Ph.D. Dissertation submitted to the school of post graduate studies, Ahmadu Bello University Zaria.
- [5]. Babalola, A (2015). "Development and characterization of zeolite Y from a Nigerian local raw material". A Thesis Submitted in the Department of Chemical Engineering to the School of the Postgraduate studies, in partial fulfilment of the requirement for the award of the degree of Doctor of Philosophy, (Ph.D) in Chemical Engineering of Covenant University, Ota, Ogun State, Nigeria.
- [6]. Olaremu A. G. (2015). "Sequential Leaching for the Production of Alumina from a Nigerian Clay". *International Journal of Engineering Technology, Management and Applied Sciences*, Volume 3, Issue (7), 103-109.
- [7]. Cho D. W., Chon C. M., Kim Y., Jeon B. H., Schwartz F. W., and Lee E. S., (2011). "Adsorption of Nitrate and Cr (VI) by Cationic Polymer-Modified Granular Activated Carbon," *Chemical Engineering Journal*, Vol. 175.
- [8]. Surajo Abubakar Ibrahim, (2017). "Industrial application and uses of clay mineralogy in oil and gas industry". PTG 311 Clay Mineralogy and Diagenesis Pp. 1-9. *Department of petroleum geosciences, Cairo University, Egypt*.
- [9]. Djomgoue Paul and Njopwouo Daniel, (2013). "FT-IR spectroscopy applied for surface clays characterization". <http://dx.doi.org/10.4236/jsemat.2013.34037>. *Journal of Surface Engineered Materials and Advanced Technology*, 2013, 3, 275-282.
- [10]. Teku Victor Dominic, (2017). "Modified kaolinite clay as catalyst for biodiesel production from waste cooking oil". A Master of Science degree dissertation submitted to the school of postgraduate studies, Ahmadu Bello University, Zaria.
- [11]. Odoma A.N, Obaje N.G, Omada J.I, Idakwo S, Erbacher J (2013) "Paleoclimate reconstruction during Mamu Formation (Cretaceous) based on clay mineral distributions. *IOSQ J Appl Geol Geophy* 1(5):40–46.
- [12]. Eman A. Emam, (2014). "Clays as Catalysts in Petroleum Refining Industry". *ARNP Journal of Science and Technology*, Vol. 3, No. 4, April 2013.
- [13]. Ugwu Ifeoma Mary and Igbokwe Onyedikachi Anthony, (2019). "Sorption of Heavy Metals on Clay Minerals and Oxides: A Review". *IntechOpen*, pp. 1-25. DOI: 10.5772/intechopen.80989.
- [14]. Gu Shiqing, Kang Xiaonan, Wang Lan, Lichtfouse Eric, and Wang Chuanyi, (2019). "Clay mineral adsorbents for heavy metal removal from wastewater: a review". *Environmental Chemistry Letters* 17:629–654, <https://doi.org/10.1007/s10311-018-0813-9>.
- [15]. Eman A. Emam, (2013). "Clays as Catalysts in Petroleum Refining Industry". *ARNP Journal of Science and Technology*, Vol. 3, No. 4.



- [16]. Yong, S., Jong, M., and Dong, W., (2008). "Microstructure and electrical conductivity of NiO-YSZ nanopowder synthesized by aerosol flame deposition". *Journal of Ceramics International*, vol. 34, pp. 873-876.
- [17]. Massaro M., Lazzara G., Milioto S., Noto R., Riela S. Covalently Modified Halloysite Clay Nanotubes: Synthesis, Properties, Biological and Medical Applications. *J. Mater. Chem. B*. 2017;5:2867–2882. doi: 10.1039/C7TB00316A
- [18]. Mukherjee S., (2013). "The Science of Clays: Applications in Industry, Engineering and Environment, Chapter 7, Pp. 113-122, DOI: 10.1007/978- 94-007-6683-9\_7, Capital Publishing Company.
- [19]. Güven, N., & Grim, R. E. (1972). X-ray diffraction and electron optical studies on smectite and  $\alpha$ -cristobalite associations. *Clays and Clay Minerals*, 20(2), 89-92.
- [20]. Murray H. H., (2007). "Applied clay mineralogy". 1<sup>st</sup> edition, Elsevier B.V., ISBN-13: 978-0-444-51701-2.
- [21]. Omisanya N. O., Folayan C. O., Aku S. Y. and Adefila S. S., (2012). "Synthesis and characterization of zeolite A for adsorption refrigeration application". *Advances in Applied Science Research*, 3 (6):3746-3754.
- [22]. Tantawy Mohamed Ahmed and Alomari Abdulaziz Ali, (2019). "Extraction of alumina from Nawan kaolin by acid leaching". *Oriental Journal of Chemistry*, Vol. 35, No. (3): Pg. 1013-1021. <http://dx.doi.org/10.13005/Ojc/350313>.
- [23]. Pranoto, Inayati, and Fathoni Firmansyah, (2018). "Effectiveness Study of Drinking Water Treatment Using Clays/Andisol Adsorbent in Lariat Heavy Metal Cadmium (Cd) and Bacterial Pathogens". *IOP Conf. Ser.: Material. Science and. Engineering*. 349, 012047., IOP Publishing. doi:10.1088/1757-899X/349/1/012047.
- [24]. Bhattacharyya K.G. and Gupta S.S. (2008). "Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Adv Colloid Interface Sci* 140(2):114–131. <https://doi.org/10.1016/j.cis.2007.12.008>.
- [25]. Zakaria R.M., Hassan I., El-Abd M.Z., El-Tawil Y.A., (2009). "Lactic acid removal from wastewater by using different types of activated clay. In: Thirteenth international water technology conference (IWTC), Hurghada, vol 13, pp 403–416.
- [26]. Rahman A, Kishimoto N, Urabe T. (2015). "Adsorption characteristics of clay adsorbents – sepiolite, kaolin and synthetic talc – for removal of Reactive Yellow 138:1". *Water and Environment Journal*, 29, 375–382. doi:10.1111/wej.12131.
- [27]. Beall Gary W, (2003). "The use of organo-clays in water treatment. *Applied Clay Science* 24, 11– 20. doi:10.1016/j.clay.2003.07.006
- [28]. El-Maghrabi Heba H. and Mikhail Sara, (2014). "Removal of Heavy Metals via Adsorption using Natural Clay Material". *Journal of Environment and Earth Science*, Vol.4, No.19, 2014, ISSN 2224-3216 (Paper) ISSN 2225-0948 (Online).
- [29]. Awasthi A., Jadhao, P., and Kumari K., (2019). "Clay nano-adsorbent: structures, applications and mechanism for water treatment". *SN Applied Sciences* 1:1076. <https://doi.org/10.1007/s42452-019-0858-9>.
- [30]. Yamina A.M., Fizir M., Itatahine A., He H., Dramou P. (2018). Preparation of Multifunctional Peg-Graft-Halloysite Nanotubes for Controlled Drug Release, Tumor Cell Targeting, and Bio-Imaging. *Colloids Surf. B. Biointerfaces*. 170:322–329. doi: 10.1016/j.colsurfb.2018.06.042
- [31]. Annan, E., Agyei-Tuffour B., Bensah Y.D, Konadu D.S., Yaya A., Onwona-Agyeman B. and Nyankson E., (2018). "Application of clay ceramics and nanotechnology in water treatment: A review". *Cogent Engineering*, 5: 1476017. 1-35. <https://doi.org/10.1080/23311916.2018.1476017>.
- [32]. Olaremu Abimbola G., Adedoyin Rotimi W., Odunayo T. Ore, Adeola Adedapo O., (2021). "Sustainable development and enhancement of cracking processes using metallic composites". *Applied Petrochemical Research*, pp. 1-18. <https://doi.org/10.1007/s13203-021-00263-1>.



- [33]. Madu A.J.C, Ugwu R.E, (2015). "Physical and Chemical Properties of Crude Oils and Their Geologic Significances". International Journal of Science and Research (IJSR) ISSN (Online): 2319-7064, Index Copernicus Value (2015): 78.96.
- [34]. Corma A., Corresa E., Mathieu Y., Sauvanaud L., Al-Bogami S., Al-Ghrami M.S., and Bourane A., (2016). "Crude oil to chemicals: Light olefins from crude oil". Catal. Sci. TechnolCatalysis science & technology., DOI: 10.1039/C6CY01886F.
- [35]. Adeyemo, A. A., Adeoye, I.O., Bello, O.S. (2015). Adsorption of dyes using different types of clay: a review". Applied Water Science, Applied Water Science. 1-29. DOI 10.1007/s13201-015-0322-y.

