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Recent Advances on the Adsorption of Pollutants from Aqueous Media Using Clay-Based Adsorbents

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***Abstract**: The sequestration of pollutants from wastewater remains an active research topic recently owing to persistent disposal of industrial wastewater to waterbodies without adequate management strategies available especially in the developing countries. Different technologies have been employed in which adsorption has found a wide range of application. Today, various low cost adsorbents have been developed and evaluated for the adsorption processes. Clay mineral is one of the low cost natural adsorbents requiring minimum modification to enhance its adsorptive capacities. To maintain a clean and safe environment the water bodies must be free of contaminants of emerging concern. The availability of potable water is a global effort, as two of the UN's seventeen Sustainable Development Goals (SDG) are centered on water which is not surprising. Goal 6 focuses on clean water and sanitation whereas Goal 14 focuses on life below the water. With this in view, the availability of potable water highlights the significance of this study, which analyzes the potential of clay minerals as a good precursor for water treatment. Therefore, this review focuses on the clay minerals, its availability in Nigeria, classification and modification of the clay adsorbent.*

***Keywords:** Clay, Water Pollution, Low-cost Adsorbent, Sustainable Economy, Adsorption Process*

1. INTRODUCTION

The persistent disposal of industrial wastewater to the waterbodies and unsustainable waste management strategies especially in urban centers constitute a very serious challenge. Natural gases, acid gases, toxic chemicals and solid waste materials impact negatively on the air, land and water quality if improperly disposed [1]. In particular, water pollution in the developing countries has a major challenge threatening the ecosystem and human health [2]. According to current research, the increasing pace of water contamination in developing countries will gravely endanger the availability and sustainability of potable water over the next three to four decades. [3,4]. Accidental ingestion of untreated wastewater poses numerous health risks, including endocrine disruption, autism spectrum disorder, neurological disorders, cervical cancer, birth defects, lungs, and skin cancer. [5–9], Hence, there are serious awareness creation efforts by government and other non-governmental organizations such as the World Health organization (WHO) on waste disposal strategies and creation of sustainable technology for the elimination of contaminants from water bodies.

Numerous technologies have been developed to sequestrate contaminants for efficient water and waste water treatment. These methods are classified into physical, biological and chemical treatment. Each of these strategies has distinct limitations related with its use [10]. Biological treatment is cost effective and simple but the process time is slow with probable toxic by-products. Chemical treatment is also beneficial, but it comes with the risk of introducing additional toxic substances into the ecosystem. Physical treatment technique is ecofriendly and operated on a solid liquid interphase with no toxic by -products. However, the challenges associated with this method is high process cost which has been successfully addressed with the use of low-cost material as adsorbents [10]. The treatment techniques includes membrane separation, photocatalytic degradation, ion exchange, coagulation, biological treatment and adsorption [2,11,12]. Among them, adsorption have found wide application and acceptability due to environment friendliness, minimal energy usage, minimal safety issues, reusability, design simplicity, sludge free and low cost. Adsorption method, therefore has become popular and utilizes solid adsorbents including activated carbon, biochar, zeolites biomass, monolith, metal organic frameworks, graft polymers and clays have been reported [1]

In recent times, clay and its composites have been prepared to have sufficient high surface area, surface hydrophilicity, cation exchange capacity, and surface electronegativity for widespread application for environmental remediation. This paper focuses on the review of clay minerals, modification methods targeting applications in adsorption process and its classification. and its classification. A critical investigation of modified clay for usage as an adsorbent to remove various contaminants is presented. Also, the future perspectives and knowledge gaps involved in the application of modified clay for the sequestration of pollutants are identified.

2. ADSORPTION PROCESS

Adsorption is a physical treatment technology that has found widespread use in water treatment due to its unique features. The adsorption operation is simple, practical, and efficient in removing trace-level chemicals present in aqueous solutions without the production of secondary contaminants [13,14]. The major drawback of adsorption process is the high cost of commercial adsorbent which recently have been addressed with the emergence of low-cost adsorbent from agricultural residues and other mineral sources [13]. Adsorption operating modes include continuous fluidized bed, batch, pulsed bed adsorption, continuous fixed bed and continuous moving bed [15]. In addition, adsorption process is sustainable because different adsorbent can be used in the system and the selection of the adsorbents depends on the environment friendliness, cost, adsorption efficiency and specificity for a particular contaminant [16,17]. Various adsorbents from inorganic and organic sources have demonstrated satisfactory performance in water and wastewater treatment [19]. Some of these adsorbents include clay minerals [18,20,21], agricultural wastes [22–24], geopolymers [25], metal organic frameworks [26] and activated carbon [27]. However, the scope of this study is limited to adsorption of pollutants onto clay minerals as adsorbents. Online-published articles from science direct were considered with the search word "adsorption of pollutants onto clays". The results of this search for a time frame of year 2010 – 2020 were shown in Figure 1. This illustrates the widespread acceptance and extensive use of adsorption in the treatment of water and wastewater.

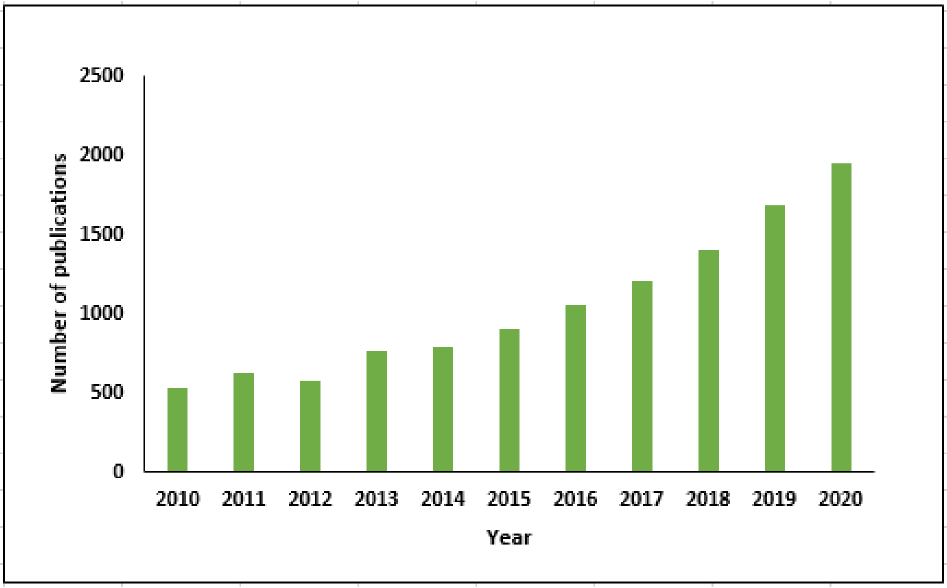

Figure 1: Publications of pollutants sequestration onto clay/clay composites since 2010-2020

3. CLAY MINERALS

3.1 General Overview of Clay Minerals in Nigeria

Clay is one of the natural solid minerals found in large quantities in different states in Nigeria including Edo, Borno, Niger, Lagos, Ogun, Oyo, Ondo, Nassarawa, Delta, Abuja (FCT), Sokoto, Akwa-Ibom and Anambra. Which implies that clay mineral deposits are found in all the six geo-political zones in Nigeria including the Federal Capital Territory (Figure 2). Raw Materials Research and Development Council of Nigeria (RMRDC) affirm this report that almost all the state in the federation have billions of tones of clay deposits [28]. Hence, the viability of it been a source of income when explored on a commercial basis in the country [29,30]. For instance, Nigeria is known to be rich in bentonite distribution in almost all the states of the federation. About 700 million metric tons of bentonite is estimated to be found in the country. This resulted in the rule of law that bans importation of bentonite clay in 2003 [31]. Consequently, Nigerians dug clay locally because these natural resources are scattered and readily available in different location which also does not require a special expertise or instrument to excavate.

Clay has unique properties such as being widely distributed, inexpensive, abundant, ecofriendly, and readily available, as well as having an exceptional ability to undergo modification (cation exchange potential) and being mechanically and chemically stable with varying structural and surface characteristics. It is economically viable in ancient times for the building construction and for production of household goods such as plates and pots. Clay has found several applications in various sectors in recent years as a result of technological advancements.

Figure 2: Map of Nigeria that indicates states with clay deposits. Source: Adapted from [32]

Ihekweme et al., used Clay in water purification technology through molecular sieving, ion exchange mechanisms and adsorption. Clay ceramic water filters are a product of these processes that are effective for removing contaminants like heavy metals, chemicals, and microbes from drinking water [32]. Dansarai et al., looked at how clay is used to make refractory materials. In the metallurgical industry, refractory materials are used for casting, mould production, smelting vessels, and furnace construction [28]. The capacity of clay to endure heat at high temperatures is one of the distinguishing features. These techniques produce reactors, kilns, crucibles, and furnace linings. The majority of these refractory materials are imported at a high cost into the country. Consequently, many researchers recently have investigated the potential of Nigerian clay deposits regarding the physical, chemical, and mechanical qualities in a bid to ascertain meeting the required standards for these applications [33]. Positive results were obtained, demonstrating that Nigerian clays are capable of meeting standard requirements for the production of refractory materials [28].

Also, tests were carried out by Jongs et al., on clay materials from five different locations at plateau state, Nigeria [34]. The evaluation of the physical, chemical and mineralogical properties oof these sample showed that the sampled clays are useful for different industrial purposes. The natural white colour of two of the sample reveals its suitability for the productions of paint, white-wares, paper, refractories and rubber/plastic. Also, it was observed that processing these samples could increase their application in pharmaceuticals and fertilizer production. Another sample from a particular location was observed to be near whitish in colour with high proportion of clay size particles and can find applications in paint, refractories, tiles and sanitary wares production. Another sample from investigation was found applicable for producing sewage pipes, pottery, clay bricks and low-grade paint. A sample was identified with a high concentration of K_2O, TiO_2, Fe_2O_3, having low shrinkage ability with a moderate plasticity and found to be suitable in building for clay bricks production.

Nigeria therefore is blessed with many varieties of clay minerals that if properly treated, can find numerous applications in industries including chemical, environmental management, oil and gas, building and construction, paint and many others. The information contains in this review is a compilation of various ways a clay mineral from different parts of the world has been treated and modified for use as adsorbent in water and wastewater treatment. Such pieces of information could be useful source of revenue and employment through developing one of the natural and ubiquitous materials for wastewater and water treatment to benefit the humanity.

3.2 Classification of Clay

Clay minerals are formed through chemical weathering, sedimentation or hydrothermal effects of aluminosilicates rocks. This process occurs gradually by low concentration of dilute solvent such as carbonic acid, which leaches the upper weathered layer through the rock [28]. They are found in different locations including the argillaceous shale rock, soil and marine sediments. Each clay mineral structure unit consists of stacked layers of one or two tetrahedral silicate sheets joined by an octahedral aluminum hydroxide sheet. Clay minerals have a large specific surface area due to the hydrous phyllosilicate sheets they contain [35]. The octahedral sheet is characterized with closely packed arrangement of six oxygen atoms or hydroxyl groups surrounding the aluminum, iron or magnesium atoms in an octahedral structure. On the other hand, in the tetrahedral sheet four oxygen atom are attached to one silicon atom or hydroxyl groups in a tetrahedral structure. The chemical composition of the aluminosilicates and tetrahedrons in layers are $Al_2(OH)_6$ and $Si_2O_6(OH)_4$ respectively[35]. In an octahedron sheet, metal cores (grey filled circles) such as aluminum, magnesium, or iron are surrounded by hydroxyl groups (black filled circles) while silicon atoms (black filled circles) are surrounded by hydroxyl groups (white filled circles) in a tetrahedron (Figure 3).

Tetrahedral sheets – silicon atoms surrounded in a tetrahedron structure by hydroxyl group

Octahedral sheets – metal centers such as magnesium, iron or aluminium surrounded in an octahedron structure by hydroxyl group

Figure 3: Typical clay (a) tetrahedral and (b) Octahedral sheets. Source: Adapted from [36]

Clay is classified according on the ratio of tetrahedral to octahedral sheets within a clay unit. Clay units are classified based on their interlayer exchangeable ions, crystalline structure, and octahedral metal centers [37]. The structure of clay minerals has plasticity properties and capability to harden when firing or dried [38]. In aqueous conditions, clay particles become fine colloidal particles due to their irregular morphology. They feature a broad particle size distribution and an isometric crystal structure. The stability of the suspension is determined by its surface area, cation exchange capacity, layer flexibility, pH, charge on basal (plane and edges) and temperature [37]. The weak electrostatic interactions and strong covalent bonds in between and in the sheets respectively impart high elastic anisotropy in form of layered structural plate-like structures between the sheets [36]. The study of the mineral composition of clay is very important to the classification of clay [35]. The elemental composition of several clay minerals reported in the literature is interpreted in Table 1.

Table 1: Chemical composition (weight % oxides) of different clay minerals measured by XRF

	Elemental composition													
Clay Minerals	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	Na_2O	SO_3	K_2O	P_2O_5	TiO_2	SrO	ZrO_2	NiO	Others	Ref.
Bentonite	71.91	19.99	1.53	1.16	3.9	0.70	0.44	0.38	0.05	0.13	0.05	0.02	0.0054		[40]
Pristine bentonite clay	59.17	18.49	1.51	3.43	6.68	4.54	-	1.51	-	-	-	-	-		[41]
Bentonite	63.12	22.59	3.45			3.42		2.37	1.26					3.79	[42]
Bentonite	71.60	12.75	-	0.31	10.77	-	0.09	0.09	0.70	1.66	-	0.04	-	1.99	[43]
Natural Bentonite	64.17	22.44	4.78	2.18	3.04	0.73	-	2.27	-	-	-	-	-	-	[44]
Sepiolite	68.14	0.14	27.42	3.51	0.72	0.09	0.79	0.21	-	-	-	-	0.41	0.2	[45]
Natural Sepiolite	63.160	6.18	23.95	2.86	2.65	0.16	-	0.55	-	-	-	-	-	-	[44]
Sepiolite	53.19	0.21	24.22	2.94	0.01	0.01	0.005	0.01	0.01	0.02	-	-	-	0.001	[46]
Sepiolite	70.40	7.04	12.80	5.05	2.08	0.07	-	0.88	-	-	-	-	-	-	[47]
Kaolinite	63.66	24.16	0.49	0.13	4.05	0.61	1.31	2.51	0.40	0.72	-	-	-	1.75	[48]
Kaolin	48.21	39.85		0.09	0.65			0.07		0.4		0.02		14.2	[49]

This shows that location is also a determinant in the composition of clay minerals. Clay minerals are structurally categorized into two primary groups: 1:1 and 2:1. The 1:1 group is defined as a structural unit layer composed of a silicon tetrahedral sheet and an alumina octahedral sheet. Serpentine, halloysite, and kaolinite are examples of such minerals. The second class, the 2:1 group, comprises of two silicon tetrahedral sheets and one alumina octahedral sheet. Example of this class includes montmorillonite, vermiculite and mica [39]. Aside the arrangement of the tetrahedral to octahedral sheets in clay mineral unit, another important property for classifying clay is the swelling capability in aqueous solution. A class of clay swells when in contact with water resulting in increase in volume and expansion in the structure. This in turn modifies the rheological characteristics and viscosity of the clay suspension [36]. Table 2 shows a brief summary of the differences between 1:1 and 2:1 clay mineral. The description of three out of the several groups is discussed in this section.

Table 2: Comparison of 1:1 and 2:1 clay structure based on selected properties

Description	**1:1 clay structure**	**2:1 clay structure**	**Reference**
Structure	One silicon tetrahedral sheets to on aluminum octahedral sheet	Two silicon tetrahedral sheets to on aluminum octahedral sheet	[39]
Types of clay minerals	Kaolinite, Halloysite, serpentine	Montmorillonite, illite, Vermiculite, Chlorite mica	[52]
Swelling capability	It does not stretch as much as 2:1 when in contact with water. That is it has lows swelling ability due to lack of interlayer space in between the particle	It expands and increase in volume when in contact with water. It has high swelling ability in the interlayer space in between the particle	[53]
Cation Exchange Capacity	Rapid and fall between 3-15 meg/100	Not as rapid as 1:1 class and its between 70 -120 meg/100	[53]
Dehydroxylation temperature	It has one distinctive dehydroxylation temperature. The process is simple to operate.	There are differences in dehydroxylation temperature, which is dependent on the interlayer and octahedral coordinated cation. It is a complex process	[54]
Plasticity property	The plasticity property of this class of clay is low compared to 2:1 type	Highly elastic and can be molded into any shape or form when it is in contact with water	[38]

i. **The smectite clay mineral:** Smectite group is formed from the weathering of mafic igneous rock that is rich in Ca and Mg. it is known to be stable in temperate, semi-arid and arid regions. The main characteristics of this type of clay is the formation of weak cationic bonds (e.g Ca^{++}) and its high swelling capability. One of the types of clay in this class is bentonite clay molded from the breakdown of volcanic ash. It has a layered structure of octahedral to tetrahedral sheets in the ratio 2:1 [50]. There are two types of bentonites including the swelling Na bentonite (montmorillonite) or the non-swelling Ca bentonite (montmorillonite). The Na bentonite swells because it expands when it is in contact with water. This in turn enhance the application as a paper filler, detoxifier, bleaching agent, binder amongst others. The molecular weight of bentonite is 422.286 mg/mol [51].

ii. **The kaolinite clay mineral:** This class of clay is formed from gradual breakdown of orthoclase feldspar. It comprises mainly of kaolin. Mineral kaolin is one of the natural clays which belongs to non-expanding kandite group with T-O structure and chemical composition of $Al_2Si_2O_5\,(OH)_4$. Kaolin is soft and whitish in colour which allow its various use as catalysts, paint extender, wine purifier, medicine, oil adsorbent, cosmetics, coating and filler in paper industry. It has a layered silicate structure of tetrahedral sheet of silica and octahedral sheet of alumina in ratio 1:1 interconnected with each other. The cation exchange capacity of kaolin range between 1 to 10 meq/100 with 258.071 g/mol molecular weight and surface area between 7 – 30 m^2/g [51]. Kaolin clay decomposed during firing at varying temperature. When kaolin clay is subjected to firing at a temperature up to 500 ^oC metakaolin is formed, (equation 1). Further increase in firing of metakaolin to 900 ^oC leads to the formation of crystalline silicon material (Equation 2). Additional heating to 1100 ^oC leads to the formation of pseudo mullite materials as shown in Equation 3 [55].

$$Al_2Si_2O_5\,(OH)_5 \rightarrow Al_2Si_2O_7 + 2H_2O \quad (1)$$

$$2(Al_2O_3.SiO_2) \rightarrow 2Al_2O_3.3SiO_2 + SiO_2 \quad (2)$$

$$2Al_2O_3.3SiO_2 \rightarrow 2(Al_2O_3.SiO_2) + SiO_2 \quad (3)$$

iii. **The Illite clay mineral:** Illite is the deep sea or marine clay also referred to as mica with shales as its main constituent. It is the most common type of clay mineral and contains greenish clay sand called glauconite. This clay mineral is formed from the breakdown of feldspar during a hydrothermal process. The weathering procedure fills the open space between the clay crystals with potassium which in turn inhibits swelling. It is in the class of 2:1 clay mineral group but the swelling capacity is lower than that of the smectite group as a result of less hydrated potassium in between the clay crystal surface [52].

4. SELECTION CRITERIA FOR CLAY ADSORBENT

A variety of factors influence the choice of adsorbents for pollution removal. The application and the impurities that need to be eliminated determine the kind of clay that is employed. Because every type of clay has different adsorption properties, maximizing its adsorption capacity may require using particular preparation and activation techniques [56].

The flow characteristics of porous material are mostly determined by their pore size distribution (structure and porosity) and permeability. Pore classification in clay is not uniform but it is categorized into three segments including: micropore-inter layer pore; pores in aggregates – meso layer pore; and pores between aggregates – interaggregate pores [57]. Also, permeability is a major property to be considered for fluid flow in clay minerals. This has a direct impact on fluid movement, pressure, and the behaviour of viscous fluids in soil materials over time [58]. The relationships among the pore structure, porosity and permeability of soil are well described by Kozeny-Carman (K-C) equation [57]. Kozeny's hydraulic equation (Equation 4) depicts this relationship with hydraulic radius (Rh) as the main focus. Kozeny Carman constant quantify the intricate geometry of the pore conduits and the pore shapes. The hydraulic radius is defined as the ratio of the pore volume to the wetted area as depicted in Equation 5.

$$k = \frac{\emptyset}{ckc} Rh^2 \tag{4}$$

$$Rh = \frac{V_p}{S} \tag{5}$$

Where $\emptyset$= porosity, k = permeability (m^2), ckc = Kozeny-Carman constant, S = pores total surface area (m^2) and Vp = pore volume (m^3). Scheidegger 1974 stated six ways in which equation 5 is versatile including: reasonable uniform pore size, random pore distribution, lack of diffusion phenomena, open pores, fluid movement through batch capillaries and acceptable porosity levels [59].

An important feature of clay mineral that aid its adsorptive capacity is the two different charges namely: surface and structural charge. The surface charge of a clay mineral appears on the sheet edge, either the tetrahedral or octahedron sheet. It is not constant but changes with respect to the pH in the clay mineral. The hydrolysis of Al-OH and Si-OH bonds produce the surface charge in the clay sheets. For a clay mineral, the net surface charge is dependent on the pH of the solution and the structure of the silica sheet. The anion and cation exchange capacity in clay develops when the pH is less than pH point of zero charge or when pH is greater than pH point of zero charge respectively. Also, the permanent charge that originates from the interior of layers is responsible for the structural charge on the clay mineral, which is caused by ion substitution [56].

The ion exchange capability of clay minerals is another important characteristic. Clay particles have the ability to adsorb and retain ionic species in their surroundings. The interlamellar zone may provide additional adsorption sites in addition to the external surface, depending on the type of clay minerals. The aluminate and silicate structural layers are not changed by ion exchange activities. In neutral pH, the ion exchange capacity of different clay minerals is measured. For clay minerals, adsorption on the basal plane and margins results in a variety of aggregate forms. Some of the factors that could influence how reactive its surfaces are surface charge, interlayer ions, surface area, and the availability of vacant ionic sites in octahedral sheets. Certain clay minerals show distinctive swelling behaviour when suspended in water. The interlamellar area is permeable to water molecules, which expands the structure and increases volume. The aqueous clay suspensions' viscosity and other rheological characteristics are altered by this event. By lessening the swelling behaviour, saline solutions can affect this characteristic of clay minerals [36].

5. MODIFICATION OF CLAY FOR ADSORPTION PROCESSES

As mentioned earlier there are different types of clay minerals which is applicable in industrial and environmental sector for several purposes. Most of these clay minerals are not utilized in its natural form but a form of modification procedure is carried out in order to get the best results for the desired application. The adsorption capacity and removal efficiency of pollutants improves when clay mineral is subjected to modification before applied for adsorption process [60]. Studying the modification strategy that will be effective for the elimination of various pollutants is therefore important. According to earlier research, Table 3 displays the maximum adsorption capacity of several contaminants onto modified clay minerals. A number of methods, including acid treatment, thermal treatment (calcination), and organic modified clay, have been used by researchers to modify clay in order to improve its usability beyond its natural state [61].

5.1 Thermal treatment

Thermal treatment also referred to as calcination process influence changes in the permeability, water content, particle size, specific gravity and cohesion properties thus enhance the adsorptive capacity of clay mineral. Thermal treatment has exhibited satisfactory result based on experimental data analysis of different studies. Several reports are documented on the improvement of the surface activity of clay material sequel to thermal modification [72]. Maier et al., investigated the effect of thermal treatment on raw clay in a preheated muffle furnace so as to evaluate its suitability as a supplementary cementitious material [54]. Sequel to calcination the material was dried at 105°C for a minimum of 12 h, crushed and grinded in a rotary disc mill for 5 min. The dehydroxylation temperature was determined using thermogravimetric analysis (TGA) and calcined 100 K above the endset temperature of the dehydroxylation reaction. Also, Cao et al., reported a significant adsorption capacity in the combine alkaline surface modification of bentonite-zeolite adsorbent in swine wastewater treatment [42]. The rice husk gasification improved the specific surface area and pore volume of the adsorbent. Consequently, Zhou et al., emphasized the significant changes in the structural and textural properties of sepiolite subjected to thermal activation [73]. Significant changes were reported in the surface area of thermal activated sepiolite compared to natural clay mineral. Derouiche and Baklouti demonstrated the benefits of combine activation using mechanical, thermal and acid activation with phosphoric acid in order to improve its adsorptive capacity [49]. Thermal treatment converts kaolin clay to an amorphous metakoalin without obstruction of the morphology. A complete amorphous metakaolin was obtained after acid activation which consists of two geopolymer.

Table 3: Maximum adsorption capacity of various clay minerals for pollutant sequestration

Group	Adsorbate	Adsorbent	Modification Type	Adsorption capacity	Best fit model	Reference
Dyes	Brilliant green dye	Bentonite-zeolite-acrylic polymer	-	90.09 mg/g	Langmuir	[40]
	Congo red dye Malachite green	Ackee apple and Bentonite composites	Inorganic chemical activation - $FeSO_4$, $FeCl_3$, and lime	1439 mg/g 706 mg/g	Liu	[60]
Pharmaceuticals	Diclofenac Acetaminophen Tetracycline	Organo Sepiolite	-	242.9 mg/g 67.7 mg/g 85.5 mg/g	Statistical physics model	[62]
	Atenolol	Corncob biochar – montmorillonite composite	Pyrolysis	86.86 mg/g	-	[63]
	Propanolol Hydrochloride	Bentonite clay	Thermal treatment	0.468 m mol/g	-	[64]
	Tetracycline	Indium oxide/kaolinite	Thermal activation	32.2 mg/g	Langmuir	[65]
	Doxycycline Hydrochloride	Bentonite	Intercalation	119.93 mg/g	Langmuir	[66]
	Ciprofloxacin	Bentonite	Thermal activation	114.4 mg/g	Langmuir	[67]
	Tetracycline	Illite	-	32 mg/g	Freundlich	[68]
Heavy metals	Cd^{2+}	Calcium Bentonite	Calcination	32.17 mg/g	Langmuir	[69]
	Phosphate Nitrate	Magnetic kaolin	Co-precipitation	92.05 mg/g	Langmuir	[70]
	Hg (II) ions	Sepiolite	-	345.3 mg/g	Langmuir	[71]

5.2 Acid Modification

The surface area and chemical composition of clay minerals improves with acid activation. Acids such as HNO_3, H_2SO_4, HCl and H_3PO_4 have been used to modify the surface activity of clay materials. Table 2 shows the various clay minerals and the specific chemical composition as reported in literature. Cecilia et al., demonstrated the modification of two fibrous clay mineral (Sepiolite and palygorskite) with nitric acid for the adsorption of CO_2 [74]. The XRF analysis shows improvement in the chemical composition of the mineral after acid activation. Likewise, the surface area of the material increased sequel to acid activation. In the other hand, Erdoğan et al., evaluated hydrogen adsorption on natural and sulphuric acid treated bentonite and sepiolite clay [44]. The acid concentration was varied and significant improvement were recorded in the chemical composition of acid treated clay minerals with increase in concentration. Likewise, the surface area increased from 291 to 564 m^2/g for sepiolite and 71 to 123 m^2/g for bentonite clay. This also reflect the effect of acid modification in the surface activity of the mineral.

5.3 Organic Modified Clay

Natural occurring clay minerals are hydrophilic and the level of hydrophilicity increases with the addition or its saturation with cations (Na+). Clay minerals such as bentonite or montmorillonite in its pure hydrophilic state will be compatible mainly with hydrophilic polymers (such as polyethylene oxide). In order to improve its compatibility for non-polar molecules the clay minerals are modified with organic molecules to form organoclay. Organoclay are hydrophobic and hence it is compatible with non-polar molecules. Organic molecules such as ammonium cations are mostly employed by ion exchange techniques. Other organic modifiers including non-ionic surfactants and quaternary phosphonium salts are employed in recent times [18,75].

Daitx, et al., modified montmorillonite and halloysite in an organic medium containing 96% ethanol [75]. In a beaker, 30 g of each clay mineral was combined with 120 mL of ethanol while continually stirring. The pH of the mixture was adjusted to 3 with acetic acid to allow the amino group to be protonated. This technique facilitates in the cation exchange between the protonated amino group and the Na+ present in the clay interlayer. A known quantity of (3-aminopropyl) triethoxysilane (APTES) was added to the mixture at a clay: silane ratio of 1:0.2 and stirred continuously for 2 hours at room temperature. The changed samples were filtered, washed with ethanol, collected, and dried for subsequent use. The results reveal that the alteration of the nanoparticles improved the clay mineral-polymer interactions on both phases via the polar portions.

6. MECHANISM OF ADSORPTION USING MODIFIED CLAY FOR POLLUTANTS SEQUESTRATION

The availability of good quality water has been considered by scientist and policy making platforms over the last decades. It follows that the focus of two of the seventeen (17) Sustainable Development Goals (SDG) of the UN is on water. Goal 14 is concerned with life below the water, goal 6 focuses on clean water and sanitation. The environment contains a number of organic and inorganic pollutants that come from various sources. The negative impacts of these contaminants on the ecosystem have drawn researchers' attention to the need for sustainable environment [25,76]. Table 3 shows the adsorption capacity of modified clay minerals in the sequestration of pollutants from aqueous solution as reported in literature.

6.1 Pharmaceuticals Pollution

Pharmaceuticals including antibiotics, anti-inflammation, analgesics and anti-steroidal drugs are used often to treat and cure diseases. The source and discharge into the water environment has been reported in so many literatures [77–80]. Adsorption of pharmaceuticals onto different adsorbents is shown in Figure 4. Because of the way that pharmaceuticals persist in the ecosystem, there is a risk to public health. Kalhori et al., used light weight expanded clay aggregate surface (LECA) to investigate the removal efficiency of metronidazole antibiotic [81]. MgO nanocomposite was used to alter LECA. The maximum adsorption capacity increased of the unmodified and MgO coated LECA, increased from 56.31 to 84.55 mg/g. Likewise, Antonelli et al., evaluated the efficiency of calcined verde lodo bentonite clay on the adsorption of ofloxacin antibiotics [67]. Thermogravimetric analysis in this study reveals that clay is thermally stable up to 1000^{o}C and the characterization studies reflects the presence of ofloxacin on the adsorbent surface. The regeneration studies shows that calcined bentonite clay can be regenerated by heat treatment up to 93%. Hence, the adsorbent is a feasible precursor for sequestration ofloxacin from water environment. In the other hand, Cristina do Nascimento et al., assessed the adsorption of Propranolol Hydrochloride on thermally treated bentonite clay [64]. Propanolol hydrochloride has been reported as persistent non-biodegradable β blocker drug used in regulating blood pressure and thus classified as emerging contaminants. The results of the characterization studies inferred that the process modified the clay surface by effective removal of the drug.

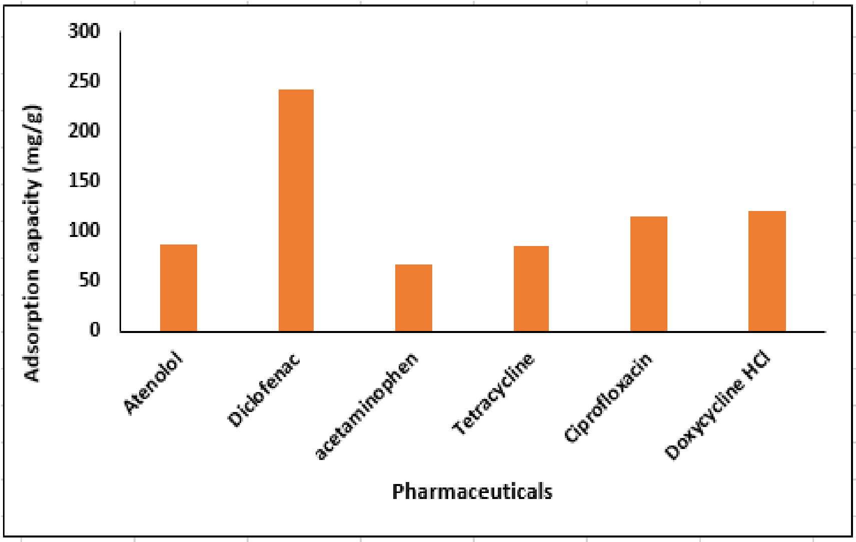

Figure 4: Maximum adsorption capacity of pharmaceuticals onto modified clay minerals

6.2 Heavy Metal Pollution

Heavy metals are discharge into the environment through different process including agricultural process, tanneries, mining and metal plating. Ingestion of these toxic metals can cause damages to the liver, brain or kidney that may result to death [82]. Zhong, et al evaluated the adsorption of four different heavy metals including Pb, Cd, Zn and Cr on modified kaolin clay. Sequel to acid/alkali modification the pore volume, pore size and specific surface area of the adsorbent increased thereby increasing the number of active sites. Also, the thermal treatment of kaolin between 900 – 1300 ^oC has a significant effect on adsorption activity of heavy metals. The reaction on the adsorbent-adsorbate interphase becomes very slow resulting in low adsorption capacity [83]. Similarly, Dim et al investigated the removal efficiency of Pb (III) and Cr (IV) using hydrochloric (HMC) and acetic (AMC) acid modified kaolin. The specific surface area of clay increased from 84.223 m^2/g of raw clay to 389.37 for HMC and 319.95 m^2/g for AMC. The desorption studies recorded desorption efficiency range 65 % to 92% for both adsorbent. This study affirms the potency of modified clay in adsorption of heavy metals. [84] Also, Dinh, *et al*., modified bentonite clay with hexadecyl trimethyl ammonium bromide (HDTMA) for the removal of Pb (II) from aqueous solution. This evaluation shows improved adsorption capacity of about 36.5% over unmodified clay sample. This can be related to availability of more active sites as a result of modification as shown in Figure 5 below [85].

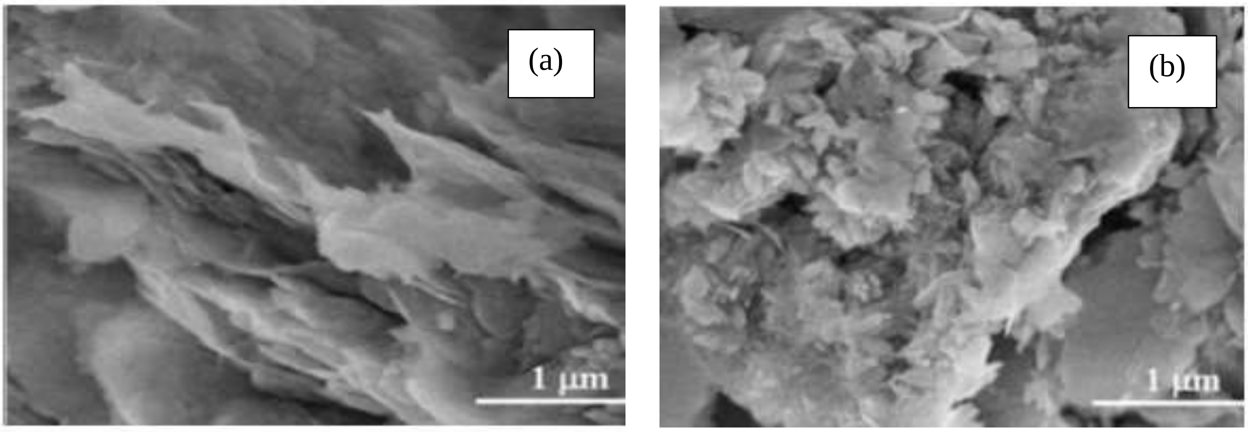

Figure 5: SEM images of (a) unmodified and (b) modified bentonite clay. Source: Adapted from [85]

6.3 Organic and inorganic Dye Pollution

The existence of coloured pigment substances in water environment is of major concern in the sustainability of a clean and safe environment [86]. Dyes are compounds used to give colours in diverse anthropogenic and industrial activities including textile, paper, bleaching, grease, leather, plastics, tannery and food industries [87]. Dyes are classified according to the source, it can either be natural or synthetic in nature. Natural dyes are extracted from plants, minerals and animals. As a result, of population increase and industrialization, natural dyes does not meet industrial demand hence the emergence of synthetic dyes. Due to wide application for various industrial purposes dye pigments are found in water bodies which pose hazardous health risk in the ecosystem [88]. The presence of dyes in water obstructs sunlight penetration which in turn reduces dissolved oxygen resulting to death of organisms. Dyes are considered mutagenic and carcinogenic hence its sequestration from water bodies is important for economic sustainability [61,89,90]. According to da Silva et al., Na^+ bentonite-chitosan nanocomposite was used in the sequestration of reactive violet dye [91]. The characterization studies using FTIR, EDX and XRD results demonstrated that the adsorbent is a good precursor for dye wastewater treatment. Similarly, Gamoudi and Srasra modified illite-smectite clay with a cationic surfactant (hexadecylpyridinium bromide salt) for the adsorption of three different dyes [92]. The suitability of the modified illite-smectite clay in the adsorption of methyl orange, indigo carmine and phenol red dye was affirmed with the results obtained. The analysis of the data suggests hydrophobic interaction mechanism as the controlling mechanism in dye adsorption process. Also, anionic exchange mechanism should be considered in some dye – clay adsorption system. On the other hand, Onu et al., performed a comparison study on the adsorption of eriochrome black T dye on clay using ANFIS, ANN and RSM [93]. To increase the adsorption capacity, hydrochloric acid was used for producing the modified clay. Improvement of the adsorption capacity after acid activation was validated by the characterization results obtained through FTIR and SEM examination.

6.4 Oil Spill

One of the aftermaths of industrialization and urbanization is oil spill, which is an inevitable challenge from the production, exploration and transportation of oil in the offshore. This has resulted in serious threat to human, aquatic and terrestrial animals in such environment [94]. For instance, crude oil contaminated water is detrimental to the growth of food crops, economic trees and soil fertility. Diseases such as cancer, hepatoxicity, hemotoxicity and renal failure are reported as the resultant effect of ingestion of crude oil contaminated water. Hence, cleaning up oil spill from water surface is a major process that must be considered for the sustainability of ecosystem in such areas [95]. Adsorption has found wide acceptance in oil spill cleanup and clay importantly has been used as adsorbent for such process [96].

In a study reported by Peng et al., acid modified kaolinite and graphene oxide sheets were coated on a melamine sponge surface to form a rough superhydrophobic surface [97]. The prepared adsorbent was used for the adsorption of several organic solvent and oil including methanol, ethanol, n-hexane, diesel oil, liquid paraffin, kerosene and motor oil. The evaluation of the experimental data shows a high super-hydrophobic surface and adsorption capacity with no discharge of secondary pollutants. In the other hand, Rotaru et al., evaluated the adsorption capacity of clay aerogel polymer composites in an oil spill system [98]. The clay sample was modified with trimethoxy(octadecyl)-silane and the adsorption capacity of motor oil and dodecane are12.25 and 10.55 mg/g respectively. Wang et al., also demonstrated the adsorptive capacity of fluorinated cationic surfactant kaolin modified melamine sponge as a suitable adsorbent for the remediation of various oil and organic solvent from water surface [99]. The results show the efficiency of the adsorbent with adsorption capacity of 87 – 197 mg/g and excellent recyclability greater than 97%.

7. RESEARCH TRENDS AND FUTURE OUTLOOKS

Acid modification of clay minerals improves adsorbent surface area and sorption capacity. In some instances, reports show reduction of adsorption capacity due to loss of cations in the clay structure. At times, modification with strong acids reduces the pH of the clay minerals which leads to subsequent increase in the pH of the aqueous medium. To enhance the potency of acid modification, some properties must be evaluated including, type of clay mineral, acid concentration, pH of the reaction, acid/clay mineral ratio and time [37,100]. On the other hand, the major challenge of organic modification is the pollution of the environment with the main surfactants (ammonium surfactants compound) used for the modification. As a result, the most effective organic material must be identified in order to reduce ammonium salt toxicity in the environment. Several studies have confirmed the benefits of thermal treatment for pollutant removal. It has also been shown that heating clay minerals may have a negative impact on their adsorption capacity at specific temperatures. Thus, the efficiency of thermal treatment is determined on the nature of the adsorbate and the adsorption mechanism. The scope of adsorption studies in most of the previous literature reports were limited to batch operational method. This operational system explores the feasibility of the process on a laboratory scale whilst not applicable in the real industrial scale. Therefore, the efficacy of the established adsorbent must be tested in a column adsorption studies in order to ascertain the findings from batch operation mode. In addition, few studies examined the reusability of spent clay mineral adsorbents. More convenient regeneration techniques must be established in order to accomplish environment friendliness, low operation cost and efficient adsorbent utilization of adsorption process.

8. CONCLUSION

The availability and quality of water is important in the drive for sustainable economy. The study of adsorption process in ameliorating water pollution has been investigated in recent times. To alleviate the major challenge of high cost of commercial adsorbent associated with adsorption studies is employ the use of low-cost adsorbents. The main objective of this review is to have knowledge of art of clay minerals in previous studies as a suitable precursor in environmental remediation. The adsorptive characteristics of clay mineral adsorbent is dependent on clay properties, size, nature of adsorbate, modification method and adsorbent dose. It can be deduced from this study that a holistic approach must be embraced to optimize the use of certain clay minerals for sequestration of specific contaminants.

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