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Clay Soil Modification Techniques for the Adsorption of Heavy Metals in Aqueous Medium: A Review

Adekeye Damilola Kayode[1*], Asaolu Samuel Sunday[2], Adefemi Samuel Oluyemi[3], Adebawore Adefusisoye Adegalu[4], Osundare Olusegun Samson[5], Ibigbami Olayinka Abidemi[6], Olumide Abisola Hellen[7]

[1-6]*Department of Chemistry, Ekiti State University, Ado-Ekiti, Nigeria*

[7]*Department of Geology, Ekiti State University, Ado-Ekiti, Nigeria*

Corresponding Author:** ***Adekeye Damilola Kayode, *Department of Chemistry, Ekiti State University, Ado-Ekiti, Nigeria*

Abstract: *Clay modification techniques have been employed to improve heavy metals adsorption properties of clay minerals for removal of the metals from their respective aqueous solutions. These modification techniques enhance the surface area, pore volume, and number of present active sites on the surface of the clay. In this study, recently developed and newly applicable techniques such as chemical, physical (thermal), biogenic and mechano-chemical treatments are reviewed and discussed as treatment techniques for modifying clay minerals. Intercalation and pillaring of clay minerals are chemical processes through which modification could be achieved. Surface doping and chemical grafting of polymer onto clay could produce superadsorbent materials with highly enhanced adsorption properties. Also, activation, structural transformation and disruption of clays could be achieved by thermal treatment. Eco-friendly mechano-chemical method which eliminates the use of solvents is also used to achieve chemical processing and transformation of clay for adsorption purpose while biogenic modification which involves the fortification of clay with organic biomass and composites is a promising technique for modification and enhancement of clay for heavy metals adsorption. The adsorption properties of different modified clay minerals are also discussed in comparison with their raw (unmodified) form.*

Keywords: *modification; techniques; physical; chemical; mechano-chemical; biogenic; polymer*

1. INTRODUCTION

Variety of clays and clay minerals play an important role in the environment and used as an effective adsorbent material for the removal of toxic metal ions from water solution (Crini, 2010). The use of clays as adsorbent have advantages upon many other commercially available adsorbents in terms of low-cost, an abundant availability, high specific surface area, excellent adsorption properties, non-toxic nature, and large potential for ion exchange (Crini and Badot, 2010; Gupta *et al*., 2013; Rao *et al*., 2014; Rao *et al*., 2015). Clays also contain exchangeable cations and anions held to the surface (Miranda-Trevino and Coles, 2003; Crini and Badot, 2010). For these reasons, the attention of scientists worldwide has been focused on using natural or modified clay materials as adsorbent for water treatment.

The uptake of heavy metals by clay minerals involves a series of complex adsorption mechanisms; such as direct bonding between metal cations with the surface of clay minerals, surface complexation, and ion exchange etc., (Churchman *et al*., 2006; Arnamwong *et al*., 2016). Clay has a property that shows plasticity through a variable range of water content, which can harden when dried (Das, 2012). The efficiency of adsorption depends on various soil characteristics such as particle size distribution, particulate shape, clay content, moisture content, heterogeneity of soil matrix, density between soil matrix and metal contaminants, magnetic properties, and hydrophobic properties of particle surface (Van *et al*., 1996; Pollard *et al*., 2006). Heavy metals have different sorption characteristics and the mechanisms depend on the adsorbents. Clays used as adsorbent show difference in the sequence of selectivity for different metals. One example is lead when compared to other metals, since it is highly attracted and adsorbed by several types of clay (Manahan, 2001).

In many cases, pre-treatment is required to enhance the adsorption capacity of clays and hence modified to increase metal uptake (O'Connell *et al*., 2010). This pretreatment enhances the surface area, pore volume, and number of present active sites on the surface. Through this treatment or modification, the clay minerals become hydrophobic, organophilic, and it thus enhances the uptake of small non-ionic organic compounds (Ismadji *et al.*, 2015). Many forms of treatment can modify clay, with a goal to increase the adsorption capacity of the raw clay material. However, researchers have also present results that treatment or modification did not increase the adsorption properties (Bhattacharyya and Gupta 2009; Al-Jlil and Alsewailem, 2009). In this review, we summarized the different techniques that have been implored for modification and synthesis of novel clay materials.

2. CLAY MODIFICATION TECHNIQUES

2.1. Chemical Treatment

This process involves the use of both organic and mineral acids, base (alkilinisation), salts and metal oxides for modification of clays achieved through pillaring and intercalation. Chemical treatment is a widely used technique for activation and functionalization of clays (Bhattacharyya and Gupta 2006; Gładysz-Płaska, et al., 2012; Kumar et al., 2012; Shen et al., 2015).

Pillaring is the process by which a layered compound is transformed into a thermally stable micro- and/or mesoporous material with retention of the layered structure (Schoonheydt and Jacob, 2001). The obtained product is a pillared compound or a pillared layered solid. Pillared clays (PILCs) constitute a special class of pillared layered solids. The goal of the pillaring process is to introduce micro and mesoporosity into clay minerals. This is achieved by combination of clay and a pillaring agent via an ion-exchange reaction, in which a two-dimensional channel network is formed (Schoonheydt and Jacob, 2001). Heating the clays imparts stability to the pillared clay by promoting permanent bonding between the pillar and the layers. The resulting materials have small cavities and a large surface area. These properties, along with their low cost, make pillared clays ideal for use as alternative catalysts to zeolites (Kloprogge et al., 2002). There are numerous oligomeric cations that could be used as pillars, some of which are Al, Zr, Ti, Cr, Fe and Ce (Pergher et al., 1999; Kloprogge et al., 2002). These cations could be used individually or mixed in different ratios (Carriazo et al., 2005; Catrinescu et al., 2011).

Several authors have extensively studied the preparation techniques and adsorption properties of aluminum-pillared clays. Research by Yu et al. (2008) revealed that Carbon modified aluminum-pillared montmorillonite has shown good uptake of Cd (II) from an aqueous system. The Cd (II) adsorption followed a mechanism based on second-order kinetics. Adsorption of Cd (II) was low at a pH level less than 6.0, but uptake increased sharply at a pH level greater than 6.0. This may be as a result of the relatively low H^+ concentration on the clay surface as the surface became negatively charged at a higher pH; this could allow for strong bonds with Cd (II). A study by Na et al. (2010) also confirmed Ti-pillared montmorillonite as an effective and a promising adsorbent for As (III) and As (V) removal from arsenic contaminated water.

Intercalation is the reversible inclusion or insertion of a molecule or ion into materials with layered structures (Stanley, 2012). The surfaces of clays have been modified through intercalation by different researchers. A meticulous study by Kumar et al. (2012), showed the intercalation of trioctylamine onto sodium montmorillonite for potential adsorption of mercury as a tetrachloromercurate (II) anion. The adsorption was facile in an acidic medium and a N_2 adsorption–desorption isotherm study confirmed the mesoporous nature of the adsorbent. The result of their study also showed that the adsorption process was thermodynamically favoured. The adsorption process was correlates to the mechanism involved in the electrostatic interaction between the tetra-chloromercurate (II) anion and the protonated amine in the improved clay.

In the treatment of a pillared Smectite clay, Guerra et al. (2008) collected raw Brazilian Smectite-bearing clay samples, and [3-(2-aminoethylamino) propyl] trimethoxy-silane was successfully anchored onto the pillared Smectite; then, active sites were improved in the clay surface through the presence of the NH groups in the modifying agent intercalated chain. This displayed improved ability for lead sorption.

2.1.1. Modification with Organic Compounds

To render layered silicates miscible with polymer matrices, one must convert the hydrophilic silicate surface to an organophilic one, making the intercalation of polymeric chain between silicate layers possible. This can be done by ion-exchange reactions with organic surface active (surfactant) agents (Ozdemir and Yapar, 2009). Several researches have shown that organically modified clay possess good and improved adsorption properties. For instance, result of a study on Cr (VI) removal using batch adsorption techniques conducted by Gładysz-Płaska et al. (2012), exploring the adsorptive properties of the natural red clay after modification by hexadecyl-trimethylammonium bromide (HDTMA) showed improved adsorption properties of the modified clay over the raw red clay. In the advancement of organically modified montmorillonite clay and for the removal of copper, a research work was conducted by Ma et al. (2016) in which organo-montmorillonites (OMts) were modified by a cationic surfactant and a zwitterionic surfactant. The adsorption capacity of the zwitterionic surfactant (Z16) modified montmorillonite towards Cu (II) was comparable with that of raw montmorillonite. The results of this work provide novel information for developing new effective adsorbents of heavy metals. Smectite was modified using hexadecyltrimethylammonium bromide which an amount to double cationic exchange capacity for the interchangeable sorption of phosphate (V) and Pb (II) (Bajda et al., 2015). Possible use of montmorillonite modified with polyethyleneimine was investigated by Goncharuk et al. (2010) for the removal of Co (II) and Ni (II) metal ions from aqueous solutions. The increased sorption of cobalt on the modified sorbent being studied (compared with the natural mineral) pointed to the binding of cobalt ions with amine groups attached to the sorbent. It was found that the employment of such a composite sorbent is promising for the purification of medium and highly mineralized wastewaters with a neutral value of pH (Goncharuk et al., 2010).

In another instance, kaolinite and montmorillonite were modified with tetrabutyl-ammonium (TBA) bromide followed by calcination and used for the adsorption of Fe (III), Co (II) and Ni (II) ions from aqueous solution as studied by Bhattacharyya and Gupta (2009). In their report, the calcined TBA clay minerals have a lower adsorption capacity compared to the parent clay minerals at the same experimental conditions; they demonstrated that the reduced adsorption capacities of the calcined TBA clay minerals were attributed the bulky TBA groups that block several negatively charged sites and most likely, the pores. Unuabonah et al. (2008) studied the sorption of Pb (II) and Cd (II) on sodium tetraborate modified kaolinite clay, and the result of their study showed increase in the sorption capacity of the kaolinite upon modification with sodium tetraborate. The increase in adsorption capacity of the modified clay was attributed to the increase in its cation exchange capacity.

Organically modified clays have been found to possess increased capabilities to remove heavy metals contaminants from aqueous solutions (Aroke and El-Nafaty, 2014). Surfactant modified clays can provide selectivity. They are produced from inexpensive base materials and are chemically regenerable. Therefore, modification of a specific clay mineral with anionic surfactant can produce an efficient adsorbent that is capable of sorbing inorganics from aqueous solutions (Tien et al., 2017). In contrast, reduced efficiency of some organically modified clays adsorbents for adsorption of heavy metals is primarily due to the fact that organic cations compete with metals for adsorption sites on the clay mineral surfaces. For instance, a study was reported on the adsorption of Pb (II) and Hg (II) by montmorillonites modified with natural organic cations (Cruz-Guzmana et al., 2006). In their study, the adsorption of Pb (II) and Hg (II) was reduced because of the competition between organic cations and heavy metals for adsorption sites and lack of organic functional groups that are capable of interacting with heavy metals.

2.1.2. Acid Activation

Treatment of clays with acids replaces exchangeable cations with H ions and leaching cations out of both tetrahedral and octahedral sites, leaving the SiO_4 group intact for binding with cations and anions (Theocharis et al., 1998). Acid activations of clay materials have been widely studied as a form of chemical treatment method for the improvement of heavy metals adsorption properties. The method involves leaching of the clays with either organic or inorganic acids, resulting into disaggregation of clay particles, elimination of mineral impurities, and dissolution of the external layers, thus altering the chemical composition and structure of the clays (Emam et al., 2016). The acid treatment is beneficial in terms of increased surface area, porosity and number of acid sites with respect to the parent clays. The acid treated clays are made up of a mixture of non-attacked clay layers and a hydrous, amorphous, and partially protonated silica phase (Belver, 2002).

Acid activations of several clay materials have been widely studied. Olu-Owolabi et al. (2010) reported the modification of Bentonite clay with a binary mixture of goethite and humic acid for the removal of Cu (II) and Cd (II) from aqueous solutions. The modification resulted in an increased cation exchange capacity by a binary mixture of goethite and humic acid reagents. An investigation of the adsorption of lead (II) onto montmorillonite clay modified by humic acid under a fixed pH condition was also conducted by Aziz et al., (2015), the results showed that adsorption of Pb (II) onto humic acid was high. Li et al. (2010) conducted a research on the influence of low molar mass organic acids, acetic acid, tartaric acid, and citric acid on Cd (II) and Pb (II) adsorption by goethite and montmo-rillonite. The effects of the acid concentrations on Cd (II) and Pb (II) adsorption were more obvious on goethite than montmorillonite according to the study. In the goethite system, Cd (II) adsorption was better increased by citric acid and tartaric acid than by acetic acid at low acid concentrations. Christidis et al. (1997) also reported that treatment of raw bentonite with hydrochloric acid resulted to an increased surface area of the clay after modification and thereby enhanced the sorption capacity of the clay sorbent in the removal of heavy metal ions from aqueous solutions. Bhattacharyya and Gupta (2006) studied the adsorption of iron oxide, Fe (III), from water by natural and acid activated clays. The study showed that the adsorption increased with pH until Fe (III) became insoluble at a pH level >4.0, and increased adsorption capacity was shown for the acid activated clay minerals when compared to the untreated clay minerals.

However, treatment of clay with acids may also result in low adsorption capacity of the clay. For instance, three types of local clays: Tabuk, Baha, and Khaiber, were tested for their abilities to adsorb Pb (II) from wastewater. The clays were then treated with hydrochloric acid to activate the adsorption sites within clay particles. Untreated Tabuk clay had the largest adsorption capacity (30 mg lead/g clay) in comparison to those of Baha and Khaiber clays. The adsorption of the metal on acid-activated clays was not enhanced and low compared to those of the untreated clays (Al-Jlil and Alsewailem, 2009).

2.1.3. Salt Modification

Modification of clay soil using both organic and inorganic salts, have been studied by several researchers. For instance, Ma et al. (2011) studied Phosphate-modified montmorillonite (PMM) for the removal of $Co^{2+,}$ Sr^{2+}, and Cs^{+} from an aqueous solution. They reported that the surface properties of the modified clay were improved; Freundlich model best explained the process of the adsorption, indicating the heterogeneous surface property of PMM. Sorptions of Co^{2+} and Sr^{2+} were strongly dependent on the solution pH. The nature of Co^{2+} sorption was endothermic, while Cs^{+} was exothermic. The strongly pH-dependent sorption of Co^{2+} indicated that surface complexation was the main mechanism of Co^{2+} sorption onto PMM. Optimisation of a two-stage batch adsorption of Pb (II) ions onto tripolyphosphate-modified kaolinite clay experiment was carried out by Unuabonah and Adebowale (2009). The mechanism of their study suggested that Pb (II) ion adsorption possibly took place at the negatively charged O-P-O sites. The presence of up to three negative charged sites per molecule of pentasodiumtripoly-phosphate adsorbed onto the kaolinite clay may have contributed to enhancing the adsorption capacity of the TPP modified adsorbent.

More so, the results of a Modified kaolinite clay with 25% (w/w) aluminum sulphate and unmodified kaolin used as an adsorbent to remove Pb (II) from an aqueous solution showed that the amount of Pb (II) adsorbed onto modified kaolin (20 mg/g) was more than 4.5-fold than that adsorbed onto unmodified kaoline (4.2 mg/g) under the optimized condition (Qin et al., 2009). High asdsorption of Cu (II), Zn (II), Cd (II), and Pb (II) onto sulphate modified goethite have been demonstrated (Swedlund et al., 2009). Kaolinite clay, in bright white lumps collected from from Ubulu-Ukwu, Delta State, Nigeria, was modified with phosphate (P-modified) and sulphate anion and thereafter used to adsorb some heavy metals (Pb, Cd, Zn and Cu) from aqueous solution of the metals. The metal ions showed greater affinity for the modified kaolinite clay mineral compared with the unmodified kaolinite clay. The phosphate modified clay however possesses greater adsorption capacity than sulphate modified clay. The order of adsorption of P-mod is presented as follows: P-mod Pb > P-modCu > P-modZn> P-modCd. Desorption studies revealed that the P-modified clay showed a very strong ability to specifically adsorb lead, copper and zinc and are therefore poorly desorbed while all the metals were easily desorbed from the unmodified sorbent. In another treatment, a Japanese volcanic soil called Akadama clay was functionalized with metal salts ($FeCl_3$, $AlCl_3$, $CaCl_2$, $MgCl_2$, and $MnCl_2$) and used to adsorb Cr (VI) from an aqueous solution (Ji et al., 2015). The adsorption showed little dependence on the pH of solution. Result of also showed that Cr (VI) was best removed by $FeCl_3$.

2.1.4. Metal Oxide Functionalization (Oxidative Modification)

The oxidation modification of clays leads to the formation of colloid-sized particles. Colloids are particles with linear dimensions between 0.001 and 1.0 µm (Hiemenz, 1986). The high specific surface area possessed by the colloid particles is an essential characteristic in adsorption phenomena. It is therefore important that the colloid particles remain stable over a period. The colloid must also be stable or resistant to Ostwald ripening or coagulation (Mayer and Jarrell 1996). Ostwald ripening is the process by which larger particles grow at the expense of smaller ones (Finsy, 2004). This occurs because the smaller particles being energetically less stable than the larger ones dissolve and precipitate onto larger particles. It has been demontrated that dissolved organic matter and inorganic anions such as phosphate and silicate inhibit the Ostwald ripening of Fe oxides (Liang and Morgan, 1990; Schwertmann and Cornell, 1991). Also, the presence of inorganic anions like phosphate and silicate is believed to make Fe oxide negatively charged and play important roles in stabilizing colloids (Sigg and Stumm, 1981; Anderson & Benjamin, 1985; Liang & Morgan, 1990). Si in the structure of ferrihydrite is capable of inhibiting the transformation of ferrihydrite to more crystalline oxides and exerts a strong influence on the crystallinity of Si-containing ferrihydrite (Ford et al., 2006). Ferrihydrite-modified clay could be produced by oxidizing the Fe (II) product slowly in the npresence of dissolved silica to the Fe (III) species (Mayer & Jarrell, 1996). The final product has been identified to be one of two Fe oxides (lepidocrocite or ferrihydrite), depending on the initial concentration of dissolved silica (Schwertmann and Thalmann, 1976; Schwertmann et al., 1984; Tipping et al., 1989). The Si/Fe molar ratio is important in determining which of the Fe oxides would be formed during the oxidation of Fe (II).

In recent years, series of aluminum and iron oxide modified Smectites have been used for comparative study of their effectiveness on heavy metal adsorption from water (Franco et al., 2016). Except for Hg (II) sorption, the starting Smectites and the obtained materials displayed higher metal adsorption properties in comparison to that of carbon that is used as the reference in their study. The adsorption properties of raw bentonite were further improved by modification with manganese oxide. The high adsorption performance exhibited by manganese oxide modified bentonite (MMB) was attributed to an increased surface area and a higher negative surface charge after modification for successful removal of traced Cu (II) from an aqueous solution (Eren and Afsin, 2008). Sari and Tuzen (2013) studied the adsorption of silver from aqueous solution using both raw (RV) and manganese oxide-modified vermiculite (Mn-MV). Results of their study showed that the adsorption surface of RV increased approximately 10 times after the modification because of the increase in negative charge onto the sorbent surface (Sari and Tuzen 2013).

2.1.5. Modification by Polymers

Clay minerals such as kaolin can also be modified by the use of polymers. This could be achieved through surface doping or chemical grafting in which the polymer is allowed to interact with the clay to form polymer-clay hybrid composites (Toor, 2010). Chen et al., (2005) proposed polyacrylamide as a polymer to be used for clay modification. Polymer clays are classified into three viz. conventional composites, intercalated composites and exfoliated composites (Masinga, 2013). The loading of polymers into clay could produce materials with enhanced adsorption properties.

Chitosan is a natural polycationic biopolymer that can form chelate with heavy metals through its amino and hydroxyl groups and its nano-composites with clays and zeolites are used for heavy metals adsorption. However, chitosan has a low surface area, with weak chemical and mechanical properties. Thus, modifications are required to overcome these limitations. On the other hand, clay has a lamellar structure with negatively charged surfaces that can interact with polycationic chitosan to form polymer-clay hybrid. Chitosan-functionalized closite 10A (Pandey and Mishra, 2011) montmorilonite (Fan et al., 2006; Bleiman and Mishael, 2010) perlite (Hasan et al., 2003; Hasan et al., 2008; clinoptilolite, 2010, alumina (Boddu et al., 2003) and bentonite (Futalan et al., 2012) have been used for the adsorption of heavy metals from aqueous medium. The functional groups of chitosan (–NH_2 and –OH) interact with heavy metals in the compounds. Chitosan-layered nanocomposites interaction with metal cations occurs through –OH and –NH_2 groups of chitosan and the maximum adsorption capacity values of these adsorbents completely depend on the used layered compounds (Kalyani et al., 2005). Wang et al. (2009) reported the use of chitosan-g-poly (acrylic acid)/attapulgite (CTS–g–PAA/APT) composites for the adsorption of Cu^{2+}. Results showed that there was reaction between attapulgite (APT) and the CTS–g–PAA polymer. Adsorption experiments carried out at pH 5.5 showed fast sorption of the Cu^{2+} and more than 90% of the metal ion was adsorbed after 15 minutes. FTIR spectra of CTS–g–PAA/APT compound before and after the adsorption of Cu^{2+} showed possible chemical interaction between the $–NH_2$, –OH groups of chitosan, –COOH groups of PAA in the composites and the Cu^{2+}. Similarly, methacrylic acid grafted chitosan/bentonite (Abdel Khalek et al., 2012), Chitosan-g-poly (acrylic acid)/vermiculite (Wang and Wang, 2012) and humic acid-immobilized-amine modified polyacrylamide immobilized on bentonite (Anirudhan and Suchithra, 2010) have been reportedly used for the adsorption of various heavy metal ions from their respective aqueous solution.

Synthesis of a novel superabsorbent composite was achieved by copolymerization reaction of partially neutralized acrylic acid (AA) on bentonite micropowder using N, N´-methylenebisacrylamide as a crosslinker (Bulut et al., 2009). The results of the study showed high maximum coverage capacity values for sorption of Pb^{2+} (1666.67 mg/g), Ni^{2+} (270.27 mg/g), Cd^{2+} (416.67 mg/g) and Cu^{2+} (222.22 mg/g).

2.2. Biogenic Modification (Fortification with Organic Biomasses and Composites)

Fortification of clay with organic biomass and composites could possibly enhance heavy metals adsorption by improving the surface area of the clay, thereby, providing additional reactive sites for cation exchange and/or surface complexation. Akpomie et al. (2017) investigated the effect of cassava peel modified kaolinite clay compared to the unmodified kaolinite clay on the adsorption of Cr (III) ion. The result showed the suitability of cassava peel modified kaolinite clay for chromium ion sorption from aqueous solution.

Plantain peels are the primary waste products of plantain fruit constituting approximately 40% of it (Akinsami et al., 2015). The presence of suitable properties and components contained in plantain peel has made it an acceptable biosorbent for removal of heavy metals and other inorganic contaminants. Venkateswarlu et al. (2013) prepared a cheap and eco-friendly Fe_3O_4 magnetic nanoparticles adsorbent using plantain peel extract via the biogenic method, the adsorbent was shown to possess high BET surface area and excellent magnetic response attribute. Opeolu and Fatoki (2012) studied the adsorption and desorption potential of plantain peel biomass for the removal of Zn^{2+} ions from aqueous solution. The result from their study showed an excellent uptake of the metal by the adsorbent. The low cost and abundance and high efficiency of biogenic adsorbents cannot be over-emphasized which makes them applicable industrially for adsorption purposes. Sanusi et al. (2016) demonstrated that feldspar clay modified with carica papaya seed showed increased the adsorption; the adsorption capacity of feldspar clay from 18.26 mg/g to 45.81 mg/g for Pb (II) from 12.57 mg/g to 46.18 mg/g for Cu (II) at 308 K upon modification. Increasing temperature and initial metal ions concentration was found to have resulted to increased adsorption of both metals onto the adsorbent.

2.3. Mechano-Chemical Treatment

Mechano-chemistry is the coupling of mechanical and chemical phenomena on a molecular scale and includes mechanical breakage, chemical behavior of mechanically stressed solids, and polymer degradation under shear etc., (Munnings et al., 2014). The method of ball milling is a widely used process in which mechanical force is used to achieve chemical processing and transformation (Carlier et al., 2013). Mechanochemical transformation eliminates the use of many solvents which makes the whole process environmentally friendly (Lim, 2016).

Mechano-chemical phenomena have been applied for clay modification. For instance, Hongo et al. (2012) carried out a research on vermiculite clay which was subjected to mechano-chemical treatment using a vibration mill. The mechano-chemical treatment led to a reduction in the particle size and a significant increase in the surface area. The mechano-chemical treatment of vermiculite resulted in a dramatic improvement in the lead (II) adsorption capacity. The removal of Pb (II), Cd (II), Cu (II) and Zn (II) from aqueous solutions using unmodified and modified (mechano-chemically activated) Serbian interstratified montmorillonite/kaolinite clay was investigated by Ksenija et al. (2013) and the results of their study showed that the modified clay exhibited greater equilibrium adsorption capacity

2.4. Physical Method (Thermal Treatment)

Physical method of clay modification could be achieved either by calcination or microwave heating. These methods are applied in order to disrupt the chemical structure of the clay material. The clay material is usually subjected to a very high temperature capable of breaking some chemical bonds and altering the arrangement of molecules in the lattice structure of the clay.

2.4.1. Calcination

This involves the exposure of the materials to high temperature capable of breaking the bonds of the components contained in the substance. This can also be referred to as conventional heating method of activation (Itodo et al., 2010). Clays are strongly dependent on temperature, and the high temperature treatment of clays destructs the crystalline structure of the clay minerals (Ionescu et al., 2011). Conventional heating technique have been regarded as one of the most adopted for the preparation and activation of adsorption materials among others, in which heat is transferred via convection, conduction and radiation mechanisms (Hesas et al., 2013). In the conventional heating of materials, the outermost parts experience the energy before the interiors, stimulating a thermal gradient amid the inner and the outer surface of individual particle (Thostensen and Chou 1999; Yadoji et al. 2003). This result to heterogeneous microstructure of materials at high heating temperature, high energy consumption and time wasting as limitations compared to other techniques (Oghbaei and Mirzaee, 2010). It could also result to overheating of the materials causing substrate and reagent degradation (Lidstrom et al., 2001).

2.4.2. Microwave Heating

The preparation of cost-effective adsorption materials can be considered on the basis of the starting materials, energy consumed and time expended in synthesis of such materials. Almost all reactions have been tested under classical conditions (thermal heating) for comparison with reactions that proceeds in the microwave field which is an improved alternative for conventional heating. It has been observed from experimental results that microwave–initiated chemical reactions occur at faster rates as great as 1000-folds of the conventional methods (Hayes, 2004).

In chemistry, microwave radiation has saved energy in chemical synthesis and production of low-cost adsorbents (Hesas et al., 2013). The principle of microwave irradiation heating is based on the fact that most molecules possess a dipole or are ionic in nature which results into orientation or movement of the poles upon interaction with the microwaves. A dipole is sensitive to external electric field and attempts to align itself with the field when rotated and in the presence of an alternating current. Hence, the electric field is reciprocated at individual variation leading to dipoles moving together to suit the reciprocated electric field Jauhari et al., 2012); thus initiating rotational and frictional forces between the molecules which dispel as internal uniform heating within the medium. Microwave radiation just like other electromagnetic radiation can be understood based on two phenomena namely viz. electric field (accountable for dielectric heating) and magnetic field. The heating is achieved through two primary pathways which are dipolar polarization and conduction mechanisms (Lidstrom et al., 2001). The irradiation frequency (2450 Hz) of microwave electric field that is commonly used alternates at the speed of 4.9 × 109/second. Therefore, microwave heating is said to be influenced directly by the dielectric characteristics of the material, namely: dielectric constant and dielectric loss.

Studies have reported that changes occur in the properties of natural clay after thermal treatment at various heated temperatures (Diffo et al., 2015). In a study, Elimbi et al. (2011) reported the calcination temperature of kaolin to be 700 °C at which geopolymers with optimal characteristics were obtained. In another study, Castelein et al. (2002) observed the transformation of kaolin into mullite under thermal influence. Kounou et al. (2015) conducted a study on Metakaolinite which was obtained from kaolinite clay soils from the South Western Region of Cameroon by heating 20 g of kaolinite at a temperature of 700 °C. The clay was used as an adsorbent to study its adsorptive capacities on the removal of zinc (II) ions. The adsorption mechanism confirmed that the physical and chemical adsorption processes controlled the zinc (II) ion uptake onto the two adsorbents (Metakaolinite and raw kaolinite). Throughout their study, it was observed that metakaolinte was an excellent adsorbent for Zn (II) removal compared to kaolinite.

A multi technique was used to investigate the interaction of Cr (VI) species with pre-fired brick clay as studied and reported by Priyantha and Bandaranayaka (2011), they found that Cr (VI) adsorption by fired brick clay was strongly dependent on the firing temperature as the maximum adsorption was found at 200 °C. Research by Rao and Kashifuddin (2012) showed that ball clay exhibited an excellent adsorption capacity toward Cd (II) ions after the sample was heated at 200 °C. The result of their research showed that percentage (%) adsorption of the fired clay decreased with increasing temperature from 200–1000 °C. However, some studies also confirm the endothermic nature of clay. For example, the maximum adsorption capacities of three types of Saudi clay were found to have increased with temperature increase (Alshammari 2015). The study concluded that adsorption process of three types of natural Saudi clays to remove cobalt ions was endothermic Alshammari. Another investigation supported this result, in which spent activated clay (SAC), a natural waste, produced in Refinery Company, was thermally treated by pressure steam treatment and then used as an adsorbent to remove Cr (VI). The study proved its beneficial use in wastewater treatment (Weng et al., 2008).

Bhattacharyya and Gupta (2009) demonstrated the modification of Kaolinite and montmorillonite with tetrabutylammonium (TBA) bromide followed by calcination and used for the adsorption of Fe (III), Co (II), and Ni (II) ions from their respective aqueous solution. However, in their study, the calcined TBA clay minerals possess a lower adsorption capacity compared to the raw clay minerals at the same experimental conditions. The result of the study also showed that the reaction of kaolinite with TBA decreased the adsorption of Fe (II) by 55%, Co (II) by 47%, and Ni (II) by 44% while the adsorption capacity of the calcined TBA-montmorillonite was reduced by 44, 41 and 42% of the raw clay for removal of Fe (III), Co (II), and Ni (II), respectively. The reduction in adsorption capacity of the calcined clays could be as a result of the bulky TBA groups that block several negatively charged sites and most likely, also the pores.

3. CONCLUSION

Clay materials have shown excellent potential for the removal of metal pollutants without any modifications, but in many studies, their removal capacities were improved through different modification techniques. Treatment techniques such as chemical, physical (thermal), mechano-chemical and fortification with organic biomasses and composites have been successfully applied to modify clay soils with the aim of improving the heavy metals adsorption capacity of the soils.

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