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Mineralogical and Chemical Characteristics of Raw and Modified Clays and Their Application in Arsenic and Fluoride Removal: Review

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Abstract

Clay and clay minerals have always been used since the ancient times for making ceramic materials and also as a building material. Over the past decades, there has been a growing trend in their applicability in different areas such as industries, environmental remediation and water treatment sectors. The growing trend is mainly associated with the fact that they are chemically and mechanically stable, have higher specific surface area and cation exchange capacity. Furthermore, clays can be modified to improve their functionalities in different sectors. In this chapter, we present a review of the structural, mineralogical and chemical properties of clay and the effect of surface modification in their structures. We further looked at their applicability in arsenic and fluoride removal in their raw and also in their modified form. Although the literature showed that modified clay minerals yields higher adsorption capacity as compared to raw clays little nothing has been reported yet in relation to the cost of modifying clays with chemical species. As such new studies should also elaborate on the cost effectiveness of modifying clay minerals with chemical species.

Keywords: clay minerals, physicochemical properties, mineralogy, surface modification, adsorption

1. Introduction

Clay and clay minerals have attracted wide interest for application in various sectors including process industries, agricultural sectors, engineering and construction sectors, environmental remediation and water treatment [1]. This is not only due to their abundance and inexpensiveness but also because of their physicochemical properties such as chemical and

mechanical stability, larger specific surface area, higher charge density, layered structure, higher cation exchange capacity [2].

By definition clays are naturally occurring aluminosilicate materials composed mainly of fine grained materials with colloid fraction of soils, rocks, sediments and water [3–5]. Clay minerals are composed of groups of small crystalline particles of one or more members of a group of minerals. These minerals originate from weathering of silicate minerals [6, 7]. Common minerals that constitute clay minerals are kaolinite, illite, mica, vermiculite and montmorillonite or smectite. This chapter presents a review on mineralogical and chemical properties of clay minerals, their surface modification and their application in arsenic and fluoride removal potential from water.

2. Structure, mineralogical and physicochemical composition of clay

The structure of the clay consists of phyllosilicate sheets that are arranged properly to form structural layers. Individual layer is made by a stack of tetrahedral and octahedral sheets that shape the frame of all the clay mineral [8, 9]. The tetrahedral (T) sheet consist of cations coordinated to four oxygen atoms and linked to adjacent tetrahedral by sharing three corners to form two dimensional hexagonal mesh [10]. The most common tetrahedral cations are Si^{4+} , Al^{3+} and Fe^{3+} .

The second sheet is called octahedral sheet (O), which is comprised of six oxygen atoms which are closely parked together and hydroxyl ions in which cations are arranged to form octahedral coordination and linked to neighboring octahedral by sharing edge. The edge of shared octahedral forms sheet of hexagonal or pseudo hexagonal symmetry and shows different topologies depending on octahedral hydroxyl position [8]. Cations in octahedral sheet are usually Al^{3+} , Fe^{3+} , Mg^{2+} or Fe^{2+} . When cation with positive valence of three (Al^{3+} or Fe^{3+}) is present in the octahedral sheet, only two-thirds of the possible positions are filled in order to balance the charges and the mineral is therefore termed dioctahedral. Conversely, when cation with positive charge of two (e.g. Mg^{2+} and Fe^{2+}) is present, all three positions are filled to balance the structure and the mineral is termed trioctahedral. The phyllosilicate sheets are joined together by sharing the apical oxygen atom or hydroxyls to form hexagonal network with each sheet in a fundamental structure. **Figure 1** depicts structures of octahedron sheets and tetrahedron sheets proposed by Grim [11]. Based on the number and ratio of the sheets in the fundamental structural units, the existing cations substitutions in the octahedrons and tetrahedrons caused for resulting charge of the layers which can be descended into two main groups of clay mineral namely 1:1 (kaoline) and 2:1 (smectite and illite) [12, 13].

2.1. Type 1:1

This group of mineral is also called kaolin minerals, which is the basic mineral for kaolinite, dickite and hallocite [14]. They consist of single tetrahedral sheet of SiO_4 and an octahedral sheet with Al^{3+} as octahedral cation. Both sheets combine to form a common a unit in such that the tip of silica tetrahedral points toward the octahedral sheet [3]. The layer of the tetrahedral sheet is invented over the octahedral sheet with oxygen atoms and hydroxyls ions present to balance the charges being shared by the silica in the tetrahedral sheet and the aluminum in

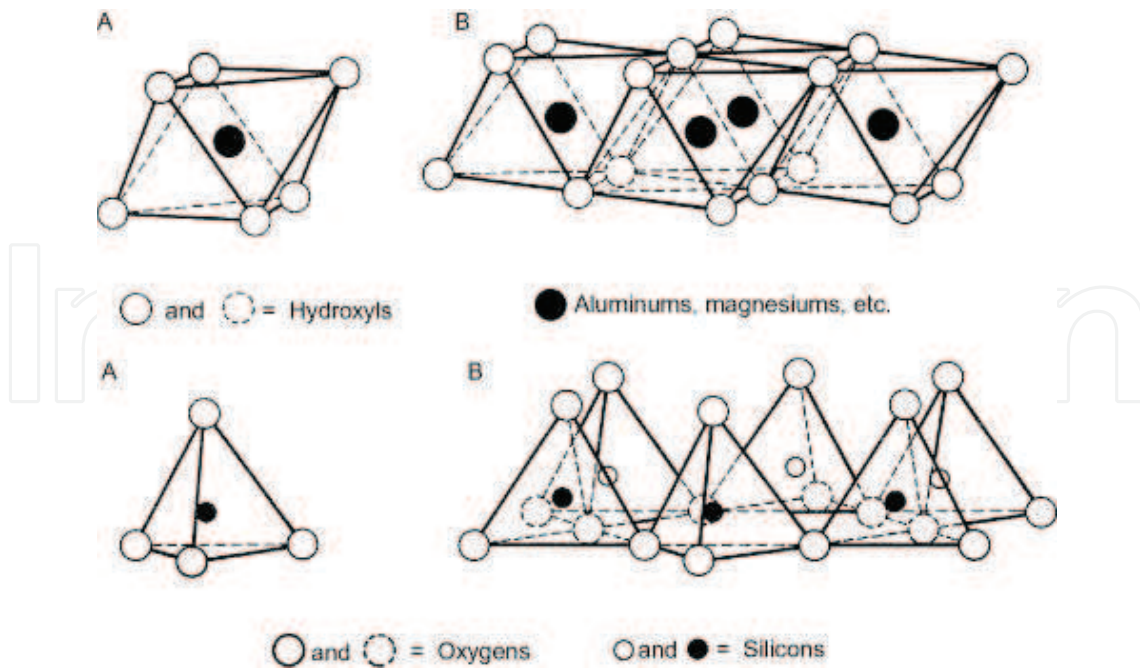


Figure 1. Schematic diagrams of octahedron and tetrahedron sheets. Top: (A) an alumina octahedron in which the central aluminum ion is coordinated to six hydroxyls; (B) an alumina octahedral sheet formed by linking octahedra through edge-sharing. Bottom: (A) a silica tetrahedron in which the central silicon ion is coordinated to four oxygens; (B) a tetrahedral sheet formed by linking silica tetrahedra through corner-sharing [11].

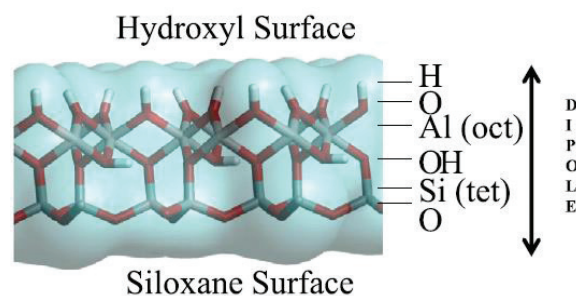


Figure 2. Typical structure of Kaoline mineral [15].

the octahedral sheet. With the layer charges close to zero, the kaolin mineral has essentially no interlayers and does not show interlayer expansion in the water because the contiguous layers within particles are strongly held together by Al-OH and O-Si-OH bonding supplemented by dipole-dipole and van der Waal interaction. **Figure 2** represents the typical structure of kaoline mineral [15].

2.2. Type 2:1

Clay mineral groups such as smectite and vermiculite are part of 2:1 type and it constitutes minerals such as montmorillonite, saponite, nontronite and beidellite. The 2:1 minerals are composed of one octahedral sheet between two tetrahedral sheets. For which the interlayer thickness is 1 nm when the sheet is closed [16]. Generally in this group of clay minerals

isomorphic substitutions are observed, for example, possible substitutions of Si^{4+} in tetrahedron by Al^{3+} or those of Al^{3+} in octahedron by Fe^{2+} [17]. Such substitution leads to permanent negative surface charge at the sheet by the presence of exchangeable cations [18]. The most common exchangeable cations in the interlayers are K^+ , Na^+ , Ca^{2+} , Mg^{2+} and H^+ . The 2:1 group minerals have higher charge density, higher surface area and higher swelling capacity [3]. The swelling capacity of these type of clay arise from their structural features that enables water to overcome the electrostatic and van der Waals interactions keeping the layers together and penetrate into surface interlayers leading to hydrolization of Al and Si atoms to aluminol (AlOH) and silanol (SiOH) resulting in expansion. **Figure 3** presents the schematic diagram of 2:1 clay minerals.

2.3. Cation exchange capacity

One of the important properties of the clay minerals is that contains cations that can be exchanged for any guest species of anion or cation by treating clay mineral with such clay mineral. The exchangeable cations are held on the outside of silica-alumina clay mineral structural units and the exchange does not affect the layout of the silica-alumina units [11]. The ion exchange capacity phenomenon is measured in terms of milli-equivalents per gram or per 100 g. The commonly used cations used to evaluate the cation exchange capacity of the clay mineral includes; Mg^{2+} , Ca^{2+} , K^+ , Na^+ , H^+ and NH_4^+ [16].

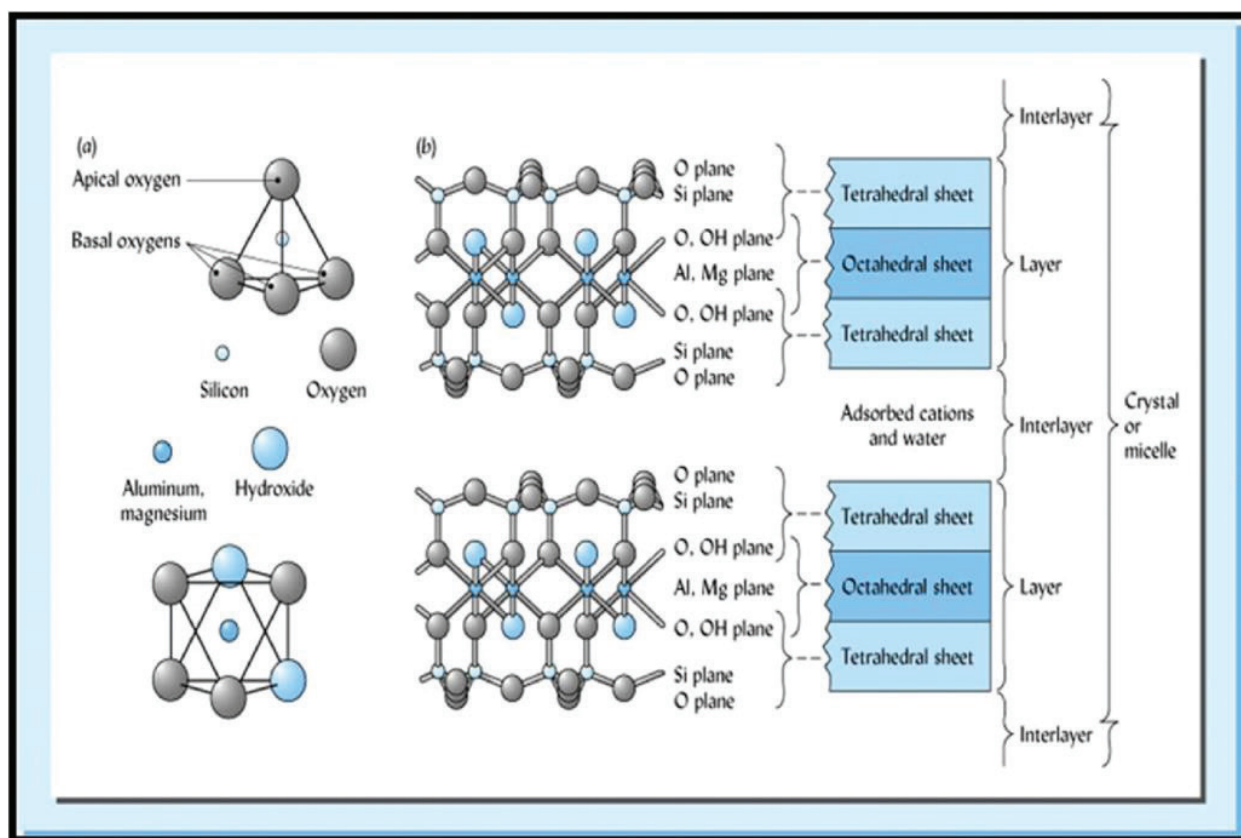


Figure 3. Typical structure of 2:1 clay [19].

Different clay minerals portray different cation capacity depending on the substitution within the lattice structure [11]. Type 1:1 clay minerals such as kaolinite have limited substitution between their lattice structure compared to type 2:1 clay minerals such as smectite, vermiculite and sepiolite and consequently they have lower cation exchange capacity [10]. Several studies have indicated that cation exchange capacity of the clay mineral decreases after modification by inorganic species [2, 20, 21]. This is because modification involves the ion exchange reaction between the exchangeable cations in the clay interlayer and the guest species. Low CEC of modified clays suggests the irreversibility of cationic exchange and thus intercalated metallic polycations are hardly exchanged [21]. **Table 1** summarizes the cation exchange capacity of different raw and modified clay minerals.

2.4. Specific surface area

One of the essential properties of clay minerals is their larger surface area. This characteristic allows clay minerals to adsorb water and other environmental contaminants [26]. Type 2:1 clay minerals such as smectite and vermiculite possess higher specific surface area as compared type 1:1 clay minerals such as kaolinite and halloysite because of their ability to swell [10]. The total specific surface area of the clay is denoted by the sum of external surface area and the internal surface area corresponding to the interlayer spaces [8].

Several authors have indicated that total specific area of the clay mineral can be increased through modification to increase their functionality in different areas of application. Hua [27] reported an increase in surface area of Na-bentonite from 34.1 to 77.2 m²/g after modification with Mn oxides. Bentonite modified with the combination of Mn oxides and poly(diallyldimethylammonium chloride) showed a sharp increase in surface area to 128.9 m²/g. The increase in total specific

| Clay mineral | CEC (meq/100 g) | Ref |
|-------------------------------------|-----------------|------|
| Unmodified smectite | 118.5 | [2] |
| Fe-exchanged smectite | 115.75 | [2] |
| Ti-Pillared smectite | 105.75 | [2] |
| Raw bentonite | 265.5 | [20] |
| Fe ³⁺ modified bentonite | 188.9 | [20] |
| Na-montmorillonite | 78 | [21] |
| Fe(OH)-montmorillonite | 12 | [21] |
| Al(OH)-montmorillonite | 14 | [21] |
| Al ³⁺ modified bentonite | 183.3 | [22] |
| Mukondeni smectite rich clay soils | 79.93 | [23] |
| Mixed mukondeni clay soils | 137.7 | [24] |
| Montmorillonite | 91.61 | [25] |

Table 1. Cation exchange capacity of raw and modified clay minerals.

area could be attributed to swelling of bentonite clay during modification. Mishra and Paride [28] also reported increased specific surface area for bentonite pillared with manganese oxides at temperature of 500°C. This was attributed to decomposition of the complex with increasing temperature to form the oxide pillar which generated the void micropores inside the clay layers. This phenomenon was also emphasized by Bertella and Pergher [29] who also observed an increased in specific surface area of bentonite clay after pillaring using Al and Co from 58 to 304 m²/g.

3. Application of clay in arsenic and fluoride removal

The presence of arsenic and fluoride has attracted worldwide attention due to their toxicity in human health after a prolonged period of exposure [30]. Excessive intake of fluoride can lead to dental and skeletal fluorosis while the intake of arsenic can lead to various types of cancer. The World Health Organization (WHO) has set the standard of fluoride and arsenic in water for human consumption at 1.5 and 0.01 mg/L, respectively [31]. Recently much attention is being driven into developing a technique that can be used to remove excess of fluoride and arsenic in drinking water to acceptable levels. Adsorption using clay mineral has emerged to be the promising technique and several studies pertaining to removal of fluoride and arsenic using clay minerals has been reported in the literature. This is because clay minerals are abundantly available in nature at little or no cost. Furthermore clay minerals are more chemical and mechanical stable, poses larger specific surface area and higher cation exchange capacity making them good adsorbents.

3.1. Arsenic removal

Mohapatra et al. [32] reported the adsorption of arsenic from water by Kaolinite, Montmorillonite and illite and its dependence on solution pH and temperature. The results indicated that As(V) adsorption is dependent on pH and optimum adsorption capacities of 0.86, 0.64 and 0.52 mg/g were achieved at pH 5 for kaolinite, montmorillonite and illite, respectively. Furthermore, it was found that increasing temperature decreases the adsorption efficiency indicating that the interaction between As(V) was exothermic. This was observed in both evaluated clay soils. When evaluating the mechanistic aspect for As(V) adsorption onto kaolinite, montmorillonite and illite, authors ascribed it to inner sphere surface complexation and strong specific ion adsorption.

The adsorptive properties of five different clay minerals namely, R-clay, Y-clay, E-clay, A-clay and Rhassoul-clay found in Morocco for As(V) removal has been evaluated by Bentahar et al. [33]. The results showed that As(V) adsorption was more favorable at acidic pH and clays containing higher iron oxide content had higher arsenic binding affinity. The maximum adsorption capacity observed was 1.076 mg/g.

3.2. Fluoride removal

The effectiveness of raw clay minerals in fluoride removal has been reported by several authors. Kau et al. [34] evaluated the fluoride retention by kaolin clay. It was observed that the degree of fluoride sorption by kaolin is dependent on solution pH and available fluoride

concentration. It was further believed that adsorption of fluoride by kaolinite clay is accompanied by slight expansion in the kaolin sheet lattice. After this study, Tor [35] evaluated the efficiency of montmorillonite clay mineral in adsorption of fluoride removal from groundwater. A maximum fluoride adsorption capacity of 0.263 mg/g was reported at initial pH of 6.

Mudzielwana et al. [23] reported the efficiency of Mukondeni smectite rich clay in fluoride removal. They observed that percentage fluoride removal decreases with increasing pH of the solution with about 92% fluoride removal noted at acidic pH of 2. Ngulube et al. [24] also observed the same trend in the adsorption of fluoride by mixed Mukondeni clays. The decrease in percentage of fluoride with increasing pH during adsorption by raw clay minerals is often attributed to abundance of OH^- at alkaline pH.

The fluoride adsorption capacity of selected South African clay soils was reported by Coetzee et al. [36]. They observed that kaolinite type clay has the lowest adsorption capacity while the gibbsite clay has the highest adsorption capacity toward fluoride ions. The adsorption capacity of South African clays can be summarized in the following increasing order: kaolinite > smectite > palygorskite > goethite > gibbsite. This was attributed to the structure of the clay, surface charges and also the chemical composition of the clay [36].

4. Modification of clays and application in arsenic and fluoride removal

It has been observed that raw clays exhibit low adsorption capacities toward arsenic and fluoride adsorption from solutions. This is attributed to the permanent negative charges on the edges of clay sheets [37]. As such clay modification by higher density charge species and organic cationic surfactant is essential to improve their binding affinity. Common techniques that have are used for modification of clays for arsenic and fluoride removal includes intercalation, coating and pillaring. Intercalation includes insertion of guest species in the interlayers of the clay mineral with preservation of the clay layered structure [38]. Guest species may be the inorganic cations such as Mn^{2+} , Fe^{3+} and Al^{3+} or organic cationic surfactants such as HDTMA and CTAB. Gitari et al. [20] intercalated Fe^{3+} ions onto South African bentonite clay, their results showed that the process involved the cation exchange between main exchangeable cations such as Mg^{2+} , Na^+ , Ca^{2+} and K^+ . This was confirmed by the subsequent decrease of the content of these chemical species in the Fe^{3+} modified bentonite. Mudzielwana et al. [39] and Masindi et al. [22] intercalated Mn^{2+} and Al^{3+} onto the interlayers of bentonite respectively, and also observed decrease in the content of Mg, Na Ca and K oxides. These results confirm that during intercalation basic exchangeable cations in the interlayers are exchanged for guest species.

Pillaring is the most commonly used procedure to transform phyllosilicate materials into microporous and mesoporous materials. It involves the formation, intercalation and subsequent fixation of polynuclear cations between the clay interlayers [29]. Thus the lamellar spacing and specific area increases, making these materials attractive adsorbents for adsorption of various inorganic contaminants. **Figure 4** presents a schematic diagram of a pillared clay [40].

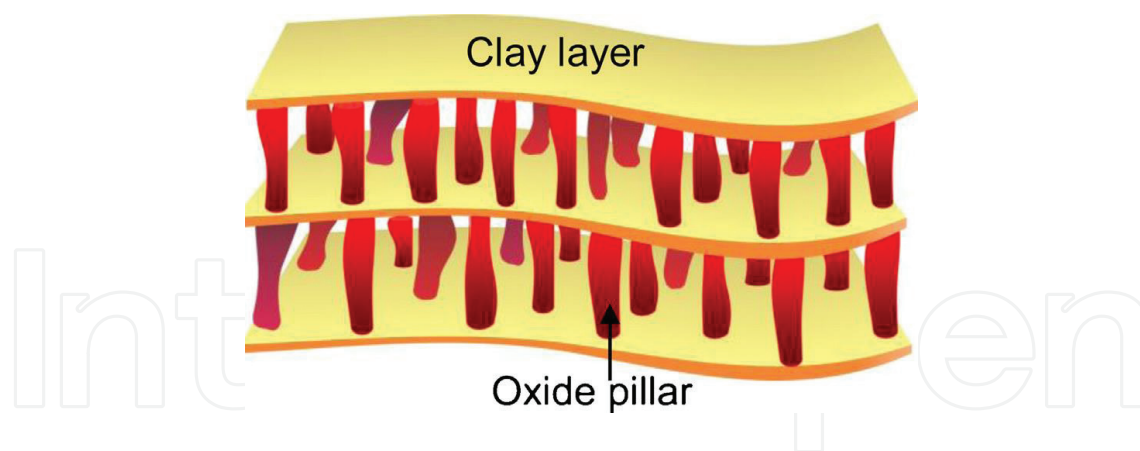


Figure 4. Schematic diagram of a pillared clay [40].

Lenoble et al. [21] pillared montmorillonite clay using titanium, iron and aluminum as pillaring solution. Their results confirmed that pillaring increases the basal spacing and the specific surface area by many folds. These results were confirmed by Mishra and Mahato [40] who also observed increased in both specific surface area for Mn and Fe pillared bentonite clay. Beside the side the change in basal spacing and chemical oxide content in the pillared clays, the whole process of pillaring does not change the mineralogical composition of the clay.

4.1. Arsenic removal using modified clay minerals

Mishra and Mahato [40] evaluated the effectiveness of Fe and Mn pillared bentonite clay in As(V) and As(III) removal from groundwater. Maximum As(III) and As(V) adsorption capacities of 17.57 and 25.77 $\mu\text{g/g}$ were observed for Fe pillared bentonite while adsorption capacities of 25.77 and 26.17 $\mu\text{g/g}$ were observed for Mn pillared bentonite clay. This was higher by many folds compared to 4.31 and 4.33 $\mu\text{g/g}$ for raw bentonite clay. This was attributed to increased surface area in the pillared bentonite and also increased charge density in the pillared clay.

Ren et al. [25] intercalated Fe polycations and cetyltrimethylammonium bromide (CTMAB) onto montmorillonite clay mineral and test it for arsenic removal. The results showed that CTMAB had diffused into the interlayers of the montmorillonite minerals while Fe polycations were adsorbed on the outer surface and had formed flocculent particles. When tested for arsenic removal, CTMAB-Fe montmorillonite and Fe montmorillonite showed a maximum adsorption capacities of 8.85 and 15.15 mg/g for As(V), respectively, and 13.89 and 16.13 mg/g for As(III). Furthermore, the optimum adsorption capacities were observed at wide range of pH of 4–10.

4.2. Fluoride removal using modified clay minerals

Several studies have been reported concerning the adsorption of fluoride using chemically modified clay minerals and the results showed improved adsorption efficiency as compared to unmodified clay soils. Kamble et al. [41] reported better sorption capacity for La, Mn and Mg oxides incorporated bentonite clay compared to bare bentonite. Efficiency of magnesium incorporated bentonite in adsorption of fluoride has also been evaluated by Thakre et al. [42] and maximum adsorption capacity of 2.26 mg/g was achieved over a wide range of pH which

| Adsorbent | CEC (meq/100 g) | Surface area (m ² /g) | Adsorbate | pH | Adsorbent dosage (g/L) | Adsorption capacity (mg/g) | Ref |
|-----------------------------|--------------------|--|----------------|------|---------------------------|----------------------------------|------|
| Kaolinite | — | 33 | As(V) | 5 | 40 | 0.86 | [32] |
| Montmorillonite | — | 58 | As(V) | 5 | 40 | 0.68 | [32] |
| Illite | — | 28 | As(V) | 5 | 40 | 0.54 | [32] |
| Moroccan clays | 35 | 22.5 | As(V) | 7 | 25 | 1.07 | [33] |
| Smectite rich clay | 79.9 | 20.35 | F ⁻ | 2 | 8 | 0.21 | [23] |
| Montmorillonite | — | 18.5 | F ⁻ | 6.0 | 8 | 0.26 | [35] |
| Mixed Mukondeni clay | 137.7 | 35.46 | F ⁻ | 2 | 150 | 0.08 | [24] |
| CTAMB-Fe montmorillonite | — | — | As(V) | 4–10 | 4 | 8.85 | [25] |
| Fe-montmorillonite | — | — | As(V) | 4–10 | 4 | 15.15 | [25] |
| Mg ²⁺ bentonite | — | — | F ⁻ | 3–10 | 3 | 2.26 | [41] |
| Fe ³⁺ bentonite | 188.9 | 49.95 | F ⁻ | 2–10 | 20 | 2.29 | [20] |
| Al ³⁺ bentonite | 183.3 | 33.1 | F ⁻ | 2–12 | 10 | 5.7 | [22] |

NB: (–) = not reported.

Table 2. Comparison of the adsorption capacity between raw and modified clay toward arsenic and fluoride.

was better than the capacity achieved with unmodified bentonite. Gitari et al. [20] reported maximum adsorption capacity of 2.91 mg/g for the Fe³⁺ modified bentonite clay which was also better than the unmodified bentonite. The main factor which was leading to improved sorption fluoride capacity was the increased surface area that corresponds to availability of more active sites for fluoride ion adsorption. Furthermore, modification of clay mineral by high density charges polycations increases the amount of positive charges in the surface of adsorbent leading to increased sorption capacity of anions.

Table 2 summarizes the comparison between raw and modified clay soils toward fluoride and arsenic adsorption from water. It is observed that the adsorption of fluoride and arsenic increases by many fold after clay modification.

5. Mechanisms for arsenic and fluoride removal using clay soils

General mechanism involved for arsenic and fluoride removal using clay mineral can be summarized by the following three main steps: (i) Mass transfer of ions to the external of the adsorbent, (ii) adsorption of ions on the external particle surface and (iii) Intra-particle diffusion of ions from the exterior surface and the exterior surface and possible exchange with elements on the pore surface inside particles [30, 43]. These major three steps were observed during the adsorption of fluoride onto MnO₂ coated bentonite by Mudzielwana et al., [44]. Besides these

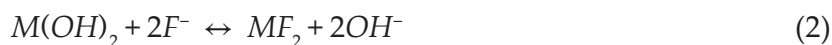
three steps, there are two adsorption processes that take place during the transfer of adsorbate ions into the adsorbent, namely, physisorption and chemisorption. Physisorption occurs when the ions are adsorbed to the surface through the weak intermolecular interactions such as Van der Waal forces, hydrogen bonding and dipole–dipole interactions [45]. Conversely, chemisorption occurs when adsorbate ions forms chemical bond through electron exchange. Lee et al. [46] evaluated the adsorption of As(III) and As(V) onto HDTMA modified clays and they concluded that the adsorption of As(III) was via physisorption while the adsorption of As(V) was via chemisorption. They further indicated that the adsorption of As(III) occurred on the outer layer of the adsorbent while the adsorption of As(V) occurred in the inner layer of the adsorbent.

Solution pH is the main factor that influences the adsorption of arsenic and fluoride onto clay minerals since it determines the surface charges [37, 47]. Several authors observed that adsorption of fluoride and arsenic by clay minerals is low at alkaline pH values due to the abundance of OH^- ions on the adsorbent surfaces that causes electrostatic repulsion. Furthermore, the adsorption of arsenic and fluoride has been observed to be favored by low pH values. This is mainly attributed to the fact that at low pH the clay surfaces are positively charges and as such ions will be removed easily through electrostatic attraction. Thakre et al. [42] used the Eqs. 1 and 2 to hypothesize the adsorption of fluoride onto magnesium incorporated bentonite under different pH conditions.

Acidic pH:



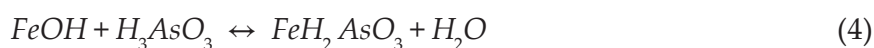
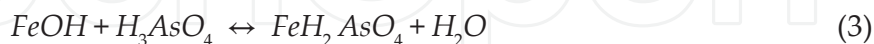
Alkaline pH:



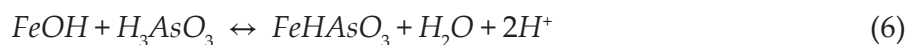
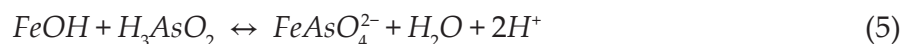
where M represents metals.

According to Ren et al. [5] the adsorption of As(V) and As(III) onto modified clay minerals at acidic and alkaline may be elucidated by Eq. 3–6:

Acidic:



Alkaline:



6. Conclusion

This chapter presented a summary of mineralogical and chemical composition of raw and surface modified clay minerals and their application in arsenic and fluoride removal from drinking water. From the review, it is noted that properties of the clay minerals such as higher cation exchange capacity and specific surface areas as well as the chemical composition of clay minerals enables them to be used as arsenic and fluoride adsorbents. Furthermore, these physicochemical properties can be improved through intercalation and pillaring which consequently improves their applicability in arsenic and fluoride removal. Modification of clay minerals does not alter their phyllosilicate structure. However, it improves the basal spacing and specific surface areas of the clay minerals. The modification is mainly through ion exchange between the basic exchangeable cations such Na^+ , K^+ , Mg^{2+} and Ca^+ with the guest species. The effectiveness of the clay minerals in adsorption of arsenic and fluoride is mainly influenced by the surface charges which are determined by the solution pH. At acidic pH the sorption is higher due to the fact that the surface is positively charged which influences the sorption of anions through electrostatic attraction. Conversely, at alkaline pH the sorption is low due to electrostatic repulsion. Recently, the attention is mainly on modification of clay minerals to enhance their application in various fields. However, little has been done on evaluating the chemical stability and the cost effectiveness of modifying clay minerals. As such future studies should be directed toward evaluating the chemical stability of modified clay minerals especially those applied for drinking water treatment. Also, studies should elaborate the cost effectiveness for modifying clay minerals with chemical species.

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