Adsorption of Radioactive Element by Clay: A Review

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Abstract. Clay is one of the most important industrial minerals that have been used to improve the quality of product and economize the production cost. Clay and their minerals, both in its natural and modified forms, have the ability to absorb various radioactive materials from aqueous solution, such as Uranium, Thorium and Caesium as discussed extensively in this review. This article presented an overview of properties and classifications of clay, current research literature on using clay minerals as an absorber, and a descriptive analysis of their adsorption behaviour. Three type of clay are the focused in this review namely Bentonite, Kaolin and Zeolites due to their excellent qualification in absorbing radioactive materials such as Uranium, Thorium and Caesium.

1. Introduction

Radioactive elements occur naturally in the earth's rocks, soils and water in varying concentrations. Many industrial operations, tend to accumulate naturally occurring radioactive materials (NORM) at concentration above normal in by-product waste streams. Massive amounts of NORM wastes produced annually by manufacturing industries around the world should receive the attention of international and national environmental protection agencies and regulatory bodies. Since the mid-1980s, both federal and state regulatory agencies have become increasingly concerned about the presence of NORM [1].

The long-lived radionuclides in radioactive waste are considered to be hazardous pollutants, and their migration along with groundwater flow is strongly affected by the adsorption of geological materials. The existence of radioactive materials in aquatic environment has been known to cause various health problems to humans and animals. They can be absorbed and accumulated in the human body and cause serious health effects such as cancer, organ damage, nervous system damage, and in extreme cases, death [2]. Additionally, improper disposal of NORM may contaminate soil and water and lead to higher indoor radon levels in nearby buildings [3].

Therefore, radioactive waste treatment is gaining worldwide attention due to the harmful effect of radiation associated with these wastes to human health and environment [4]. Several techniques such as ion exchange, solvent extraction, adsorption and electrochemical treatment have been used to remove these hazardous pollutants [5]. Among these, adsorption has been proven to be a successful method for removal of radioactive materials from wastewater. This technique is highly effective, inexpensive, availability and easy to operate compared to other techniques [6-7].

Clay is a naturally occurring earth’s subsurface material composed primarily of fine-grained minerals, which has high plasticity index when moist and become hard when dried or fired [8]. Clay
and clay minerals play an important role in the environment and can be used as an effective adsorbent for the removal of radioactive materials in water solution. The use of clays as adsorbent has significant advantages in terms of low production cost, availability, non-toxic nature, high specific surface area and excellent adsorption properties [9]. In addition, clays also have great potential for ion exchange (cations and anions) mechanism, thus, many researchers and scientists worldwide has focused on the use of natural or modified clay materials as an adsorbent for water treatment [10].

The main goal of this review is to provide detailed information on natural or modified forms of clay minerals and their excellent adsorption capacities for various radioactive materials such as Thorium, Uranium and Caesium from aqueous solution. This review presents the characteristic and classification of various types of clay minerals, current research literature on adsorption studies using Bentonite, Kaolin and Zeolites as an absorber, and a descriptive analysis of their adsorption behaviour using X-ray Diffraction (XRD).

2. Properties and classification of clays
Clay has a variety of physical properties such as plasticity, hardness, fineness of grain, shrinkage under fire and under air-drying, colour after firing and catalytic properties [11]. Clays and clay minerals have small particle size and complex porous structure with high specific surface area, which allows strong physical and chemical interactions with dissolved species. These interactions are due to the electrostatic repulsion, crystallinity and adsorption or specific cation exchange reactions [12].

Grim (1962) proposed a classification of clay minerals to outline the nomenclature and differences between various clay minerals. According to Grim, the major groups of clay minerals are kaolinite, montmorillonite, and illite. Almost, all clays composed of one or more members of these three groups [13]. Figure 1 shows Grim’s classification and lattice structure of clay minerals [13].

Figure 1. Classification of clay minerals according to Grim.
Clays are hydrous aluminosilicates which composed of mixtures of fine-grained clay minerals, crystals of other minerals and metal oxides [14]. On the basis of such qualities, clays are variously divided into classes or groups such as kaolinite, mica (illite), vermiculite, smectites (montmorillonite), chlorite, and pyrophyllite (talc) as shown in Figure 2 [15].

![Figure 2. Clay minerals; (a) kaolinite, (b) mica (illite), (c) vermiculite, (d) smectite (montmorillonite), (e) chlorite, and (f) pyrophyllite (talc).](image)

2.1. Structure of clays

The structure of some most important clay minerals is briefly summarised as follows:

- **Kaolinite** structure possesses great advantages in many processes, due to its high chemical stability, cation exchange capacity, and low expansion coefficient [16]. Kaolinite layers composed of one tetrahedral sheet linked to an octahedral sheet. Therefore, they classified as 1:1 type layer silicates. The structure of kaolinite is a tetrahedral silica sheet, alternating with an octahedral alumina sheet (Figure 3a).

- **Montmorillonites (Smectite)** have a 2:1 layer structure consist of an octahedral alumina sheet sandwiched between two opposing tetrahedral silica sheets [17]. (Figure 3b).

- **Illites** are also 2:1 type minerals, but the interlayers are bonded together with potassium ion (K+) to satisfy the charge and lock the structure [18]. (Figure 3c).

![Figure 3a. Kaolinite (1:1)](image)
Figure 3. Diagrammatic representation of crystal structures (a) Kaolinite (b) Montmorillonite (smectite) (c) Illite.

3. Cases study (Research literature)

The use of natural and modified clay as a potential adsorbent in the removal of metal ions from aqueous solution have been extensively studied for many years [19-21]. There are three types of clay that has been focused in this review which are Bentonite, Kaolin and Zeolites, as adsorbents for uptake of Uranium, Thorium and Caesium from aqueous solution.

3.1. Bentonite

Bentonite has attracted great interest in nuclear waste management due to its high swelling property, good self-sealing ability and cation exchange capacity [22]. Bentonite is also used as buffer or backfill material according to its function and location in the nuclear waste disposal field [23].

Khalili et al. studied the sorption behavior of purified Jordanian bentonite towards UO$_{2}^{2+}$ and Th$^{4+}$ metal ions in aqueous solutions using both batch and column techniques [17]. The main objective of this study was to investigate the sorption capability of purified Jordanian bentonite at different pH (i.e. 1.0, 2.0, and 3.0), at different temperatures (i.e. 25°C, 35°C, and 45°C) and at different contact times (i.e.). The purification of raw bentonite was done by the removal of quartz. This include mixing the raw bentonite with water and then centrifuge it at 750 rpm, the process being repeated until white purified bentonite is obtained. XRD technique is used for the characterization of purified bentonite.

The characteristic XRD peaks for the minerals in raw bentonite are shown in Table 1. Raw Jordanian bentonite consists of montmorillonite (M) as major clay mineral, whereas quartz (Q) and calcite are present as impurities, as well as anorthite is present as minor constituent. The XRD patterns for raw bentonite and purified bentonite (stirring with distilled water) are shown in Figure 4.
Table 1. The major XRD peaks for raw bentonite.

| Mineral                  | $2\theta$ | $D$ (Å) |
|--------------------------|-----------|---------|
| Montmorillonite (bentonite) (M) |           |         |
|                          | 19.89     | 4.457   |
|                          | 35.36     | 2.536   |
|                          | 40.30     | 2.236   |
|                          | 61.84     | 1.499   |
| Quartz (Q)               | 20.88     | 4.251   |
|                          | 26.67     | 3.340   |
|                          | 50.18     | 1.817   |
| Anorthite                | 13.71     | 6.452   |
|                          | 21.98     | 4.041   |
|                          | 28.43     | 3.137   |
| Calcite                  | 29.84     | 2.991   |

Figure 4. XRD patterns for (I) raw bentonite and (II) purified bentonite, M: montmorillonite, Q: Quartz, and C: calcite.

From their experiments, the Jordanian bentonite has shown high metal ion uptake capacity toward uranium(VI) than thorium(IV). The influence of different pH on metals uptake also showed that the metal ion uptake by bentonite increased with pH and reached a maximum at pH = 3 for Th$^{4+}$ and UO$^{2+}$ as shown in Table 2. The maximum absorption capacity of bentonite was high for Th$^{4+}$ and the extent of metal ions uptake followed the order: Th$^{4+}$ > UO$^{2+}$ at pH = 3 and 25°C. The equilibrium for each metal ion on the surface of bentonite occurs at 18 hours to achieve maximum uptake level.
Table 2. Uranium(VI); and Thorium(IV) percentage uptake by bentonite at pH 1.0, 2.0 and 3.0 at 25°C and concentration 50 ppm.

| pH | Percentage Uptake By Bentonite | Uranium(VI) | Thorium(IV) |
|----|--------------------------------|-------------|-------------|
| 1  | 40%                            | 57%         |
| 2  | 55%                            | 75%         |
| 3  | 81%                            | 78%         |

3.2. Kaolin

A number of studies on kaolin and kaolinite used to adsorb metal ions from aqueous solution have been reported [24-27]. The most common mineral in the kaolin group of minerals is kaolinite. Typically, kaolinite has a low cation exchange capacity (CEC), which is 0.03–0.15 meq/g [28][29]. Although kaolinite has low CEC, their adsorption capacity can be improved if chemically modified [30-31].

A study conducted by Wang et al. (2009) proved that the modified kaolin has greatly enhanced the adsorption of uranium (VI) [17]. They modified kaolin by calcination process and followed by acid-activation. The modified kaolin samples were dispersed in uranium(VI) solution of a given concentration and pH value for 1 hour at 25 °C, then centrifuged at 4000 rpm for 10 minutes. The adsorption capacity of modified kaolin for uranium(VI) increased with the contact time and reached adsorption equilibrium within 60 minutes (Table 3). Compared with natural/non-modified kaolin, the adsorption was strongly increased after modification. The adsorption also increased with increasing pH as shown in Table 4. Calcined and acid-activated kaolin is a favorable adsorbent for uranium(VI) removal from aqueous solutions.

Table 3. Influence of contact time on the adsorption of uranium (VI) \([\text{UO}_2^{2+}\] =20 mg/L, Adsorbent mass=50 mg, pH=5.0, T=25 °C).

| Time (min) | Absorption capacity (mg/g) |
|------------|----------------------------|
| 10         | 2.70                       |
| 20         | 3.00                       |
| 30         | 3.25                       |
| 40         | 3.30                       |
| 50         | 3.35                       |
| 60         | 3.40                       |
Table 4. Influence of pH on the adsorption of uranium (VI) $[\text{UO}_2^{2+}] = 20 \text{ mg/L}$, Adsorbent mass=50 mg, T=25 °C).

| pH | Removal efficiency |
|----|--------------------|
| 2  | 4%                 |
| 3  | 6%                 |
| 4  | 32%                |
| 5  | 53%                |
| 6  | 65%                |
| 7  | 70%                |

3.3. Zeolite

Zeolite is a natural and synthetic hydrated aluminosilicates with a three-dimensional framework. Along with the isomorphous replacement of Si by Al, negative charges are generated, and zeolites have the capacity to adsorb metal cations including heavy metal cations [32-33].

Johan et al. conducted a Cs⁺ adsorption experiment using two natural zeolites, namely mordenite and clinoptilolite [21]. Similar experiments were also performed using synthetic zeolite A, synthetic zeolite X, and artificial zeolite Na-P1 as references. Synthetic zeolite A and zeolite X were purchased from WAKO pure chemicals industry, Japan. Meanwhile, Na-P1 was an artificial zeolite made from coal fly ash by mixing 10.0 g of coal fly ash with 80 mL of 2M NaOH, followed by heating at 100 °C for 24 hours.

The purpose of this study was to investigate the potential of natural zeolites on the adsorption of radioactive Cs⁺. The results show that the CEC of the natural zeolites was much lower compared to the synthetic and artificial zeolites as shown in Table 5. The higher CEC of the synthetic zeolites (zeolite A and zeolite X) is due to the lower Si/Al ratios (around 1.0 to 1.2) and higher crystallinity, as shown in the XRD patterns of Figure 5. On the other hand, the lower CEC of the natural zeolites is due to their higher Si/Al ratios and impurities contained.

Table 5. CEC values of the zeolite samples.

| Zeolite samples | CEC (cmol kg⁻¹) |
|----------------|----------------|
| Mordenite      | 266            |
| Clinoptilolite | 211            |
| Na-P1          | 325            |
| Zeolite A      | 615            |
| Zeolite X      | 556            |
Although the CEC of the natural zeolites was much lower compared to the synthetic and artificial zeolites, the adsorption capacity of Cs$^+$ was much greater than the synthetic and artificial zeolites as illustrated in Figure 3. The order of the adsorption capacity of Cs$^+$ was mordenite > clinoptilolite > Na-P1 >> zeolite A > zeolite X. It indicates that natural zeolites are promising materials in the removal of radioactive Cs$^+$. 

4. Discussions
Adsorption is one of the most important processes of metal uptake with several properties that take place at the mineral-solute interface. The performance of clay materials and the adsorption process in the reported studies have been verified by examining the effect of various factors such as pH, temperature, contact time and initial concentration. From the experiment conducted by Khalili et al. [19], the influence of different pH on metals uptake indicated that the metal ion uptake by bentonite increased with pH and reached a maximum at pH = 3 for Th$^{4+}$ and UO$_2^{2+}$. Meanwhile, experiment conducted by Wang et al. [20], showed that the adsorption of uranium(VI) by modified kaolin also increased with increasing pH at pH = 7. In terms of contact time, the equilibrium for each metal ion on the surface of bentonite occurs at 18 hours to achieve maximum uptake level. Meanwhile, the adsorption capacity of modified kaolin for uranium(VI) increased with contact time and reached adsorption equilibrium within 60 minutes. In most of the reported works, adsorption experiments that were conducted by using the batch technique have confirmed their applicability and selectivity of the maximum adsorption capacities towards targeted pollutants [19].

Many clay materials have shown their excellent potential for the removal of metal pollutants without any modifications, but in many studies, their removal capacities can be improve through certain chemical modifications as discussed in this review. Wang et al. [20] modified kaolin by calcination process and followed by acid-activation. The result showed that compared with natural kaolin, the adsorption was strongly increased after modification. Therefore, the adsorption properties also depend on the extent of chemical treatment, activation, and modification of the adsorbent.

5. Conclusion
Through the analysis of 30 papers from different clay prospect studies, many clay materials have shown their excellent potential in removing metal ions from aqueous solutions. Clay, inexpensive, locally available, and effective adsorbent material, will surely offer many promising benefits in the future. In addition, high specific surface area, non-toxic nature, excellent adsorption capacity and large potential for ion exchange give tremendous importance to clay minerals and can be demonstrated in
future research. Bentonite, Kaolin and Zeolites have shown an excellent performance in absorbing radioactive materials such as Uranium, Thorium and Caesium as strongly discussed in this review.

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Acknowledgements
The work was financially supported by GGPM-2017-042. The author express gratitude to the staffs of the Universiti Kebangsaan Malaysia (UKM) for their assistance throughout the research.