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Adsorption Studies of Radionuclides by Turkish Minerals: A Review

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Abstract: Hazardous radionuclides are produced during normal operation of nuclear power plants and research facilities. They can also be spread to the environment due to fallout from nuclear accidents and nuclear weapon tests. The removal of hazardous radionuclides and the safe management of radioactive waste are of vital necessity. Natural minerals have been widely used for the removal of heavy metals and radionuclides because of their low cost, high capacity, and radiation resistance properties. Turkey has abundant natural mineral deposits. These deposits include clinoptilolite, bentonite, montmorillonite, kaolinite, vermiculite, illite, red clay, sepiolite, diatomite, perlite, and volcanic tuff. Within the scope of this review, Turkish minerals were classified as three main groups: zeolites, clay minerals, and other minerals. The review consists of sections on the general properties of natural minerals such as zeolites and clays, the characteristics of Turkish minerals, and the adsorption performance of these minerals against some radionuclide ions (Sr, Cs, U, Th and Po).

Keywords: Adsorption, radionuclide, clay, zeolite, Turkish mineral

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INTRODUCTION

Nuclear power plants play a key role in meeting the increasing energy demand with continuous energy generation as a base load source. Liquid radioactive waste (LRW) is generated as a result of the operation, repair, and disposal activities of nuclear power plants. Removal of radionuclides from the LRW is required prior to discharge. Developments and improvements are ongoing for the safe management of radioactive waste. On the other hand, dangerous radionuclides can be released into the environment as a result of nuclear weapons tests and radiological accidents (1). ^{137}Cs and ^{90}Sr are fission products that are generated during the splitting of uranium atoms in reactor core. These radioisotopes are the major sources of heat and radiation in high-level waste (2). The half life of ^{90}Sr is about 30 years. It tends to accumulate in human bones and is considered one of the most hazardous pollutants (3). Uranium emerges as a pollutant in the environment as a result of activities from nuclear fuel cycle, use of coal, and processing of depleted uranium munitions. In addition, groundwater seeps can occur with natural erosion of igneous rocks and ore bodies (4).

Thorium is more abundant than uranium in the earth's crust. Even trace amounts of this toxic and dangerous radionuclide pose a threat to human physiology and other biological systems and can cause various diseases (5). Activities such as nuclear fuel reprocessing and exploitation of thorium-containing ores can also contribute to thorium concentrate (6). Thorium is stable at ambient temperature and therefore has low toxicity (7). However, due to the risk of thorium-containing liquid wastes to leak to the surface and mix with groundwater, this situation raises concerns for environmental safety.

Polonium is an important isotope from the uranium series (8,9). When absorbed in large quantities, even low concentrations make it one of the most dangerous radionuclides (10). ^{210}Po is a high energy (5.304 MeV) alpha emitter. It is effectively biomagnified by phytoplankton and zooplankton in the aquatic environment and enters the marine food chain (10–12).

The adsorption process is one of the most efficient methods for the treatment and removal of inorganic or organic pollutants and radionuclides from polluted water and wastewater (13). Natural sorbents such as zeolites and clay minerals are widely used in water purification processes due to their frequent occurrence in nature, low cost as compared with synthetic materials, and remarkable properties with respect to adsorption, ion exchange, and filtration. They have been employed for the removal of heavy metals and radionuclides, owing to their relatively large surface area and high adsorption capacity (14–18).

Today, sepiolite, diatomite, zeolite, industrial sand, dolomite, talc, wollastonite, kyanite, perlite, and calcite are also commercially produced in Turkey (19). Among these minerals, particularly zeolites and clay minerals have a key role in the adsorption processes. A program for the establishment and operation of a nuclear power plant in Turkey has been initiated, and the process continues with determination. The first unit of the nuclear power plant, which is under construction in Mersin Akkuyu, is expected to produce energy in 2023 (20). For this reason, it has become compulsory for Turkey to carry out necessary studies on the control and safe management of radioactive waste.

In this context, the objective of this study is to investigate the removal of the activity of radioactive waste with natural minerals obtained from deposits in various regions of Turkey. We focused on the adsorption of radionuclides such as strontium, cesium, uranium, thorium, and polonium by zeolites, clay minerals, and other minerals of Turkey. We present data in terms of adsorption conditions, kinetics, isotherm and thermodynamic studies. This review is a preliminary study on the usability of natural minerals in Turkey in the removal of some hazardous radionuclides found in radioactive wastes from energy production in nuclear power plants built in Turkey's nuclear program or that may occur as a result of radiation accidents.

TYPES OF NATURAL MINERALS

Zeolites and Properties

Zeolite minerals are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations. They are characterized by reversible hydration/dehydration abilities and exchangable cations in their structure. Zeolite minerals have aroused interest due to their ion exchange, adsorption, and molecular sieve properties as well as their geographically widespread abundance and have been used in a wide range of applications (21). The general formula for natural zeolites has been proposed as follows (22):

$$(M_x^{+}, M_y^{2+})\ [Al_{(x+2y)}\ Si_{n-(x+2y)}O_{2n}] \cdot mH_2O$$

where M^+ denotes monovalent cations with stoichiometry x, and M^{2+} denotes divalent cations with stoichiometry y. M^+ and M^{2+} are the exchangeable cations. Al and Si are the structural cations. They form the framework of the structure together with oxygen. The value of m is the number of water molecules in the structure.

Clinoptilolite is the most abundant naturally occurring zeolite among more than 40 zeolite species with a solid microporous structure (23,24). It is composed of a three-dimensional structure consisting of AlO_4 and SiO_4 tetrahedral bonded together by a common oxygen atom. The micropores in the structure are narrow enough to allow the entry and exchange of cations and water molecules (25). This ability is based on the replacement of SiO_4 by AlO_4^-. By this way, a negative charge is formed and this has to be balanced by exchangeable cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} (26). The formation of 3D crystalline structure of zeolite from primary building units (PBU) and secondary building units (SBU) along with the channels in the structure are shown in Figure 1.

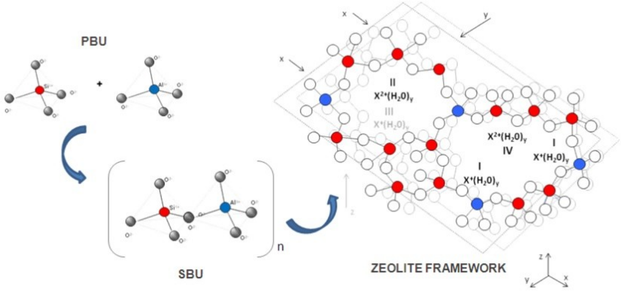

Figure 1: The structure of natural zeolite-clinoptilolite (The represented structure has been used from ref. (27)).

Natural zeolites have been investigated for their potential use in the treatment of nuclear wastewaters, municipal and industrial wastewaters (28–31), and acid mine drainage waters (32) due to their selectivity for specific cations such as Cs^+, Sr^{2+}, and NH_4^+. Their potential use in the remediation of sites contaminated with fission products such as ^{90}Sr and $^{135,\ 137}Cs$ (33–35) has also been studied. The adsorption of radionuclide ions in zeolite structure can be depicted as in Figure 2.

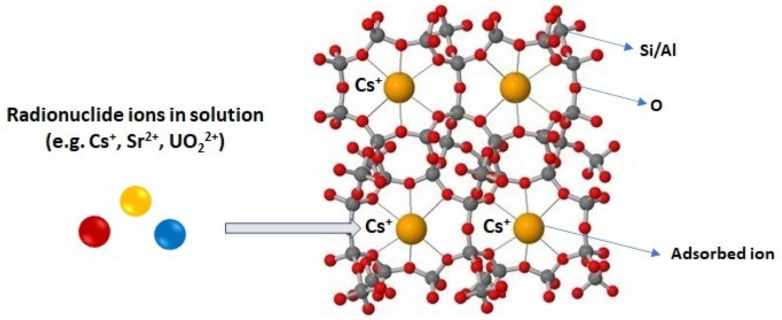

Figure 2: A simplified illustration of radionuclide adsorption in zeolite structure (The illustration has been adapted and modified from ref. (36)).

Clay Minerals and Properties

Clays are hydrous aluminosilicate structures. They consist of mixtures of fine grained clay minerals, crystals of other minerals, and metal oxides (37). Clays are classified into groups such as smectites (montmorillonite, saponite), mica (illite), kaolinite, vermiculite, serpentine, pyrophyllite (talc), and sepiolite (38). Grim (1962) was the first to propose the classification and naming of clay minerals in 1962 (39). Grim (1962) stated that the most significant groups of clay minerals are montmorillonite, kaolinite, and illite. Clays and clay minerals have high specific surface areas and porous structure. This results in interactions with dissolved species caused by electrostatic repulsion, crystallinity, and adsorption/ion exchange reactions (40).

Kaolinite has a chemical formula of $Al_2Si_2O_5(OH)_4$ and is composed of Al_2O_3 (39.53%), SiO_2 (46.53%), and H_2O (13.94%), theoretically. Kaolinite has a 1:1 layered structure consisting of a tetrahedral SiO_4 sheet and an octahedral sheet containing Al^{3+} as the cation. Hydroxyl groups located above and below the two Al atoms form a central hexagonal structure in a single plane. Although the surface charge of kaolinite is neutral, it has a small net negative charge at the fractured edges of the crystals (41,42). Kaolinite is used in the paper, ceramics, pharmaceutical, and cosmetic industries (43,44) . In addition, the use of kaolinite in water treatment is increasing rapidly. With the release of H^+ ions from the layered structure in acidic solutions, heavy metal ions are adsorbed (45).

Bentonite has an aluminum phyllosilicate structure mainly composed of montmorillonite. It is a sedimentary rock consisting of clay, with a smectite structure. Na^+, Ca^{2+} and Li^+ ions are located between its layers. The octahedral and tetrahedral sheets are in such a combination that a single layer is formed by the edges of the tetrahedra in each silica sheet and one of the hydroxyl layers in the octahedral sheet. Montmorillonites are smectite clays and are abundant in the environment. They have a chemical formula of $(Na, Ca)_{0.33}(Al, Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$ and are comprised of plate-shaped particles with an average diameter of approximately 1 μm (46). In the structure, the octahedral aluminum layer in the center was surrounded by two tetrahedral silica layers. Interactions between the sheets generally take place via –OH groups in the octahedral layer and the edges of the tetrahedral layer. Montmorillonite tends to swell due to lattice expansion caused by polar molecules such as water. In addition, interlamellar gap may be unbalanced due to cation exchange between the silicate sheets (47).

Figure 3 shows a diagram of the structure of Na-montmorillonite and the adsorption mechanism of metal ions. Si^{4+} cations in the tetrahedral layer and Al^{3+} cations in the octahedral layer are replaced by lower valence cations. As a result, a negative charge is formed. Ions such as Sr^{2+}, Cs^+, UO_2^{2+}, Th^{4+} are adsorbed by replacing exchangeable ions between tetrahedral layers and forming ion pairs with negative charge centers. Also, adsorption may occur as the complexation of metal cations on Na-montmorillonite surface (48,49).

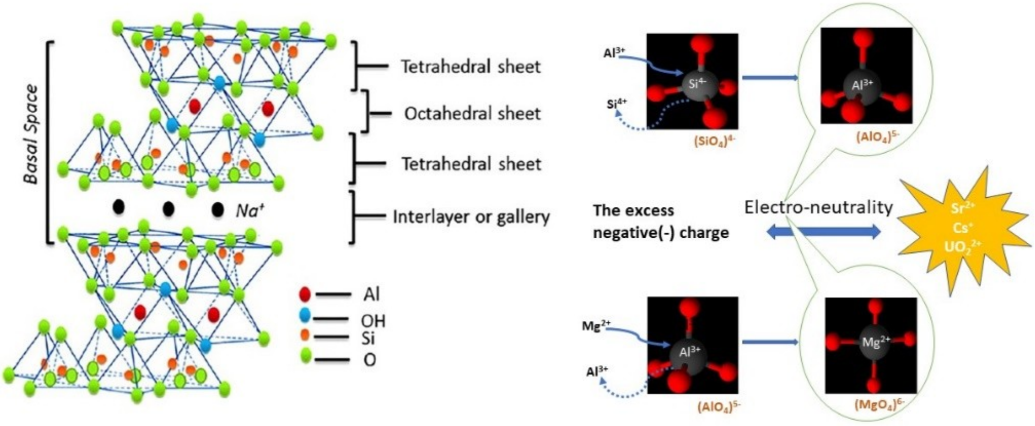

Figure 3: A general illustration of radionuclide adsorption onto Na-montmorillonite (adapted and modified from ref. (50)).

Vermiculite is a common clay mineral. It has a 2:1 aluminosilicate structure composed of a tetrahedral layer of silica and two layers of $MgO_2(OH)_4$ octahedra. Silicon is partially substituted by aluminum, and it forms a stable mica. The lack of positive charge in the parallel layers is compensated by cations in the interlayer space such as K^+, Na^+, Ca^{2+}, and Mg^{2+}. The structure formed by combining two layers in this way is called a 2:1 layered silicate structure (51,52).

Other Minerals

Perlite is an acidic volcanic glass. It expands with heat and becomes lighter and porous. Perlite rocks may differ from each other in terms of color and structural properties. Changes in the color of raw perlite can be observed from transparent light gray to bright black. In its expanded form, the color turns completely white. Perlite contains 2.5% water in its hydrated glassy silica structure, and this feature makes it stable. When perlite is suddenly heated in the range of 750-1200°C, it expands with the effect of the steam formed and aggregates into glassy particles. When it expands up to 20 times its original volume, the product known as expanded perlite is obtained. Properties that make expanded perlite commercially important include low density in small volume, physical flexibility, chemical stability, low sound permeability, and fire resistance. Perlite is used in many areas in construction, agriculture, and industry. It is used as an additive, facilitating the cementing process, as a filling material in packaging and in removing water pollution (53).

Diatomite is used as an industrial raw material. Diatomite is a rock consisting of clay, sand, volcanic ash, and other organic remains, as well as diatom skeletons, a single-celled algae species living at shallow (0-35m) depths, where photosynthesis occurs intensively in fresh and saltwater reservoirs located in regions with high volcanic activity. Diatom skeletons contain $SiO_2.nH_2O$. Diatomites are resistant to many chemicals, but are affected by strong bases at high temperatures. Diatomites, whose whiteness can go up to 90% depending on their content, find the opportunity to be used in many different areas of industry with their features such as low densities, moderate refractoriness, high absorption capacities, friability to small grain size, and high surface area value. The usage areas of diatomite products can be listed in order of importance as follows: filter aid material, filling material, insulation (heat, sound, electricity) material, adsorbent, catalyst carrier, light building material, refractory material, silica source, and regulator in fertilizers (54).

Volcanic tuff is used to express consolidated pyroclastic rocks. These rocks react with water and zeolite can be formed by the transformation of volcanic glass (55) . It is extensively used as a growth substrate for plants (56). The sorption behavior of volcanic tuffs is explained by the uptake of cations on their porous surfaces, which are connected to each other by channels. This makes tuffs an important alternative material with high selectivity for many heavy metals, toxic cations (57,58) and radionuclides (59,60) in wastewater treatment.

NATURAL MINERALS OF TURKEY

Zeolites

Important zeolite formations in our country consist of clinoptilolite, chabasite, mordenite, erionite, and analcime minerals (61). Turkey's zeolite deposits are mainly composed of clinoptilolite ores and are estimated to be around 50 billion tons. Significant clinoptilolite reserves can be found in the Balıkesir-Bigadiç and Manisa-Gördes deposits. The clinoptilolite reserve identified in the Bigadiç-Balıkesir deposit is approximately 500 million tons (62). Analcime deposits are widely distributed in Bahçecik, Gölpazarı, Göynük, Polatlı, Mülk, Oğlakçı, Avaş, Mallıhan, Kalecik, Çandır, Şabanözü, Hasavaz regions. There are clinoptilolite, chabazite, mordenite, and erionite deposits in the Kapadokya region (61).

Elemental composition of zeolites may differ according to the deposit. Table 1 provides data on the chemical composition of various types of Turkish zeolites (63–65). Results show that zeolites are composed of silica and alumina as major constituents, iron(III) oxide, calcium oxide, magnesium oxide, sodium oxide, potassium oxide and titania as minor constitutents. The loss on ignition values is relatively low, and this indicates less carbon and higher mineral content.

Table 1: Chemical composition of Turkish zeolites.

Zeolite	**Elemental composition (weight, %)**										**Ref.**
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	H_2O	Ignition loss, %	
Manisa-Gördes	69.31	13.11	1.31	-	2.07	1.13	0.52	2.83	6.88	-	(63)
Balıkesir-Bigadiç	77.96	13.17	1.06	0.08	3.80	1.53	0.16	2.20	-	-	(64)
Kütahya	67.25	14.20	1.00	0.35	2.80	1.45	0.15	5.20	-	6.95	(62)
Çanakkale-Biga	70.00	12.85	0.75	0.07	2.60	1.65	0.90	4.30	-	6.24	(65)
Çankırı-Çorum	64.85	13.70	1.01	0.30	3.30	1.00	5.50	1.00	-	9.66	(65)

Clay Minerals

The most commonly used Turkish clay minerals in adsorption studies of radionuclides are bentonite, montmorillonite, kaolinite, and sepiolite. Illite, red clay, and vermiculite are among the other clays studied.

As mentioned earlier, montmorillonite is classified under smectite group and it is the major component of bentonite. Bentonite shows stratification in an irregular manner within the magmatic rocks and volcanic units in Turkey. In the market, bentonite is sold in raw, milled bulk, and bagged and activated forms. It is known in our country as drilling, packaging, medicine, filling, casting, and bleaching types of (66). As of 2019, Turkey’s bentonite reserves (proven+probable) are 370 million tons (67). Bentonite pitches in Turkey are in Biga peninsula, Gelibolu peninsula and north, Eskisehir-Ankara regions, Çankırı-Tokat region, Ordu-Trabzon region, Kayseri-Nevsehir-Nigde region and Malatya-Elazıg. There are many bentonite deposits of various sizes in these regions and their immediate surroundings (68).

According to the Republic of Turkey Ministry of Trade report (67), Turkey's probable kaolin reserves are over 100 million tons. Kaolin deposits are located in Balıkesir, Nevşehir, Niğde, Bolu, Çanakkale and East Black Sea region. In 2017, the total export value of kaolin reached 4 million USD.

Sepiolite is a raw material whose resources are extremely limited in the world compared to other industrial minerals and whose economic deposits are only limited to Spain and Turkey. Although meerschaum type sepiolite is a mineral that has been known for centuries and is one of our traditional export products in our country, scientific research on bedded type sepiolite deposits with sedimentary formation was initiated in 1988 with the projects of the MTA General Directorate. In particular, thanks to the joint technology studies developed with the Japanese Research Institutes, a significant part of the sepiolite deposits in Turkey has been characterized (69). Turkey's industrial and layered types of sepiolite deposits that may be considered economically, are located in Eskişehir, Çanakkale, Bursa, Kütahya and Isparta (70).

Elemental composition of various types of clay minerals (66-71), obtained from Turkish deposites, is shown in Table 2. Montmorillonite, red clay and bentonite contain silica and alumina in major quantities but in addition to these, iron(III) oxide and magnesium oxide are present at major levels in the vermiculite structure. However, sepiolite is composed of only silica and magnesium oxide, with an ignition loss of 13.50%.

Table 2: Chemical composition of Turkish clay minerals.

Clays	**Elemental composition (weight, %)**									**Ref.**
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Ignition loss, %	
Kula montmorillonite	67.37	19.74	2.31	0.46	0.38	0.13	2.37	3.38	3.81	(71)
Turgutlu montmorillonite	62.86	14.80	6.20	0.82	2.68	1.63	2.84	2.29	5.66	(71)
Bandırma kaolinite	48.00	36.60	0.92	0.05	0.07	0.3	0.1	2.00	11.96	(72)
Eskişehir red clay	59.10	19.05	6.35	1.03	4.00	1.50	1.50	1.00	6.50	(73)
Eskişehir sepiolite	56.91	0.085	0.043	0.008	1.40	27.25	0.019	0.013	13.50	(74)
Çankiri bentonite	60.32	14.78	4.90	-	3.90	2.20	3.05	1.48	9.20	(75)
Sivas-Yıldızeli vermiculite	36.3	14.8	12.4	2.70	4.20	14.6	0.3	4.80	9.10	(76)

Other Minerals in Turkey

Perlite

The world's largest perlite producers are Turkey, Greece, and the United States, with 41, 26, and 18%, respectively. The perlite reserve in Turkey has the potential to contribute significantly to the economy. It is estimated that the world's perlite reserves are around 8 billion tons (77), and 5.7 billion tons of this amount is in Turkey (Industrial Raw Materials Coordinator Mustafa Kırıkoğlu, MİGEM (General Directorate of Mining Affairs), in Turkey). It has been reported that perlite in Turkey contains SiO_2 in the range of 71-75% and Al_2O_3 in the range of 12-18% as main constituents (78).

Diatomite

Turkey's diatomite reserves are generally in the form of beds suitable for open pit production. Before starting the operation, the production method is determined by determining the quality and size through drilling, and production is ensured by excavating and transporting machines. The humidity of the diatomite, whose humidity is up to 50%, is transferred to the facilities by reducing the humidity in the field by open field drying. Mining cost in the production of finished goods is around 10%. In the facilities, production is carried out with appropriate processes selected according to the usage areas of diatomite. Turkey Sugar Factories Inc., In order to obtain filtration products in sugar production, a pilot plant was established in 1974. The plant started production in 1980, and the plant was closed in 1994 as perlite was used instead of diatomite. Diatomite consumption areas are generally defined as 66% filtration industry, 21% filling, 1% insulation, and 12% other uses (54).

Volcanic Tuff

Volcanic tuff deposits are widely distributed in Turkey (79). Tertiary and quaternary-age volcanic rocks cover approximately 155,000 sq. km of area in the country, including tuffs. Studies were conducted on the geology of the quaternary volcanic centers in eastern Turkey and the chemical and mineralogical compositions of the Tendurek tuffs (80).

ADSORPTIVE REMOVAL OF RADIONUCLIDES BY TURKISH MINERALS

The removal of hazardous metal ions by natural minerals via adsorption technique offers simplicity and low investment cost. Figure 4 demonstrates the basics of experimental procedure used for radionuclide removal using adsorption.

In the adsorption studies of radionuclides using Turkish minerals, mostly zeolite and clay minerals have been reported. However, a few studies have also been carried out with diatomite, volcanic tuff and perlite. The majority of the studies reported in this context have focused on the removal of strontium, cesium, and uranium ions. Studies on thorium and polonium adsorption have also been mentioned. In some of the studies, the inactive isotope of the radionuclide to be removed was used, while in some studies, experiments were carried out by adding radioactive tracers. For this reason, studies may contain differences in terms of experimental steps of batch method, elemental analysis techniques used, and outputs obtained. The main focus is to reveal the adsorption performance of Turkish minerals depending on the effecting parameters such as pH, contact time, radionuclide concentration, and temperature. The data obtained as a result of examining the adsorption isotherms, kinetic and thermodynamic behaviors of minerals are presented.

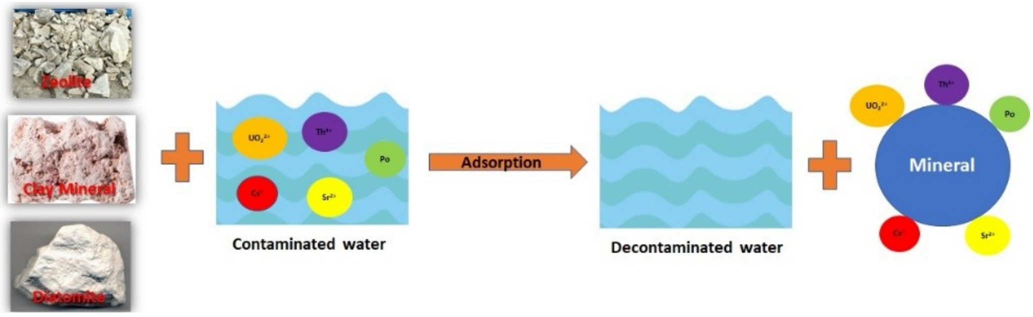

Figure 4: Illustration of adsorption process for the removal of radionuclides from contaminated water using natural minerals as adsorbent.

Adsorption studies by zeolites

Natural zeolites

Manisa-Gördes zeolite is one of the most reported zeolties. There are 18 million tons of natural zeolite reserves in this area. Uranium adsorption onto Manisa-Gördes zeolite was studied by Kilincarslan and Akyil (63). The influence of process parameters such as initial uranium concentration, pH, contact time, and temperature was investigated. The authors reported that they determined the maximum adsorption efficiency at 125 µg/mL when the uranium concentration was increased from 25 to 175 µg/mL. It is also reported that the uranium sorption is strongly pH dependent and is favored by weakly acidic value. Maximum adsorption efficiency was observed at pH 5. The adsorption of UO_2^{2+} ions increased with increasing pH up to pH 5 and then started to decrease at higher pH values. The dominant species in the solution are as follows: free uranyl ion up to pH 6, UO_2OH^+ at pH 5, and $UO_2(CO_3)_3^{4-}$ in the range of pH higher than 7. From pH 4 to pH 8, the predominant uranium complex would be the neutral $UO_2CO_3^0$ (81). Equilibrium was reached within 120 min. The adsorption efficiency of uranium on Manisa-Gördes zeolite was found to be 83 ± 1.8% at optimum conditions. The adsorption isotherm is used to describe the adsorption process and evaluate the adsorption capacity. It can be defined as the ratio of the metal concentration in the adsorbent phase to the metal concentration in the liquid phase at a given temperature (82). Uranium adsorption behavior of zeolite were best described by the Langmuir adsorption model (R^2=0.9218). The data obeying Langmuir isotherm indicate transfer of uranium(VI) from aqueous solution to the surface of zeolite as adsorption and bond formation between uranium(VI) and adsorbent may be chemical in nature. The value of E was calculated as 11.18 kJ/mol from D-R isotherm.

In another study carried out with Manisa-Gördes zeolite, Atun and Bodur (83) investigated Cs sorption using mixtures of zeolite and commercial bentonite in different proportions. ^{137}Cs was spiked as a tracer and experiments were carried out in NaCl solutions of different concentrations. Cs sorption parameters such as K_d, X, and X_m for zeolite were higher than those found for bentonite at all conditions. The observed K_d(mix) values were smaller than calculated K_d(mix) values except at 1 mol/L NaCl. In the study, it is stated that sorption is achieved by settling 3.45 Å Cs ions in the main channel of the zeolite, which has a cavity size of approximately 3.50 Å. While adsorption in bentonite with decreasing NaCl concentrations was compatible with both Freundlich and D-R isotherms, the situation in zeolite fitted with D-R at all concentrations and Freundlich isotherm at only low concentrations. K_d values increased with increasing zeolite fractions.

Sorption studies of strontium on Manisa clinoptilolite and Sındırgı kaolinite were conducted by Akar et al. (84). Kinetic studies were performed between 5 and 2880 min of contact time. The initial pH of the solution was kept in the pH range of 6.2 to 7.7. The sorption process followed pseudo second order kinetics. Isotherm data were explained well with Freundlich and Dubinin–Radushkevich isotherm models. Clinoptilolite showed a higher strontium sorption capacity than kaolinite. Thermodynamically, the activation energy of Sr^{2+} sorption by clinoptilolite was −18.4 kJ/mol. The sorption process was spontaneous and endothermic at all the studied concentrations, with ΔH^o being 9.8 kJ/mol for sorption on clinoptilolite.

Osmanlıoğlu (30) focused on the performance of natural zeolite as a sorbent for the disposal of low level liquid waste from Cekmece Waste Processing and Storage Facility (CWPSF). The batch ion-exchange capacities of the five different zeolites (Polatlı-Ankara, Bigadiç-Çanakkale, Saphane-Balıkesir, Gediz-Kütahya) and Gördes-(Manisa) in Turkey were tested for ^{137}Cs, ^{60}Co, ^{90}Sr, and ^{110m}Ag. Gördes zeolite was found to be the most suitable sorbent for LLW for radionuclides. The decontamination factors (DF) of natural zeolites for ^{137}Cs at different pH levels were investigated. It was determined that DF of the natural zeolites is very good for ^{137}Cs at pH is about 10. Stored liquid waste in storage tanks was transferred from the collection tank to the precipitator for developing precipitation strategy. At this stage, natural zeolite (particle size 0.5 mm) has been added from dosage tanks and pH has been increased to 10. Then, after settling of the sludge, the clarified solution was pumped to decantation tank. With this treatment, a decontamination factor of 430 has been achieved by using 0.5 mm clinoptilolite at 303 K.

Hicsonmez et al. (85) removed ^{209}Po using a natural zeolite mineral from Manisa-Gördes, Turkey. Polonium is one of the most significant isotopes in the uranium series (8,9). It is very dangerous, even at low concentrations, when absorbed in high enough quantities (10). The effect of initial ^{209}Po activity concentration was investigated in the range of $1.85x10^{-10}$ to $1.85x10^{-9}$ Ci/mL. The adsorption efficiency slightly increases as the initial polonium activity concentration increases. When the pH of the solutions was increased from 2 to 8, the adsorption removal efficiency of ^{209}Po onto zeolite quickly decreased from 90 to 20%, so pH had an important effect on the adsorption of ^{209}Po. The results demonstrate that adsorption process is rapid and effective. The authors found that the ^{209}Po adsorption efficiency is 90 ± 2% at optimal experiment conditions (pH<3, 298 K and 40 min of contact time). The adsorption data were compatible with both Freundlich (R^2=0.92) and Dubinin-Raduskevich (R^2=0.92) isotherms. Freundlich isotherm assumes that the adsorbent surface is coated as multilayers (86). Activation energy (Ea), calculated as 0.1008 J/nmol, indicates that the interaction between polonium and zeolite occurs through physical adsorption. When comparing polonium's K_d values with other minerals, they said that the barrier material has very good performance and selectivity for the adsorption of polonium ions with a K_d value of $4.5x10^2$ L/g. The results show that polonium adsorption onto the zeolite is very fast and effective.

Akyuz (65) investigated Cs^+ and Sr^{2+} sorption capacity of zeolite samples obtained from Kütahya, Çanakkale-Biga, Çankırı-Çorum and Manisa-Demirci regions of Anatolia. Na and Ca content of Çorum zeolite is higher than the others, whereas the Si content is less. The natural zeolites (100 mg) had been treated with 0.1 mol/L solutions of Cs^+ and Sr^{2+} chlorides, in bottles at room temperature for one day. Chemical analysis of the washed and dried filtrates was performed on an EDXRF spectrometer. The author has indicated that the Clinoptilolite type zeolite from the deposits of Çankırı-Çorum Basin was the best sorbent for both Cs^+ and Sr^{2+} ions and it can be used for the treatment of radioactive waste water. Chemical analysis also proved the superiority of Çankırı-Çorum clinoptilolite for Cs^+ and Sr^{2+} ions.

Olmez Aytas et al. (64) reported a study dealing with the adsorption of uranium on clinoptilolite-rich zeolite from Bigadiç-Turkey. Before the adsorption studies, clinoptilolite-rich zeolite ($(Na_6(AlO_2)_6(SiO_2)_{30})\cdot 24H_2O$ (Si/Al:5) was treated with 0.1 mol/L HCl at room temperature. The authors compared the U(VI) adsorption capacities of zeolites in granular (32-48 mesh) and powdered (below 200 mesh) form. The results showed that powdered zeolites exhibited greater adsorption capacities compared with the granular form. Cation exchange capacity was found to be 1.70 mmol of H^+/g of the natural zeolite. The influence of pH on adsorption was investigated in aqueous solutions from pH 2.0 to 9.0. High adsorption capacity at pH 2 is explained by the displacement of H^+ ions and uranyl ions in the active sites. The adsorption efficiency values decreased with the increase in temperature. Uranium adsorption behavior of zeolite was best described by the Langmuir isotherm model (R^2=0.967). In addition, the leachability of uranium has been studied. Zeolite samples were calcined at 873, 1073, 1273, and 1373 K. The leachability of uranium decreased with increasing calcination temperature. The authors stated this situation as an advantage of possible application for the storage of uranium in radioactive wastes.

Yıldız et al. (87) have studied the sorption behavior of Cs^+ ions onto kaolinite (Bozhöyük, Bilecik), bentonite (Çankırı) and zeolite (Bigadiç, Balıkesir). A ^{137}Cs tracer was added to simulated ground water. In all samples, equilibrium was reached in about 2 days at 5°C. Zeolites with crystalline and hydrated aluminosilicates contain regular channels or interlinked voids whose diameters are in the micropore range, depending on the structure type. Because the size of Cs^+ ion is suitable for these channels, the sorption order of cesium ion was found to be zeolite>bentonite>kaolinite. On kaolinite, there are no cations in the interlayer space and only surface bonding of cations occurs. In the adsorption experiments, the higher distribution ratios were obtained with lower Cs^+ concentrations. From the fitting of Freundlich isotherm model, the value of *k* constant was calculated as 0.8019, 7867, and 0.0916 in the order of bentonite, zeolite, and kaolinite. Desorption studies were performed to check the reversibility of the sorption of Cs^+ on bentonite, zeolite and kaolinite. In all cases, there was no significant activity, indicating that the sorption process was irreversible. From this study, it was suggested that these minerals can be used as backfill materials in geological repositories for the storage of ^{137}Cs containing radioactive wastes.

Modified Zeolites

Yusan and Erenturk (88) prepared PAN/zeolite composite for the adsorption of strontium from aqueous solution. The zeolite was obtained from Manisa-Gördes/Turkey. The percentage of adsorption increased with increasing strontium concentration (25-175 µg/mL) and remained almost constant at 150-175 µg/mL range. pH tests showed that the adsorption efficiency of Sr(II) on PAN/zeolite increased up to pH 5. The pH of the solution was an effective parameter in Sr adsorption. The uptake of Sr slightly increased with increasing contact time, and 20 min was sufficient for equilibrium. Various adsorption models were tested and it was found in the following order: Temkin>D-R>Freundlich>Langmuir. According to D-R model, X_m and the mean free energy (E) were determined to be 6.47 mmol/g and 0.91 kJ/mol, respectively.

Akyıl Erenturk and Kılıncarslan Kaygun (89) reported batch sorption studies of ^{210}Po from aqueous solution using the composite zeolite/PAN (Manisa-Gördes, Turkey). In order to work with zeolite in the column, a granular composite adsorbent has been prepared by mixing polyacrylonitrile (PAN) in a flask with reflux as a reactor. The effective parameters such as initial activity concentration of ^{210}Po, pH of the aqueous solution, contact time, and temperature were examined in a column system. Unlike natural zeolite, the highest adsorption levels (66.7%) for zeolite/PAN adsorbent was found between pH 4.0 ± 0.1 and 6.0 ± 0.1. Adsorption efficiency of ^{210}Po onto composite adsorbent was determined as 75.00 ± 0.15% in optimum conditions. Experimental equilibrium data was well fitted and found to be in good agreement with the Temkin model. Temkin isotherm explains the interaction between the adsorbent and adsorbate molecules. This model assumes the following conditions: adsorption heat of all molecular interactions is linear rather than logarithmic, and there is a uniform distribution of binding energies (90–92). Adsorption thermodynamics and kinetics of polonium were studied. It was found that the process for ^{210}Po was exothermic.

As can be seen from the above studies, Manisa-Gördes zeolite and its composite were used for the removal of uranium, cesium, strontium, and polonium ions from aqueous solutions. pH of the working solutions had a remarkable effect on the adsorption behaviours. The highest removal efficiencies of uranium and polonium were obtained at pH=5 and at pH<3, respectively. Unlike natural zeolite, the maximum adsorption efficiency of the zeolite based composite for polonium between pH=4-6. In addition, at pH=5, strontium adsorption efficiency was maximized using the same composite.

Due to the affinity of polyacrylonitrile (PAN) for uranium ions, a mineral/polyacrylamidoxime (PAO) with modification of polyacrylonitrile was prepared by Şimşek and Ulusoy (93). They obtained bentonite (B-PAO) and zeolite (Z-PAO) composites. Ion concentration, temperature, and contact time on the adsorption of Pb^{2+} and UO_2^{2+} were investigated. It has been found that the adsorption capacities of B/Z-PAO composites are higher than those of pure PAO, and their K_L values increase in the order of Z-PAO>B-PAO>PAO for two ions, particularly for U(VI). This situation has been explained by the authors with two effects. Initially, the additional electrostatic force contribution present in the negatively charged Si-O and Al-O minerals of the amidoxime terminals significantly increases the electrostatic attraction for the cations. Consequently, the choice of UO_2^{2+} should probably be related to the high stability of complexes formed with uranil ions and to the active sites of PAO and/or minerals. On the other hand, it has been determined that the monolayer adsorption capacity of the adsorbents for UO_2^{2+} was lower than that of Pb^{2+}. Because, the required number of chelating amidoxime terminals for UO_2^{2+} (94) was greater than that of Pb^{2+}. 1 mol/L HCl has been used as a regeneration solution. After five sequential treatments, it was observed that there was no change in the B-POA and Z-POA structures, but the PAO gelled completely on the first use. Table 3 summarizes the reported use of Turkish zeolites for radionuclide removal.

Adsorption studies by clay minerals

In this section, kaolinite, montmorillonite, bentonite, sepiolite, illite, red clay, and vermiculite type clay minerals have been reported for the adsorptive removal of various radionuclides.

Strontium sorption studies on kaolinite using radiotracer technique were conducted by Keçeli (95). Kaolinite based clay sampes were obtained from Çanakkale-Çan region of Turkey. The composition of the clay was; 90% kaolinite, 9% free quartz, and 1% other impurities such as Na- and K-feldspar. Kinetic and equilibrium studies were performed by batch experiments and adsorption data were evaluated by adsorption efficiency (%), uptake capacity (q) and distribution coefficient (K_d) values. According to Keçeli (95), capacity, affinity, and selectivity results obtained in this study demonstrate that the locally available kaolinite mineral can be successfully used for selective sorption of Sr radionuclides in waste disposal sites.

Data on the effect of temperature on the adsorption of radionuclides with Turkish zeolites, discussed in the text, are given in Table 4.

Table 3: Data on adsorption performance of Turkish zeolites for radionuclide ions.

Adsorbent	**Target radionuclide**	**Metal Concentration**	**Initial pH**	**Contact time (min)**	**Removal efficiency (%)**	**Ref**
Manisa-Gördes zeolite	Uranium	25-175 µg/mL	2-9	5-420	82.9	(63)
Manisa-Gördes zeolite	Cesium	$5x10^{-5}$-$5x10^{x2}$ mol/L	-	420	-	(83)
Manisa clinoptilolite	Strontium	10-500 mg/L	6.2-7.7	5-2880	-	(84)
Manisa-Gördes zeolite	Polonium	-	2-8	40	90.0	(85)
Manisa-Gördes zeolite/PAN	Strontium	25-175 µg/mL	2-8	5-300	84.6	(88)
Manisa-Gördes zeolite/PAN	Polonium	-	4-6	1-180	75.0	(89)
Balıkesir-Bigadiç clinoptilolite-rich zeolite	Uranium	10-100 mg/L	2-9	5-360	88.0	(64)

Table 4: Effect of temperature on the adsorption of radionuclides by Turkish zeolites.

Zeolite	**Target radionuclide**	**Temperature range (K)**	**Adsorption process**	**Ref.**
Manisa-Gördes zeolite	Uranium	293-323	Endothermic	(63)
Manisa-Gördes zeolite	Polonium	293-323	Endothermic	(85)
Manisa clinoptilolite	Strontium	298-333	Endothermic	(84)
Manisa-Gördes zeolite/PAN	Strontium	293-323	Exothermic	(88)
Manisa-Gördes zeolite/PAN	Polonium	293-323	Endothermic	(89)
Balıkesir-Bigadiç clinoptilolite-rich zeolite	Uranium	293-303	Exothermic	(64)

Erten et al. (96) studied sorption characteristics of Cs^+ and Sr^{2+} on Reşadiye montmorillonite and Mihaliççık kaolinite type clays and soil fractions from various regions of Turkey using the batch method. ^{137}Cs and ^{90}Sr were used as tracers. The initial concentrations ranged from 10^{-8} to 10^{-2} mol/L. Chemical composition of clay species, water composition, and the properties of the sorbent affect the sorption beahaviours of Cs^+ and Sr^{2+}. Equilibrium was reached in 4-7 days for Cs^+ and 7-11 days for Sr^{2+}. K_d values of Mihaliççık kaolinite for Cs^+ and Sr^{2+} were obtained to be 200 and 100 mL/g, whereas K_d values of Reşadiye montmorillonite for Cs^+ and Sr^{2+} were found to be 3500 and 1500 mL/g, respectively. The experimental data reveals that montmorillonite clay adsorbs Cs^+ and Sr^{2+} much more than kaolinite clay due to their different structural characteristics. The distribution coefficients increased with decreasing grain size, suggesting mainly surface sorption.

In another study, sorption and desorption behaviors of uranyl ion on Turgutlu and Kula montmorillonites were studied by Akçay and Kurtulmuş (71). The experimental data has shown that pH, solid/aqueous ratio, uranyl concentration, and clay particle dimension could have a significant impact on the sorption of uranium. The influence of contact time was investigated up to 50 h when soil/aqueous ratio, temperature, and pH were kept at 1/2, 293 K and 7.3, respectively. A contact time of 10 h was found sufficient for the establishment of equilibrium. The effect of clay size was examined when the other parameters were kept constant. +0.1 – 0.2 mm dimension range showed the maximum asdorption performance. The effect of initial uranium concentration was studied between 200 and 3000 mg/L. With the increase in the concentration, uranium uptake capacity of both clays increased. Kula clay has higher uranium uptake capacity than Turgutlu clay. pH studies were carried out in acidic (pH=3-6), neutral (pH=7) and basic medium (pH=8-10). In the acidic region, hydrogen ions were competing for cation exchange sites, and uranium uptake was relatively low. A fairly constant retention was observed in the pH range of 4-6, consistent with the ion-exchange process being dominant. In the basic region, the distribution coefficient demonstrates a gradual increase with pH. The sorption and desorption ability of uranium is defined by the distribution coefficient and Langmuir's affinity constants, which encompass surface retention. The migration of uranium will be reduced, probably due to the formation of hydrolyzed and polymeric species. Diffusion of uranyl ions into the particles probably decreases desorption tendency. The data fitted to the Freundlich equation gave a nonlinear isotherm. The quantities of sorbed and desorbed uranium ions were lower than its theoretical CEC's. This was attributed to a blocking of montmorillonites' CEC by uranium islands sorbed in the interlayer. The experimental results indicate that the montmorillonites studied should be effective components of the buffer and backfill material and lead to eventual immobilization of uranium from solutions.

Kinetic and thermodynamic parameters of Sr^{2+} sorption on Sındırgı kaolinite and Manisa clinoptilolite was investigated by Akar et al. (84). Batch tests were conducted at 25 and 60°C for a contact time range of 5-2880 min. The pH of the solution was kept in the pH range between 6.2 and 7.7. Similar trends were observed for both temperatures. The sorption process followed pseudo second order kinetics, with faster sorption on kaolinite compared to clinoptilolite. Freundlich and Dubinin-Radushkevich isotherm models described data more adequately than Langmuir model. The activation energy of Sr^{2+} sorption by kaolinite was found to be -8.5 kJ/mol. The sorption process was spontaneous and endothermic at all the studied concentrations, with $\Delta H°$ being 11.3 kJ/mol for sorption on kaolinite.

Akçay and Kilinç (97) conducted sorption and desorption studies of thorium from aqueous solutions using West Anatolian montmorillonite. The authors stated that the migration of thorium will be reduced, probably due to the formation of hydrolyzed and polymerized species. Moreover, desorption coefficients are higher, probably due to the diffusion of thorium into the particles. The sorption and desorption data were described well by the Freundlich isotherm model. The sorption of thorium on West Anatolian montmorillonite was found to be concentration dependent but nonlinear.

Akyüz et al. (73) conducted a study to investigate Cs^{+} and Sr^{2+} sorption onto Sivrihisar-Eskişehir red clay samples using EDXRF spectrometry. XRD analysis revealed that red clay is composed of montmorillonite, illite, albite, chlorite, and quartz. For the sorption experiments, cation treated clays were prepared by immersing the natural red-clay samples in Cs^{+} and Sr^{2+} bearing solutions with a concentration range of 20-400 mg/L. At low Cs^{+} or Sr^{2+} concentrations (20 mg/L) high K_d values were obtained. With the increase in inital metal concentrations, a decrease in K_d values was determined. When the cation concentration was 120 mg/L, the uptake capacities of Cs^{+} and Sr^{2+} were 5.07 and 0.88 mg/g, respectively. The authors stated that the sorption of Cs^{+} or Sr^{2+} ions on red-clay is concentration dependent but non-linear. Freundlich equation was the best to explain the relationship between the amount of Cs^{+} or Sr^{2+} adsorbed by the red-clay. From the E value of D-R isotherm model, it was found that both Cs^{+} and Sr^{2+} sorption were governed by ion-exchange. It was reported that, red clay has high affinity for Cs^{+} and Sr^{2+} and it can be considered as a promising material for nuclear waste management.

Bilgin et al. (98) studied the adsorption of strontium on illite type clay as a function of shaking time, the ratio of solution volume to weight of clay, and the concentration of strontium. ^{90}Sr was used as a tracer. Clay samples were collected from Van region in Turkey with a high percentage of illite type clay mixture. 89% of the total Sr^{2+} sorption was attained in the first 10 min. The rapid adsorption reveals that Sr adsorption on illite is an ion exchange process. K_d value decreased with increasing Sr ion concentration. The effect of the initial volume of solution to that of solid (V/m) was studied for 10^{-4} mol/L initial Sr^{2+} concentration. Initially, the K_d value increased strongly with increasing V/m up to V/m=250, whereafter a plateau region was reached. When all of the available sorption sites are covered with strontium, a further increase in the V/m ratio does not appreciably change the K_d value. the variation of the K_d value with Sr loading was investigated. The adsorption experiments were carried out using the batch method and initial Sr^{2+} ion concentrations ranged from 10^{-6} to 10^{-1} mol/L. The authors reported that, Sr is adsorbed predominantly by an ion exchange mechanism in the low Sr loadings. The shapes of the curves suggest the existence of at least two types of adsorption, one taking place at high and the other at low Sr ion concentrations. The influence of Ca^{2+} and Ba^{2+} cations on Sr adsorption was also studied. In the binary Sr-Ba system, strontium uptake capacity was 211.2 mg/g. These effects are correlated with the ionic radii of alkaline earth ions present in the solution. The Freundlich and Dubinin Radushkevich (D-R) isotherms have been applied to the data and the parameters of the isotherm equations were calculated. It was found that the experimental data fit both isotherm models well.

Donat and Aytas (75) prepared algae (*Ulva sp.)*-Na bentonite composite adsorbent for the separation of U(VI) from aqueous media. Dry and powdered algae were mixed with Na bentonite. The mixture was contacted with deionized water and then mixed to ensure homogeneity. The resulting paste was heated and dried. It was reported that the wetting and drying steps are significant to maintain the maximum contact between algae and Na-bentonite.

The influence of selected parameters such as pH, U(VI) concentration, temperature, and contact time was investigated. The influence of pH on U(VI) adsorption was studied in the pH range of 2-9. The change in solution pH affects both the surface properties of adsorbent and species in the solution. It was reported that maximum U(IV) adsorption efficiency was found at pH 3 and the uranium was in the form of UO_2^{2+}. The sorption of U(VI) was examined as a function of U(VI) concentration in the range of 10-175 mg/L. It was reported that the adsorption efficiency increased with the increase in concentration up to 125 mg/L and then a decrease was observed. Sorption isotherm data fitted Frendlich and D-R isotherm well. The effect of contact time on adsorption was studied between 7.5 and 240 min. It was determined that the sorption process was very fast and the maximum adsorption efficiency was reached within minutes. 15 min was selected as the optimum contact time. At this point, the adsorption efficiency of U(VI) was 78% ± 1.2. Thermodynamic studies were conducted between 293 and 343 K. It was found that adsorption of uranium is endothermic, spontaneous, and more favorable at higher temperatures.

Donat (74) investigated the adsorption of U(VI) from aqueous solution onto Eskişehir sepiolite by batch method. The effect of contact time was examined in the range of 15-1440 min, and 92% of the U(VI) ions were adsorbed in the first 240 min. Solution pH was investigated between pH=2.0-9.0 and sepiolite has a maximum sorption efficiency at pH 3.0. This can be explained by the presence of free UO_2^{2+} ions in the solution. The influence of U(VI) concentration was studied in the range of 100-500 mg/L and maximum U(VI) sorption capacity of sepiolite was found to be 34.61 mg/g. The sorption data fitted Langmuir isotherm well. Thermodynamic parameters indicated the exothermic heat of adsorption and the feasibility of the process. It has been stated by the author that sepiolite has the potential to replace activated carbon because it is cheap and abundant.

Eskişehir sepiolite has also been tested for the removal of Th(IV) from aqueous solution by Esen Erden and Donat (99). The influence of contact time, initial pH, Th(IV) concentration and temperature were examined using one factor at a time approach. The adsoption of Th(IV) was rapid in the initial stages and equilibirum was established in 45 min. Th(IV) removal efficiency (%) sharply increased between pH 2 and 3. Above pH 3.5, the uptake of Th(IV) decreased. It is known that when pH is >4, Th(IV) ions precipitate as $Th(OH)_4$ due to the low solubility ($K_{sp}=2.0x10^{-45}$) (100). The authors mentioned that the formation of strong surface complexes is the mechanism responsible for the sorption rather than ion exchange. Removal efficiency was 61.81% when the initial Th(IV) concentration was 40 mg/L. Langmuir isotherm demonstrated slightly better fit to the adsorption data than Freundlich and D-R isotherms with a monolayer Th(IV) capacity of 49.91 mg/g. The effect of temperature was studied in the range of 293-323 K. A positive value of $\Delta H°$ indicated an endothermic process. The spontaneity of Th(IV) adsorption could be explained by negative $\Delta G°$ values.

Bayülken et al. (101) conducted a study for the investigation of Cs^+ adsorption by Çankırı-Şabanözü bentonite, Manisa-Gördes zeolite, Eskişehir-Sivrihisar sepiolite, and Balıkesir-Sındırgı, Düvertepe kaolinite. The effects of Cs^+ concentration, pH, contact time, and temperature on the adsorption were examined using ^{137}Cs radiotracer method. Bentonite was shown to exhibit the highest capacity and sorption affinity towards Cs^+. The best fits for adsorption isotherms were with Freundlich and D-R models. The second order rate constant of cesium sorption was the highest for kaolinite among the clays. Cs^+ adsorption proceeds essentially by ion exchange and partly by specific adsorption mechanisms. The results showed that especially bentonite and zeolite can be used as effective barrier materials for sorptive hindrance of an expanding Cs^+ radioisotope plume.

Akalın et al. (76) investigated the cesium adsorption performance of raw vermiculite obtained from Sivas-Yıldızeli region of Turkey. Experiments were carried out with nonradioactive Cs^+ (CsCl). Results demonstrated that adsorbed Cs^+ ions gradually increased with the increasing adsorbent dosage and did not depend on contact time. The percentage of adsorbed Cs^+ ions at equilibrium increased with increasing pH up to pH 9.2. Maximum adsorption capacity (Q_{max}) was determined as 29.67 mg/g and 8.037 L/g from Langmuir and Freundlich isotherm models, respectively. Thereby, the adsorption process has both chemical and physical characters. In addition, the adsorption process is fitted to Temkin isotherm model. Cesium adsorption was investigated in the presence of K^+ ion and the amount of Cs^+ adsorbed at equilibrium was found to be 16.22 mg/g.

In another study, Tekdal (102) investigated the decontamination of low-level radioactive wastes containing ^{137}Cs radioisotope by using clay minerals. K_d is a parameter used to determine the ratio of ions adsorbed to the solid to the ions in the liquid phase (103). The results of these experiments were used to calculate the K_d values for the adsorption of cesium on clay minerals. In order to prepare the artificial waste solution, the ^{137}Cs isotope was provided by the Çekmece Nuclear Research Center, Health Physics Department. Five different clay samples were used as waste-retention material. These samples were collected from; No.2: Çukurova region, No.3: Konya region, No.7: Söğüt region, No.10: Söğütlü region, No.19: Çınar-Diyarbakır region. The adsorption capacities of clay samples were determined by radiometric method. For this purpose, column inlet and outlet activity measurements were made by gamma spectrometry. In all experiments, background and sample counting times were counted by taking 5 mL samples. The K_d values for clay samples are calculated to be 48.15 mL/g for sample No.2, 642.59 mL/g for sample No.10, 52.46 mg/g for sample No.7, 513.27 mL/g for sample No.19, and 380.92 mL/g for sample No.3. According to these findings, samples No.10, 19 and 3 are clay samples with the highest activity adsorbents. IR analyzes have shown that these clays are smectite group clay minerals. The selectivity of the smectite group clay minerals for ^{137}Cs is due to the fact that the odd and divalent ions in the wick change with the Cs^+ ion in addition to physical adsorption. Additionaly, the Cs^+ ion is large in ionic mobility, as it has the smallest hydrate radius (2.28 Å) and the number of hydrides (~ 9.9) in group I ions. For this reason, the ion exchanger is held in great force (Coulomb Force) by the material. The results of this study revealed that clay minerals have significant radioactivity retention capacities. This situation brings to mind the concern that clay deposits in Turkey may be used for radioactive waste storage and may threaten human health. Table 5 summarizes the reported use of Turkish clay minerals for radionuclide removal.

Adsorption studies by other minerals

Talip et al. (104) used expanded perlite for the removal of thorium ions from aqueous solution. The expanded perlite samples are the most economical commercial products and were provided by Eti Mine Works Perlite (İzmir, Turkey). Before adsorption tests, expanded perlite samples were mechanically washed in water for 24 h and used without chemical treatment. It was suggested that adsorption of thorium is mainly affected by the surface hydroxyl groups of the perlite. Silicon atoms on the surface are bonded to oxygen by forming a tetrahedral structure. They attach to monovalent hydroxyl groups and form silanol groups. Silanol and hydrous oxide groups on the surface are responsible for adsorption (105). The effects of particle size, solution pH, initial thorium concentration, contact time, V/m ratio, and temperature on the adsorption of thorium using expanded perlite were investigated. There was no significant effect of particle size on the adsorption. The adsorption efficiency (%) has been found to be strongly influenced by pH and thorium concentration. The adsorption of thorium onto expanded perlite was investigated from pH 2 to 7 at 303 K and efficiency increased from 20% to over 80% with the increase in pH from pH 3 to 5. This behaviour was explained by the adsorption of positively charged Th(IV) hydrolysis products. The influence of Th(IV) concentration was examined from 25 to 250 mg/L. After 50 mg/L Th(IV) concentration, the adsorption have been sharply decreased. The adsorption equilibrium was established within 60 min at pH 4.5. Results indicated that the temperature had a minor effect on the adsorption of thorium by expanded perlite. Maximum adsorption efficiency of Th(IV) onto expanded perlite was determined as 84 ± 4%. The adsorption isotherm was best modeled by Langmuir isotherm. The negative value of ΔG^o indicates the spontaneous and the negative value of ΔH^o shows the exothermic nature of the process. This study showed that expanded perlite can be used as an efficient adsorbent material for the adsorption of thorium from contaminated aqueous solutions, due to its high adsorption capacity, low cost, and ready availability.

Yusan et al. (106) reported a study using calcined and flux calcined diatomites for the adsorption of Th(IV) ions from radioactive waste. Diatomite samples were obtained from Turkish Sugar Factories Inc., Etimesgut-Ankara, Turkey. SiO_2 content of calcined and flux calcined diatomite were 92.68 and 89.81%, respectively. The removal of Th(IV) was affected by the alteration of solution pH. At pH 4.0, Th(IV) adsorption efficiency was maximum to be 99%. Above pH 4.0, the decrease in adsorption efficiency was observed due to hydrolization of Th(IV). Within 20 min of contact time, 98% and 89% of Th(IV) ions were adsorbed by calcined and flux calcined diatomites, respectively. The influence of inital concentration on Th(IV) uptake was studied between 25 and 150 mg/L. The adsorption data was well described by Freundlich isotherm for both adsorbents. The effect of temperature was investigated in the range of 288-328 K. $\Delta H°$ values for calcined and flux calcined diatomites were obtained as 35.99 kJ/mol and 23.62 kJ/mol, respectively. These values indicate the physical nature of the adsorption. The negative values of ΔG^o demonstrate the spontaneity of the removal process. Sorption kinetic studies were carried out to determine the possible adsorption mechanism. The authors mentioned that kinetic data fitted pseudo-second order equation better, suggesting that the rate-limiting step is chemical adsorption.

The removal of uranium from aqueous solutions with diatomite samples supplied from the same origin was investigated by Ölmez Aytaş et al. (107). Calcination and flux calcination (with Na_2CO_3 at 1650 ºC) were applied to samples to improve their mechanical properties. As a result of the preliminary tests, it was determined that the sample coded as No. 2 (Flux calcined) had the highest uranium capacity (94.82 mg/g). Further studies were performed using No. 2 (Flux calcined) sample. Adsorption efficiency of uranium was examined as a function of pH in the range of 2-7, a contact time of 24h at 303 K. Up to pH=5, authors observed a slight increase in the uranium uptake. However, uptake values decreased in the pH range of 6-7. This behaviour may be explained by the presence of UO_2^{2+} below pH 5 and stable carbonate complexes around pH 7. Within 15 min of contact time, maximum adsorption efficiency was 77% at pH 5. 97% of uranium adsorption. A decrease in the adsorption percentage of uranium was observed with the increase in temperature from 298 to 333 K. The authors suggest that the adsorption mechanism was physisorption. Langmuir isotherm model was used to describe the equilibrium between uranium and diatomite. Monolayer capacity of the adsorbent was calculated as 38.58 mg/g for uranium. Diatomite has been reported to be an inexpensive, high-affinity adsorbent for the removal of uranium from waste solutions from uranium refining and mining.

Yusan et al. (92) investigated uranium sorption on volcanic tuff collected from the deposits located at the Tendürek, Eastern Turkey. The effects of solution pH, contact time, initial uranium concentration, and temperature were investigated one factor at a time. The effect of pH was examined between 2.0 and 9.0. Other parameters were kept constant as follows: initial concentration; 100 mg/L, temperature; 303 K, and contact time; 2 h. The maximum removal efficiency of U(VI) was found to be 69% at pH 5.0. Initial U(VI) concentration parameter was studied in the range of 50-250 mg/L while the other parameters were kept constant. The adsorption efficiency increased gradually, up to 95% when the uranium concentration was 75 mg/L. Adsorption isotherm models were utilized to describe the uranium adsorption. Langmuir model was the best to explain adsorption equilibrium data. The maximum monolayer adsorption capacity was calculated as 2.62 mg/g. The effect of temperature on uranium adsorption was examined between 298 and 323 K and thermodynamic parameters were calculated. Adsorption efficiency gradually decreased from 94% to 76% with the increase in temperature from 298 to 323 K. It was reported that the positive value of ΔH^o points out that this adsorption process has an endothermic character. Moreover, the decrease in ΔG^o values with the increasing temperature indicates that the adsorption process is physisorption. The authors stated that Tendürek volcanic tuff is a naturally abundant material and it has a high capacity for the efficient removal of uranium ions from aqueous solutions.

Table 5: Data on adsorption performance of Turkish clay minerals for radionuclide ions.

Adsorbent	**Target radionuclide**	**Metal Concentration**	**Initial pH**	**Contact time**	**K_d (mL/g)**	**Removal efficiency (%)**	**Q (mg/g)**	**Ref**
Reşadiye montmorillonite	Cesium Strontium	10^{-8}-10^{-2} mol/L (Cs) 10^{-8}-10^{-2} mol/L (Sr)	-	4-7 d (Cs) 7-11 d (Sr)	3500(Cs) 1500(Sr)	-	-	(96)
Kula montmorillonite	Uranium	200-3000 mg/L	7.3	600 min	-	-	-	(71)
Sındırgı kaolinite	Strontium	10-500 mg/L	6.2-7.7	5-2880 min	-	-	-	(84)
Eskişehir red clay	Strontium Cesium	20-400 mg/L	7	1440 min		-	-	(73)
Van illite	Strontium	10^{-6}-10^{-1} mol/L	-	0-60 min	-	-	211.2	(98)
Algae (Ulva sp.)-Na bentonite composite	Uranium	10-175 mg/L	2-9	7.5-240 min	-	78.2	-	(75)
Eskişehir sepiolite	Uranium	100-500 mg/L	2-9	15-1440 min	2400	96.00	34.61	(74)
Eskişehir sepiolite	Thorium	40-150 mg/L	2-5	5-360 min	-	92.90	49.91	(99)
Sivas-Yıldızeli vermiculite	Cesium	100-300 mg/L	3-10	60-480 min	-	87.00	29.67	(76)

Data on the effect of temperature on the adsorption of radionuclides with Turkish clay minerals, discussed in the text, are given in Table 6.

Table 6: Effect of temperature on the adsorption of radionuclides by Turkish clay minerals.

Adsorbent	**Target radionuclide**	**Temperature range (K)**	**Adsorption process**	**Ref**
Sındırgı kaolintie	Strontium	298-333	Endothermic	(84)
Algae (Ulva sp.)-Na bentonite composite	Uranium	303-333	Endothermic	(75)
Eskişehir sepiolite	Uranium	298-313	Exothermic	(74)
Eskişehir sepiolite	Thorium	293-323	Endothermic	(99)
Sivas-Yıldızeli vermiculite	Cesium	298-323	Exothermic	(76)

CONCLUSION

Nuclear power generation, rare-earth mining, reprocessing, nuclear medicine, and nuclear research are the main sources of radioactive isotopes released into the environment. They are dangerous to human health due to their long half life and solubility in water. This review attempts to cover a wide range of Turkish mineral adsorbents that have been used so far for the removal of radionuclides from aqueous solutions. Based on the literature reviewed, the following concluding remarks can be made:

For Turkish zeolites;

- U(VI) adsorption was investigated using Manisa-Gördes zeolite under varying parameters (pH, initial concentration, temperature, contact time, etc.), and it was determined that alteration of pH was remarkably effective. The adsorption efficiency is 82.9% at the following experimental conditions: U(VI) concentration 125 mg/L, pH=5, contact time=2 h. The process is compatible with the Langmuir model. The E value is 11.18 kJ/mol according to D-R isotherm.

- Manisa-Gördes zeolite is very stable for ^{137}Cs in LLW at pH 10.

- pH is a significant factor for Po removal and the adsorption efficency is 90% at pH<3 with a 40 min contact time. Freundlich model is the most appropriate for fit of the experimental data, and E value is 0.1008 J/nmol.
- PAN modified zeolite is promising for Sr at pH>5 and E value was calculated as 0.91 kJ/mol from D-R isotherm. However, the composite adsorbent is effective between pH 4-6 for Po at column and E value was found to be 1.7226 J/nmol.

- The clinoptilolite type zeolite from the deposits of Çankırı-Çorum basin was the best sorbent for both Cs and Sr ions.

- The powdered form of Bigadiç zeolite treated with 0.1 mol/L HCl showed better adsorption properties for U(VI) compared to the granular form. Adsorption equilibrium data were well-fitted with Langmuir model. Uptake of U(VI) decreased with increasing calcination temperature.

- Bigadiç zeolites adsorp ^{137}Cs better than bentonite and kaolinite. Experimental adsorption data can be described by Freundlich isotherm.

- The bentonite (B-PAO) and zeolite (Z)-PAO composites were investigated for U(VI). K_L value was found to be higher on (Z)-PAO composite.

For Turkish clay minerals;

- Kaolinite based clay obtained from Çanakkale-Çan region was proposed as a reasonable candidate for the selective adsorption of Sr in waste disposal sites. On the other hand, Reşadiye montmorillonite has higher K_d values for Cs and Sr than Mihalıççık kaolinite depending on structural properties.

- For the sorption of U(VI) ions on Turgutlu and Kula montmorillonites, optimum contact time for the establishment of equilibrium was determined to be 10 h. For both clays, the maximum uptake was achieved with +0.1 –0.2 mm particle size. The increase in U(VI) concentration has a positive effect on uptake capacity. However, Kula clay showed a higher affinity for U(VI) than Turgutlu clay. K_d values of U(VI) increased in basic pH range.

- When Sr adsorption of Sındırgı kaolinite and Manisa clinoptilolite is compared, clinoptilolite shows a higher sorption capacity than kaolinite. The adsorption isotherm was best modeled by Freundlich isotherm.

- West Anatolian montmorillonites and Eskişehir-Sivrihisar red clay have been used for Th and Sr, Cs adsorption, respectively. Adsorption processes using both clays were found to be concentration dependent. Adsorption data was fitted to Freundlich isotherm. The responsible mechanism for the removal of Sr and Cs was found to be ion exchange.

- Sr affinity of Van illite was relatively high, and the maximum removal efficiency (%) was achieved in 10 min. Experimental data was fitted to Freundlich and D-R isotherms. Adsorption occurs via ion exchange in the relatively low Sr concentration range.

- The maximum U(IV) sorption efficiency using algae (Ulva sp.)-Na bentonite composite and Eskişehir sepiolite was reported at pH 3. The equilibrium was attained in 15 min for algae (Ulva sp.)-Na bentonite, whereas it took 240 min for sepiolite. Sorption isotherm data for modified bentonite fitted Frendlich and D-R isotherm well while for sepiolite it was compatible with Langmuir isotherm.

- Sivas-Yıldızeli vermiculite demonstrated high affinity for Cs^+ in basic medium. Process has both chemical and physical characters.

- The highest K_d for ^{137}Cs in low-level radioactive waste was obtained by Söğüt region clay as 642.59 mL/g.

For other Turkish minerals;

- The use of expanded perlite was suggested as a high capacity and low cost adsorbent material for the removal of Th(IV) ions. The adsorption process has been found to be strongly influenced by pH and Th(IV) concentration. Adsorption equilibrium was established within 60 min at pH 4.5. Maximum adsorption efficiency of Th(IV) onto expanded perlite was determined as 84 ± 4%. Adsorption data are compatible with Langmuir adsorption isotherm.

- Diatomite samples were used for the removal of Th(IV) and U(VI) ions. 99% of Th(IV) ions were adsorbed at pH 4 whereas the maximum adsorption efficiency of U(VI) was 77% at pH 5. Th(IV) adsorption was described well by Freundlich isotherm, however U(VI) adsorption was Langmuir type. 20 and 15 min of contact time were sufficient for the attainment of equilibrium for Th(IV) and U(VI), respectively. For both ions, the adsorption mechanism was physisorption, depending on thermodynamic data.

- Tendürek volcanic tuff is a naturally abundant material and it has a high capacity for the efficient removal of U(VI) ions from aqueous solution. Adsorption efficiency of U(VI) increased gradually up to 95% when the uranium concentration was 75 mg/L. The adsorption data fitted to Langmuir model and maximum monolayer adsorption capacity was found as 2.62 mg/g. Thermodynamic data point out an endothermic process and physisorption mechanism.

Turkish minerals (natural and modified) have been successfully used for the adsorption of Sr, Cs, U, Th and Po from aqueous solution. Adsorption studies on these minerals should be continued for binary or multiple mixtures of hazardous radionuclides, and thus information about their adsorption performance in the case of a mixed solution should be obtained.

We believe that this article will shed light on the studies to be carried out in terms of the immediate supply and use of our own minerals in the event of nuclear pollution caused by both radioactive waste and atmospheric fallout.

CONFLICT OF INTEREST

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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