

Sorption-Desorption Assessment to Characterize Radionuclides Contaminated Soils (overview)

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Abstract: Knowledge of radio-nuclides environmental pathways, and exposure, is an important aspect of any strategy to protect the public and the natural environments. The prediction of radionuclides fate and behavior in the environment is largely governed by sorption/desorption processes.

Models for the description of metal sorption are still mostly based on empirical solid-liquid distribution coefficient (K_d) values. a K_d value, which quantifies the distribution of a dissolved element between the solution and the solid phases present along relevant transport pathways. In any case, the evaluation of the distribution coefficient, K_d , is operationally needy and firmly differ due to a few variables. To assess the risk derived from the absorption of radionuclides in soils; after a continuous or an accidental release; sorption-desorption assessments at a laboratory scale are required.

Competitive sorption between sorbates has been recognized as an important factor in determining contaminant migration in the environment. This review paper discusses the most significant aspects of sorption processes and properties of the soil-water interface.

Keywords: Radionuclides, Sorption isotherm, Sorption reversibility, Risk assessment.

1 Introduction

Radionuclides are critical soil contaminants, particularly cesium (Cs-137) and strontium (Sr-90) are harmful due to their high radiotoxicity and metabolic similarity to major soil nutrients (e.g. K^+ , Ca^{2+}) [1,2]. Radionuclides contaminated environmental spheres may cause harmful effects as radioactive contamination. Accidentally released radionuclides along with their decay products ends up naturally in soil, water, and air ecosystems leading to linked health risks.

Interaction of radionuclides with various soil-water components present in the environmental systems represents a key factor in affecting their environmental speciation and mobility (Figure.1).

It has been reported that the migration and mobility of radioisotopes in the presence of a soil system play a vital role in forecasting the environmental impacts in the case of an unplanned release. Many investigations have suggested that the sorption-desorption process is one of the most important factors affecting the fate and behavior of radionuclides and contaminants in the environment [3].

Various steps must be considered to assess the risk derived from radionuclide incorporation in soils. Information needed include; the qualitative and quantitative

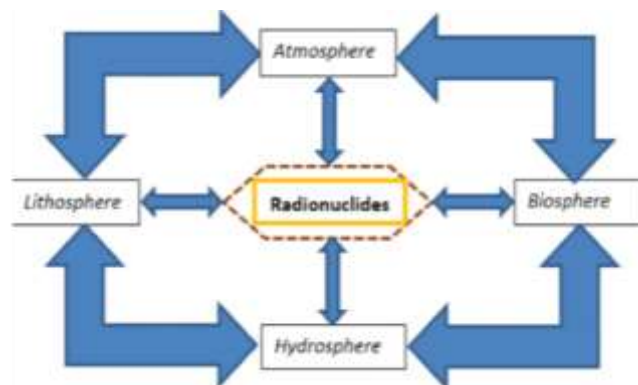


Fig.1: Interconnectivity of radionuclides in the environment.

description of the source term (e.g., to determine whether the source is particulate or soluble; whether it is formed by a single metal or it is multi-metallic), the knowledge of soil properties, as well as the establishment of metal concentration and distribution in the affected area. The mechanisms of soil-radionuclide interaction include; structural incorporation, co-precipitation, complexation, specific sorption, ion-exchange and electrostatic attraction (Fig.2).

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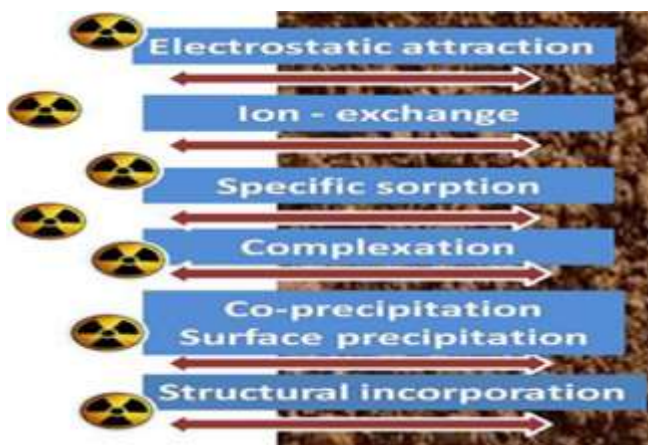


Fig. 2: Mechanisms of soil-radionuclide interaction.

The knowledge of metal soil interaction may also be useful to forecast how changes in environmental conditions (e.g., changes in soil pH) may affect metal mobility. Metals mobility can be examined and predicted by experiments carried out at the field and/or at a laboratory scale. Laboratory experiments represent lower-cost tests than field experiments or continuous soil monitoring campaigns, and they permit them to acquire the knowledge of the interaction mechanisms. Data from laboratory tests are easily used as input data for prediction models in which the Environmental Decision Support Systems are based, to establish and characterize the soil quality, and to perform the risk assessment exercise. However, laboratory tests are operational and data from the same soil-metal combination may vary in various orders of magnitude due to several factors.

While field experiments (e.g., soil-plant transfer or sampling soil profiles to examine metal vertical migration) permit obtaining in situ information in real-time, they are usually high-cost, long-time studies, with results difficult to be extrapolated to other scenarios due to the absence of elucidated mechanisms controlling metal mobility.

To date, there is a significant lack of harmonized and standardized protocols, although recommended methods are available from several organizations [4,5].

It is well-known that the transport behavior of radionuclides, their bioavailability, their uptake in different food chains, and their toxicity are governed by chemical and physical properties, mainly speciation [6,7].

Despite the vital importance of speciation for their behavior in the environment (Fig.3), our knowledge remains scarce. At its most fundamental, very often the more extensive knowledge about the speciation of non-radioactive trace elements and heavy metals can be appreciably extrapolated to radionuclides [8]. Radionuclides can be present in different physio-chemical forms influencing transport/mobility and bioavailability. Radionuclide species depend on sources and release conditions and transformation processes occurring in the environment [9].

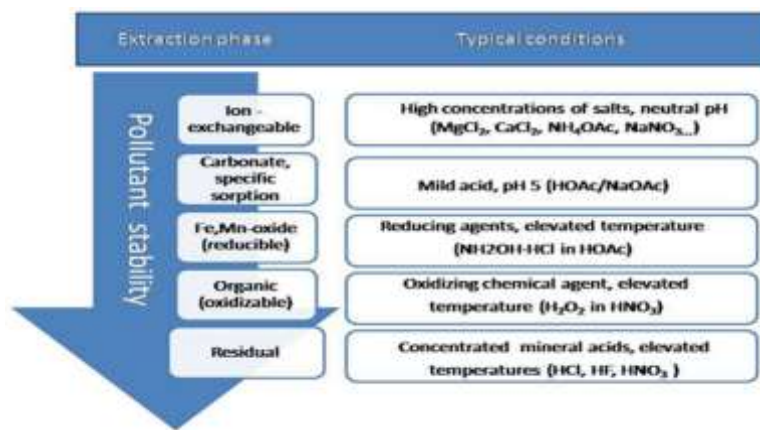


Fig. 3: pollutant stability.

2 Chemical Characteristics of Radionuclides

To assess the transfer and fate of radioactive contaminants in the atmosphere terrestrial and marine environment the information on physical and chemical parameters of radionuclide carriers is required. The release of radionuclides associated with particles of different sizes and mineralogical composition into the environment can considerably affect their transport and bioavailability. Thus, after nuclear explosions different spreading velocities and downward movement of ¹³⁷Cs, ⁹⁵Zr, ⁹⁵Nb, ²²Na aerosols and gaseous ¹⁴C(¹⁴CO₂) were observed [11]. In addition, low chemical reactivity is characteristic of highly insoluble refractory oxides of uranium and plutonium formed in nuclear explosions and they are very kinetically stable and remain in a form in which they are injected into environment for a long time. They were distinguished for their behavior in the environment from radionuclides released into environment processing plants and laboratory research. The emission of radiocesium from combustion of contaminated firewood can also contribute to the radiational situation in Lithuania. The analysis of activity concentrations, meteorological situation, types of particle are important for understanding the sources and possible impact on given location [10].

The chemistry of both radionuclides and heavy metals is far from being uniform for their behavior and speciation relationship. It has been reported that if the radionuclide is a chemical analog of an essential nutrient, absorption of the radionuclide by biota will increase if the nutrient is scarce. Empirical knowledge of the chemical behavior of stable elements in the same chemical group is vital to assessing and gaining insights into the potential for uptake into food chains and exposure pathways. Radionuclides and nuclides discharged in the biosphere might be assembled by their substance properties. It has been accounted for that their compound conduct will in general copy stable components in a similar concoction bunch especially the overwhelming metal components.

3 Sorption Theoretical Concepts

The behavior of radionuclides in the environment is greatly influenced by the process of sorption in a given scenario according to Links among environmental media, exposure media, and exposure pathways as well the interactive effects between them. However, the emphasis of the sorption concepts will be on radionuclides-liquid-soil systems. In considering such systems, the migration of radionuclides ions and colloidal particles will be dictated by the movement of fluid and geochemically, being represented by sorption (i.e., adsorption, desorption, diffusion) behavior. Evidence of this was illustrated in the research reported by Konoplev and Pflingsten et al., [11,12].

It is well known that the sorption behavior of radionuclides in the environment, their toxicity, and uptake in the biosphere are primarily influenced by Physico-chemical properties, namely their speciation and to a lesser degree by their concentration. Dissolved metal ions in the soil solution can bind to solid surfaces by several processes often classified under the broad term of sorption.

Gutten and Benes [13], indicated that the sorption and desorption behavior of nuclides are strongly affected by the physical, geochemical and biological processes that are occurring at specific field sites. They further concluded that the mobility of a nuclide in an aquifer system depended strongly on the relevant negative, neutral or positive charges and the nature of mineral surfaces and dissolved species. Differences in soil-pH and/or redox state may change the identity of the primary species.

Sorption occurs either as physical adsorption, a phenomenon referred to as physisorption, or chemical adsorption also called chemisorption. Scientists agree that sorption is a complicated process. It depends largely on the system pH and Eh. The composition of the fluid phase, surface chemistry of the host sorbate, and chemical speciation of radionuclides. When sorption occurs both repulsive and attractive forces become balanced. Much definitive work relating to the sorption of radionuclides has been published by Mishra et al. and Muhammad et al [14,15].

Jones et al, [16] investigated the mechanisms of sorption in many different cases and some relationships between structural properties of sorbate and sorbent. The behavior of radionuclides can then be correlated to stable elements in the same chemical group concerning their sorption. Consequently, sorption mechanisms can be readily deduced accordingly. It is well known that the mechanisms of radionuclides sorption process is based on the attraction force between the individual molecules, atoms, or ions of a sorbate and the sorbent surface [17,18].

Bucur et. Al., [19] indicated that Sorption/desorption experiments results showed that cesium is strongly and almost irreversible sorbed on the loess and clay samples from Saligny site. The high distribution coefficients determined for ^{137}Cs is explained by the presence in

relatively high percent of clay minerals that are well recognized for their high cation exchange capacity (CEC). The chemical form and speciation of metals strongly affect their movement through environmental media and uptake by biota. Specifically, the way that metal is bound to solids eventually controls the amount of metal in the solution, which directly influences the fraction of metal that may be incorporated by organisms.

Models for the description of metal sorption are still mostly based on empirical solid-liquid distribution coefficient (Kd) values. a Kd value, which quantifies the distribution of a dissolved element between the solution and the solid phases present along relevant transport pathways. The Kd value thus represents the sorption process, encapsulating both adsorption and desorption of the contaminant between the solid surface and the aqueous phase. It combines the effects of various processes determining the reversible partitioning between the solid and liquid phases, including surface complexation and ion-exchange. The distribution coefficient (Kd) is defined as the ratio of the mass normalized sorbed concentration of an element "X" to its dissolved concentration:

$$K_d = \frac{\text{amount of element "X" sorbed per unit mass of substrate}}{\text{amount of element "X" dissolved per unit volume of solution}} \quad (1)$$

and typically has units such as mL/g, L/kg or m³/kg. The amount of contaminant (in both the numerator and denominator) can be expressed in convenient units (such as moles, milligrams, or, for a radioactive isotope, Bq). One of the attributes of a Kd value is that it can be incorporated into transport models, including those used for migration predictions associated with the deep disposal of high level radioactive waste, as well as near-surface repositories for low-level waste. However, in almost all applications Kd values are considered as constant in time and space, thus lacking any account for heterogeneity and dynamics of environmental conditions. This approach is the simplest sorption model available and is the ratio of the concentration of metal sorbed on a specified solid to the metal concentration in a specified liquid phase at equilibrium (Kd, L/kg).

4 The Methodological Approaches to Quantify Kd

The different methodological approaches to quantify Kd values can be grouped into three general categories: in-situ, dispersed or batch and compacted or column [20].

4.1 In-Situ Method

The in situ method is based on the quantification of Kd values as the ratio of the concentration levels of the target element determined in the contact solution (e.g., run-off soil solution; groundwaters) and in the solid particles of the soil sample (i.e., once the liquid phase, or porewater, has been removed from the bulk matrix of the soil), collected

directly at field [20].

Since in situ K_d values are determined directly using quasi-undisturbed field soil samples and contact solutions, the main advantages of this approach are that representative solution composition and solid phase mineralogy can be used, if required, for further modelling and, on the other, that a true equilibrium between the solid and the liquid phases may have been attained. On the other, the disadvantages of the in situ method are less apparent but nevertheless appreciable. Depending on the method used to determine the RN concentration in the solid soil matrix (e.g., by means of total or pseudo-total digestion of the sample), this approach may lead to K_d values determined by including fraction of RN not reversibly bound to the soil matrix and, thus, not available for exchange with the liquid phase. Therefore, in situ values may be higher than those derived from methods aiming at estimating reversible K_d .

Besides this, with the in situ method it is not possible to distinguish between sorption and precipitation of the target element in the matrix of the environmental sample.

Since some transport and risk assessment models treat sorption and precipitation processes differently, which require that K_d values only account for the element sorption processes, the use of in-situ K_d data for this purpose is unsuitable since it may overestimate the element-soil interaction. Finally, the in situ method is not cost effective, which makes its application to be very limited, and thus, the number of available in-situ K_d data of RNs in soils are scarce. This scarcity of in situ K_d data jeopardizes their use to assess the interaction of RNs in other scenarios than those already studied.

4.2 Batch Method

In the batch method dispersed soil samples are mixed with contact solutions during a given period of time. It represents the most widely applied approach to estimate the K_d values for a given RN in soils. In this type of test, a known amount of unconsolidated or disaggregated, clean soil sample, is put in contact with a volume of an aqueous solution spiked with the target RN. "Clean" refers to an initial RN activity concentration in the solid sample which is negligible compared with the sorbed activity concentration after contact with the solution. After shaking the mixture for a short period of time, from hours to few days, the solid and liquid phases of the resulting suspension are separated and K_d values are calculated as the ratio of the RN concentration determined in both phases.

Quantification of the K_d may be affected by experimental conditions, such as temperature, filtration of the resulting solution, contact time, and L/M ratios, albeit K_d variability due to experimental conditions is normally much lower than those arising from RN and solid phase characteristics. Because of the operational nature of this method, recommendations on experimental conditions are often given by international guidelines [21,22] to facilitate comparability of the results and representativeness of the

K_d data measured. For instance, it is recommended to use contact times long enough to achieve sorption equilibrium, which should be checked in advance; to keep L/M ratios in batch sorption tests between 10:1 and 50:1 L/kg, which are not fully representative for soils at field; and, when possible, to use contact solutions with a composition (e.g., ionic strength, pH, presence and concentration of ligands and/or other species, etc.) as similar as possible to that of the liquid sources expected to cause the radioactive soil contamination (e.g., using solutions sampled at field or synthetic solutions prepared by mimicking the composition of real ones).

The batch method also has the added benefit that the assumptions of "reversibility" and "steady-state" of the K_d measurements can be demonstrated. Moreover, batch sorption tests are particularly useful for doing inexpensive, relatively convenient, series of K_d measurements in which a given characteristic of the soil system, potentially impacting K_d values, (e.g., pH of soil/solution suspension, ionic strength, redox potential, concentration of organic or inorganic ligands, etc.) is kept reasonably constant or, in the other way around, is intentionally varied under controlled conditions, in order to develop an understanding of RN sorption mechanisms. Besides batch sorption tests are often completed with tests aiming at predicting processes related to the re-mobilization of RNs from contaminated soils, the so-called batch desorption tests. Such methods consist in performing a leaching test to soil samples containing the target RN, such as soils affected by past contamination episodes or soils intentionally spiked (e.g., sorption test soil residues). According to which scenario wants to be reproduced and, thus, to which RN remobilisation process wants to be assessed, extractant solutions of different composition are applied.

K_d values gathered in soils from desorption tests tend to be higher than those obtained when sorption tests are applied, even when the same experimental conditions (i.e., same contact solution, contact time, L/M ratio, etc.) are used in both types of test. The differences between sorption and desorption K_d values can be taken as representative for the effect of sorption dynamics, which is RN dependent and tends to increase as the time elapsed since the RN was incorporated to the studied soil increases. With the exception of those RNs with a high sorption K_d (e.g., over 104 L/kg), it is relevant to estimate how much higher the desorption K_d would be, as this may be of major significance for risk assessment exercises.

Regarding batch experiments, many factors affect the quantification of the K_d , since it is not only extremely dependent on the soil-metal combination, but also on the operational conditions applied in the sorption tests, such as contact time, volume/mass ratios, and filtration of the resulting solution, especially if the target metals exhibit an association with colloids.

Moreover, there is a crucial effect of the composition of the contact solution, specifically the pH and the concentration of the major elements. Finally, the way the source term is

simulated in the batch experiments will also determine how representative the K_d values are. The simple K_d -based model relies on the hypothesis that the metal on the solid phase is in equilibrium with the metal in the solution, and thus can exchange with it.

5 Compacted or Column Methods

The column method entails the study of a solution containing the target RN as it flows through soil samples. In this case, K_d values can be derived from the diffusion-based mass transport pattern of a RN in undisturbed soil cores or compacted soils. The approach takes into account the retardation of the RN due to interactions with soil particles. Mass transport experiments are used to simulate the migration of RNs through soils under saturated and/or unsaturated conditions. They allow observation of RNs migration rates without significant solid particle alteration caused by grinding, as in batch experiments, and often produce results more representative of the field conditions than those obtained by the batch method. Mass transport experiments are usually carried out with columns. Experimental setup includes a reservoir to the column, a cylindrical holder to contain the crushed or intact soil sample being tested, and a sample collector for the column effluent.

Several operational problems with column experiments have been identified, such as homogeneity of column packing, potential short-circuit effects, and residence time required for experimentation [23]. Besides these experimental complications, the associated equipment costs, time constraints and variability of the obtained data limit the use of this approach. Thus, alike the case of in situ K_d data of RNs in soils, scarce K_d data derived from mass transport experiments in soils are available. $K_d(S)$ -Cs was found to be in the range of 65 to 2100 L/kg.

6 Sorption and Sorption Reversibility

Since the radionuclides will compete for the open sorbing sites, several scenarios may be proposed. In multiple component systems of sorption, the sum of the desorbed and input concentration for each contaminant becomes an adimensional concentration. Abdehagh et al. [24] reported for multiple component systems, a large number of interaction sites are available on the sorbent and all the contaminants in the solution mixture are easily sorbed. However, with the lowest affinity contaminants for the active sites are desorbed from the sorbent and replaced by sorbates with a higher affinity. Multicomponent sorption phenomenon has also been reported in industrial applications by Noroozi and Sorial [25], and Abdehagh et al. [24].

Figure. 4 shows that desorption of Cs and Sr by montmorillonite seemed to match the sorption curves of these metals i.e. hysteresis phenomenon could characterize the sorption-desorption reaction. It was mentioned that Cs

is mainly adsorbed by montmorillonite on ion exchange sites which are characterized by rapid and reversible adsorption. Accordingly, Ca can easily substitute Cs and Sr on the surfaces of the montmorillonite clay mineral. Freundlich isotherm was found to be the best model fitting the sorption

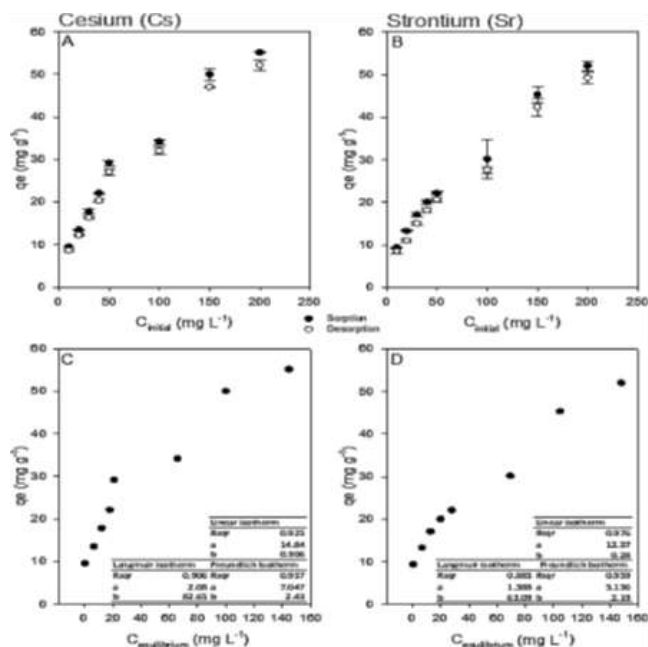


Fig.4: Sorption-desorption of Cs and Sr by montmorillonite: pH=7, $K=298$, sorbent/water ratio=1g L⁻¹.

of Cs by montmorillonite, while the linear isotherm seemed to be the best model fitting Sr sorption by montmorillonite. Probably, specific adsorption mechanism may account for Cs sorption on clay minerals. However, the sorption process of Cs ion on such sorbent surfaces seemed to be a reversible process.

On the other hand, it was reported that sorption-desorption behavior of the two contaminants (Cs and Sr) was different [26]. Cesium showed the highest sorption in arable silty loam soil, followed by forest sandy-clay loam and lowest in arable loamy sand. Strontium sorption was nearly half compared to cesium in all soils with higher sorption in silty loam and almost similar sorption in loamy sand and forest soils. Despite lower soil pH but most likely due to higher clay content and chemical nature of organic matter, Sr retention in forest soil was larger than in amended arable soils. Temperature variation in the range (5-35°C) did not cause a substantial effect on the sorption-desorption of the two radionuclides in opposition to the soil type.

The reversibly sorbed fraction depends on the previous sorption step (e.g, sorption sites; sorption conditions, such as ionic status of the sorption solution and application of drying-wetting cycles after the sorption step; time elapsed after metal sorption), and it can rarely be predicted from soil and sorption data.

7 Factors Affecting the Data Derived from Sorption-Desorption Tests

The sorption of long-lived radionuclides of cesium, strontium and cobalt (^{134}Cs , ^{85}Sr and ^{60}Co) on bentonite under various experimental conditions, such as contact time, pH, sorbent and sorbate concentrations have been studied [27]. The uptake of Cs and Sr was rapid and equilibrium was reached almost instantaneously in both the cases, while Co sorption was time dependent. The sorption of these nuclides increased by increasing pH. The uptake of Cs, Sr and Co increased with increasing the amount of the bentonite clay. The percentage sorption for Cs, Sr and Co decreased with increasing metal concentrations. The desorption studies with 0.01M CaCl_2 and ground water at low-metal loadings on bentonite showed that about 95% of Cs, 85-90% of Sr and 97% of Co were irreversibly sorbed. These results could be helpful for nuclear waste management, for waste water effluents containing low concentrations of cesium, strontium and cobalt

7.1 The Effect of the Contact Time in Sorption Experiments

The effect of contact time in the adsorption of Co(II) by bentonite clay for different initial concentrations can be seen in Figure. 5. The adsorption of Co(II) increases with increasing time and reaches a maximum value within 24 h [28], and thereafter it remains constant. The decreasing removal rate towards the end suggests formation of a monolayer of Co(II) ions on the outer surface of clay and intraparticle diffusion onto the inner surface of the adsorbent particles through the film. Adsorption of metal ions from the aqueous solution onto many conventional adsorbents, such as clay and activated carbons, have been reported to be a long process because the levels of metal ion adsorption on these porous adsorbents, mainly controlled by inner surface diffusion process which is much slower than bulk ion diffusion of metal ions in solution [29]. The equilibrium times were found to be the same for all the concentrations studied. Similar results were reported by some researchers for a variety of adsorbate-adsorbent systems [30].

Regarding the K_d values, the effect of the contact solution was more significant at low concentrations, where the existence of specific sites was evidenced, leading to higher K_d values, while at the high concentration range the effect of the composition of the contact solution was almost negligible, with low K_d in all scenarios.

7.2 The Effect of the Initial Metal Concentration

The influence of the initial concentration of U(VI) and Th(IV) on uptake percentage of HQ-bentonite is shown in Figure 6 [31]. They indicated that a decrease in the uptake

percentage by increasing the initial concentration of metal ions. The poor adsorption capacity at high metal ion concentrations is attributed to the increased ratio of sorption quantity of U(VI) and Th(IV) ions on the HQ-bentonite surface to available vacant sites.

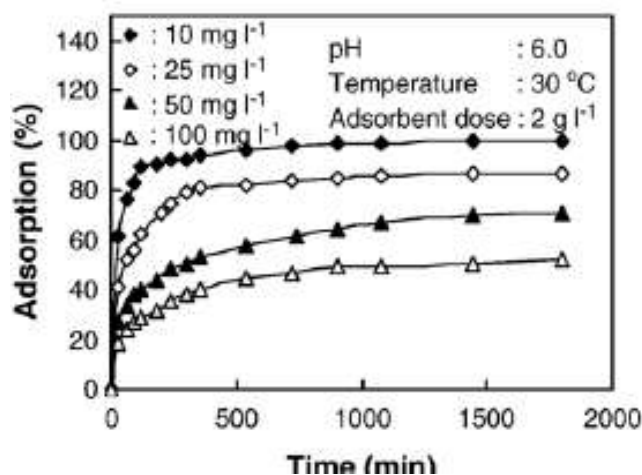


Fig. 5: The effect of contact time and initial concentration on the adsorption of Co(II) onto Bentonite clay.

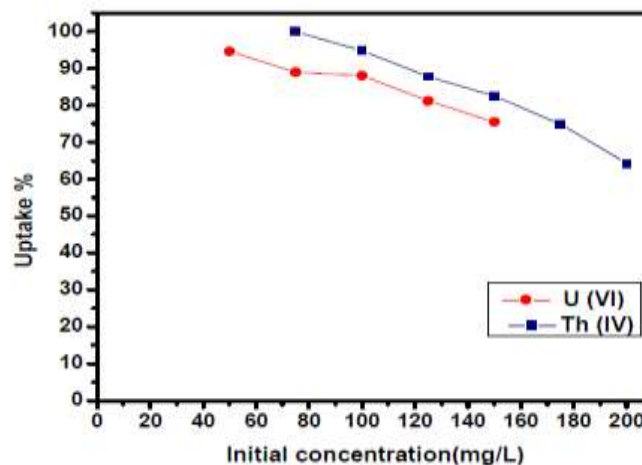


Fig. 6: Effect of metal ions initial concentration on U(VI) and Th(IV) ions sorption onto HQ-bentonite.

Conditions: 0.1 g HQ-bentonite; 50 mL solution; U(VI) (pH 4), Th(IV) (pH 3); shaking time U(VI) (15 min.), Th(IV) (8 min.); temperature 303 K.

7.3 Effect of Solution pH

Solution pH is known as an imperative parameter in adsorption process which affects degree of ionization and speciation of adsorbate as well as surface charge of the adsorbent [32]. Therefore, the rate of adsorption varies with the pH of an aqueous medium. The effect of solution pH on heavy metal adsorption can be investigated at different pH by adding NaOH or HCl solutions while keeping other

variables (e.g., adsorbent dosage, metal ion concentration, temperature, contact time) constant. The experimental results for the effect of pH on metal ions adsorption are shown in Figure. 7. The results showed that, Zn, Fe, Ni, Cu and Cr ions adsorbed poorly adsorbed on reactive silica at pH lower than 4 and the adsorption increased significantly with the rise in pH (within 6-8). At low pH value, the high concentration of hydrogen ion at the interface repels positively charged metal ions electrostatically and prevents their approach to the reactive surface [32]. At pH 4, the adsorbed amount of Fe and Cr is much more as compared with Zn, Ni and Cu ions. This may be possible due to selectively removal of Fe and Cr ions from aqueous solutions, containing the Zn, Ni and Cu ions by carefully adjusting the pH values and the other reaction conditions [33].

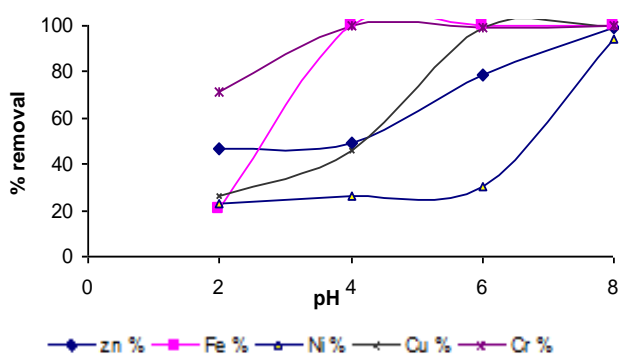


Fig.7: Effect of pH on the removal of Zn, Fe, Ni, Cu and Cr%.

7.4 Effect of Temperature

The effect of temperature on the sorption of U(VI) and Th(IV) metal ions onto HQ-bentonite was studied [31]. As illustrated in Figure 8. with increasing the temperature, the number of reacting moles having excess energy increased, this led to an increase in the uptake percentage of U(VI) and Th(IV) ions, so the sorption rate and the rate of mass transfer of the diffusion was increased.

7.5 The Effect of the Sorbent Mass

In the uptake process, the amount of adsorbent used is an important parameter because it determines the adsorbent's uptake capacity at a specific concentration of metal ions. Usually, the adsorption efficiency increases by increasing the adsorption dose due to the enhancement of active sites and the easy penetration of ions into the adsorbent's active sites [34]. Figure 9 shows the effect of sorbent mass on the sorption of Cs, Sr and Co on bentonite [27].

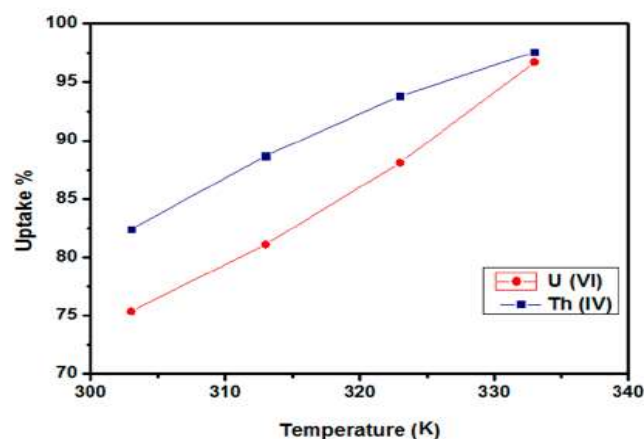


Fig. 8: Effect of temperature on U(VI) and Th(IV) ions sorption onto HQ-bentonite. Conditions: 0.1g HQ-bentonite; 150 mg/L metal ion; 50 mL solution; U(VI) (pH 4), Th(IV) (pH 3); shaking time U(IV) (15 min.), Th(IV) (8 min.).

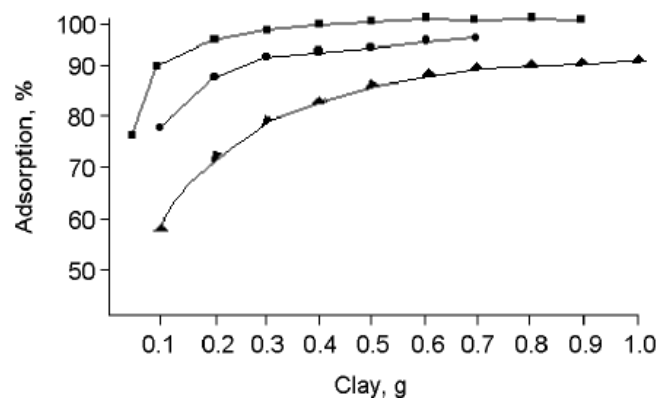


Fig. 9: effect of sorbent mass on the sorption of Cs, Sr and Co on bentonite [28].

7.6 The Effect of the Composition of the Contact Solution

Sorption isotherms are usually obtained under the same background electrolyte conditions to permit comparing results of the soil samples [35]. By comparing the sorption isotherms of Cd in two soils (organic and clay saline soils), and in two ionic media (in 0.02 eq/L CaCl₂ and in a medium that simulates the cationic composition of the soil solution), the effect of the changes in the concentration of major cations (i.e., Ca, Mg, K, and Na) in the contact solution on the K_d values were evaluated [36]. For the clay saline soil, the K_d values obtained in the soil solution medium were from one to two orders of magnitude lower than those quantified in the 0.02 eq/L CaCl₂ solution, especially at the low initial metal concentration range. This was due to the higher ionic strength and higher concentrations of the major elements in the soil solution of

this soil (around 75 meq/L in Ca; 180 meq/L in Mg; 470 meq/L in Na; and 6.5 meq/L in K) concerning the CaCl₂ background solution. On the contrary, higher K_d values were quantified in the organic soil in the soil solution medium, due to the lowest ionic strength of the solution simulating the cationic composition of the soil solution (1.3 meq/L) [37].

Regarding the K_d values, the effect of the contact solution was more significant at low concentrations, where the existence of specific sites was evidenced, leading to higher K_d values, while at the high concentration range the effect of the composition of the contact solution was almost negligible, with low K_d in all scenarios. The changes in the extraction yield due to the variations in the metal initial concentration and the composition of the contact solution did not follow a clear pattern concerning the initial metal concentration, although in general, they increased in the soil solution medium when decreasing the initial metal concentration.

It is recommended that sorption tests should be done that simulate real field conditions as much as possible as is reproducing the cationic composition or the ionic strength of the soil solution in the sorption medium [39]. Figure 10 illustrates how the sorption of Zn, as a target metal, is affected by the presence of a competitive metal (Pb), at two concentrations (0.2 and 10 meq/L), in two soils of contrasting properties [38]. When Pb was present at a low concentration, there was a minor, although significant, the effect of the presence of Pb on the Zn sorption, especially in the mineral soil.

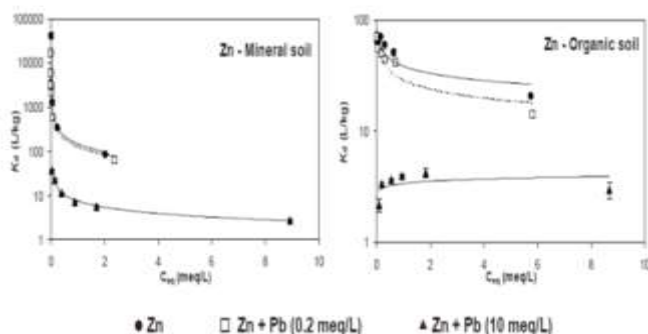


Fig. 10: Effect of the presence of a competitive metal (Pb) on the sorption of a target metal (Zn).

However, when the concentration of the competitive metal increased, the sorption of Zn decreased various orders of magnitude in both soils and, as seen in the organic soil, the sorption isotherm even changed its pattern, since the increase in the Zn concentration led to an unexpected increase in the K_d (Zn), which was not observed in the monometallic solution. This fact relates to the ability of Zn to compete with Pb for the sorption at selective sites, and thus increasing the K_d (Zn), only when its concentration increased.

8 Sorption–Desorption Behavior of Radionuclide / Heavy Metals

Sorption–desorption properties of cobalt(II) and strontium(II) ions were studied by Smiciklas et al.[39], using a soil sample from the vicinity of the Serbian radioactive waste processing and interim storage facilities. Their study aimed to evaluate the sorption/desorption properties of Co²⁺ and Sr²⁺ in the soil and to make recommendations on possible remediation techniques based on the cation's mobility.

According to the batch kinetic and isotherm studies, Sr²⁺ sorption was initially faster but with lower maximum sorption capacity compared to Co²⁺. Correlations between the amount of Ca²⁺ and H⁺ ions released during sorption of Co²⁺ and Sr²⁺ indicated their different sorption mechanisms. The addition of Sr²⁺ ions end-up predominantly in exchangeable fraction, whereas Co²⁺ distributed largely between carbonate phase and Fe, Mn oxides. They concluded that increasing metal concentration in the soil enhanced mobility of both cations, while increasing aging time provoked relocation of Co²⁺ from carbonate to Fe, Mn oxide fraction. Desorption studies revealed that acidic media and solutions of competing cations (Ca²⁺) induced more effective release of Sr²⁺ from the soil, while complexing agents such as citric and tartaric acids used at their natural pH (~2) leached more Co²⁺ than Sr²⁺.

Mishra, et al.,[14] investigated the sorption–desorption behavior of uranium (U), cesium (Cs), and strontium (Sr) by quantification of the solid-liquid distribution coefficients (K_d) using a batch method in typical podzol soils from Ukraine. Uranium shows reversible sorption and there was no isotopic fractionation observed with a known isotopic U composition using as a tracer. Cs sorption mostly occurred irreversibly. Soil clay content and exchangeable K play an important role in Cs fixation. Sr adsorption is observed to be reversible and mainly controlled by cation exchange and shows the highest mobility in the soil-water system.

Apart from CEC, the concentration of natural Sr and Ca in the aqueous and solid phases, pH and solution ionic strength controls the Sr sorption in soil and the reversible process could be easily desorbed from the surfaces of soils [20, 40].

Cesium competes with potassium for adsorption sites. The sorption of Cs is more correlated with the mineral composition and is controlled by the frayed edge sites of micaceous clay minerals and adsorbs mostly in an irreversible manner [41]. The higher K_d value for Cs (almost 3-fold) observed in the desorption process than adsorption shows the irreversibility of Cs sorption on the soil. The lowest K_d value was observed for Sr and compared with the results for Chernobyl soil reported earlier using ⁹⁰Sr as a tracer [41]. The extent to which Sr partitions from the aqueous phase to the solid phase is expected to be controlled primarily by the CEC of the solid phase [20].

Mishra et, al. [14] concluded that K_d values for Sr by both

adsorption and desorption were found to be almost similar indicating the reversibility of the sorption process. However, the association of these nuclides in different soil components and desorption considering the aging effect must be studied in detail for a better understanding of sorption–desorption behavior. The K_d values and the interaction mechanisms for the soils with typical characteristics can be used for contaminant transport models and can be extrapolated in case of similar scenarios.

9 Conclusions

In general, the characteristics of radionuclides will depend on the source and their properties. A better characterization of speciation is necessary for gaining a better understanding of processes and mechanisms governing their sorption and thereby their behavior and fate in the environment. This paper discussed the most significant aspects of radionuclides sorption processes and properties at the soil–water interface, the mechanisms involved, and various mathematical relationships. Furthermore, knowledge of environmental transport, environmental pathways and exposure pathways to radionuclides is an important component of any strategy to protect every biotic and abiotic environmental component. Much work remains to be done in facilitating the practical applications of the sorption–desorption characteristics of radionuclides in the environment.

Sorption-desorption tests increase the understanding of the mechanisms of the metal-soil interaction, and they are suitable tools to predict metal mobility after their incorporation in soil. They must be applied not only when assessing the risk derived from a contamination event, but also to back up the design of remediation strategies (e.g., use of soil amendments to decrease metal mobility in contaminated soils).

Regarding the data derived from the application of the sorption-desorption tests, the use of the K_d , adjusted (the K_d divided by the reversibly sorbed fraction) is suggested as the most appropriate input data for the risk assessment models.

The characteristics of the source term (e.g., concentration of the target metal; presence and concentration of potential competitive metals) and of the field scenarios (e.g., soil characteristics; cationic composition of the soil solution) must be considered in the design of the sorption-desorption tests. Sorption-desorption tests must be harmonized and standardized, since to date, there is still a lack of validated protocols and (certified) reference materials, especially dealing with sorption tests.

The determination of the K_d of a target metal also depends on the presence of other metals that may be sorption competitive. This is because the selective sites in the solid phase of soil, which lead to the highest K_d for a given metal, are not sufficiently metal-specific for a given element, but metals with a similar chemical behavior may compete for sorption at the same sites.

Finally, the combination of field and laboratory data is required for an optimum risk assessment, especially because the validity of the laboratory tests must be checked with field experiments.

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