The retention of multivalent pollutants in mineral layers

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HIGHLIGHTS

- The multivalent species will be more abundant in the double layer for high values of surface charge density.
- The retention capacity is dependent on the valency of the pollutants.
- The surface charge density has a big effect on the retention capacity.
- The retention coefficient for multivalent pollutants is decreased by increasing its concentration in the bulk.

GRAPHICAL ABSTRACT
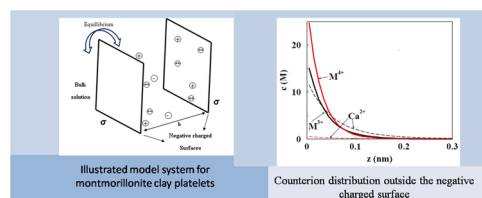
ABSTRACT

Radioactive waste treatment is earning worldwide awareness due to the harmful impact of radiation emitted from these wastes to human health and environment. Clay can be used as effective adsorbent in order to remove radioactive pollutants in aqueous solution, and have great potential for ion exchange technique. In our study we investigated the montmorillonite clay using primitive model Grand canonical Monte Carlo (MC) simulations to describe the ion exchange or competition between the counterions of different valences. Throughout the study we introduced a formula representing the retention coefficient to quantify the ion exchange, which is essentially proportional to the more common distribution coefficient K_d, and has the advantage of being dimensionless and more suitable for theoretical cases. we emphasized on the effect of surface charge density of clay platelets assumed to be negative, valence of the pollutants, and ground water reservoir concentrations of pollutants and of other cations. It is found that the retention is increased by increasing the valence of the pollutants, and the surface charge density, while it is decreased by increasing bulk concentration of pollutants and of other cations. Also it is found that the presence of high concentration of monovalent is less serious for the retention than the presence of multivalent ones.

1. Introduction

Water can be polluted with radioactive materials as a result of mining activities, nuclear weapons production, nuclear energy, laboratory experiments and other activities [1]. Removing water of these pollutants is important, especially for clean environment. Most of radioactive ions are harmful for the people and environment because of their toxicity, even in low concentrations, attenuated by their long

lifetimes, and elimination it is an important aspect in liquid waste treatment. An effective method for removing these pollutants from aqueous solutions is to be adsorbed on a solid matrix, for which efficient and cheap adsorbents are required [2–7].

In different countries, such as Canada, Spain, Sweden, France, Japan etc., they design the radioactive pollutants repositories in rocks, salts, or clay sediments, by combining natural and engineered barriers in order to achieve long term confinement [8,9]. Another way is to put the

nuclear waste into underground copper containers, fixed firmly and deeply in bentonite clay, which is characterized by its high swelling pressure, low permeability, and high cation exchange capacity, enabling self sealing and cation retention. The high retention capacity of clay minerals allows them to be used as ion exchangers providing an effective barrier against radioactive migration. These properties, besides the stability of the clay under varying conditions, can assure the success of such a containment. Stability of the clay means to be able to tolerate changes in the surrounding groundwater especially salt concentration, and still serves as effective hydraulic barrier.

Dry bentonite is made of nanometric platelets with a thickness of approximately 1 nm and lateral dimension of several hundred nanometers [10]. Montmorillonite, which is the main part of the bentonite is consist of one octahedral and two tetrahedral unit. The two tetrahedral sheets consisting of oxygen coordinating Si^{+4}, surrounded the octahedral part which consists of Al^{+3}, arranged with oxygen. The unit cell formula for the bentonite (montmorillonite) is $Al_2(OH)_2(Si_2O_5)_2$ [11]. Exchanging Al^{+3} with Mg^{+2} and/or Fe^{+2} will produce a negatively bentonite platelets. Interlayer cations such as Na^+ or Ca^{2+} can balance the negative charge to obtain electroneutrality. The platelets are usually modeled as an electrical double layer, where counterions valence and surface charge density are important factors can affect on the stability and swelling of the platelets in salted solutions [12–17]. However, the platelets are not an ideal electrical double layer sometimes called tactoides typically consisting of 5–20 platelets [18–21].

Radioactive leakage should be avoided when storing nuclear waste. Many attempts have been taking place to evaluate the sealing properties of bentonite clays from different sources [13,22–24]. Different studies concentrated on the sorption capacity of pollutants in bentonite both experimentally [2,4,25–28] and by simulations [29,30]. Many factors such as concentration of ions in polluted water, pH, contact time, and temperature effect on the sorption process of ions in clay minerals from aqueous solution which always mean cation exchange.

Segad et al. concluded from experimental and theoretical studies that large swelling is predicted for a Ca/Na montmorillonite system in equilibrium with a bulk solution where the cations are pre-dominantly monovalent [12–16,21,31], while a limited swelling is occurred if divalent cations dominate. One or two order of monovalent cations concentration must be higher than divalent cations for the monovalent ones to dominate. In presence of divalent cations, the swelling is limited because of ion-ion correlations [32], which reduces the entropic repulsion and gives rise to an attractive component in the total osmotic pressure.

In this work we try to quantify the retention of multivalent species when the polluted aqueous reservoir contains several types of cations with different valences using Monte Carlo (MC) simulations. The focus is on the importance of electrostatic interactions, while any specific chemical interaction is not included in our treatment. In addition to clay relevant parameters, we have studied higher surface charge densities more appropriate for cementitious materials.

2. Model

Dispersions of charged particles can be modeled as electric double layers with various geometries [33]. Infinite charged planar sheets separated by a narrow water slit containing neutralizing counterions and added salt can often represent platelets like montmorillonite and other clay minerals (Fig. 1). Assuming that the lamellar structure to be in equilibrium with an infinite salt reservoir of known salt concentration (bulk solution). One of the cornerstones of DLVO theory is the Poisson-Boltzmann (PB) equation which has been traditionally describing the statistical mechanical problem [34,35]. The PB equation can be described as a mean field and neglects ion-ion correlations which is important in the presence of divalent counterions and highly charged Particles [32].

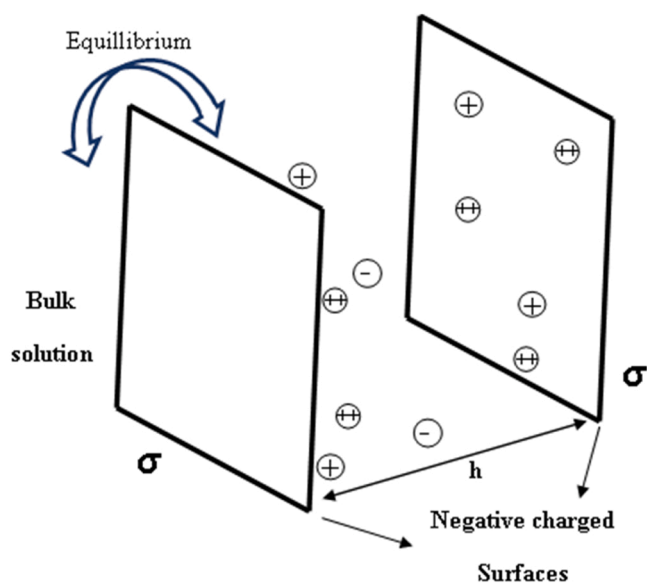For clays, ion-ion correlations play a significant role already with

Fig. 1. Illustrated model system for the platelets with two infinite parallel sheets with a uniform negative surface charge density. The slit is in equilibrium with an external bulk solution containing various salts.

multivalent ions, as divalent, trivalent or tetravalent ions.

In the model system, consider two surfaces having a negative uniform surface charge density, σ, and separated by a distance represented by h. The primitive model is adopted, in which the water is entered into the model by its dielectric constant with a relative dielectric permittivity, $\epsilon_r = 78$, and all ions are represented by hard spheres. The interaction, between two particles i and j separated a distance r_{ij}, can be given as:

$$u(r_{ij}) = \frac{z_i z_j e^2}{4\pi\epsilon_0\epsilon_r r_{ij}} \quad r_{ij} > d_{hc} \tag{1}$$

$$u(r_{ij}) = \infty \quad r_{ij} \leq d_{hc} \tag{2}$$

where z_i is the ion valence, e is the elementary charge of an electron, and ϵ_0 is the permittivity of vacuum. The hard core diameter of the ion, d_{hc}, was kept fixed equal to 0.4 nm in all simulations. The interactions between the ions and the charged surfaces took place in a rectangular simulation box and included an external potential to take care of interactions ranging outside the simulation box [36,37]. Periodic boundary conditions were utilized in the directions parallel to the surfaces, and the traditional minimum image method was applied. The number of ions varies between 100 and 1000 based on salt concentration and the distance between the two surfaces.

3. Monte Carlo simulations

The Monte Carlo simulations were achieved with the Metropolis algorithm [38] in grand canonical ensemble (μVT) [39]. The system is in equilibrium with a salt reservoir of finite concentration (bulk electrolyte). The chemical potential in electric double layer is the same as it is in the bulk, while the concentration of the species can differ. To explore the retention of highly charged elements, we used a bulk contains a reasonable concentration of NaCl, $CaCl_2$, and low concentration, covering a range of 10^{-8} to 10^{-3} M, of a trivalent (M^{3+}) or tetravalent (M^{4+}) ions representing the radioactive pollutants. Low concentration of ions is a typical one used in previous experimental studies for sorption of radioactive ions onto motmorollonite or other solid sorbents [40,41]. Initially, we considered a bulk contains monovalent and divalent cations assuming the divalent cation as pollutant. In this case a competition for the charged surface occurred to neutralize the charged surface,

but strongly varying degree. Several factors effect on the competition, the valence of counterion M, surface charge density, and the bulk concentration of all charged ions.

The chemical potential can be written as a sum of a standard part, an ideal, and an excess part

$$\mu = k_B T ln \Lambda^3 + k_B T ln c + \mu^{ex} \tag{3}$$

Where Λ is the thermal wavelength, c is the ion concentration, k_B is Boltzmann constant, T is the temperature, and μ^{ex} is the excess chemical potential. In the grand canonical ensemble, the total chemical potential in the bulk is the same as it is in electric double layer for a given species, but it is not a similar case for excess and ideal terms where their values are differed in the bulk (B) and in the electric double layer (DL), thus, $\mu_B^{ex} \neq \mu_{DL}^{ex}$. As the competition is strong, a relatively small concentration of multivalent counterions in the bulk is enough for these ions to dominate the double layer [32].

We have chosen to quantify the ion exchange or competition with a "retention coefficient"

$$\gamma = \frac{< C_{DL}{}^{n+} > + \quad C_B}{C_B} \tag{4}$$

C_B represents the concentration of a cation in the bulk and $< C_{DL}{}^{n+} >$ is defined as the average double layer concentration in molarity of a cation with valence n, and can be calculated according to the following

$$< C_{DL}{}^{n+} > = \quad \frac{< N_{M^{n+}} >}{(L \times L \times h) \times N_A} \tag{5}$$

Where L is the length of the rectangular simulation box, h is the distance between the two charged surfaces represents the width of the box, and N_A is Avogadro number.

The quantity of γ in Eq. (4) is essentially proportional to the more common "distribution coefficient" K_d [25]. The retention coefficient, γ, has the advantage of being dimensionless and is also more suitable in a theoretical context. Meanwhile, we stress that it is simply related to K_d. However, the retention coefficient could be suggested as

$$\gamma = \frac{< C_{DL}{}^{n+} >}{c_B} \tag{6}$$

and will give a similar results as Eq. (4) especially, in our study, the surface potential is high and $C_B << C_{DL}$, the only difference will be in the minimum limit for γ. The minimum limit of γ will be 2 if we apply Eq. (4), while it will be 1 when applying Eq. (5), so it is a matter of vertical shifting by 1. Another choice for γ could be

$$\gamma = \frac{< C_{DL}{}^{n+} > - c_B}{c_B} \tag{7}$$

In this case we will get $\gamma \geq 0$, and log γ could be negative when $\gamma < 1$, so to avoid the negative logarithm we eliminated this choice.

To describe the competition between the counterions, we can calculate the fraction of counterions in the slit as

$$\propto_{frac} \quad = \frac{< N_{M^{n+}} > \times n}{< N_{M^{1+}} > \times (1) + < N_{M^{2+}} > \times (2) + \ldots + < N_{M^{n+}} > \times n} \tag{8}$$

where M^{n+} is a cation with valence n+, and $< N_{M^{n+}} >$ is the average number of M^{n+} in the slit which is modeled as double layer (DL).

4. Results and discussion

We will throughout consider a double layer system in equilibrium with a bulk that contains a prescribed concentration of the various mono-, di-, tri- and tetravalent cations in addition to a neutralizing monovalent anion. Sometimes we will refer to the mono-and divalent species as Na^+ and Ca^{2+}. It is assumed that the surface charge density is negative and of a magnitude corresponding to clay and cementitious materials.

Fig. 2 describes a typical competition between mono- and divalent counterions. This is, for example, illustrated by the fact that in order to have an equal degree of neutralization from mono- and divalent counterions, then the bulk concentration of monovalent species has to be more than 1000 times higher than the bulk concentration of divalent counterions.

The surface charge density is an important parameter affecting the competition between the different cationic species. The multivalent species will be more abundant in the double layer for high values of $|\sigma|$. This is clearly described in Fig. 3a, which shows that already micromolar concentrations of a trivalent cation in the bulk is enough for it to dominate over a divalent species in the double layer. In this case the divalent concentration in the bulk is 4 mM, three orders of magnitude larger than the trivalent species. Fig. 3b shows that for a tetravalent cation the same happens already at nanomolar concentrations. The amount of monovalent counterions in the double layer is too low to be seen in Fig. 3. The domination of trivalent or tetravalent cations in the double layer over the divalent and monovalent cations is mainly due to the electrostatic screening correlations μ_{SC} which is proportional to z_i^2 and contributes to cation adsorption [42].

Fig. 4 shows the spatial distribution of the cations in the double layer with the same bulk concentrations of mono- and divalent species as in Fig. 3 and with the tri- and tetravalent concentrations equal to 10 μM. The distribution of divalent and trivalent cations are rather similar while tetravalent species completely dominate over divalent ones. Both Figs. 3 and 4 are simulated for a double layer width of 3 nm, noting that reasonable changes of the separation will not change behavior of the curves.

Fig. 5 shows how the double layer becomes saturated with trivalent species. That is, a change from 0.001 to 0.01 M in the bulk has a significant effect on the double layer content of M^{3+}, while a further increase only leads to a marginal increase of the concentration in the double layer.

The surface charge densities used here, 0.7–3 e/m^2, are such that in the presence of di- or multivalent cations ion-ion correlations will play a spectacular role. That is, the "normal" double layer repulsion will disappear and the systems will only show a limited swelling typically of the order of 1 nm [21].

Fig. 6 again demonstrates the strong competition and how the multivalent ions completely dominate the neutralization of the charged surfaces even at μM concentrations. One can note that sub μM concentrations are enough to saturate the double layer, that is the surface is neutralized by tetravalent ion only. This means that the retention coefficient becomes a linear function of log c_B^{4+} as shown in Fig. 6b. For trivalent ion, the linearity depends on the bulk concentration and the surface charge density, where the linearity is clear at larger surface charge density. The retention capacity is dependent on the valence of the pollutant, as it is also dependent on the surface charge density as it is shown in Fig. 6. The retention coefficient for multivalent ions is decreased by increasing the multivalent bulk concentration which is in agreement with the results previously reported for sorption of various ions on a variety of sorbents [25], in which the Cr^{3+} distribution coefficient was found to decrease by increasing its concentration in the solution.

It is, however, also dependent on the bulk concentrations of other cations - mono- or divalent ones as shown in Fig. 7. As could be expected, the concentration of divalent cations has a more significant influence than that of monovalent ones. The tetravalent ion dominant in neutralization for the surface charge over the other cations even at low pollutant concentration and at low divalent concentration, The trivalent starts to be dominant at higher pollutant concentration and depends on the divalent concentration.

Fig. 8 also demonstrates the effect of mono- and divalent cations on the retention of tri-and tetravalent pollutants. High concentration of
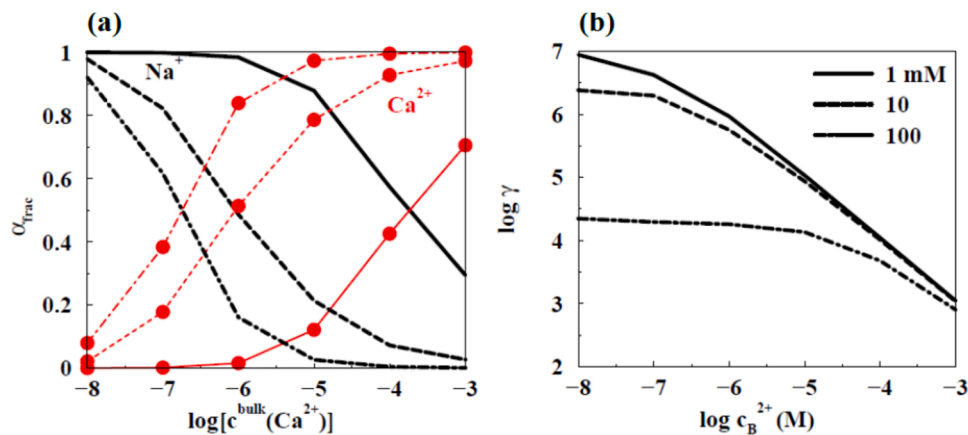
Fig. 2. a) Fraction of different counterions in the slit as a function of divalent cation concentration in the bulk. The slit is in equilibrium with a bulk containing various amounts of NaCl. Fraction of sodium ions is shown as lines without symbols and fraction of calcium ions as lines with symbols. Solid lines = 100, dashed lines = 10 and dot-dashed lines = 1 mM NaCl. The surface charge density is 2 e/nm². b) Retention coefficient as a function of calcium concentration in the bulk solution, which contains a mix of sodium and calcium ions. The sodium concentration is indicated in the figure for the three curves. The surface charge density has been kept constant at 2 e/nm².
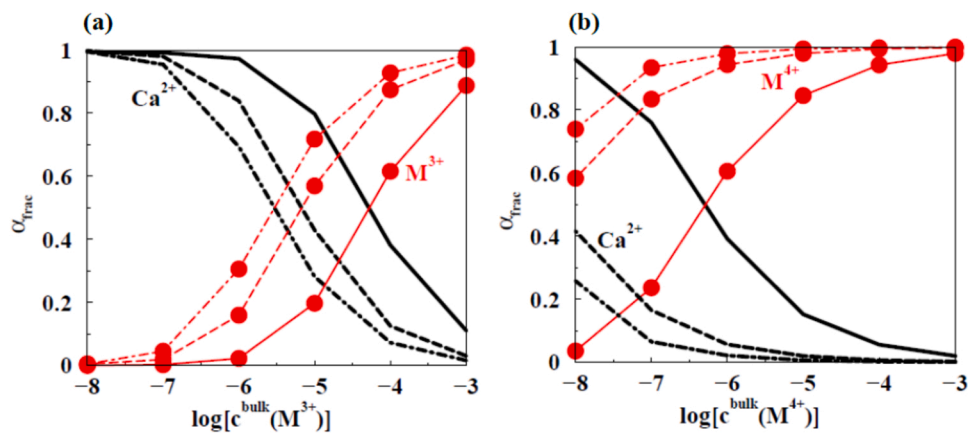

Fig. 3. Fraction of different counterions in the slit as a function of multivalent cation concentration in the bulk. The slit is in equilibrium with a bulk containing 1 mM NaCl, 4 mM CaCl₂ (typical ground water) and a varying amount of multivalent cation. Fraction of calcium ions is shown as lines without symbols and fraction of multivalent ions as lines with symbols. The fraction of sodium ions in the slit is too low to be seen in the graph. The surface charge density has been varied; solid line = 0.7, dashed line = 2 and dot-dashed line = 3 e/nm². a) Trivalent and b) tetravalent cation.
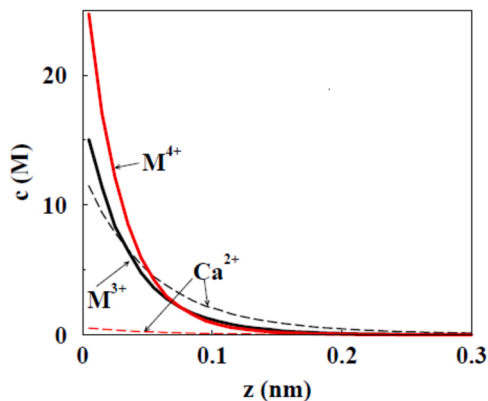

Fig. 4. Counterion distribution outside the charge surface. Two different bulk systems are shown with 1, 4 and 0.01 mM of Na⁺, Ca²⁺ and Mⁿ⁺ ions, respectively. The surface charge density is 2 e/nm² and the slit width is 3 nm. The Na⁺ concentration is virtually zero and is not plotted in graph.

Fig. 5. Concentration of trivalent cations outside the charged surface. The surface charge density is 0.7 e/nm² and the bulk solution contains 1 mM of NaCl, 4 mM of CaCl₂ and varying amount of trivalent cations as indicated in the graph.

monovalent species is less serious for the retention than the presence of divalent cations. A consequence is that the regeneration of the retention matrix has to be done with divalent species. Also, the figure includes the retention coefficients calculated with Poisson-Boltzmann (PB) theory, which underestimates the retention by one or two orders of magnitude. This is a consequence of the neglecting of ion-ion correlations in the mean-field PB theory.

The average double layer concentration of trivalent cations is dependent on the surface charge density as shown in Fig. 9, where the
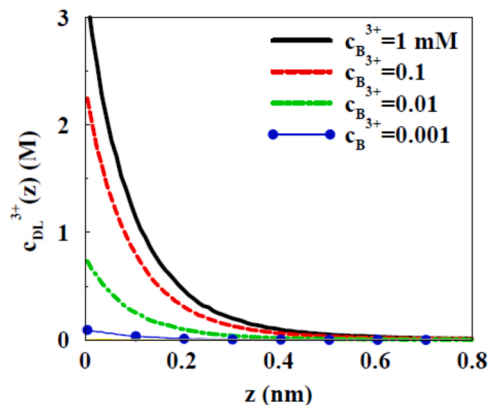
system is in equilibrium with a bulk containing 100 mM of monovalent and 10 mM of divalent cations in addition to trivalent species. Three different surface charge densities are displayed and the distance between the two charged surfaces is 30 Å. The concentration of trivalent cations is increased by increasing the surface charge density, and by increasing the concentration of trivalent cations in the bulk. This increment is clear and large when the surface charge density is 0.03 e/Å² relative to the small value of surface charge density of 0.007 e/Å². The dependence of *DL* concentration of trivalent cations can be explained by
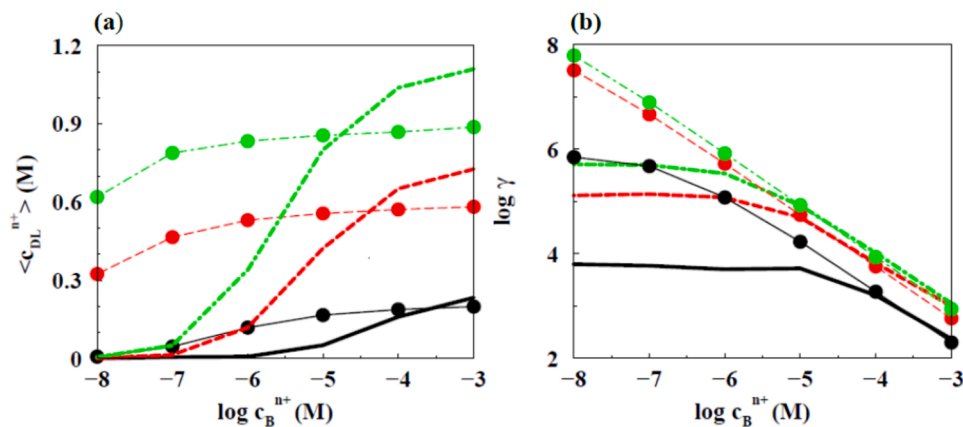
Fig. 6. a) Average double layer concentration of the trivalent (lines without symbols) and tetravalent (lines with symbols) cations as function of the bulk concentrations. The surface charge density has been varied: solid lines = 0.7, dashed lines = 2 and dot-dashed lines = 3e/nm^2. The bulk also contains 1 mM of NaCl and 4 mM of CaCl$_2$. b) The retention coefficient calculated from the curves in (a).
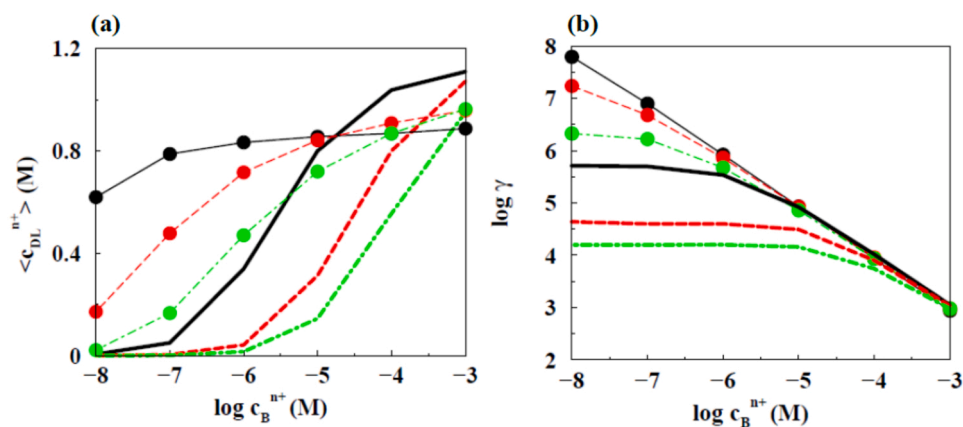

Fig. 7. a) Average double layer concentration of the trivalent (lines without symbols) and tetravalent (lines with symbols) cations as function of the bulk concentrations. The surface charge density has been kept constant at 3 e/nm^2, but the bulk conditions have been varied: solid lines = 1 mM NaCl + 4 mM CaCl$_2$, dashed lines = 100 mM NaCl + 10 mM CaCl$_2$ and dot-dashed lines = 500 mM NaCl + 10 mM CaCl$_2$. b) The retention coefficient calculated from the curves in (a).
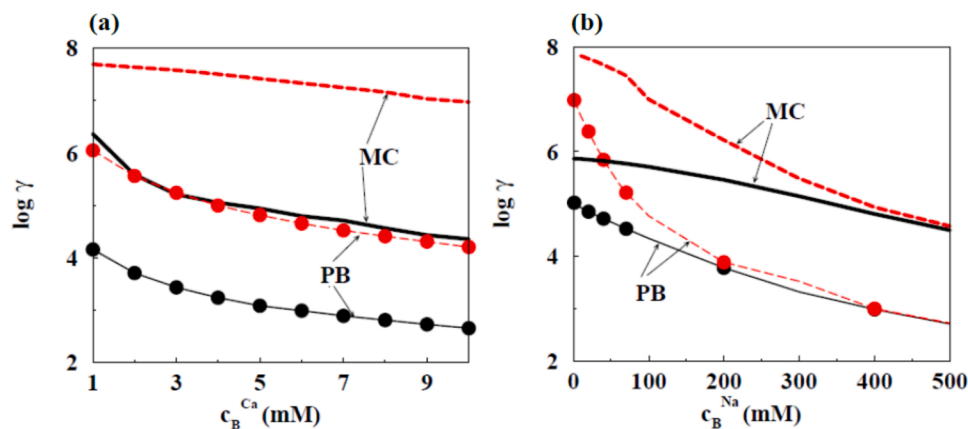

Fig. 8. a) Retention coefficients for trivalent (solid lines) and tetravalent cations (dashed lines) as a function of calcium concentration in the bulk, the bulk concentration of the multivalent cations is 10^{-8} M while the bulk sodium concentration is zero. Lines without symbols are from MC simulations, while the lines with symbols are obtained from the Poisson-Boltzmann (PB) equation. The surface charge density is 2 e/nm^2. b) As in a) but with retention coefficients for multivalent cations as a function of sodium concentration in the bulk with zero calcium bulk concentration.

the contact density theorem which was described by Voukadinova et al. and shows that the total contact density grows as σ^2 [42]. The theorem is strong because it is accurate for primitive model, and contains a lot of definitive information especially when $|\sigma|$ is large and whenever one ion species prevail the contact density.

5. Conclusion

The high retention capacity of clay minerals allows them to be used as ion exchangers providing an effective barrier against radioactive migration. In our study we applied the grand canonical Monte Carlo (MC) simulations to describe the ion exchange or competition between the counterions of different valences. Our study shows that the surface
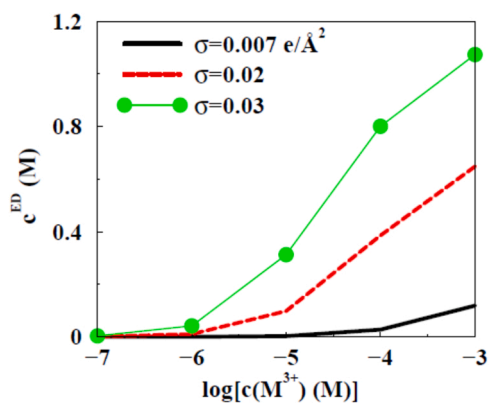
Fig. 9. The average double layer concentration of a trivalent cation for a system in equilibrium with a bulk containing 100 mM of a monovalent and 10 mM of a divalent cation in addition to the trivalent species. The distance between the two charged surfaces is 30 Å and three different surface charge densities are displayed.

charge density is an important parameter affecting the competition between different cationic species, and the multivalent species will be more abundant in the double layer for high values of $|\sigma|$, where the surface charge densities used here, 0.7–3 e/nm^2, are such that in the presence of di- or multivalent cations ion-ion correlations will play a spectacular role. These results are in good agreement with what Voukadinova et al. describe in their study for the energetics of counterion adsorption in the electrical double layer [42]. The retention capacity of the pollutants quantified by the proposed equation for retention coefficient γ is dependent on the valence of the pollutants, the surface charge density, and on the bulk concentrations of the pollutants and of other cations, monovalent, or divalent ones. It is found that the retention is increased by increasing the valence of the pollutants, and the surface charge density. While it is decreased by increasing the bulk concentration of the pollutants and of other cations in agreement with the results previously reported for sorption of various ions on a variety of sorbent [25]. The retention coefficient calculated with Poisson-Boltzmann (PB) theory is underestimated by one or two orders relative to the one calculated with Monte Carlo (MC) simulations because of the neglect of ion-ion correlations in the mean-field PB theory. Our results prove that the primitive grand canonical Monte Carlo (MC) simulations is an excellent and safe method to analyze the sorption of multivalent radioactive pollutants by montmorillonite clay modeled as *DL*. Also, prove that the proposed equation for retention coefficient γ is a good tool to quantify the ion exchange between the counterions of different valences in montmorillonite clay. Furthermore, the agreement of our results with the previous studies emphasizes the strength and the credibility of our approach. This approach and γ equation for retention coefficient may be of great help in analyzing ion exchange method for extracting and recovering radioactive pollutants from aqueous solutions to assure clean and healthy ground water.

CRediT authorship contribution statement

Khawla Qamhieh: Conceptualization, Methodology, Data curation, Writing – original draft, Visualization, Investigation. **Zeid N. Qamhieh:** Visualization, Investigation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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