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**Faculty of Graduate Studies**

# **Hexavalent Ions Sorption on Bentonite Clay**

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### III

## Dedication

To my kind parents, who are impossible to be thanked adequately for everything they have done for me and my future and who encourage me to be ambitious person. They always support me to get the best degrees. They are really the best model for perfect parents and they are the main cause of success in my life. God bless them.

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## الإقرار

أنا الموقع أدناه مقدم الأطروحة التي تحمل عنوان

### **Hexavalent Ions Sorption on Bentonite Clay**

أقر بأن ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص, باستثناء ما تمت الإشارة إليه  
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## List of Abbreviations

SKB	Swedish Nuclear Fuel and Waste Management Company
pH	Is the Potential of Hydrogen
EDL	Electrical Double Layer
$\Phi(r)$	Potential at distance $r$
$k_B$	Boltzmann constant
$\nu_i$	Valency of ion $i$
T	Absolute temperature
$k_d$	Distribution coefficient
V	Volume
$\langle C_{EDL} \rangle$	Average electrical double layer concentration of a cation
$C_B$	Concentration of a cation in the bulk solution
$\gamma$	Retention coefficient
$\sigma$	Surface charge density
SKB	Swedish Nuclear Fuel and Waste Management Company
V	Volume
$\epsilon_0$	Vacuum permittivity
$\epsilon_r$	Relative dielectric permittivity
P	Probability
E(r)	Energy at distance $r$
Z	Random number
N	Number of particle
Z	Grand canonical partition function
Q	Canonical partition function
$\langle K \rangle$	Average of any quantity
$\lambda$	Thermal de Broglie wavelength
$\mu^{exc}$	Excess chemical potential
mM	Millimolar
$\alpha_{frac}$	Fraction
$M^{+6}$	Cation with valency +6
$\mu$	Chemical Potential

XIV  
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**Abstract**

Radioactive ions, even in low concentration, form a potential threat to the environment and humans due to their strong radiation and long half-life times. The treatment of this serious problem is obviously of great concern and can be investigated by several techniques. The focus of this study is on studying the retention of hexavalent pollutants in bentonite clay. The sorption of hexavalent radioactive pollutants from ground water on Bentonite Clay has been studied using Monte Carlo Simulation.

Primitive model has been used where the water is included as solvent with constant dielectric permittivity ( $\epsilon_r = 78$ ), and the ions are treated as spheres with same diameter and the Bentonite clay is treated like as electrical double layers. Series of simulations have been performed with systematic variations of different parameters to investigate the sorption of the ions. The parameters including Ionic strength of cations in the aqueous solution, the concentration of ions in the aqueous solution, the surface charge density of the parallel planer surfaces and the temperature of the aqueous solution are checked. The results of this study indicate that: the sorption process is affected by the previous parameters and it can be explained by calculating the retention coefficient of sorption and average electrical double layer

concentration. In particular, the average electrical double layer concentration and the surface charge density increase as the concentration of ions increases. By contrast, the average concentration decreases by increasing ionic strength of aqueous solution. In addition, the retention coefficient ( $\gamma$ ) of hexavalent ions decreases as hexavalent concentration and ionic strength increasing, and this coefficient ( $\gamma$ ) increases by increasing the surface charge density ( $\sigma$ ). The results obtained by Monte Carlo simulation method are compared with some available experimental results and found to be in good agreement.

## **Chapter one**

### **Introduction**

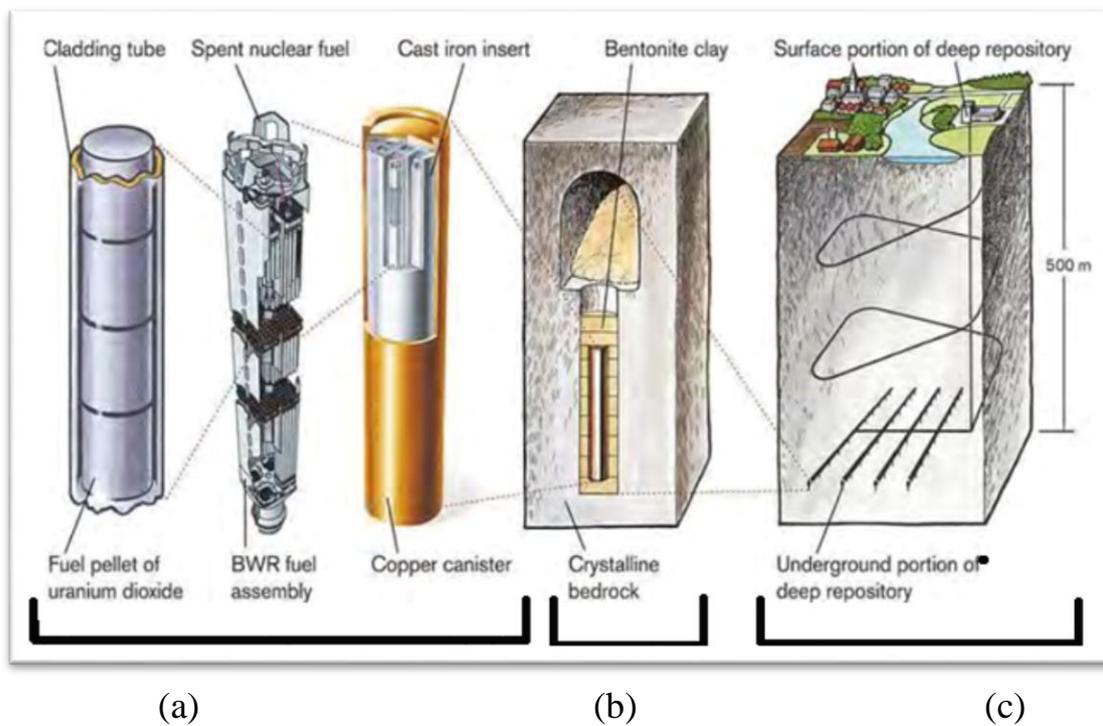
Radioactive waste is mainly produced by nuclear power generation in nuclear reactors, ships, planes and nuclear power plants. This waste might pollute the ground water or soil causing diseases for human and all other living creatures. The treatment of this serious problem is obviously of great concern and can be investigated by several techniques such as fixing the radioactive ions in porous media and removal of ions from the solution by using dead microbial cells (Zakrzewska, 2003).

#### **1.1 Techniques of Treatment of radioactive Waste Water**

For treating radioactive waste, several techniques can be used (Karlheinz et al., 1977). One of them is fixing the radioactive ions in porous media by injecting the ions into the porous media water-soluble organic monomers (Mercer et al., 1979). Another method is the removal of ions from the solution by using dead microbial cells (Tsezos and Volesky, 1981). Moreover, evaporation, adsorption and ionic exchange methods can be used to treat liquid radioactive wastes (Buckley et al., 2004). However, the evaporation of the radioactive wastes needs high costs and may cause air pollution. In another method, the radioactive waste are being treated by adsorption method which needs effective materials that can store the radioactive wastes for very long time, but is also a costly method. In reality, the ionic exchange method is more efficient method that can be used to treat the radioactive wastes (Saleh and Bayoumi, 2014). This low

cost method has been applied by Swedish Nuclear Fuel and Waste Management Company known as SKB (Svensk Kärnbränslehantering Aktiebolag) . In this method, the following effective multiple barrier method for final disposal of radioactive wastes has been used (Elam and Sundqvist, 2009):

- 2 The radioactive wastes are enclosed in canisters made of copper with iron insert. The iron strengthens the canister and the copper is used for corrosion resistance (fig (1.a)).
- 3 Bentonite clay is used as a buffer around the canisters to protect them from rock movement. It also prevents water from leaking to the canister fig (1.b).
- 4 The canister including radioactive wastes are embedded underground at depth 500 m (fig (1.c)).
- 5 After all, the tunnels and all rock caverns are sealed.



**Figure (1.1):** The effective multiple barrier method used in SKB: (a) copper canister, (b) bentonite clay, (c) the system is at 500 m underground (Anders 2014).

## 5.1 Literature Review

The sorption of  $\text{Ag}^{+1}$  and  $\text{Cr}^{+3}$  on Bentonite clay and the effects of some parameters on the sorption process such as the concentration of ions in aqueous solution and pH of aqueous solution was studied experimentally (Khan et al., 1995). The result of that study showed a decrease in adsorption of ions with the increase of their concentration in aqueous solution, and an increase in adsorption of ions with the increase of the potential of hydrogen (pH) of the aqueous solution

Studying the adsorption of Uranium (VI) and Thorium (IV) on Bentonite by batch experiment was also performed (Khalili et al., 2012). In the conclusion of that study, an increase in adsorption of ions occurs with increasing the pH of the aqueous solution and the sorption time.

The effect of the pH of the solution and the amount of Bentonite clay on the sorption of  $\text{Cr}^{+6}$  on Bentonite clay was studied (Tewari et al., 2005). The result of that study showed that the sorption increases as the pH of the solution increases until (pH is 2.0). Beyond this value (pH > 2.0) the sorption starts to decrease. In addition, when the amount of clay increases the sorption decreases.

Experimental research for the sorption of hexavalent chromium ( $\text{Cr}^{+6}$ ) by activated carbon and Bentonite was studied (Salah et al., 2012). From this study, it is obvious that the sorption of  $\text{Cr}^{+6}$  increases by increasing the time of the sorption process, and it increases slightly by increasing the

temperature of the system. Moreover, the sorption decreases by increasing the initial amount of the sorbent. The main result of this research showed that Bentonite is more efficient in adsorbing ions compared with the activated Carbon.

The study of the sorption of hexavalent Uranium ions ( $U^{+6}$ ) on Bentonite clay was performed (Broder and Baritta, 2010). Several factors were found to affect the sorption process of such ions. For example, by increasing the pH of the aqueous solution up to 7, the sorption increases. However, beyond this value of pH the sorption starts to decrease slowly, and by increasing the temperature of the system the sorption increases very slightly. It was noticed that increasing the initial concentration of the solution decreases the sorption of  $U^{+6}$  ions.

The sorption is also affected by the properties of the clay. For example, the sorption of ions into a substance containing Fe and Mn minerals in the form of magnetite ( $Fe_3O_4$ ) or in the form of groutite ( $MnOOH$ ) differs from the substance which doesn't contain Fe and Mn. However, studying the sorption of  $Pu^{+5}$  into Bentonite clay showed that the sorption increases by increasing pH of the solution, and also the sorption rate is affected by presence of Fe and Mn in Bentonite clay (Zavarin et al., 2012).

Monte Carlo simulation method has been recently extensively used for studying the sorption process of multivalent ions. For example, the effect of valency on sorption process on Ca/Na montmorillonite using Monte Carlo simulation method has been studied (Qamhieh and Jönsson under preparation). More specifically, the sorption of trivalent and tetravalent

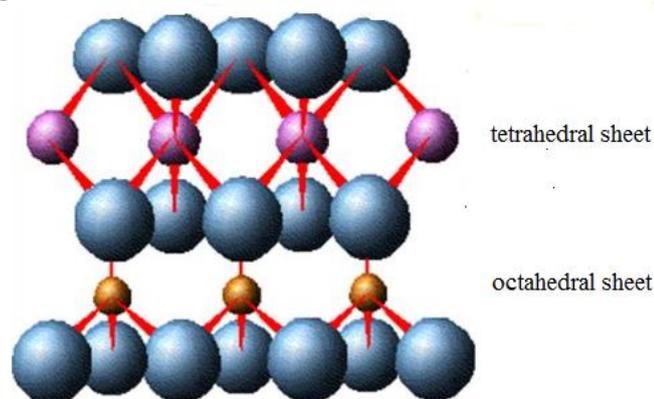
cations from sea water on Bentonite clay has been performed by the same method (Maraaba et al., 2014). The results of such study tell that the retention coefficient decreases as the ion concentration increases. In another study, the sorption of pentavalent ions on Bentonite clay was studied (Odeh et al., 2015). The conclusion of this study is similar to the previous one, so that the retention coefficient becomes less as the pentavalent concentration increases.

## Chapter Two

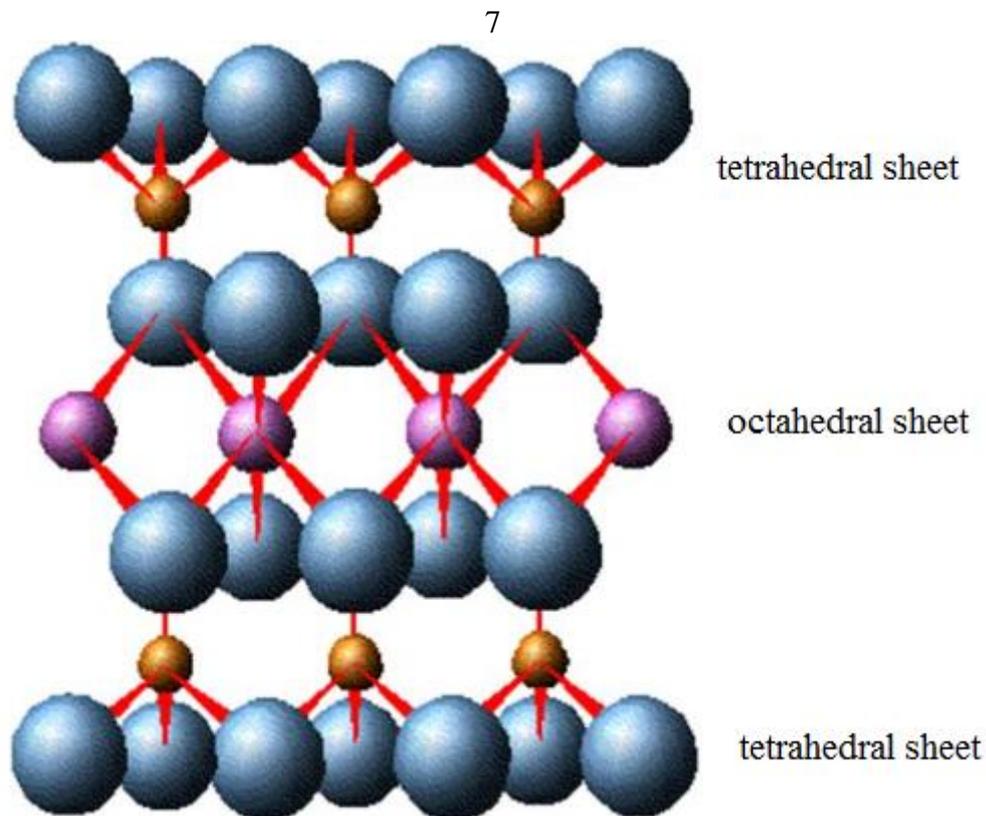
### Theoretical Background

#### 6.1 Clay Minerals

Clay minerals are hydrous aluminum phyllosilicates or can be with other elements such as  $\text{Fe}^{+2}$  and  $\text{Mg}^{+2}$  which are useful to humans' life (Church et al. 2003). The uses of clay minerals depend on their type (1:1 layer type structure or 2:1 layer type structure). However, 1:1 layer type structure (figure (2.1)) has one tetrahedral silica sheet and one octahedral alumina sheet. This type is called kaolin group ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) of minerals and has small specific area. Examples of this type are kaolinite ( $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ ) and serpentine ( $\text{D}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$  where  $\text{D} = \text{Mg, Fe, Ni, Mn, Al, Zn}$ ). On the other hand, 2:1 layer type structure is one octahedral sheet sandwiched between two tetrahedral sheets (figure (2.2)), and example of this type is vermiculite ( $\text{Mg}_3(\text{Al}_4\text{O}_{10})(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$ ) ( Nelson 2015).

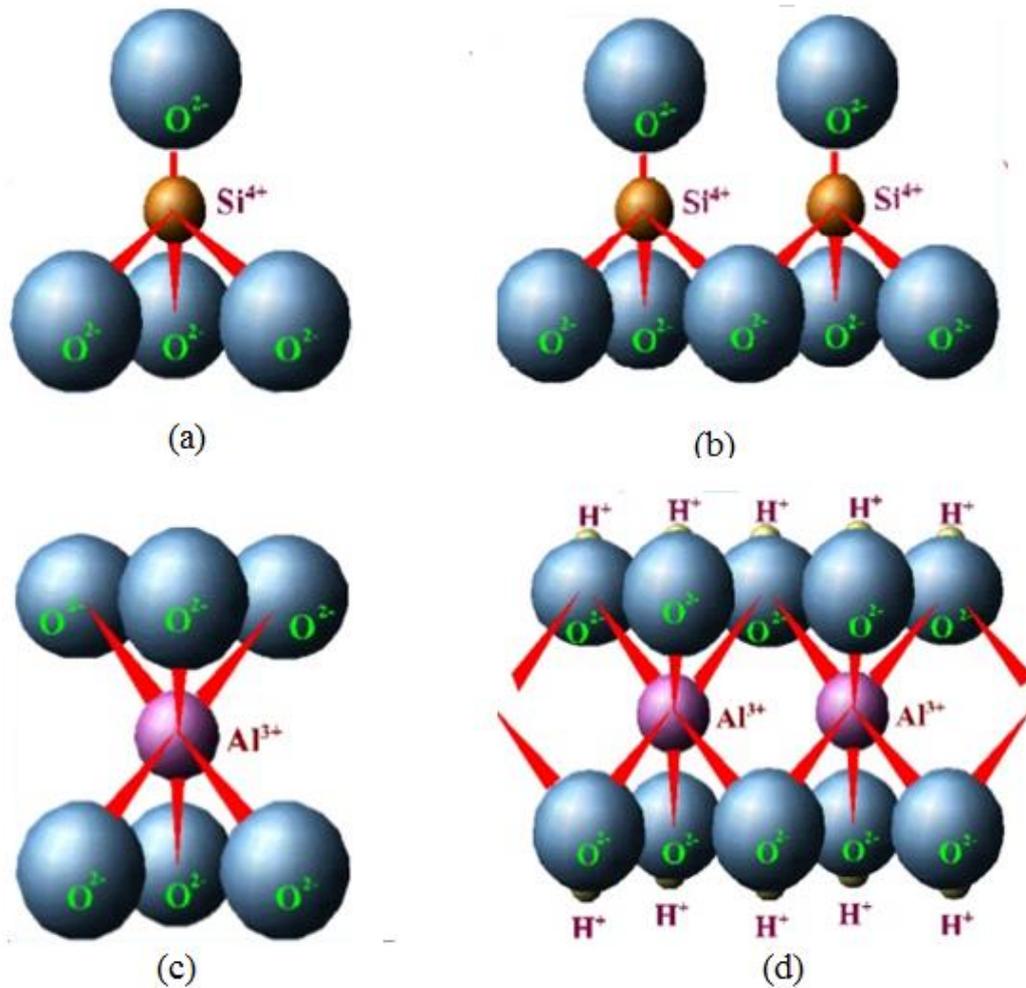


**Figure (2.1):** The structure of 1:1 clay minerals which composed one tetrahedral sheet and one octahedral sheet



**Figure (2.2):** The structure of 2:1 clay minerals which is composed of one central octahedral sheet sandwiched by two tetrahedral sheet.

The tetrahedral sheet is composed of tetrahedral units which are composed of one central silica atom and four oxygen atoms (figure (2.3.a)). Any oxygen atom of these may be shared with other neighboring tetrahedral unit forming a tetrahedral sheet (figure (2.3.b)). On the other hand, the octahedral sheet is composed of octahedral units (figure (2.3.c)) constitute of one central Mg or Al atom sharing with six oxygen atoms. Moreover, any oxygen atom of these may be shared with other neighboring octahedral unit forming octahedral sheet (figure (2.3.d)) (Grim 1968).

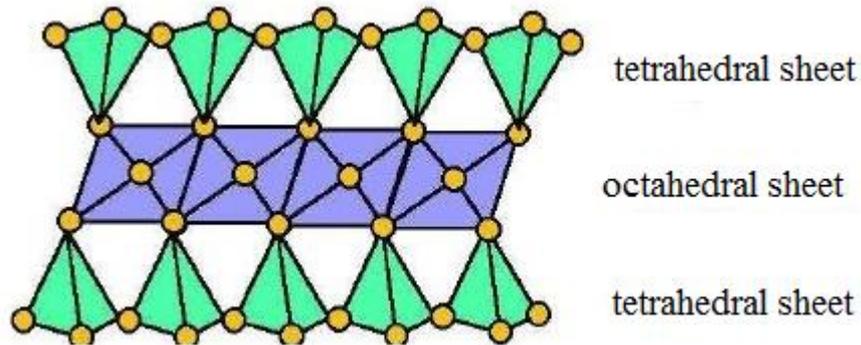


**Figure (2.3):** (a) Tetrahedral unit which is one central silica atom sharing with four oxygen atoms (b) the octahedral unit which is one central aluminum atom sharing with six oxygen atoms (c) the tetrahedral sheet which is composed of multiple tetrahedral units (d) the octahedral sheet which is composed multiple of octahedral units.

## 6.2 Bentonite Clay

Bentonite is an adsorbent aluminium phyllosilicate which was named by Wilbur C. Knight in 1898. The main component of bentonite is montmorillonite which is the phyllosilicate group of minerals that typically form in microscopic crystals forming a clay (Deer 1969). Montmorillonite was named by the French Montmorillon and is known to be 2:1 clay having

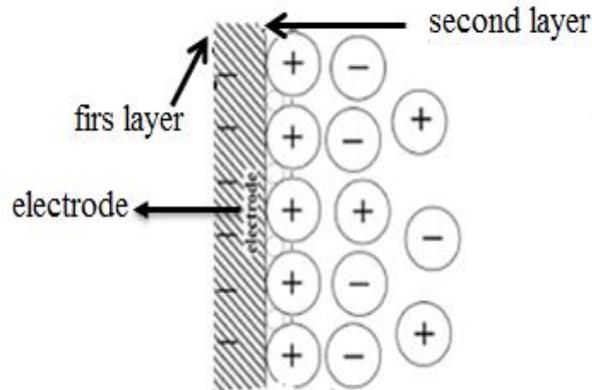
two tetrahedral sheets sandwiching a central octahedral sheet. These three sheets (figure (2.4)) are forming one nanometer thick platelet (Trauger 1994).



**Figure (2.4)** : Schematic of montmorillonite structure – tetrahedral silica sheets sandwiching a central cation octahedral sheet (Trauger 1994).

Each silica atom in tetrahedral sheet combines with four oxygen atoms, and each  $\text{Al}^{+3}$  atom in octahedral sheet combines with six oxygen atoms. The two sheets together form the lamellar structure. Furthermore, the lamellar structure forms electrical double layer model in the presence of electrolyte solution (figure (2.5)) (Trauger 1994).

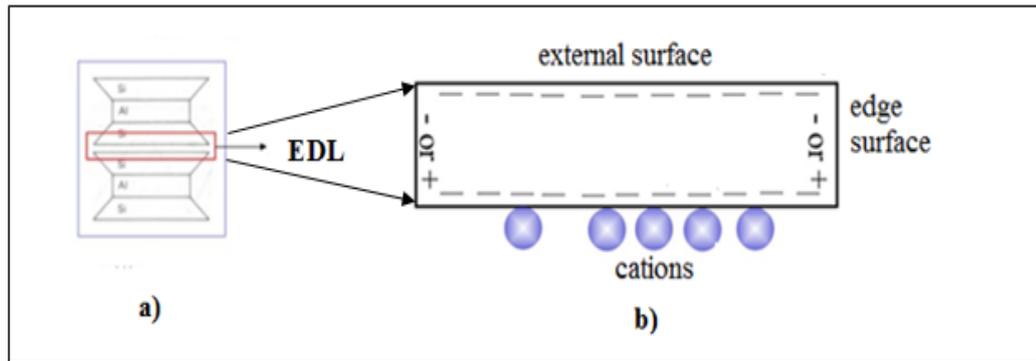
The electrical double layer refers to two parallel layers. The first layer is the surface charge (either positive or negative) comprises ions adsorbed onto surface due to chemical interaction. The second layer comprises ions attracted to the surface charge via Coulomb force (figure (2.5)) (Chem 1998).



**Figure (2.5):** The electrical double layer structure where the first layer is charge surface with net negative charge density and the second layer is composed the positive charge due to coulomb force

The platelets' surface has negative net charge due to ion exchange, such as, the changing of  $\text{Si}^{+4}$  with  $\text{Al}^{+3}$  in silica tetrahedral layer or  $\text{Al}^{+3}$  with  $\text{Fe}^{+2}$  in alumina octahedral layer. However, cations such as  $\text{Ca}^{+2}$  and  $\text{Na}^{+1}$  neutralize this negative charge at the surface (Metropolis 2007).

The electrical double layer, which has been used as a model for Monte Carlo simulation and other techniques (Metropolis 2007), is formed by clay platelets in the presence of electrolyte aqueous solution. The Bentonite platelet has two surfaces: the external surface and the edge surface (figure (2.6)). The external surfaces have negative charge because of the ions exchange, and the edge surfaces may have positive or negative net charge according to the reactions between ions.



**Figure (2.6):** a) The electrical double layer, b) EDL's external surface and edge surface: the external surface has positive or negative charge but the edge surface has negative net charge.

It should be noted that the adsorption of water molecules occurs at the external surface of EDL (figure (2.5)). In addition, the reactions between the ions and water molecules depend on the pH of the aqueous solution (Jonsson et al., 2008). When the pH of the aqueous solution is less than 7 (acidic solution), the following reactions between water and ions may occur:



where  $M^{+}$  is metallic ion at the surface. But if the pH of the aqueous solution is more than 7 (basic solution), the decomposition of MOH into ions is described by the following equation:

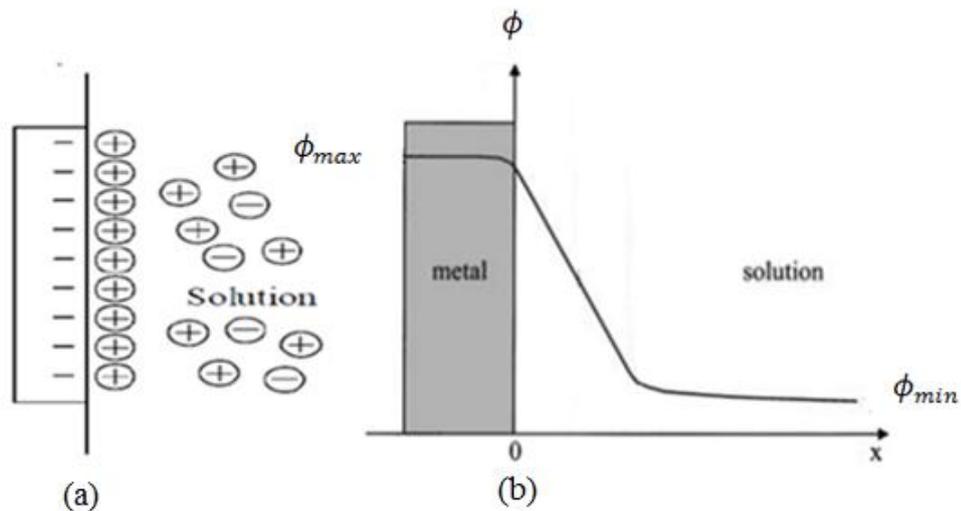


So, the net negative charge at the surface will be increasing by increasing the PH of the aqueous solution. But this negative charge can be neutralized by cations between layers of different valences (Trauger, 1994).

### 6.3 Electrical Double Layer (EDL)

Electrical Double Layers (EDL) diffuse the charge at their surfaces. The EDL refers to the distribution of the cations on the clay platelet and the net negative charge on the layer. The ions exchange process occurs by impressing the clay into aqueous solution. So that, the distribution of ions in the solution will change (Mitchell, 1993).

Helmholtz model is a practical model to the structure of the EDL (figure (2.7)). This model can be described as two layers having opposite charges: the negative charge (clay platelet) and the positive charge (cations in the solution). The cations are adsorbed into the surface because of the attraction force (figure (2.7.a)). The electric potential is decreasing as the distance from the surface is increasing and it has the maximum value  $\phi_{max}$  at the surface of layer (figure (2.7.b)) (Scholz 2002).



**Figure (2.7):** (a) The distribution of the charge in Helmholtz double layer model (b) the change in electrical potential as a function of the distance from the surface layer (similar to discharge capacitor) (Scholz 2002).

In general there are some assumptions which are important while doing calculation for EDL and Helmholtz model (Olphen, 1977):

1. The permittivity value of the medium between the two layers should be constant.
2. The distribution of the charges on the surface of the layer should be uniform.
3. The interactions between the interlayer charges are neglected.
4. The EDL thickness is about 30 nm.
5. The charges are considered to be point charges (Endo et al., 2002).

The Boltzmann equation for the distributions of ions in electric field can be defined by the equation (Meunier, 2005):

$$C_i = C_{i0} e^{\left(\frac{v_i e \phi}{k_B T}\right)} \quad (2.3)$$

where,  $C_i$  is the ionic concentration of particle  $i$ ,  $v_i$  is the ion valency,  $e$  is electron charge,  $C_{i0}$  is the ionic concentration at the surface with electrical potential  $\phi_{max}$ ,  $k_B$  is Boltzmann constant and  $T$  is the absolute temperature.

#### 6.4 Distribution Coefficient

The distribution coefficient ( $k_d$ ) describes the sorption of the radioactive ions in Bentonite clay, where  $k_d$  can be defined as:

$$k_d = \frac{\text{nuclide concentration in the solid phase}}{\text{nuclide concentration in the liquid phase}} \times \frac{V}{m} \quad (2.4)$$

where  $V$  is the volume of the solution and  $m$  is the mass of the Bentonite (Xu et al., 2008).

The ion exchange process can be explained in terms of the retention coefficient ( $\gamma$ ) defined by (Qamhieh and Jönsson, under preparation):

$$\gamma = \frac{\langle C_{EDL} n^+ \rangle + C_B n^+}{C_B n^+} \quad (2.5)$$

where  $\langle C_{EDL} n^+ \rangle$  is the average electrical double layer concentration of cations that has valence ( $n^+$ ) and  $C_B n^+$  is the cations concentration in the bulk solution. And since the average electrical double layer concentration is much more than the bulk concentration, the  $C_B n^+$  can be neglected in the numerator. Accordingly, the retention coefficient can be simplified to:

$$\gamma = \frac{\langle C_{EDL} n^+ \rangle}{C_B n^+} \quad (2.6)$$

### 6.5 The Factors Affecting Sorption Process

The sorption process of ions into Bentonite clay can be affected by some factors such as (Lujaniene et al., 2006):

1. The properties of the metal in the solution such as its size or valence.
2. The type of Bentonite clay such as kaolinite and vermiculite.
3. The solution properties such as ionic strength, pressure on the bulk, pH, the temperature, the contact time and the concentration of radioactive ions.

### 6.6 Ions Exchange and Surface Complexation

To understand the sorption process of radioactive ions on Bentonite clay there are two concepts that should be considered which are the ions

exchange process and the surface complexation. First, the ions exchange between cations neutralizes the net negative charge on the surface of Bentonite, since the cations with higher valence were replaced by cations with lower valence (Poernomo, 2010). However, the ions exchange process is characterized by the following:

1. Taking place at basal surface (second surface (figure (2.5))).
2. independent of acidity (pH).
3. Are a result of the interactions between the ions in the solution and the charges on the surface (Fletcher and Sposito, 1989).

The reaction of ion exchange, for example between  $L^+$  and  $G^+$ , can be expressed as:



where  $Z$  is the solid exchanger and  $L^+$  and  $G^+$  are ions in the solution.

Second, surface complexation includes the hydroxyl group  $OH^-$  and Oxygen atoms. There are two types of complexes namely: inner-sphere and outer-sphere. If there are no water molecules between the ions and the functional group, the reaction result is an inner-sphere, and attributed to more covalent bonds. On the other hand, if at least there is one water molecule attached to the functional group, the complex is classified as an outer-sphere, and corresponds to electrostatic attraction (Cronstrand, 2005).

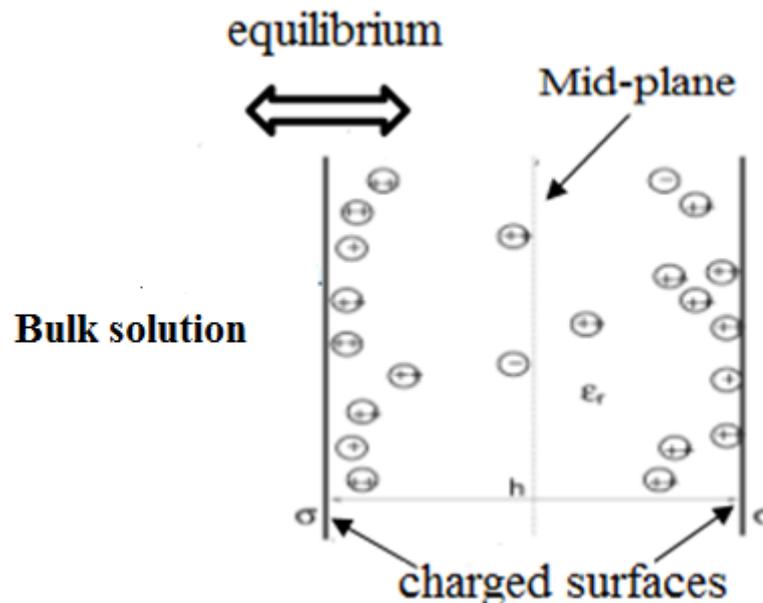
## Chapter Three

### Methodology

#### 7.1 Lamellar Structure

The montmorillonite structure is lamellar structure (fine layers) which can be modeled by two infinite parallel planer surfaces separated by distance  $h$  as shown in figure (3.1) and with negative uniform surface charge density at the surface of planers (Chem 1998). The assumptions for this lamellar structure model are:

1. The bulk solution is at equilibrium with lamellar structure system.
2. The charges are treated as spheres with fixed diameter ( $d$ ).
3. The solvent in this system is the water with constant dielectric permittivity ( $\epsilon_r = 78$ ) (salah et. al 2012).



**Figure (3.1):** The two parallel planer surface with net negative charge density at the surface  $\sigma$  separated by distance  $h$  (Segad et al., 2010).

The Coulomb's interaction law for the electrical interaction between two charged particles can be described by these equations:

$$\phi(r) = \frac{q_i q_j}{4\pi \epsilon_0 \epsilon_r} \quad r > d \quad (3.1)$$

$$\phi(r) = \infty \quad r \leq d \quad (3.2)$$

where  $\phi(r)$  is the electrical potential between the particles  $i$  and  $j$ ,  $q_i$  is the charge of the particle  $i$ ,  $q_j$  is the charge of particle  $j$ ,  $\epsilon_0$  is the electrical permittivity of the free space,  $d$  is diameter of atom and  $\epsilon_r = 78$  is the dielectrical permittivity of the water.

## 7.2 Monte Carlo Simulation Method

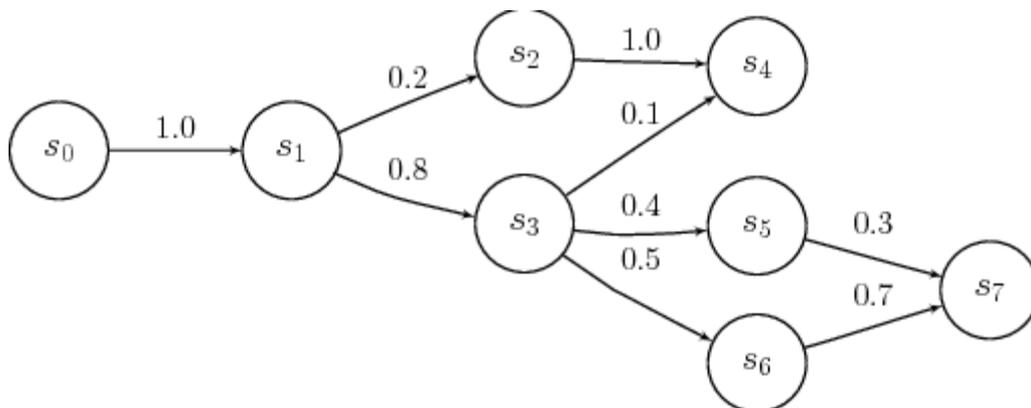
To study the behavior of electrical double layer in statistical mechanics there are different methods such as the Poisson Boltzmann equation and Monte Carlo simulation method. Monte Carlo simulation method is computation technique which can account the risk in quantitative analysis by finding the possible range of the outcome values and probability distribution for them. Moreover, Monte Carlo method perform tens of thousands recalculation of the simulation to produce distributions of the possible outcome values (Valleau, 1991).

It is also an efficient method to solve high dimension problem, it can be implemented in several ensembles such as grand canonical ensemble and isobaric–isothermal ensemble.

Canonical ensemble is the statistical ensemble that represents possible states of a mechanical system in thermal equilibrium with a heat bath as

fixed temperature. The system can exchange energy with heat bath, so that the states of the system will deferent total energy.

The Monte Carlo method depends on Markov chain and metropolis algorithm (Giorgio et al. 2010). Markov chain can be described by a set of state  $S = \{s_1, s_2, s_3, \dots\}$ . The process starts at one of these states such as  $s_i$  then the transition is possible to other state such as  $s_j$ , this transition is described by the transition probability  $p_{ij}$ . However, if there is no transition to a new state the probability is  $p_{ii}$  (Tildesley, 1987). The transition probability from state  $n$  to state  $n+1$  depends on the current state  $n$ , but not on the previous state  $n-1$ , figure (3-2).



**Figure (3.2):** Example for markov chain for random system, the probability to move from state  $s_0$  to state  $s_1$  is one exactly, and the total summation of probability out form any state is one.

Markov chain is the method used in metropolis algorithm which was introduced by Metropolis in 1953. This algorithm constructs random process (Markov process) and the probability ( $P$ ) of particular point in this process is related to Boltzmann factor ( $\beta = 1/k_B T$ ) as follows:

$$P \propto \exp(-\beta E(r)) \quad (3.3)$$

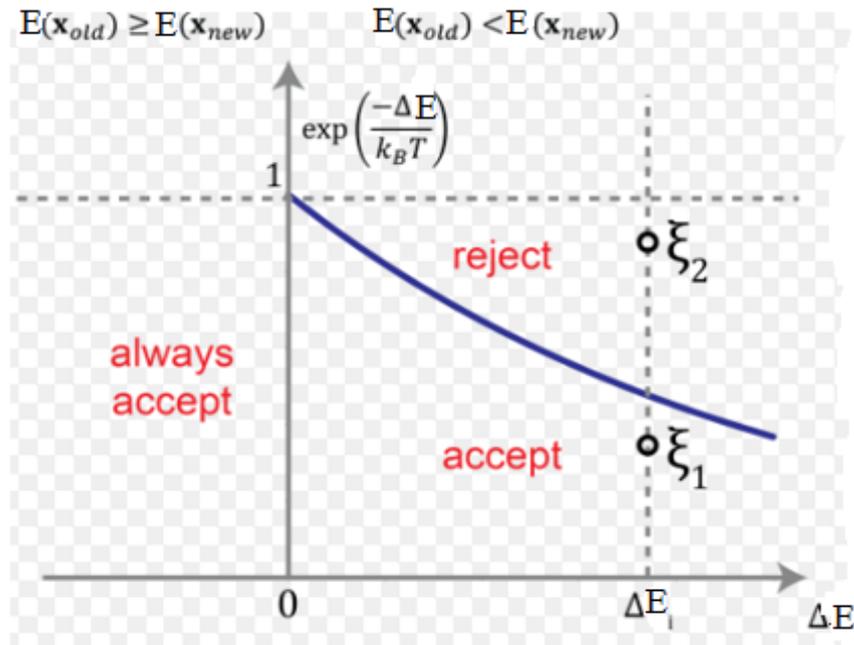
Where  $E(r)$  is the energy of the particle at displacement  $r$  and  $k_B$  is Boltzmann constant To make random process, first the particle is chosen randomly and its energy ( $V(r_i)$ ) is calculated, then the displacement is changed to  $r_j$  and the new energy ( $V(r_j)$ ) can be calculated. Finally, the probability of transition from state  $i$  to state  $j$  can be defined by this equation (Tildesley, 1987):

$$P_{ij} = \text{minimum} (1, \exp -\beta ( E(r_i) -E(r_j))). \quad (3.4)$$

From equation (3.4) we can conclude that the probability is an exponential function it takes values equal or less than one. Moreover, to explain the transition accepted or rejected the potential energy difference must be defined as follows:

$$\Delta E_{ij} = E(r_j) -E(r_i) \quad (3.5)$$

The transition is accepted with probability  $P =1$  if  $\Delta E_{ij} < 0$ , then the particle is at state  $s_j$ . If  $\Delta E_{ij} > 0$  then the random number  $\xi$  (where  $\xi$  is potential difference between old and new states) is generated from the transition which is accepted if  $\xi < P_{ij}$  then the particle is at state  $s_j$ . Otherwise, the transition is rejected and the particle is still at state  $s_i$  (figure (3.3)).

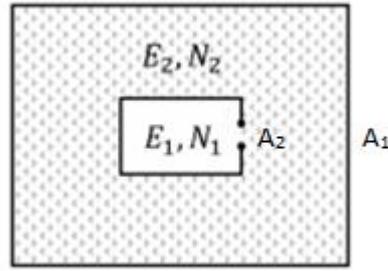


**Figure (3-3):** The exponential function which defines the transition from state  $i$  to state  $j$  is accepted or rejected since if  $E_{old} \geq E_{new}$  the transition is accepted but if  $E_{old} < E_{new}$  so the random number  $\xi$  is selected and if  $\xi < P$  the transition is accepted otherwise the transition is rejected since  $E(x_{old}) = E_i$  and  $E(x_{new}) = E_j$ , where  $x_{old}$  is the position of state  $i$  and  $x_{new}$  is the position of state  $j$ .

### 7.3 Grand Canonical Ensemble

The grand canonical ensemble is a generalization of the canonical ensemble which is restricted to some of laws. In canonical ensemble the total number of particles is constant, and in grand canonical ensemble the total number of particles and the total energy of ensemble are constant.

Consider the system  $A_1$  and particle reservoir  $A_2$  in figure (3.4):



**Figure (3.4):** The system  $A_1$  with its energy  $E_1$  and the number of particle is  $N_1$ , and the particle reservoir system  $A_2$  with its energy  $E_2$  and total particle is  $N_2$ .

Assume the system  $A_2$  is larger than the system  $A_1$ , and the two systems are in thermal equilibrium at temperature  $T$  and with chemical potential  $\phi$  so:

$$E_2 > E_1 \quad (3.6)$$

$$N_2 > N_1 \quad (3.7)$$

And in this grand canonical ensemble there are two boundary conditions which are

$$N_1 + N_2 = N = \text{constant.} \quad (3.8)$$

$$E_1 + E_2 = E = \text{constant} \quad (3.9)$$

In sorption study, the best ensemble should be chosen is grand canonical ensemble, because in this ensemble the adsorbent particles is still in equilibrium with Reservoir system (Bentonite clay). The chemical potential ( $\mu$ ) and the temperature inside and outside the clay are equal. Moreover, the volume of system and reservoir are still constant, for this conditions the grand canonical ensemble is called  $(\mu VT)$ - ensemble (Smit, 1996).

The partition function ( $Z(\mu, V, T)$ ) of grand canonical ensemble can be given by the equation:

$$Z(\mu, V, T) = \sum_N e^{(N\mu\beta)} \left( \sum_J e^{-\beta E^{NJ}} \right) \quad (3.10)$$

where  $\mu$  is chemical potential of the ensemble,  $V$  is volume of the ensemble,  $T$  is temperature of the ensemble,  $\beta$  is Boltzmann factor and  $E^{NJ}$  is the potential energy of the ensemble at number of particles  $N$  and at state  $J$ .

In general, the partition function of canonical ensemble can be defined by the equation:

$$Q(N, V, T) = \sum_J e^{-\beta E^{NJ}} \quad (3.11)$$

By inserting eq. (3-10) into eq. (3-11) the partition function for  $(\mu VT)$ -ensemble is given as:

$$Z(\mu, V, T) = \sum_N e^{(N\mu T)} Q(N, V, T) \quad (3.12)$$

Since the probability is normalized so:

$$1 = \sum_{J, N} P_j(N) \quad (3.13)$$

Then the partition function  $Z(\mu, V, T)$  is:

$$Z(\mu, V, T) = \sum_N \left( \frac{e^{N\mu\beta}}{\lambda^{3N}} \int_0^L \dots \int_0^L dr^N e^{-\beta E(r^N)} \right) \quad (3.14)$$

where  $r$  is the radial distance,  $N$  is the number of particles and  $\lambda$  is de Broglie wavelength and  $L = 30$  nm. (McQuarrie, 1976):

The average of any quantity  $K$  can be defined by the following equation:

$$\langle K \rangle_{\mu VT} = \frac{\sum_{N=0}^{\infty} (N! \lambda^{3N})^{-1} e^{N\mu k_B V^N} \int dS X(S) e^{-k_B E(S)}}{Z(\mu, V, T)} \quad (3.15)$$

where K could be volume, temperature, energy, entropy, number of particles or other quantity. In  $(\mu VT)$ - ensemble, the bulk reservoir and lamellar structure are in equilibrium. So, the total chemical potential for each charge in bulk solution and in electrical double layer is the same. However, in grand canonical ensemble, if the particle moves from state i to state j then the probability of moving the particle between these states is defined by equation (3.3) (Metropolis et al., 1953). However The probability of removing the random particle is given by:

$$P_{ij} = \text{minimum} \left( 1, \frac{N\lambda^3}{L^3} e^{(-\beta\{\mu + \Delta\phi_{ij}\})} \right) \quad (3.16)$$

Whereas The probability to add random particle is  $\phi_{ij}$ :

$$P_{ij} = \text{minimum} \left( 1, \frac{V}{(N+1)\lambda^3} e^{(-\beta\{\Delta\phi_{ij} - \mu\})} \right) \quad (3.17)$$

In this simulation the particles are confined in simulation box of a certain dimension, which is assumed to be periodic. In addition, each box contains N particles, and if the particle moves to a higher box then the image charge particle comes from the lower box (Metropolis et al., 1953).

#### 7.4 Methodology

The results of this work were obtained by Monte Carlo simulations in grand canonical ensemble using Metropolis algorithm. The bulk solution includes different concentrations of NaCl and CaCl<sub>2</sub> which depend on the kind of water. In sea water for example, the concentrations are 100 mM NaCl and 10 mM CaCl<sub>2</sub>. On the other hand, the concentrations in ground water are 1mM NaCl and 4 mM CaCl<sub>2</sub>. In addition, the water contains

radioactive ions such as hexa-, penta-, tri-, tetra-, di-, and monovalent radioactive ions, but in this research we have considered hexavalent ions. However, the simulation is performed in rectangular box  $W \times W \times L$ , where  $L = 30$  nm is the separation between the two parallel planer surface and  $W$  is width and height of rectangular box. The chemical potential can be written as:

$$\mu = k_{\beta} T \ln \lambda^3 + k_{\beta} T \ln c + \mu^{exc} \quad (3.18)$$

where  $T$  is the temperature in kelvin,  $k_{\beta}$  is Boltzmann constant,  $\lambda$  is the thermal de Broglie wavelength,  $c$  is the average concentration of aqueous solution. The term  $(k_{\beta} T \ln \lambda^3)$  is the standard term,  $(k_{\beta} T \ln c)$  is the ideal term and  $\mu^{exc}$  is excess chemical potential term. However, The average electrical double layer concentration can be defined by the following equation (Odeh et al., 2015) :

$$\langle C_{EDL} \rangle = \frac{\langle M^{n+} \rangle}{W \times W \times L} 1660.54 \quad (\text{molarity}) \quad (3.19)$$

$$\langle C_{EDL} \rangle = \frac{\langle M^{n+} \rangle}{W^2 \times 30} 1660.54 \quad (\text{molarity}) \quad (3.20)$$

where the number 1660.54 is multiply to transfer the unit from  $M/m^3$  to  $M$ . Moreover, the fraction of  $M^{+6}$  ions in bulk solution which contains NaCl and  $CaCl_2$  can be defined by equation (3.21) with bulk concentration  $C_B$ , and the surface charge density at surface of planers is  $\sigma$  with temperature of the system is  $T$  (Hansen and McDonald, 2006).

$$\alpha(M^{+6}) = \frac{\langle M^{+6} \rangle * 6}{\langle Na^{+} \rangle * 1 + \langle Ca^{+2} \rangle * 2 + \langle M^{+6} \rangle * 6} \quad (3.21)$$

where  $\alpha(M^{+6})$  is the fraction of  $M^{+6}$  ions in bulk solution which contains NaCl and  $\text{CaCl}_2$ . In addition, the ions exchange coefficient or the retention coefficient is:

$$\gamma = \frac{\langle C_{EDL} \rangle + C_B}{C_B} \quad (3.22)$$

## Chapter Four

### Results and Discussion

The sorption of hexavalent ions from ground water and sea water on Bentonite clay was studied by doing a series of Monte Carlo simulation.

During this study, several assumptions were considered:

- \* The bulk solution is in equilibrium with electrical double layer.
- \* The distribution of charges at the surface of platelet is uniform.
- \* The bulk solution has different concentrations of hexavalent ( $M^{+6}$ ) radioactive ions.

In this chapter, there are four sections: the effects of the bulk concentration (sec 4.1), the effects of surface charge density of electrical double layer (sec 4.2), the effects of temperature of the system (sec4.3) and the effects of ionic strength of aqueous solution on the sorption process (sec 4.4).

#### 8.1 The Effects of Bulk Concentration

The effects of bulk concentration on the sorption process appears on the following: 1) On cations fraction in electrical double layer (sec 4.1.1).

2) On the average electrical double layer concentration (sec 4.1.2).

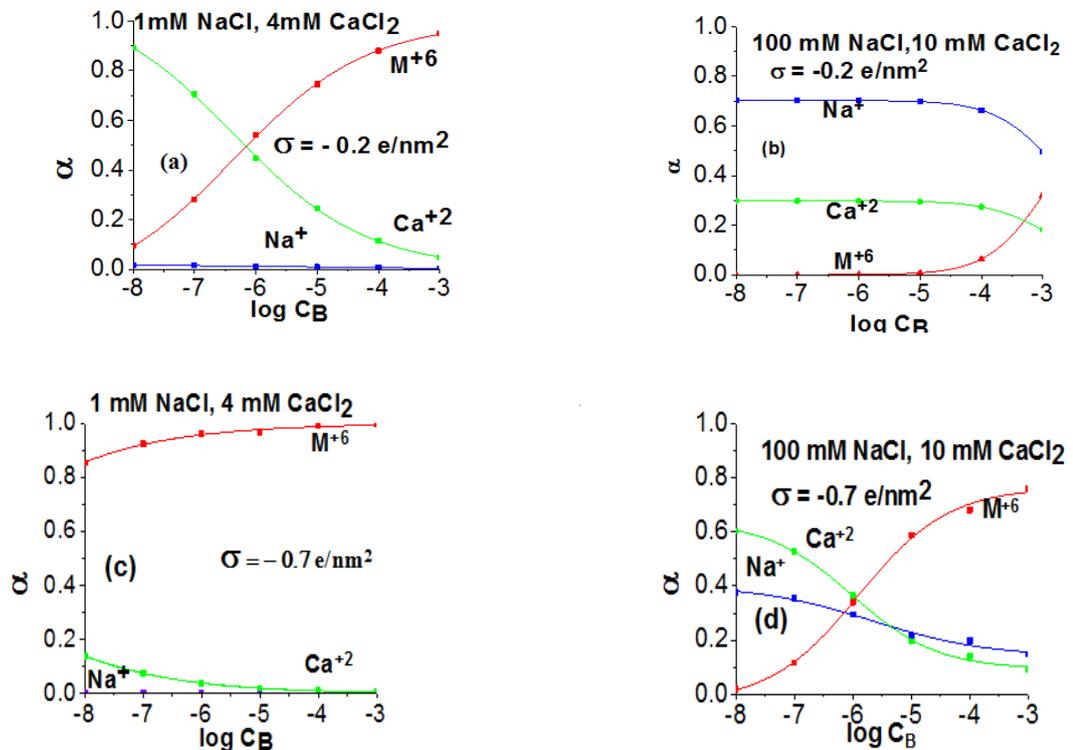
3) On the retention coefficient (sec 4.1.3).

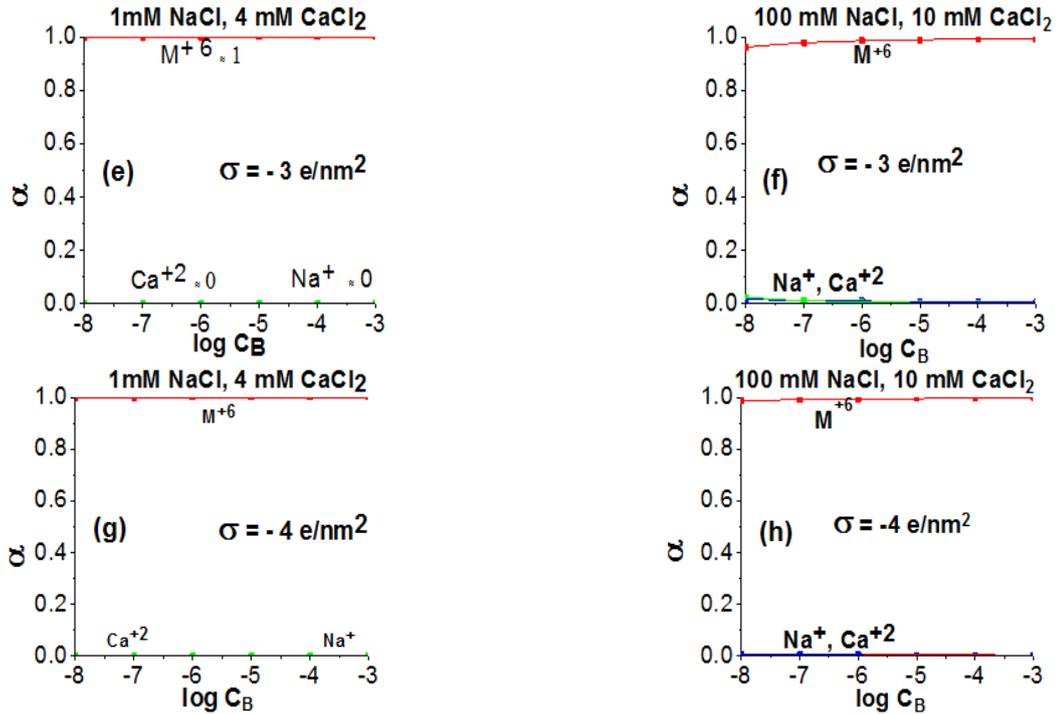
##### 8.1.1 The Effects on Cations Fraction in Electrical Double Layer

The fraction of three ions ( $Na^+$ ,  $Ca^{+2}$  and  $M^{+6}$ ) in the EDL as a function of the bulk concentration with different values of surface charge density ( $\sigma$ )

are shown in figure (4.1). The fraction of the three ions are computed at room temperature (298 K) and the range of hexavalent ions concentration in the bulk solution from  $10^{-8}$  to  $10^{-3}$  M.

It is clear from figure (4.1) that the fraction of hexavalent cations  $\alpha$  ( $M^{+6}$ ) in the bulk solution of ground water (1mM NaCl, 4mM  $CaCl_2$ ) and sea water (100mM NaCl, 10mM  $CaCl_2$ ) increases by increasing its concentration in the bulk. Meanwhile, the fraction of  $Ca^{+2}$  and  $Na^+$  decreases dramatically. This demonstrates the concept of sorption process in which the concentration of hexavalent ions at the surface of platelets increases as the bulk concentration increases (Salah and Mohammad, 2012).

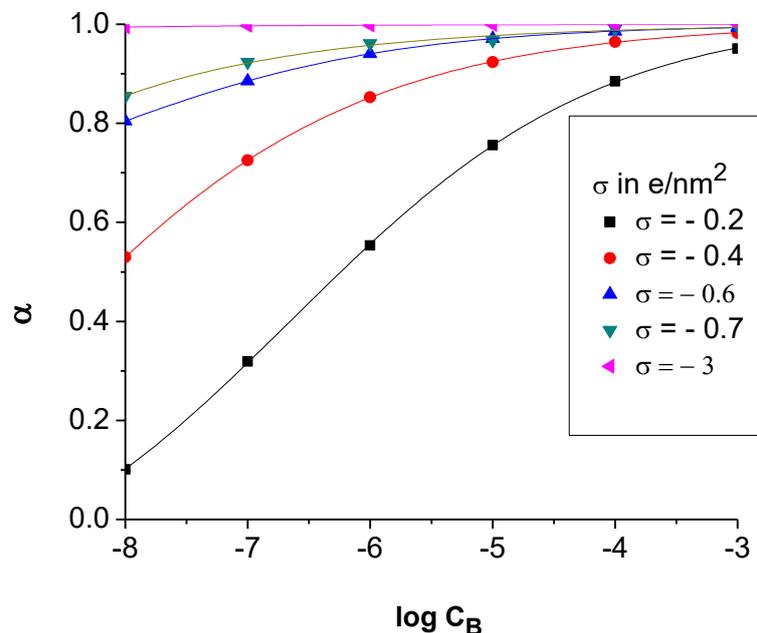




**Figure (4.1):** The fractions of ions in the electrical double layer ( $\alpha$ ) against the logarithm of bulk concentration  $\log C_B$  at room temperature and at 1mM NaCl, 4mM CaCl<sub>2</sub> and at 100mM NaCl, 10mM CaCl<sub>2</sub> concentrations with different values of surface charge density: (a) and (b)  $\sigma = -0.2$ , (c) and (d)  $\sigma = -0.7$ , (e) and (f)  $\sigma = -3$ , (g) and (h)  $\sigma = -4\text{ e/nm}^2$ .

In addition, one of the main parameters that affects the fraction and the abundance of the cations is the surface charge density. In general, the fraction of the hexavalent ions increases by increasing the surface charge density of platelets. It can be noticed that by increasing the surface charge density (sec 4.2) from  $-0.2$  to  $-3\text{ e/nm}^2$  the abundance of hexavalent ions in electrical double layer increases (figure (4.2)). For example, in ground water concentration from figure (4.1.a) when the  $\sigma = -0.2\text{ e/nm}^2$  and the bulk concentration  $\langle C_B \rangle = 10^{-6}\text{ M}$ , the fraction of  $M^{+6}$  is  $\alpha(M^{+6}) = 0.5402$ . However, from figure (4-1-e) when  $\sigma = -3\text{ e/nm}^2$  and  $\langle C_B \rangle = 10^{-6}\text{ M}$ , the fraction of hexavalent ions is  $\alpha(M^{+6}) = 0.9995$ . In contrast, the abundance

of monovalent and divalent ions in the electrical double layer decreases when  $\sigma$  increases. For example, in sea water concentration from figure (4.1.b) at  $\sigma = -0.2$  and  $\langle C_B \rangle = 10^{-7}$  M the fraction of monovalent ions  $\alpha(\text{Na}^+) = 0.7022$  and divalent ions  $\alpha(\text{Ca}^{+2}) = 0.2977$ . At the same bulk concentration and at  $\sigma = -3 \text{ e/nm}^2$ , the fractions are  $\alpha(\text{Na}^+) = 0.0112$  and  $\alpha(\text{Ca}^{+2}) = 0.0105$  as shown in figure (4.1.f).



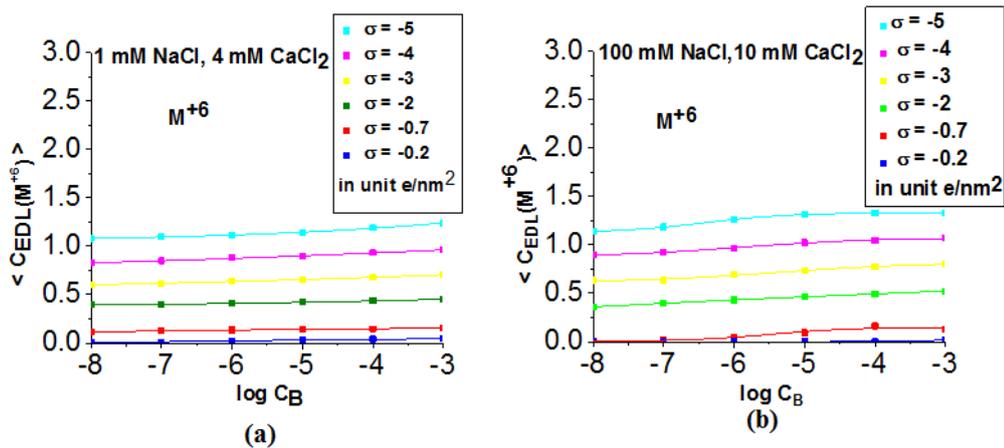
**Figure (4.2):** The fraction of hexavalent ions as function of logarithm of the bulk concentration for different values of surface charge density ( $\sigma = -0.2, -0.4, -0.6, -0.7$  and  $-3 \text{ e/nm}^2$ ) in ground water concentration (1mM NaCl, 4mM CaCl<sub>2</sub>).

The abundance of monovalent ions in ground water concentration is less than the abundance of divalent ions, while in sea water the abundance of monovalent ions is large, this because the salt concentration NaCl is large in sea water. In addition, at low surface charge density the sorption of hexavalent ions is more efficient at ground water concentration than sea water concentration.

For high values of surface charge density  $\sigma = -4$  and  $-5 \text{ e/nm}^2$ , the fraction of all ions is approximately constant since  $\alpha(\text{Na}^+)$  and  $\alpha(\text{Ca}^{+2})$  vanish while  $\alpha(\text{M}^{+6})$  is completely dominant since as  $\sigma$  increases the negative net charge at the surface increases. We can conclude that at these values of  $\sigma$  there is no effect on fraction of ions in electrical double layer when the bulk concentration changes as shown in figure(4.1.g) and figure (4.1.h).

### 8.1.2 The Effects on Average Electrical Double Layer Concentration

The effect of hexavalent ions concentration  $C_B$  on average electrical double layer concentration  $\langle C_{EDL} \rangle$  is computed at (1mM NaCl and 4mM CaCl<sub>2</sub>) and (100 mM NaCl 10 mM CaCl<sub>2</sub>) and room temperature ( $T= 298 \text{ K}$ ) as shown in figure (4.3). This figure shows that the average electrical double layer concentration  $\langle C_{EDL}^{+6} \rangle$  is slightly increasing at a rate 0.05 in (1mM NaCl 4 mM CaCl<sub>2</sub>) and in (100 mM NaCl 10 mM CaCl<sub>2</sub>). This explains how hexavalent ions neutralize the charge at the surface of platelets.

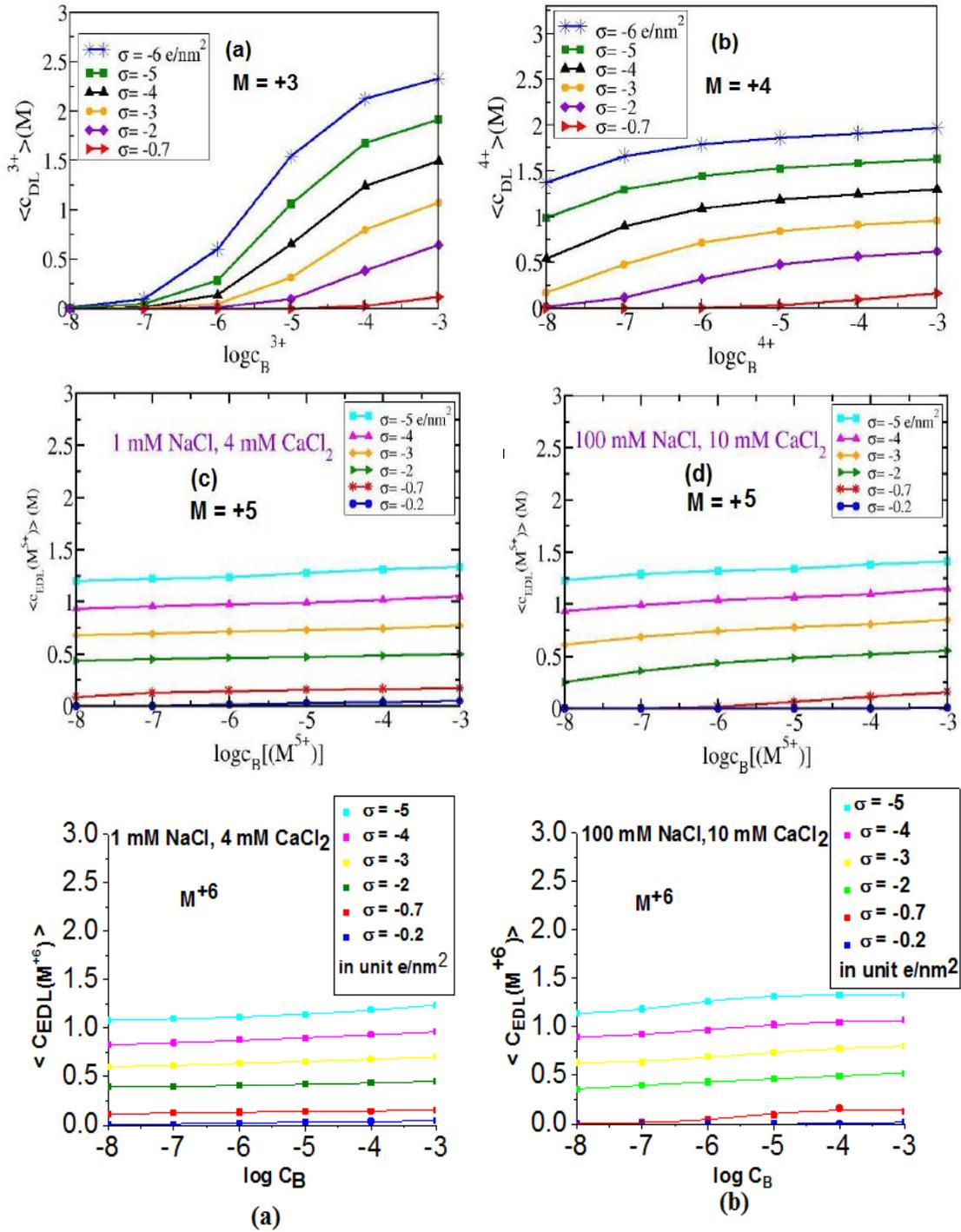


**Figure (4.3):** The average electrical double layer concentration against logarithm of bulk concentration with different values of surface charge density  $\sigma$  at room temperature ( $T= 298$ ), and the bulk include (a) ground water (1mM NaCl and 4 mM CaCl<sub>2</sub>), (b) sea water (100mM NaCl and 10 mM CaCl<sub>2</sub>).

The relation between the electrical double layer concentration  $\langle C_{EDL}^{+6} \rangle$  and the bulk concentration  $C_B$  at room temperature and different values of the charge density is shown in figure (4.3). First, this figure shows that  $\langle C_{EDL}^{+6} \rangle$  increases linearly and steadily as  $C_B$  increases. Second the curve takes higher values of  $\langle C_{EDL} \rangle$  at the same value of  $C_B$  as the surface charge density increases (figure (4-3)).

For example, from figure (4.3.a) at  $C_B = 10^{-5}$  M and  $\sigma = -0.7$  e/nm<sup>2</sup> the  $\langle C_{EDL} \rangle = 0.1400$  M, while at  $C_B = 10^{-5}$  M and  $\sigma = -5$  e/nm<sup>2</sup> the  $\langle C_{EDL} \rangle = 1.1411$  M. This result agrees with the study of the sorption of hexavalent Cr<sup>+6</sup> ion (Tewari et al., 2005), in which the increasing in concentration of Cr<sup>+6</sup> ions in the bulk solution causes similar increasing of the concentration in Bentonite clay. Moreover, by increasing  $\sigma$  the  $\langle C_{EDL} \rangle$  increases for Cr<sup>+6</sup> ions at surface of platelets.

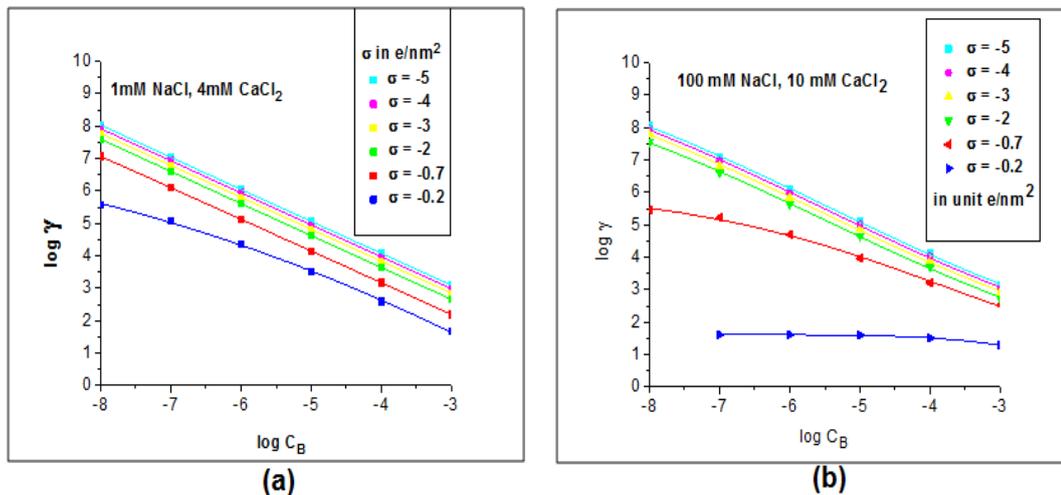
The effect of  $C_B$  on  $\langle C_{EDL} \rangle$  can be shown in figure (4.4) for four different valences: Tri-, tetra- (Marabaa et al. 2014), penta- (Odeh et al. 2015) and hexavalent ions, this figure shows that as the valence (M) increases, the average electrical double layer concentration ( $\langle C_{EDL} \rangle$ ) increases and the curves become linear with slopes approaching to zero in the same bulk concentration  $C_B$  range ( $10^{-8}$  -  $10^{-3}$ ).



**Figure (4.4):** The electrical double layer concentration as function of logarithm of bulk concentration at room temperature and (1 mM NaCl 4 mM  $CaCl_2$ ) (a): trivalent (b) tetravalent (c) pentavalent(d) hexavalent ions sorption into Bentonite clay and in, (e) in sea water in sea water (100 mM NaCl, 10 mM  $CaCl_2$ ) for sorption of (f) pentavalent (g) hexavalent ions into Bentonite clay.

### 8.1.3 The Effects on the Retention Coefficient $\gamma$

The retention coefficient describes the sorption process of hexavalent ions on Bentonite clay. This coefficient is affected by some parameters like concentration of such ions in the bulk solution  $C_B$ . In figure (4.5), the retention coefficient of hexavalent ions decreases as the concentration of hexavalent ions in the bulk solution increases this because the increasing in concentration of hexavalent ions neutralized the negative charge at the surface. This is obviously decreasing linearly except at low surface charge density such as  $\sigma = -0.2 \text{ e/nm}^2$  in sea water (100 mM NaCl, 10 mM  $\text{CaCl}_2$ ) the retention coefficient becomes constant as the bulk concentration increases as shown in figure (4.5.b).



**Figure (4.5):** The logarithm of retention coefficient  $\log Y$  as function of logarithm of concentration of hexavalent ions in the bulk solution  $\log C_B$  with different values of surface charge density ( $\sigma = -0.2, -0.7, -2, -3, -4$  and  $-5 \text{ e/nm}^2$ ) at room temperature ( $T = 298 \text{ K}$ ) and (a) (1 mM NaCl, 4 mM  $\text{CaCl}_2$ ), (b) (100 mM NaCl, 10 mM  $\text{CaCl}_2$ ).

The results shown in figure (4.5) are in good agreement with the results of the sorption of  $\text{Cr}^{+6}$  ions using activated carbon Bentonite. In the sorption of  $\text{Cr}^{+6}$  as the initial concentration of  $\text{Cr}^{+6}$  ion increases the adsorption of

hexavalent ions from aqueous solution increases (Salah and Mohammad, 2012).

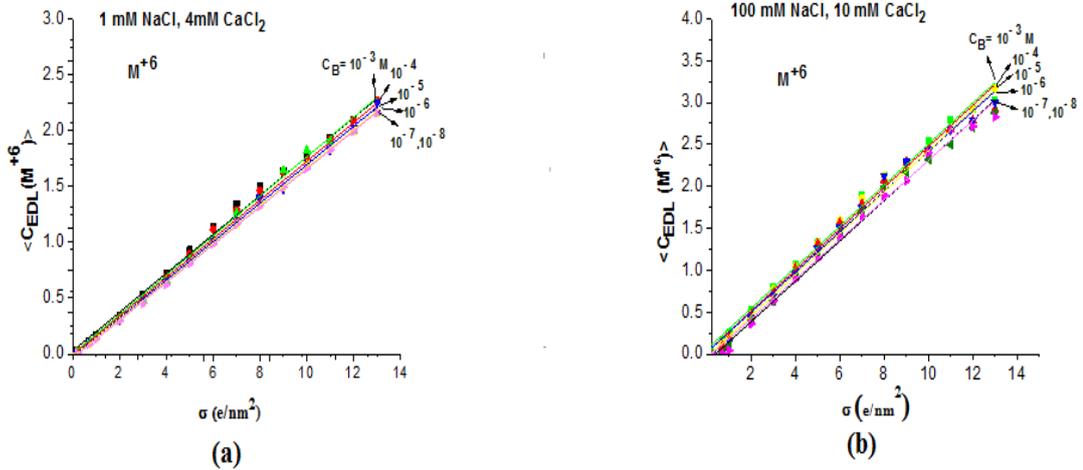
## **8.2 The Effects of Surface Charge Density**

In ground water and sea water, the effect of surface charge density ( $\sigma$ ) is studied. First, on the average electrical double layer concentration ( $\langle C_{EDL} \rangle$ ) (section 4.2.1). Second, on the retention coefficient ( $\gamma$ ) (section 4.2.2).

### **8.2.1 The Effects on the Average Electrical Double Layer Concentration**

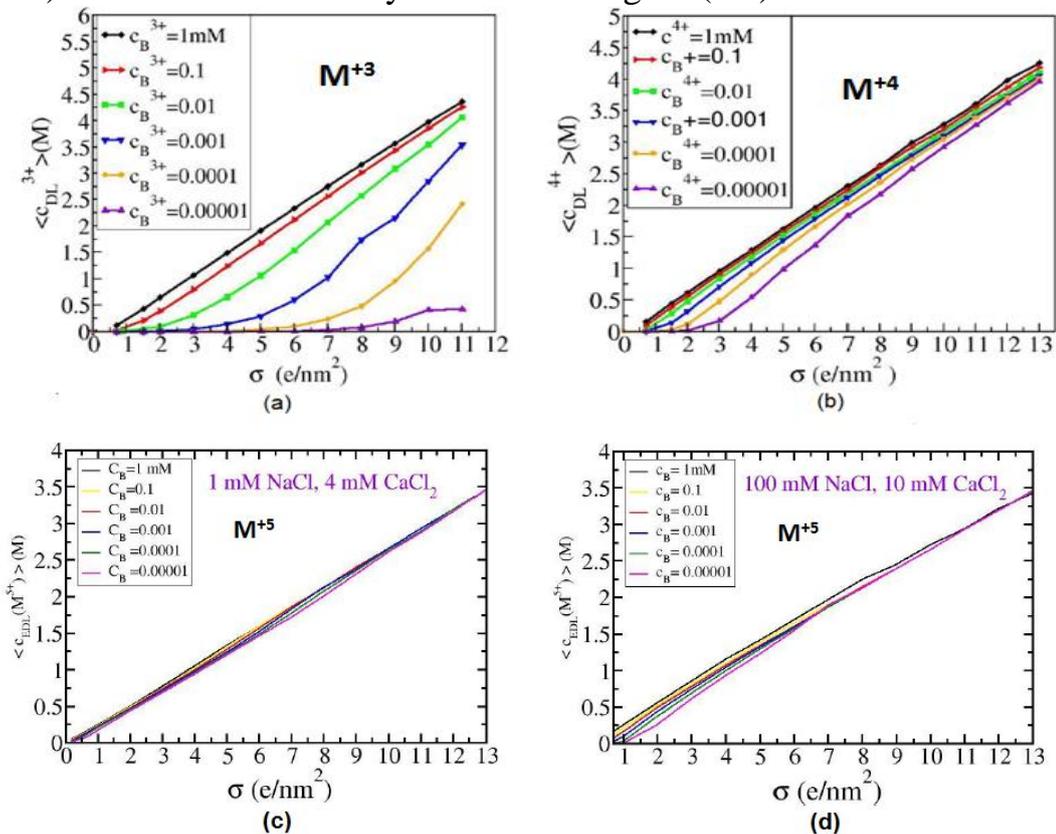
The sorption process of  $M^{+6}$  ions on Bentonite clay is influenced by changing the value of surface charge density  $\sigma$  of the two platelets. The effect of the surface charge density on  $\langle C_{EDL}^{+6} \rangle$  and the retention coefficient is studied by changing the values of  $\sigma$  from 1 to 13 e/nm<sup>2</sup> at the same bulk concentration and room temperature ( $T= 298$  K).

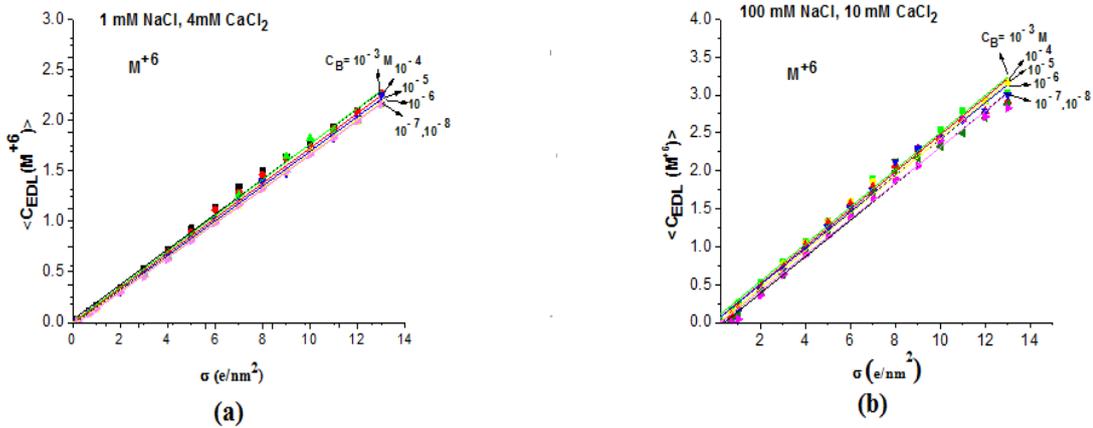
Figure (4.6) shows that the average electrical double layer concentration  $\langle C_{EDL}^{+6} \rangle$  as function of surface charge density is a linear relation. However, at low bulk concentration  $C_B$  the average electrical double layer concentration ( $\langle C_{EDL} \rangle$ ) is almost independent of the bulk concentration  $C_B$  since the lines at  $C_B = 10^{-7}$  and  $10^{-8}$  are identical and coincide on each other. Moreover, the concentration of electrical double layer is slowly increasing when the bulk concentration  $C_B$  is increasing since as increasing  $\sigma$  means the increasing of hexavalent ions concentration at parallel platelet.



**Figure (4.6):** The average electrical double layer concentration ( $C_{EDL}$ ) as function of magnitude of surface charge density ( $\sigma$ ) of two platelets in bentonite with different bulk concentration ( $C_B= 10^{-3},10^{-4},10^{-5},10^{-6},10^{-6},10^{-7}$  and  $10^{-8}$  M) at room temperature ( $T= 298$  K) and (a) 1mM NaCl, 4 mM CaCl<sub>2</sub> (b) 100mM NaCl, 10 mM CaCl<sub>2</sub>.

These results can be compared with the results of studying the sorption of trivalent, tetravalent (Marabaa et al. 2014) and pentavalent (Odeh et al. 2015) ions on Bentonite clay as shown in figure (4.7).





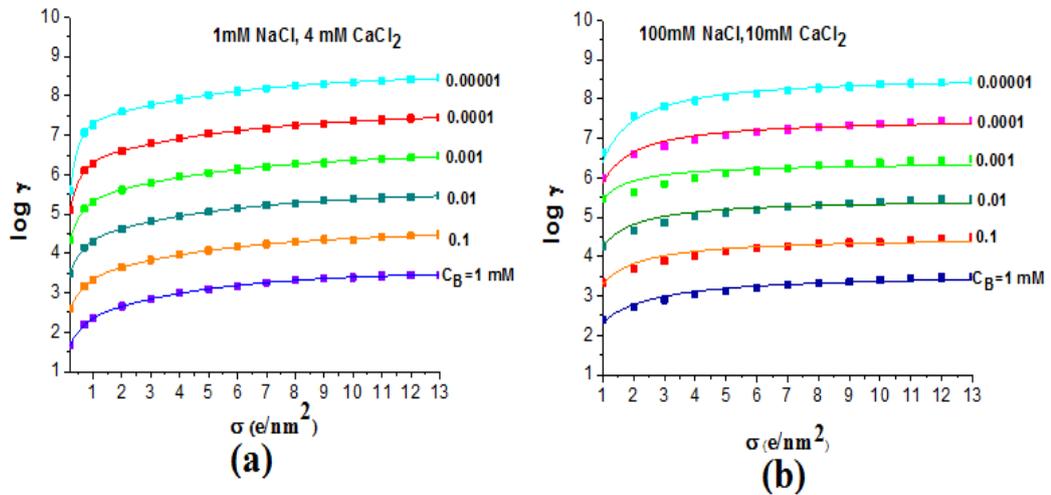
**Figure (4.7):** The average electrical double layer concentration as function of surface charge density of two platelets on Bentonite at room temperature ( $T= 298$  K) for sorption of (a) trivalent ions in ground water, (b) tetravalent ions in ground water, (c) pentavalent ions in ground water and, (d) pentavalent ions in sea water, (e) hexavalent ions in ground water and (f) hexavalent ions in sea water on Bentonite clay.

It can be noticed that if the valence of the electrical double layer increases, its concentration becomes independent of the bulk concentration (the curves become very close to each other as the valence increases as in figure (4.7.c and d)) since as the valence increases the electrical force between the charge increases. In addition, the maximum value of the curves at different valence are decreasing as the valence increasing. In other words, at high surface charge density the electrical double layer decreases as the valence increases.

### 8.2.2 The Effects on the Retention Coefficient

The retention coefficient  $\gamma$  is also affected by changing the values of  $\sigma$  and  $C_B$  as can be noticed from figure (4.8). The retention coefficient increases until it reaches saturation value at higher surface charge density (the

increasing in electrical double layer leads increasing the concentration of  $M^{+6}$  at the surface). In addition, it increases as the bulk concentration decreases. Moreover, the retention coefficient goes to saturation point more quickly at sea water (figure (4.8.b)) more than at ground water (figure (4.8.a)).



**Figure (4.8):** The logarithm of retention coefficient ( $\log(Y)$ ) as function of surface charge density  $\sigma$ , at various bulk concentrations ( $C_B = 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}$  and  $10^{-8}$  M) at room temperature ( $T=298$  K) and (a): 1mM NaCl, 4mM CaCl<sub>2</sub> (ground water) (b): 100mM NaCl, 10mM CaCl<sub>2</sub> (sea water).

In reality, there is a relation between the surface charge density and pH of the solution (Anah and Astrini, 2017). The hydroxyl groups in alkaline solution can dissociate as expressed in the following equation:



So, by increasing the pH of the bulk solution the number of negative ions at the surface of platelets increases which leads to the increase in the total surface charge density.

The influence of pH of the aqueous solution on the sorption of  $\text{Cr}^{+6}$  was studied (Anah and Astrini, 2017). their results agree with our results as the pH of aqueous solution increases above 7 the sorption of  $\text{Cr}^{+6}$  increases.

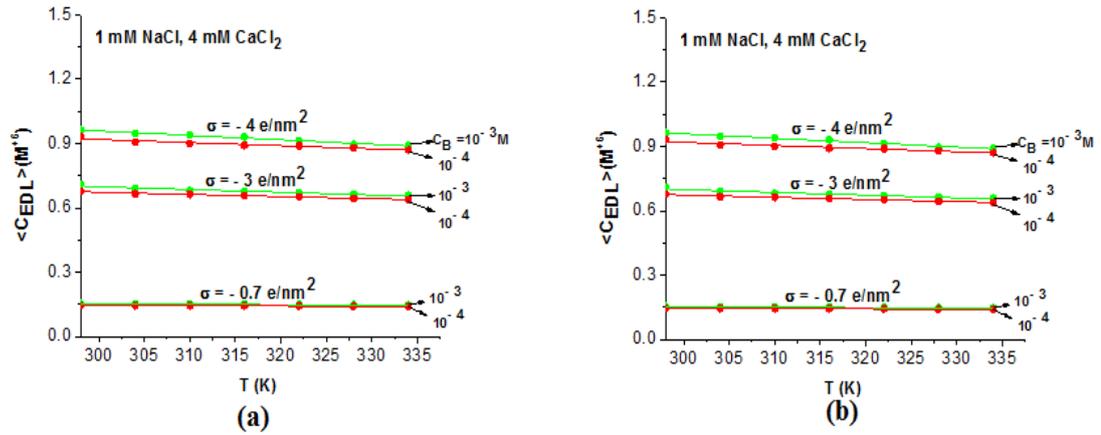
### **8.3 The Effect of Temperature on $\langle C_{\text{EDL}} \rangle$ and $\gamma$**

The effect of changing the temperature from 298 K to 334 K for three fixed values of surface charge density ( $\sigma = -0.7, -3$  and  $-4 \text{ e/nm}^2$ ) for ground water (1mM NaCl 4mM  $\text{CaCl}_2$ ), and for sea water (10mM NaCl 100mM  $\text{CaCl}_2$ ) was studied.

- a. The effect on the electrical double layer concentration  $\langle C_{\text{EDL}} \rangle$  (sec (4.3.1)).
- b. The effect on the retention coefficient  $\gamma$  (sec (4.3.2)).

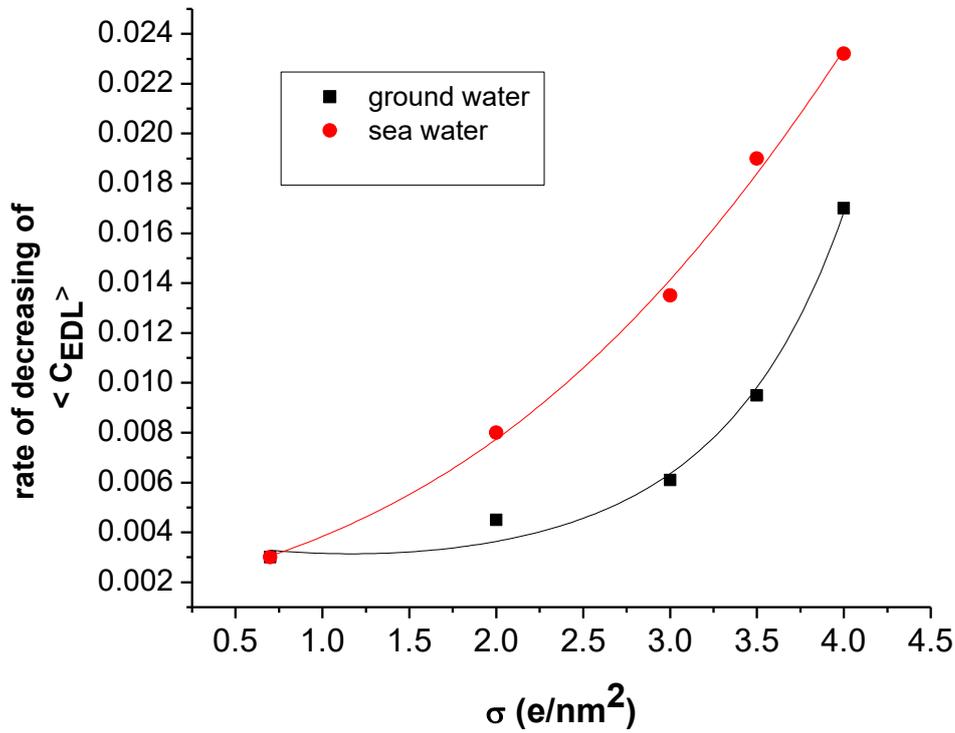
#### **8.3.1 The effect on electrical double layer concentration $\langle C_{\text{EDL}} (\text{M}^{+6}) \rangle$**

As shown from figure (4.9) the average electrical double layer concentration  $\langle C_{\text{EDL}} \rangle$  is linear and decreases slightly (the rate of decreasing is  $10^{-4} \text{ M/K}$  at  $\sigma = -0.7 \text{ e/nm}^2$ ). However, the electrical double layer concentration at sea water (figure (4.9.b)) is more than at ground water because the high salt concentration in sea water (figure ((4.9.a)) for the same temperature. Furthermore, the  $\langle C_{\text{EDL}} \rangle$  increases as the surface charge density increases. The increase in T causes increase in the entropy S of the system as well as increase in the number of hexavalent ions that leave the surface of Bentonite clay to bulk solution. These ions cause a decrease in  $\langle C_{\text{EDL}} \rangle$  which agrees with the previous results.



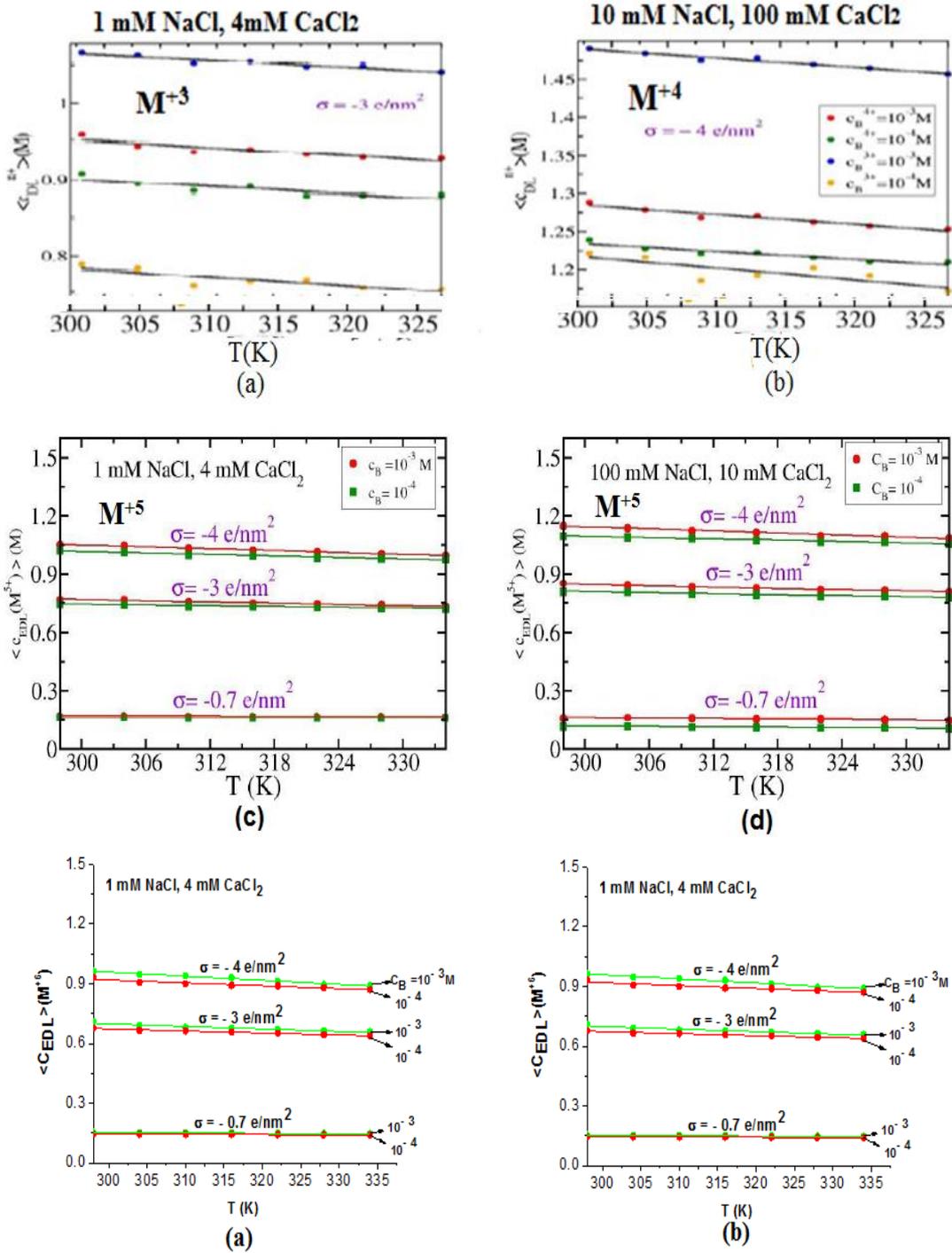
**Figure (4.9):** The average electrical double layer concentration as function of the temperature of system with different values of surface charge density ( $\sigma = -0.7, -3$  and  $-4$  e/nm<sup>2</sup>) at (a): 1 mM NaCl, 4 mM CaCl<sub>2</sub> (b): 100 mM NaCl, 10 mM CaCl<sub>2</sub>. The red lines for  $C_B = 10^{-4}$  M, and the green lines for  $C_B = 10^{-3}$  M.

The rate of decreasing the electrical double layer concentration as function of surface charge density  $\sigma$  was shown in figure (4.10), so this rate is quadratic increasing as  $\sigma$  increasing.



**Figure (4.10):** The rate of decreasing of the electrical double layer concentration (CDL) as function of absolute value surface charge density  $\sigma$  for sorption of hexavalent ions into Bentonite clay in (a): ground water (1 mM NaCl, 4 mM CaCl<sub>2</sub>), (b): sea water (100 mM NaCl, 10 mM CaCl<sub>2</sub>). The dots are from the simulated values, and the lines are quadratic fits.

figure (4.11) compares the results of the electrical double layer concentration as a function of temperature for sorption of trivalent, tetravalent, pentavalent and hexavalent ions into bentonite clay. From this figure it can be concluded that the lines are the same, so the relation between  $\langle C_{EDL} \rangle$  and temperature is not affected by the valence of ions at small surface charge density such as at  $\sigma = -0.7 e/nm^2$ .

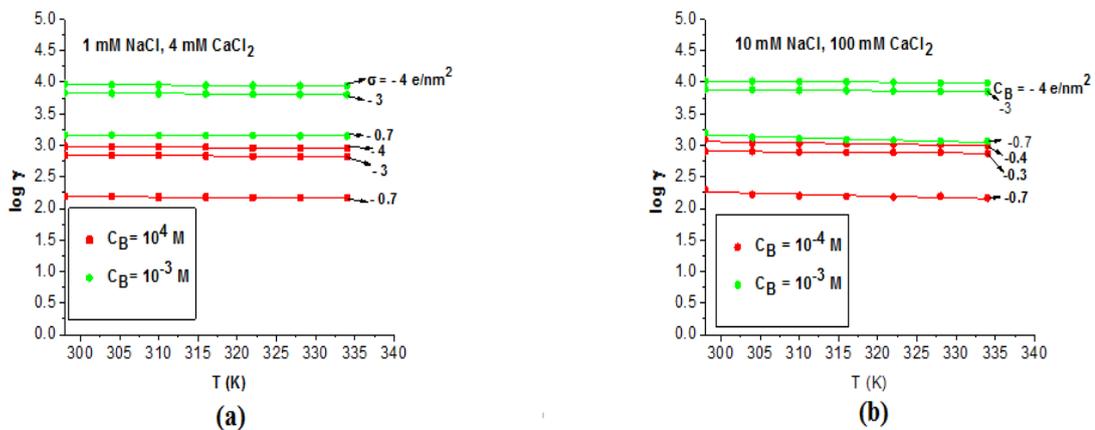


**Figure (4.11):** The electrical double layer concentration as function of temperature for sorption of (a) trivalent ions in ground water, (b) tetravalent ions in ground water, (c) pentavalent ions in ground water and, (d) pentavalent ions in sea water, (e) hexavalent ions in ground water and (f) hexavalent ions in sea water on Bentonite clay.

### 8.3.2 The Effect on the Retention Coefficient $\gamma$

The relation between the retention coefficient and temperature of system is shown in figure (4.12). It can be noticed that the retention coefficient decreases slightly at an average rate of  $10^{-4}$  ( $K^{-1}$ ) as the temperature increases. This is because, the increase in T causes increasing in the entropy S of the bulk system so the retention coefficient decreases.

The effect of temperature on the sorption process of hexavalent ions into Bentonite Clay denotes that this process is exothermal process, so that energy is released to surrounding as heat, light or other forms ( Kuipers and Van 1971).



**Figure (4.12):** The logarithm of retention coefficient as function of temperature of system with two different value of  $C_B$  ( $C_B = 10^{-3}$  and  $10^{-4}$  M) and with three different values of surface charge density ( $\sigma = -0.7, -3$  and  $-4$  e/nm<sup>2</sup>) at (a): 1 mM NaCl, 4 mM CaCl<sub>2</sub>, (b): 100 mM NaCl, 10 mM CaCl<sub>2</sub>.

### 8.4 The Effect of Solution Ionic Strength on Sorption Process

The ionic strength of bulk solution indicates the value of the concentration of different ions in the bulk solution such as Na<sup>+</sup> and Ca<sup>+2</sup> ions. In this

section the effect of ionic strength on the sorption process was studied by changing the concentration of divalent ions ( $\text{Ca}^{+2}$ ) (sec (4.4.1)), and monovalent ions ( $\text{Na}^+$ ) (sec (4.4.2)).

#### **8.4.1 The Effect of the Divalent Ionic Strength on sorption process**

The effect of changing the concentration of  $\text{CaCl}_2$  on the sorption process was studied at fixed values of the concentration of  $\text{NaCl}$  at 1 mM and room temperature ( $T= 298 \text{ K}$ ). The slit width is taken to be 1 nm for two different surface charge densities ( $\sigma = -3$  and  $-4 \text{ e/nm}^2$ ).

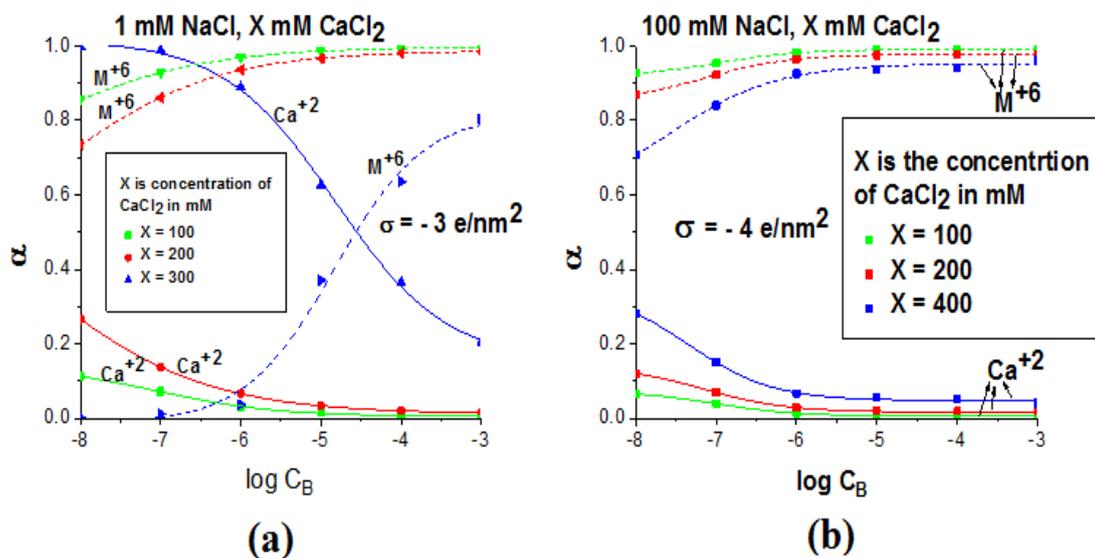
First, the concentration of  $\text{NaCl}$  was fixed at 1 mM and the concentrations of  $\text{CaCl}_2$  were 100, 200 and 300 mM. After that, the relation between the fraction of ions ( $\text{Na}^+$ ,  $\text{Ca}^{+2}$  and  $\text{M}^{+6}$ ) and logarithm of bulk concentration for two different systems  $\sigma = -3 \text{ e/nm}^2$  (figure (4.12.a)) and  $-4 \text{ e/nm}^2$  (figure (4.12.b)) is studied.

Second, the concentration of  $\text{NaCl}$  was fixed at 100 mM and the concentration of  $\text{CaCl}_2$  were 100, 200 and 400 mM. After that, the relation between the fraction of ions ( $\text{Na}^+$ ,  $\text{Ca}^{+2}$  and  $\text{M}^{+6}$ ) and logarithm of bulk concentration for two different systems  $\sigma = -3 \text{ e/nm}^2$  (figure (4.14.a)) and  $-4 \text{ e/nm}^2$  (figure (4.14.b)) is also studied.

Figure (4.13) indicates that at  $\sigma = -3 \text{ e/nm}^2$  as the concentration of  $\text{CaCl}_2$  in the bulk solution increases the fraction of  $\text{Ca}^{+2}$  increases while the fraction of hexavalent ions decreases. Moreover, by increasing the surface charge density to  $\sigma = -4 \text{ e/nm}^2$  the curves have the same behavior but shifted to the left, this means at  $\sigma = -4 \text{ e/nm}^2$  the curves need more concentration of

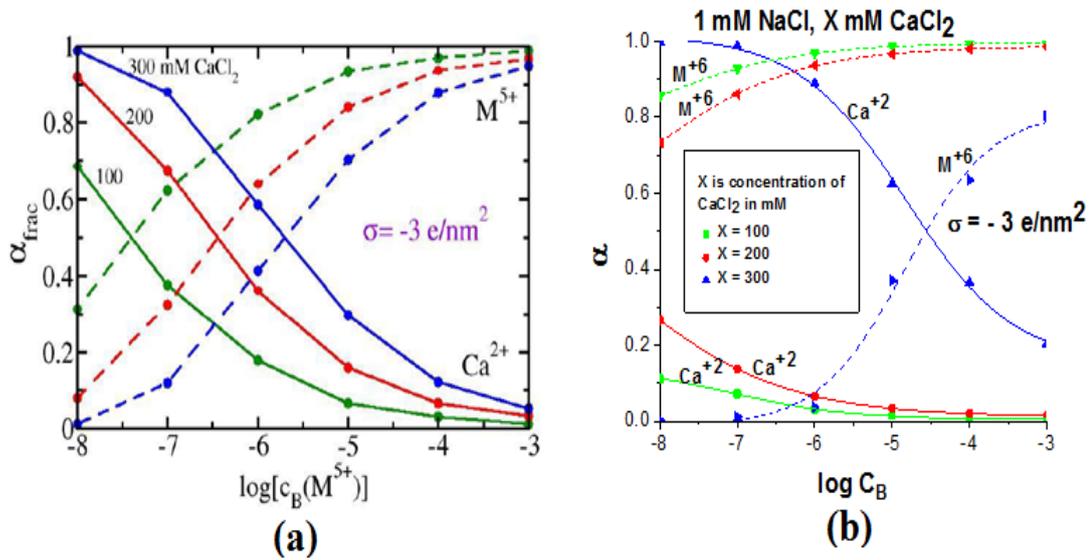
bulk solution than  $\sigma = -3 \text{ e/nm}^2$  to reach the saturation region. For example, at  $\sigma = -3 \text{ e/nm}^2$  with 1mM NaCl 100 mM CaCl<sub>2</sub> and at  $\langle C_B \rangle = 10^{-6}$  the fraction of ions are:  $\alpha_{\text{frac}}(\text{Ca}^{+2}) = 0.8893$  and  $\alpha_{\text{frac}}(\text{M}^{+6}) = 0.0368$ , while by increasing  $\sigma$  to  $-4 \text{ e/nm}^2$  the fractions are:  $\alpha_{\text{frac}}(\text{Ca}^{+2}) = 0.2915$  and  $\alpha_{\text{frac}}(\text{M}^{+6}) = 0.7084$  since Ca<sup>+2</sup> ions are exchange with M<sup>6</sup> ions because the high valence of hexavalent ions.

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**Figure (4.13):** The fraction of ions ( $\text{Ca}^{+2}$  and  $\text{M}^{+6}$ ) as function of logarithm of the bulk concentration at 1 mM NaCl, X mM CaCl<sub>2</sub>, where X takes three values 100, 200 and 300 Mm, at room temperature  $T = 298 \text{ K}$  and two values for surface charge density (a)  $\sigma = -3 \text{ e/nm}^2$ , (b)  $\sigma = -4 \text{ e/nm}^2$ .

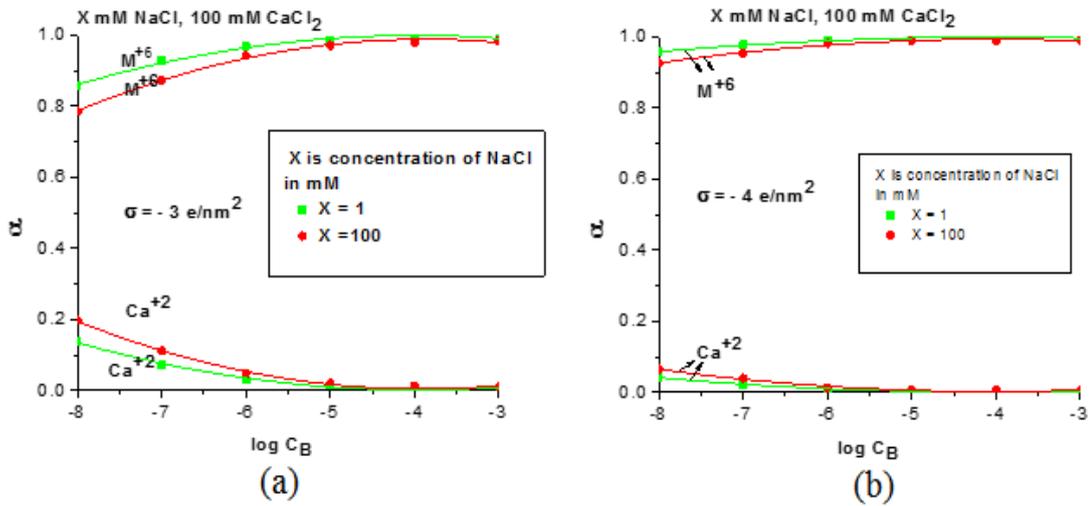
By comparing this result with the result of pentavalent ions sorption on Bentonite clay (Odeh et al., 2015), the two results are the same, but in hexavalent the sorption is more efficient than the sorption of pentavalent ions at 100 and 200 mM CaCl<sub>2</sub> as shown in figure (4.14.a) and figure (4.14.b).



**Figure (4.14):** (a) The fraction of ions ( $\text{Ca}^{2+}$  and  $\text{M}^{5+}$ ) as function of logarithm of the bulk concentration at  $1 \text{ mM NaCl}$ ,  $X \text{ mM CaCl}_2$ , where  $X$  takes three values 100, 200 and 300 mM, at room temperature  $T = 298 \text{ K}$  and surface charge density  $\sigma = -3 \text{ e/nm}^2$  (odeh et al., 2015), (b) The fraction of ions ( $\text{Ca}^{2+}$  and  $\text{M}^{6+}$ ) as function of logarithm of the bulk concentration at  $1 \text{ mM NaCl}$ ,  $X \text{ mM CaCl}_2$ , where  $X$  takes three values 100, 200 and 300 mM, at room temperature  $T = 298 \text{ K}$  and surface charge density  $\sigma = -3 \text{ e/nm}^2$ .

#### 8.4.2 The Effect of Monovalent Ionic Strength

By changing the concentration of monovalent ions  $\langle \text{NaCl} \rangle$  from 1 to 100 mM and finding the relation between the fraction of ions and the bulk concentration at same surface charge density is shown in figure (4.15). The fraction of  $\text{Ca}^{2+}$  increases while the fraction of  $\text{M}^{6+}$  decreases at increasing the concentration of  $\text{CaCl}_2$  (figure (4.15)), but the efficient of the sorption is decreasing as increasing the concentration of  $\text{NaCl}$  this because as increasing the concentration of  $\text{NaCl}$  salt leads to increasing  $\text{Na}^+$  ions at the surface as shown in figure (4.15.a) and figure (4.15.b).



**Figure (4.15):** The fraction of ions ( $\text{Ca}^{+2}$  and  $\text{M}^{+6}$ ) as function of logarithm of the bulk concentration at  $X$  mM NaCl 100 mM  $\text{CaCl}_2$ , where  $X$  takes two values 1 and 100 mM, at room temperature  $T = 298$  K and two values for surface charge density (a)  $\sigma = -3$   $\text{e}/\text{nm}^2$ , (b)  $\sigma = -4$   $\text{e}/\text{nm}^2$ .

Interestingly, the lowest value for concentration of  $\text{CaCl}_2$  (100 mM) is better choice to have more efficient sorption for hexavalent ions on EDL, which is at (1 mM NaCl ,100 mM  $\text{CaCl}_2$ ) and at (100 mM NaCl, 100 mM  $\text{CaCl}_2$ ). So in conclusion the sorption of  $\text{M}^{+6}$  is more efficient at:

1. higher surface charge density.
2. lower  $\text{Ca}^{+2}$  and  $\text{Na}^+$  concentration.
3. higher  $\text{M}^{+6}$  concentration.

## Chapter Five

### Conclusion

The sorption of hexavalent ions on bentonite clay was studied by using Monte Carlo simulation method using primitive model of NaCl and CaCl<sub>2</sub> electrolytes next to planar uniformly charge surfaces with net negative charge on it, and the bulk concentration was ranging from 10<sup>-8</sup> to 10<sup>-3</sup> M. However, the following can be concluded:

1. Monte Carlo simulation is effective for describing the sorption process of hexavalent ions on bentonite clay. Moreover, the Bentonite clay is efficient material to adsorb the radioactive ions from waste water.
2. The sorption process of hexavalent ions on Bentonite Clay is affected by some parameters such as: concentration of hexavalent ions in the bulk solution, surface charge density, temperature of the system and the ionic strength of bulk solution.
3. By increasing the bulk concentration  $C_B$  the fraction of hexavalent ions ( $\alpha(M^{+6})$ ) on the bulk solution was increasing, while the fraction of monovalent ( $\alpha(Na^+)$ ) and divalent ions ( $\alpha(Ca^{+2})$ ) on the bulk solution was decreasing (figure (4.1)).
4. By increasing the surface charge density  $\sigma$  of parallel planer surface the ( $\alpha(M^{+6})$ ) was increasing, while the ( $\alpha(Na^+)$ ) and ( $\alpha(Ca^{+2})$ ) were decreasing (figure (4.1)).
5. The average electrical double layer concentration  $\langle C_{EDL} \rangle$  is:
  - A. Increasing by increasing  $\sigma$  (figure (4.6)) and  $C_B$  (figure (4.3)).

- B. Decreasing slowly by increasing the temperature  $T$  of the system ((figure (4.9)).
  - C. Decreasing by increasing the ionic strength of monovalent (figure (4.15)) and divalent ((figure 4.13)) ions in the bulk solution.
6. The retention coefficient  $\gamma$  of the sorption process of  $M^{+6}$  is:
- A. Decreasing by increasing  $C_B$  ((figure (4.5) and ionic strength of monovalent and divalent ions.
  - B, Increasing by increasing  $\sigma$  ((figure (4.8)).
  - C. Decreasing slowly by increasing  $T$  (figure (4.12)).
7. When the valency of radioactive ions increases then the:
- A. The ionic strength on the sorption process is increased (figure (4.14)).
  - B. The effect of  $T$  on the sorption process is decreased (figure (4.11)).
  - C. The effect of the bulk concentration is decreased (figure (4.4)).

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جامعة النجاح الوطنية  
كلية الدراسات العليا

# امتصاص الأيونات سداسية التكافؤ بواسطة طينة البنتونايت

إعداد

لؤي علي مناصرة

إشراف

د. زيد قمحية

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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الفيزياء في كلية الدراسات العليا في جامعة النجاح الوطنية - نابلس.

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ب

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## الملخص

الأيونات المشعة، حتى وإن كان تركيزها قليلاً، تشكل مخاوف حالية على البيئة والإنسان بسبب إشعاعها القوي ونصف عمرها الطويل. من الواضح أن علاج هذه المشكلة الخطيرة يحظى باهتمام كبير ويمكن أن يتم بعدة وسائل. إحدى هذه الوسائل الفعالة هي امتصاص الأيونات بواسطة السوائل، التربة أو الطين. تم التركيز في هذا العمل على دراسة حفظ الملوثات سداسية التكافؤ من المياه البحرية والجوفية في طينة البنتونايت وذلك باستخدام محاكاة مونت كارلو.

تم استخدام النموذج البدائي، حيث تم اعتبار الماء هو المذيب وله قيمة ثابتة لثابت النفاذية وقيمته تساوي  $(\epsilon_r = 78)$ ، والأيونات عبارة عن كرات لها قطر ثابت، وطينة البنتونايت اعتبرت كطبقة كهربائية مزدوجة. تم استخدام

محاكاة مونت كارلو لدراسة العوامل المؤثرة على عملية الامتصاص وتتضمن: تركيز أيونات المحلول الموجبة، تركيز المواد المشعة في المحلول، كثافة الشحنة على سطح صفيحة الطين، وحرارة المحلول. نتائج هذه الدراسة تشير إلى أن: عملية الإمتصاص تتأثر بالعوامل السابقة ويمكن توضيح ذلك من خلال حساب معامل امتصاص الأيونات و معدل تركيز الأيونات على الطبقة الكهربائية المزدوجة. بشكل خاص يزداد معدل تركيز الأيونات على الطبقة الكهربائية المزدوجة بزيادة كثافة الشحنة على سطح صفيحة الطين، وبزيادة تركيز الأيونات في المحلول. وعلى النقيض، فإن معدل التركيز يتناقص بزيادة تركيز أيونات المحلول. بالإضافة إلى ذلك، فإن معامل امتصاص الأيونات سداسية التكافؤ ينخفض بزيادة تركيز المواد المشعة سداسية التكافؤ وبزيادة تركيز أيونات المحلول، وهذا المعامل يزداد من خلال زيادة كثافة شحنة السطح.