Optimal Design of Adsorbents for NORM Removal from produced water in Natural Gas Fracking. Part 1: Group Contribution Method for Adsorption

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Abstract

Natural gas has become an essential energy resource in the U.S. due to the increasing demand of energy, the high oil prices, and the need of foreign oil independency. The improvement in the drilling technology has allowed the rapid expansion in gas production, especially for unconventional gas such as shale gas. Shale gas is natural gas trapped within fine-grained sedimentary rocks called shale formations. Hydraulic fracturing is used to extract natural gas from these formations. Although natural gas is cleaner-energy source than coal or oil, there is a lot of controversy due to the environmental impact related to the water consumption and treatment. Hydraulic fracturing generates significant volumes of wastewater that contain dissolved chemicals, high content of salts, and significant levels of natural occurring radioactive material (NORM). Hence, one of the biggest challenges of this industry is to develop techniques for the prevention, remediation, and appropriate disposal of NORM. The overall objective of this work is to develop and implement a novel computational tool for high-throughput screening and selection of new adsorbents for NORM removal. In the first part of this paper series, we study the adsorption theory for NORM removal and applied group contribution methods (GCMs) to predict specific properties of adsorbents based on their thermodynamics. Then, in the second part of this paper we develop a computer-aided molecular design (CAMD) framework that generates potential adsorbent candidates according to the properties developed by the GCMs.

Key words: *Natural gas, Hydraulic fracturing, produced water, natural occurring radioactive material (NORM), group contribution method (GCM), Adsorbate solid solution theory (ASST).*

1. INTRODUCTION

The increase of the world's energy demand and the high oil prices has led to the exploration of new resources such as the extraction of natural gas from unconventional shale plays like shale gas. Natural gas production from shale gas formation is one of the fastest-growing divisions in the U.S. oil and gas industry, and it is a promising resource to achieve the foreign oil independency. The U.S. Energy Information Administration estimates U.S natural gas reserves at 2203 trillion cubic feet (tcf), enough to last about 92 years (U.S. Department of Energy Website, 2014). Advances in drilling technology have rapidly expanded natural gas production. According to a reference case reported on the Annual Energy Outlook of 2014 (U.S. Department of Energy Website, 2014b), the production of natural gas will grow steadily, with a 56% increase between 2012 and 2040, when production will reach 37.6 tcf. This substantial growth in shale gas production comes with new environmental concerns.

Shale gas is natural gas trapped within fine-grained sedimentary rocks called shale formations. Two important shale plays are the Barnett Shale in Texas and the Marcellus Shale in the eastern of the U.S which is shown in Fig. 1 (Replica Engineering INC, 2014). It was deposited around 390 million years ago in the shallow sea that once covered the region. Shale is composed of tiny mud particles and organic

matter, which, because of the properties of radioactive elements present in the sea water, often contains concentrations of naturally occurring radioactive material (NORM). Black shale, such as that contained in the Marcellus, often contains trace levels of uranium (U), thorium (Th), and potassium (K), and in higher concentrations than found in less organic-rich grey shale. Natural gas fracking in the Marcellus shale brings out NORM to the surface in a concentrated form, which could pose a radiation safety hazard and it is the focus of these series of papers.

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The first stage of shale gas production requires large volumes of fresh water (e.g. 4 to 5 million of gallons according to Smith, 2012) that may affect the availability of water for other uses as well as aquatic habitats. About 15-25% of the water injected during hydraulic fracturing returns to surface as “flowback water” within the first 30 days while produced water, which is the water produced at the end of the flowback, continues to flow for the life of the well at a reduced rate (Silva et al., 2012). Moreover, hydraulic fracturing generates significant volumes of contaminated wastewater which may contain dissolved chemicals and other contaminants that require a special treatment before final disposal or reuse. In Marcellus gas shale, the overall estimated volume of wastewater (3.1×10^6 to 3.8×10^6 cubic meter

per year) has increased during the last years and there is an average of 0.15 to 0.3 MM gallons per day of produced water that must be properly disposed (Silva et al., 2012). It has been found that the salinity of shale gas wastewater varies from 5000 mg/L to >200000mg/L (Warner et al., 2013). Much of the flowback and produced waters such as those generated in the Marcellus contain concentrated amount of hardness species (e.g. Ca^{++} , Mg^{++} , Mn^{++} , Br^{++} , Cl^-) and metals such as barium and strontium. As stated earlier, added to this high salinity, many flowback and produced waters contain significant levels of NORM in the form of radium isotopes with activities of 185 to 592Bq/L (Warner et al., 2013). Although 95% of the flowback water is reused, the supply of flowback and produced water is expected to exceed the reuse capacity due to the rapid increase in shale gas extraction. This situation has become a big issue in the safe disposal of liquid waste in the U.S. given their large volume and typically high levels of contaminants. Most oil-gas field NORM waste is stored at production sites awaiting for disposal in specially designated and permitted landfills, disposal wells, injections wells, or treat it in a publicly owned treatment plant or wastewater treatment plants. If the production site cannot handle the final disposal of these waters, then these waters must be sent to other water treatment facilities which increase the costs of operation. However, as the natural gas production increases, these alternatives will not be enough to support its final –safe- disposal. In some states, these alternatives are not available or allowed due to the lack of regulations or appropriate geology for deep-well injection sites. Moreover, there is still potential for drinking water contamination due to spill in the surface and leaks from improperly cemented well casing. Even though multiple layers of steel casing are inserted into the wellbore to avoid contamination, there has been found some documented cases of localized releases of fluids at the surface causes by spill and casing ruptures (Lustgarten, 2009). Therefore, one of the biggest challenges of this industry is to develop techniques for the prediction, prevention, remediation, and appropriate disposal of oil-field NORM. Currently, it is not possible to selectively remove NORM from produced water

so that brines could be reduced in volume to concentrated salt solutions or dry salts producing a waste material that does not have radionuclide safety issues.

In this work, we concentrate on the adsorption process for NORM removal specifically the radium and barium isotopes. Computer-aided molecular design (CAMD) is used to develop new adsorbents with desired properties that can remove these materials. CAMD is generally the reverse use of the group contribution method (GCM) that is used to generate molecules having desirable properties. A GCM is a technique to estimate and predict thermodynamic and other properties from molecular structures of compounds. In the first part of this paper, we focus on developing group GCMs to predict the desired properties based on their thermodynamics. We use experimental data of known adsorbents and their adsorption equilibrium to predict the properties such as activity coefficient. A modified UNIFAC method is used for calculation of activity coefficient. In the second part of this paper (Benavides and Diwekar, 2014), we use CAMD framework to generate new adsorbent having the desirable properties. As a result, the GCM along with CAMD based optimization methods identify existing and new potential groups of adsorbents for the NORM removal.

2. BACKGROUND

2.1 *Natural occurring radioactive material (NORM)*

The natural environment contains many naturally radioactive substances also known as NORM that emit low levels of radiation. Among some radioactive material are: uranium (U), radium (Ra), thorium (Th) and radon (Rn). These elements are found dissolved in very low concentration during normal reactions between water and rock or soil that also contain oil and gas (Zielinski and Otton, 1999). As stated earlier, the black shale found at Marcellus shale often contains trace levels of radioactive material (^{238}U , ^{235}U , and ^{232}Th) which are brought out to the surface in a concentrated form. ^{238}U and ^{232}Th are both potentially hazardous radioactive products since they decay to more soluble ^{226}Ra and soluble ^{228}Ra , respectively

(Marcellus shale, 2011). On the other hand, it has been found that mixtures of carbonate and sulfate minerals are present in the coating and sediments in the production equipment. One of these sulfate minerals is Barite (i.e. Barium Sulfate), which is known as the primary host NORM (Zielinski and Otton, 1999). Therefore, the focus of this work is on the adsorption of NORM specifically radium and barium isotopes.

Radium (Ra) is a radioactive element that may represent a potential health hazard (i.e. as carcinogen and other disorders) if it is released into the environment because radium and its decays product radon emit alpha particles that can kill and mutate cells. In produced water, NORM species typically comprise two forms: ^{226}Ra and ^{228}Ra (Zielinski and Otton, 1999). Due to the long half-life of 1600 years, ^{226}Ra is of principal interest compared to ^{228}Ra which has a half-life of 5.8 years. Although it is expected that both forms will behave similarly in the removal process, we focus on the adsorption of ^{228}Ra . Radioactive isotopes are commonly quantified in terms of activity concentration or simply “activity”. These concentrations are generally reported as picocuries/gram (pCi/g) of solid material or picocuries/liter (pCi/L) of water or air. A picocurie equals 0.037 Becquerel (Bq) which is another form to express the activity. Marcellus shale produced water samples contain more radium than non-Marcellus samples. For instance, the range of radium activities for samples from Marcellus shale (median value is 2460pCi/L) overlaps the range for non-Marcellus reservoirs (median value 734pCi/L) (Rowan et al., 2011).

Barium is a major fission product resulting from the fission of plutonium and uranium. High concentration of barium has been associated with multiple sclerosis and neurodegenerative diseases (Purdey, 2004). The toxicity of barium is related to its solubility and for insoluble salts the solubility increases with decreasing pH. The EPA allows a maximum of 0.002mg/g of barium in drinking water (U.S.EPA, 2014).

2.2 Adsorption process

Adsorption is a separation process consists adhesion of molecules of liquids, gases and dissolved substances (i.e. adsorbate) into the surface of solid (i.e. adsorbent) because of physical and chemical processes (Yang, 2003). The most fundamental property in adsorption is the adsorption equilibrium which can be describe by adsorption isotherms (Suzuki, 1990). The isotherms are illustrated in many mathematical forms such as the Langmuir shown in Eq.1.

$$\frac{1}{q} = \frac{1}{b} + \frac{1}{(bK)C} \quad \text{Eq.1}$$

Where q the amount adsorbate adsorbed in a unit mass of adsorbent and C is the equilibrium concentration of adsorbate in the solution. b and K are constant values. Another typical equation used to describe the isotherm is the Freundlich equation as shown in Eq2. In this case, k_f and n_f are the Freundlich parameters determined from correlation of adsorption data.

$$q = k_f C^{n_f} \quad \text{Eq.2}$$

Adsorption can perform many separations that are impossible or impractical by conventional techniques such as distillation, absorption, and even membrane-based systems. However, adsorption is rarely employed as a separation process due to the lack of both experimental data and suitable models used to predict the equilibrium behavior of multicomponent mixtures (Berti et al., 2000). In addition, the calculation of the measurements involved in the equilibrium is very time-consuming and cost-intensive. Therefore, distillation processes have assumed a dominant role in separation technology. GCM Method has shown a great success for the design of the most common separation processes and similar approaches are suggested for the calculation of adsorption processes.

2.3 Adsorbate solid solution theory (ASST)

In contrast to the classical formulation of adsorption equilibrium, the adsorbate solid solution theory (ASST) describes the adsorption behavior of liquid mixtures on solid surfaces using G^E -models (i.e. Gibb

excess free energy models). The approach, discussed by Berti et al., 1999 and Berti et al., 2000 considers the adsorbed phase to be a mixture containing the adsorbed species and the adsorbent as additional component (see Fig.2a). The relation of the phase equilibrium for component i is shown in Eq.3:

$$x_i^b \gamma_i^b = x_i^s \gamma_i^s \exp \left(\frac{g_i^{ad} - g_{oi}^{ad}}{RT \Gamma_{mi}^s} \right) \quad \text{Eq.3}$$

Here, x_i^b and x_i^s are the fractions of component i in the bulk phase and surface phase, respectively. γ_i^b and γ_i^s are the activity coefficients in each phase, g^{ad} is the free energy of immersion of the adsorbed solution and g_{oi}^{ad} is the free energy of immersion of the pure adsorbed species i. T, R and Γ_{mi}^s are temperature, the ideal gas constant, and surface phase capacity of component i, respectively (Berti et al., 1999 and Berti et al., 2000). The surface phase capacity Γ_{mi}^s is given by Eq.4, when assuming pore-filling model of adsorption, v_p is the pore volume of the adsorbent and v_{oi} is the molar volume of the respective fluid:

$$\Gamma_{mi}^s = \frac{v_p}{v_{oi}} \quad \text{Eq.4}$$

Berti et al., 1999 and Berti et al., 2000 argued that for the pure component adsorption, the respective activity coefficient equals 1, however, the measurable enthalpy of immersion proves the existence of interactions between adsorbent and the liquid. Therefore, they formulated a new thermodynamic framework that incorporates the adsorbent's properties by conceiving adsorption systems as a solution of the solid and the liquid adsorbate. In that sense, the influence of different structural groups of the adsorbent on the adsorption behavior is taken into account. This framework is described in Fig. 2b (Berti et al., 2000). Then, the relation of the phase of equilibrium for this new framework is presented by Eq. 5 based on the chemical potential in both phases.

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$$x_i^b \gamma_i^b = x_i^* \gamma_i^* \exp \left(\frac{(\varphi^* - \varphi_{oi}^*)}{RT \Gamma_{mi}^s} \right) \quad \text{Eq. 5}$$

Where x_i^* is the fraction of component i in the adsorbate solid solution, γ_i^* is the activity coefficient of the same component, and the expression $(\varphi^* - \varphi_{oi}^*)$ is the difference between the chemical potential of the wetted solid and the chemical potential of the wetted solid at adsorption of the pure component i (Berti et al., 1999 and Berti et al., 2000). This last term can be computed by Eq.6

$$\phi^* - \phi_{oi}^* = \frac{1}{m_0} (G^{E*} - G^{Es} - G_{oi}^{E*}) \quad \text{Eq.6}$$

Here, m_0 is the mass of adsorbent, and G^{E*} , G^{Es} , G_{oi}^{E*} , are the Gibbs excess free energy of the ASS, Gibbs excess free energy of the surface phase and the Gibbs excess free energy of the pure component adsorption all in Joules, respectively. Usually, it is more convenient to express the Gibbs excess free energy in terms of activity coefficients, therefore, for the adsorbate solid solution:

$$\frac{G^{E*}}{RT} = \sum_{i=0}^k n_i^* \ln \gamma_i^* \quad \text{Eq. 7}$$

where the index 0 refers to the adsorbent and the activity coefficient is computed using the UNIFAC model (Berti et al., 1999).

Similarly, the definition of the activity coefficients for the surface phase yields their connection with the Gibbs excess free energy as show below:

$$\frac{G^{Es}}{RT} = \sum_{i=1}^k n_i^s \ln \gamma_i(x_i^s) \quad \text{Eq. 8}$$

where n_i^s is the molar quantity in the surface phase for component i and it is computed using the following equation:

$$n_i^s = x_i^s n_T^*(1 - x_0^*) \quad \text{Eq.9}$$

And x_i^s (fraction of component i in the surface phase) can be calculated by:

$$x_i^s = \frac{x_i^*}{(1-x_0^*)} \quad \text{Eq.10}$$

Finally, for the pure component adsorption, the respective activity coefficient γ_{oi}^* is given by Eq. 11:

$$\gamma_{oi}^* = 1 + \frac{1}{\Gamma_{mi}^s M_o} \quad \text{Eq.11}$$

2.4 Group Contribution Method (GCM) and the modified UNIFAC model

GCM is used to estimate properties of compounds based on known experimental data of well-defined pure components and mixtures. Many examples can be found in the literature (Lydersen, 1955; Joback and Reid, 1987; Marrero and Gani, 2001). The objective of GCMs is formulating a property of a given compound as a statistical correlation like multi-linear regression. The parameters involved in this regression are determined by summing the frequency of each group occurring in the molecule times its contribution. The ASST offers an excellent basis to incorporate group contribution methodology that takes into account the influence of different structural groups of the adsorbent with respect to adsorption. This theory uses the UNIFAC method which is also used to predict information for the Vapor-liquid equilibrium (Fredenslund et al., 1977). UNIFAC stands for functional-groups activity coefficients and this method is resulted from the model called UNIQUAC (Universal Quasi-Chemical). Thus, for the first evaluation of a group contribution method, a modified UNIFAC model presented by Berti et al., 2000 is

used to compute the activity coefficient in the adsorbent solid solution. In the modified model, the pure component adsorption (γ_{oi}^*) has to be incorporated as shown in Eq.12:

$$\ln \gamma_i^* = \ln \gamma_{oi}^* + \ln \gamma_{GE,i}^* \quad \text{Eq.12}$$

where $\gamma_{GE,i}^*$ is the concentration dependant part of the activity coefficient and it is divided into a combinatorial part (γ_i^{C*}) and residual part (γ_i^{R*}):

$$\ln \gamma_{GE,i}^* = \ln \gamma_i^{C*} + \ln \gamma_i^{R*} \quad \text{Eq.13}$$

For the combinatorial and residual part Eq.14 and Eq.15 can be used:

$$\ln \gamma_i^{C*} \equiv \ln \gamma_{GE,i}^{C*} (x_i^*) - \ln \gamma_{GE,i}^{C*} (x_{oi}^*) \quad \text{Eq.14}$$

$$\ln \gamma_i^{R*} \equiv \ln \gamma_{GE,i}^{R*} (x_i^*) - \ln \gamma_{GE,j}^{R*} (x_{oi}^*) \quad \text{Eq.15}$$

For the adsorbent each of the second terms is dropped. The combinatorial and the residual part is given as it is presented by Fredenslund et al., 1977. $\gamma_{GE,i}^*(x_{oi}^*)$ represents the activity coefficient of a binary ASS, that is, the pure adsorbed liquid and the adsorbent.

3. ADSORPTION OF RADIUM AND BARIUM

In this section, we study the adsorption equilibrium of radium and barium on different adsorbents. Based on experimental data reported in the literature, we predict the interaction parameters of the functional groups that are commonly contained in adsorbents of radium and barium.

3.1 Problem description of radium removal

The first problem considers the adsorption of radium from aqueous solutions on different minerals. The experimental data was reported by Ames et al., 1983. In the paper, the authors presented radium adsorption efficiencies as a function of temperature determined in a 0.01M NaCl solution. In the initial solution, when no adsorbent is added, the components involved are: radium (1), sodium chloride (2), and water (3). The equilibrium is reached after 30 days of mineral solution continuous contact. At this point, two new phases are presented: bulk phase and the adsorbate solid solution (see Fig. 2b). The bulk phase contains part of the radium that was not adsorbed, sodium chloride, and water while in the ASS phase contains the adsorbed radium and the adsorbent as shown in Fig.3.

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Table A3 of the Appendix 3 presents the minerals used by Ames et al., 1983 with their properties which used the Freundlich equation (Eq.2) to describe the adsorption equilibrium. The values of k and n are given by Ames et al., 1983. These values depend on the temperature and type of adsorbent. Therefore, for the purpose of this paper we use the information reported at 25°C of adsorption temperature for experimental results.

3.2 Mass balance of the adsorption process

The first two quantities that can be compute with the given information are the moles of adsorbent (n_0^*) and radium (n_1^*) in the ASS, as it is presented in Eq 16 and Eq. 17, respectively:

$$n_0^* = \frac{m_0}{M_0} \quad \text{Eq.16}$$

$$n_1^* = q * m_0 \quad \text{Eq.17}$$

Then, the amount of radium in the bulk phase (n_1^b) is determined by subtracting the moles of radium contained in the solid (n_1^*) from the initial feed of moles contained in the solution (n_1^1):

$$n_1^b = n_1^1 - n_1^* \quad \text{Eq.18}$$

where n_1^1 is calculated with Eq. 19. C_I (mol/L) is the initial concentration of radium and V_{sln} as the volume of solution (1L from which 0.88 L were water):

$$n_1^1 = C_I V_{sln} \quad \text{Eq.19}$$

Finally, the molar fractions of radium, NaCl, and H₂O in the bulk phase (x_i^b) can be computed as presented in Eq.20,

$$x_i^b = \frac{n_i^b}{n_T^b} \quad \forall i \in [1 \dots 3] \quad \text{Eq.20}$$

The molar fraction of radium and adsorbent in the ASS phase (x_i^*) can be calculated as presented in Eq.21:

$$x_i^* = \frac{n_i^*}{n_T^*} \quad \forall i \in [0 \text{ and } 1] \quad \text{Eq.21}$$

Where n_T^b and n_T^* are the total moles in the bulk phase and in the ASS, respectively.

3.3 Activity coefficient for bulk phase and adsorbate solid solution

As mentioned before, the UNIFAC model is divided in two parts: combinatorial and residual. In the case of bulk phase, Eq.22 can be written as:

$$\ln \gamma_i^b = \ln \gamma_i^{Cb} + \ln \gamma_i^{Rb} \quad \text{Eq.22}$$

For combinatorial part of component i:

$$\ln(\gamma_i^{Cb}) = \ln\left(\frac{\varphi_i}{x_i^b}\right) + 5q_i \ln\left(\frac{\theta_i}{\varphi_i}\right) + l_i - \frac{\varphi_i}{x_i^b} \sum_1^j x_j^b l_j \quad \text{Eq.23}$$

where:

$$l_i = 5(r_i - q_i) - (r_i - 1) \quad \text{Eq.24}$$

$$\theta_i = \frac{q_i x_i^b}{\sum_j^M q_j x_j^b} \quad \text{Eq.25}$$

$$\varphi_i = \frac{r_i x_i^b}{\sum_j^M r_j x_j^b} \quad \text{Eq.26}$$

θ_i and φ_i represent the molecular surface area and volume fraction of species i, respectively, and j: 1,2 ... M represent the number of components. The van der Waals volume species/functional group/component is computed by Eq.27 while the van der Waals surface area using Eq.28, respectively:

$$r_i = \sum_g^{N_{gt}} \vartheta_g^{(i)} R_g \quad \text{Eq. 27}$$

$$q_i = \sum_g^{N_{gt}} \vartheta_g^{(i)} Q_g \quad \text{Eq. 28}$$

In this case, $g = 1, 2 \dots N_{gt}$, g is the groups index and N_{gt} total functional group in the molecule. R_g and Q_g are the constants of group sizes and surface areas that are obtained from atomic and molecular structure data. The R_g and Q_g can be viewed in Table A1 of the Appendix 1.

For residual part for group k:

$$\ln \Gamma_g = Q_g \left[1 - \ln\left(\sum_1^m \theta_m \psi_{mg}\right) - \sum_1^m \left(\frac{\theta_m \psi_{gm}}{\sum_1^n \theta_n \psi_{nm}}\right) \right] \quad \text{Eq.29}$$

where **m** and **n** represent all groups. Eq.29 also holds to $\Gamma_g^{(i)}$

The group fraction and group surface area fraction is calculated by Eq.30 and Eq.31, respectively:

$$X_m = \frac{\sum_1^j \vartheta_m^{(i)} x_j^b}{\sum_1^j \sum_1^n \vartheta_m^{(i)} x_j^b} \quad \text{Eq.30}$$

$$\theta_m = \frac{Q_m X_m}{\sum_1^n Q_n X_m} \quad \text{Eq.31}$$

Finally, in Eq.29 the parameter ψ_{nm} is given by:

$$\psi_{nm} = \exp(-a_{nm}/T) \quad \text{Eq.32}$$

a_{nm} contains the group interaction parameters for the UNIFAC model and T is the temperature. The group interaction parameter is the measure of the difference in the energy of interaction between a group n and a group m and between two same groups m (Fredenslund et al., 1977). Table 1 presents the known and unknowns values of a_{nm} for the groups used. As it can be seen, there are 6 unknown interaction parameters in which all of them are related to radium group.

Table 1
UNIFAC interaction parameters (ab_{nm}) for bulk phase

Groups (g)	Ra	Na ⁺	Cl ⁻	H ₂ O
Ra	0	ab_{12}	ab_{13}	ab_{14}
Na ⁺	ab_{21}	0	6342.2 ^(a)	-165.0 ^(a)
Cl ⁻	ab_{31}	14548 ^(a)	0	-230.2 ^(a)
H ₂ O	ab_{41}	22.38 ^(a)	-982.5 ^(a)	0

(a) The known values of a_{nm} can be found at Kikic and Fermeglia, 1991.

To compute the activity coefficient for the adsorbate solid solution (γ_i^*), the UNIFAC model presented in Section 2.3 is used. Table A2 of Appendix 2 presents the van der Waals volume and surface values for each functional group of the different adsorbents used. On the other hand, Table 2 shows the interaction parameters involved in the ASS where there are 14 unknown interaction parameters in which all of them are related to radium group. According to Berti et al., 1999 the interaction parameters between the groups on the solid are zero [18].

Table 2
UNIFAC interaction parameters (aa_{nm}) for ASS

Groups (g)	Ra	SiO ₂	Al ₂ O ₃	Na ₂ O	MgO	Fe ₂ O ₃	K ₂ O	CaO
Ra	0	aa_{12}	aa_{13}	aa_{14}	aa_{15}	aa_{16}	aa_{17}	aa_{18}
SiO ₂	aa_{21}	0	0	0	0	0	0	0
Al ₂ O ₃	aa_{31}	0	0	0	0	0	0	0
Na ₂ O	aa_{41}	0	0	0	0	0	0	0
MgO	aa_{51}	0	0	0	0	0	0	0
Fe ₂ O ₃	aa_{61}	0	0	0	0	0	0	0
K ₂ O	aa_{71}	0	0	0	0	0	0	0
CaO	aa_{81}	0	0	0	0	0	0	0

3.4 Problem description for barium removal

Produced water can also contain barium at high concentration. Therefore, in order to reach high efficiency of the recovery of water, the barium must be removed. The experimental data was obtained from two papers: Chavez et al., 2010 and Arafa et al., 1974. In the first paper, the adsorption isotherms were determined by contacting 0.2g of two adsorbents: clinoptilolite tuff and montmorillonite clay with 10ml of a solution that contained barium chloride (BaCl₂) and calcium chloride (CaCl₂). Similarly to radium adsorption, two phases are presented after reaching equilibrium (See Fig.4). The second paper -by Arafa et al., 1974 - 5g of adsorbent were mechanically shaken with 100cm³ of a solution of barium chloride and sodium chloride (0.01M) for three hours. Fig. 4 can also be used to represent the adsorption scheme process presented by Arafa et al., 1974. However, in the latter case, the adsorbent used was the β -Mn₂O and the bulk phase composition contained barium chloride that did not react, sodium chloride and water. Table A4 in the Appendix 3 presents the chemical structure of the adsorbents used for adsorption of radium and their molecular weight.

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343 The adsorption equilibrium of Ba^{+2} by Ca-Cln and by Ca-Mnt are described by the Langmuir equation
 344 shown in Eq.1. The constant values of **b** and **K** can be found in Chavez et al., 2010. On the other hand,
 345 the adsorption equilibrium of barium by β -Mn₂O is taken from the adsorption isotherm presented in the
 346 paper by Arafa et al., 1974. Its isotherm was of the Langmuir type and it was reported at pH 7.5 and 35°C
 347 of temperature. We use the same procedure presented for radium adsorption to estimate the moles and
 348 mole fractions in the bulk and ASS phase. Table 3 presents the known and unknown values of interaction
 349 parameters based on the groups used in each problem in the bulk phase (ab_{nm}). The van der Waals
 350 volume and surface parameters for each functional group can be found in Table A1 of the Appendix 1. As
 351 it can be seen in these tables, there are four unknown interaction parameters in each problem, in which
 352 all of them are related to barium group.

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Table 3

UNIFAC interaction parameters (ab_{nm}) for bulk phase for adsorption of barium onto Ca-Cnt and Ca-Mnt and adsorption onto β -Mn₂O

Groups (g)	Ba ²⁺	Ca ²⁺	Cl ⁻	H ₂ O	Na ⁺
Ba ²⁺	0	ab_{12}	ab_{13}	-558.57 ^(a)	ab_{15}
Ca ²⁺	ab_{21}	0	4166.3 ^(a)	-838.2 ^(a)	NA ^(b)
Cl ⁻	ab_{31}	21983 ^(a)	0	-230.2 ^(a)	14548 ^(a)
H ₂ O	-374.92 ^(a)	-897.2 ^(a)	-982.5 ^(a)	0	22.38 ^(a)
Na ⁺	ab_{51}	NA ^(b)	6342.2 ^(a)	-165.0 ^(a)	0

(a) The known values of ab_{nm} for can be found at Kikic and Fermeglia, 1991.

(b) There is not interaction parameter between Na and Ca since each of them belongs to different adsorption problem

Finally, Table 4 show the interaction parameters involved in the ASS phase (aa_{nm}) for the two adsorption problems, respectively. For problem one (i.e. barium adsorption onto Ca-Cnt and Ca-Mnt) there are twenty unknowns while for problem two (i.e. barium adsorption onto β -Mn₂O) there are only two unknowns (i.e. aa_{112} and aa_{121}). The optimization problem presented in the main paper was used to find these interaction parameters.

Table 4

UNIFAC interaction parameters (aa_{nm}) for ASS phase onto Ca-Cl_n and onto Ca-Mnt and onto β -Mn₂O

Groups (g)	Ba ²⁺	SiO ₂	Al ₂ O ₃	(AlO ₂) ⁻	FeO	MgO	CaO	Na ₂ O	K ₂ O	Ca ²⁺	K ⁺	β -MnO ₂
Ba ²⁺	0	aa_{12}	aa_{13}	aa_{14}	aa_{15}	aa_{16}	aa_{17}	aa_{18}	aa_{19}	aa_{110}	aa_{111}	aa_{112}
SiO ₂	aa_{21}	0	0	0	0	0	0	0	0	0	0	NA ^(a)
Al ₂ O ₃	aa_{31}	0	0	0	0	0	0	0	0	0	0	NA ^(a)
(AlO ₂) ⁻	aa_{41}	0	0	0	0	0	0	0	0	0	0	NA ^(a)
FeO	aa_{51}	0	0	0	0	0	0	0	0	0	0	NA ^(a)
MgO	aa_{61}	0	0	0	0	0	0	0	0	0	0	NA ^(a)
CaO	aa_{71}	0	0	0	0	0	0	0	0	0	0	NA ^(a)
Na ₂ O	aa_{81}	0	0	0	0	0	0	0	0	0	0	NA ^(a)
K ₂ O	aa_{91}	0	0	0	0	0	0	0	0	0	0	NA ^(a)
Ca ²⁺	aa_{101}	0	0	0	0	0	0	0	0	0	0	NA ^(a)
K ⁺	aa_{111b}	0	0	0	0	0	0	0	0	0	0	NA ^(a)
β -MnO ₂	aa_{121}	NA ^(a)	NA ^(a)	NA ^(a)	NA ^(a)	NA ^(a)	NA ^(a)	NA ^(a)	NA ^(a)	NA ^(a)	NA ^(a)	0

(a) There is not interaction parameter between β -MnO₂ and the other groups since β -MnO₂ belongs to the second problem by Arafa et al., 1974.

4. ESTIMATION OF THE INTERACTION PARAMETERS: AN OPTIMIZATION PROBLEM

As mentioned before, our objective is to find the unknown values of the UNIFAC interaction parameters (i.e. ab_{nm} and aa_{nm}) by fitting different adsorption systems and compared them with the information found in the literature. Therefore, we use optimization techniques to solve the two parameter estimation problems presented in the previous section (i.e. radium and barium adsorption). The parameter estimation problem deals with solving a system of equations based on measured or empirical data so that the values of the parameters can be estimated by optimizing an objective function. We use an error function (**Err**) (mean square error) as an objective function for this problem. This function represents the square root of the difference between the adsorption capacity from the experimental values (q^{exp}) given by the adsorption equilibrium and a new calculated q^{cal} . This adsorption capacity difference is applied for each adsorbent used. For the radium adsorption problem, we considered 4 adsorbents (kaolinite, montmorillinite, glauconite, and clinoptinolite) since they contain all the functions group needed for the prediction of the interaction parameters. For the barium adsorption problem, we solved two problems: adsorption of barium onto Ca-Cln and Ca-Mnt and adsorption of barium onto β -MnO₂. Then, using the interaction parameters as the decision variables, the objective function whose goal is to minimize the sum of this square of errors is expressed as:

$$\min \text{Err} = \min \sum_1^{AD} \sum_1^{Eq} \left[q_{Eq,AD}^{cal} - q_{Eq,AD}^{exp} \right]^2 \quad \text{Eq.33}$$

where **AD** is the adsorbent used, and **Eq** is the total number of equation used to solve the problem, we used around 20 to 40 experimental data points (i.e. 20 to 40 equations) depending on the problem. To calculate q^{cal} , we use Eq.34:

$$q^{cal} = \frac{x_1^* n_T^*}{m_0} \quad \text{Eq. 34}$$

To find n_T^* , we use the equations of the adsorption equilibrium formulation presented in the previous sections which include the equilibrium equation (Eq.5) and the difference of the chemical potential of the

adsorbent (Eq.6). This last equation involves the calculation of the Gibbs excess free energy in three parts:
adsorbate solid solution (Eq.35), surface phase (Eq.36), and for the pure component (Eq.37),

$$G^{E*} = RT(n_0^* \ln \gamma_0^* + n_1^* \ln \gamma_1^*) = RT(x_0^* n^* \ln \gamma_0^* + x_1^* n^* \ln \gamma_1^*) \quad \text{Eq.35}$$

$$G^{Es} = RT(n_1^s \ln \gamma_1(x_1^s)) = RT(n^s x_1^s \ln \gamma_1(x_1^s)) \quad \text{Eq.36}$$

$$G_{oi}^{E*} = RT n_{oi}^* \ln \gamma_{oi}^* = RT x_{oi}^* n^* \ln \left(1 + \frac{1}{\Gamma_{mi}^s M_o} \right) \quad \text{Eq.37}$$

Where $x_{oi}^* = x_1^* =$ since there only one adsorbate (either radium or barium) in the ASS phase. G^{Es} is the Gibbs excess free energy of the surface phase and in this case is equal to zero since only involves the activity coefficient for pure component ($x_1^s=1$), therefore, replacing Eq.34, 35 and 36 into Eq.6, we obtain an expression to calculate n_T^* :

$$n_T^* = \frac{(\phi^* - \phi_{oi}^*) m_o}{RT \left((x_0^* \ln \gamma_0^* + x_1^* \ln \gamma_1^*) - x_{oi}^* \ln \left(1 + \frac{1}{\Gamma_{mi}^s M_o} \right) \right)} \quad \text{Eq.38}$$

The surface phase capacity Γ_{mi}^s is given by Eq.4. The pore volume values of the adsorbents used are listed in Table A2 of the Appendix 2. Finally, to compute $(\phi^* - \phi_{oi}^*)$, if Eq. 5 is used, then:

$$\phi^* - \phi_{oi}^* = -R T \Gamma_{mi}^s \ln \left(\frac{x_i^b y_i^b}{x_i^* y_i^*} \right) \quad \text{Eq.39}$$

The nonlinear programming (NLP) optimization solution methods are used to determine the UNIFAC interaction parameters using Matlab software. As an example, we present the calculation steps to compute the adsorption capacity for Kaolinite in the Appendix 4 (Table A5 and Table A6).

We used the nonlinear least square fit for this purpose. We took 41 experimental points and converted it into a single objective function of sum error square between these experimental values and calculated values. We applied nonlinear optimization technique to obtain parameters. As the number of experimental points are not small and the data was not too noisy (as can be seen from the errors), we do not have the problem of over fitting here.

5. RESULTS AND DISCUSSION

Table 5 presents the values of the 20 UNIFAC interaction parameters determined between all possible functional group that could be part of the new adsorbent for radium adsorption. We can observed the strong interaction between radium and different groups such as water and sodium oxide since these parameters represent the energy of the interaction between the functional groups.

Table 5
Values of interaction parameter in the adsorption of radium

Bulk Phase				
Description	Variable	CI lower bound	Parameter Value	CI Upper Bound
Ra- Na ⁺	ab ₁₂	Not sensitive	8968.1*	Not sensitive
Ra-Cl ⁻	ab ₁₃	73.5- 3.0774e-06	73.5	73.5+3.0774e-06
Ra-H ₂ O	ab ₁₄	Not sensitive	94335.5*	Not sensitive
Na ⁺ -Ra	ab ₂₁	2020.8- 4.2511e-05	2020.8	2020.8+4.2511e-05
Cl-Ra-	ab ₃₁	1335.7- 5.7699e-06	1335.7	1335.7+5.7699e-06
H ₂ O-Ra	ab ₄₁	6627.4	6627.5	6627.6
ASS Phase				
Ra-SiO ₂	aa ₁₂	-846.7- 1.8356e-12	-846.7	-846.7+1.8356e-12
Ra-Al ₂ O ₃	aa ₁₃	-3298.1- 5.9439e-12	-3298.1	-3298.1+5.9439e-12
Ra-Na ₂ O	aa ₁₄	Not sensitive	14014.5*	Not sensitive
Ra-MgO	aa ₁₅	1161.9- 7.4082e-08	1161.9	1161.9+7.4082e-08
Ra-Fe ₂ O ₃	aa ₁₆	796.5-	796.5	796.5+4.7693e-

			4.7693e-08		08
Ra-K ₂ O	aa ₁₇	-1078.1- 7.6953e-12	-1078.1	1078.1+ 7.6953e-12	- 12
Ra-CaO	aa ₁₈	-7410.9- 2.3802e-11	-7410.9	7410.9+ 2.3802e-11	- 11
SiO ₂ -Ra	aa ₂₁	-71.2- 7.4115e-09	-71.2	-71.2+ 7.4115e-09	- 09
Al ₂ O ₃ -Ra	aa ₃₁	6030.39	6045.7	6061.01	
Na ₂ O-Ra	aa ₄₁	4527.6	4527.7	4527.8	
MgO-Ra	aa ₅₁	-620- 2.4368e-09	-620	-620+ 2.4368e-09	- 09
Fe ₂ O ₃ -Ra	aa ₆₁	1988.8- 3.1639e-05	1988.8	1988.8+ 3.1639e-05	- 05
K ₂ O- Ra	aa ₇₁	6438.8	6487.6	6536.4	
CaO-Ra	aa ₈₁	474.7- 1.0245e-06	474.7	474.7+ 1.0245e-06	- 06

Note: The values of interaction parameters are presented within their confidence interval CI. The value of the parameter is shown in bold. In some cases there was no confidence interval, meaning that the results are very good and have tight bounds. * The CI is not estimated since the objective function was insensitive to those parameters.

As mentioned before, these parameters were determined by fitting adsorption systems of four different adsorbents: Kaolinite, Clinoptinolite, montmorillonite, and glauconite. The isotherms (calculated and experimental) of these systems are presented in Fig.5. In this figure, we compared the capacity of adsorption (q^{exp}) from the experimental results and the calculated adsorption capacity (q^{cal}) with the interaction parameter showed in Table 5. It can be seen that the experimental and the estimated adsorption capacity values of q are in good agreement. These results are also reflected in the error

function value obtained (i.e. 1.86×10^{-4}) which it corresponds to the value of the objective function shown in Eq.33.

Fig. 5. Isotherm for adsorption of radium using Kaolinite, Clinoptilolite, Montmorillonite and Glauconite. Comparison of the experimental adsorption capacity found in the literature and the calculated adsorption capacity.

On the other hand, Table 6 reports the values of UNIFAC interaction parameters between all possible functional group that could be part of the new adsorbents for barium adsorption. In this case, the energy interaction of barium is very high especially with the anion chloride and the potassium oxide.

Similarity, we compared the capacity of adsorption for barium from the experimental (q^{exp}) and estimated (q^{cal}) values and the results can be shown in the isotherms of Fig.6.1 and Fig.6.2. The results

453 are for the 3 adsorbents used: Ca-exchange Clinoptilolite tuff, Ca-exchange Montmorillonite clay and
 454 βMnO_2 . There is an excellent agreement between of the experimental and the estimated values of q
 455 with error values are $5.21\text{e-}10$ for the first problem and $5.44\text{e-}12$ for adsorption onto $\beta\text{-MnO}_2$ problem.

456 Table 6
 457 Values of interaction parameter in the adsorption of barium onto Ca-Cln and Ca-Mnt and onto $\beta\text{-MnO}_2$

Bulk Phase				
Description	Variable	CI lower bound	Parameter Value	CI Upper Bound
Ba- Ca_2^+	ab12	-4109.7- 7.7208e-10	-4109.7	-4109.7+7.7208e-10
Ba- Cl^-	ab13	Not sensitive	47935.9*	Not sensitive
Ba- Na^+	ab15	4210	4211.2	4213
Ca_2^+ -Ba	ab21	1033.9- 1.7907e-02	1033.9	1033.9+1.7907e-02
Cl^- -Ba	ab31	-1536.6- 8.8259e-07	-1536.6	-1536.6+8.8259e-07
Na^+ -Ba	ab21	-42726- 7.8335e-10	-42726	-42726+7.8335e-10
ASS Phase				
Ba- SiO_2	aa12	1274.5	1275.3	1276
Ba- Al_2O_3	aa13	948.1	949.2	950.3
Ba- AlO_2^-	aa14	Not sensitive	10867.8*	Not sensitive
Ba-FeO	aa15	-55794- 2.3249e-07	-55794	-55794+2.3249e-07
Ba-MgO	aa16	Not sensitive	8872.1*	Not sensitive
Ba-CaO	aa17	Not sensitive	29906.7*	Not sensitive
Ba- Na_2O	aa18	-1870.32- 1.6181e-08	-1870.32	-1870.32+1.6181e-08
Ba- K_2O	aa19	Not sensitive	33090.4*	Not sensitive
Ba- Ca_2^+	aa110	-124244- 1.6013e-07	-124244	-124244+1.6013e-07

Ba-K+	aa111	1402.6	1418.7	1434.7
Ba-βMnO2	aa112	5710	5712.9	5716
SiO ₂ -Ba	aa21	Not sensitive	6029.7*	Not sensitive
Al ₂ O ₃ -Ba	aa31	Not sensitive	2856.3*	Not sensitive
AlO ₂ ⁻ -Ba	aa41	Not sensitive	6338.5*	Not sensitive
FeO-Ba	aa51	-44287.3- 1.7231e-02	-44287.3	- 44287.3+1.7231e-02
MgO-Ba	aa61	Not sensitive	5044.6*	Not sensitive
CaO-Ba	aa71	Not sensitive	-4072.6*	Not sensitive
Na ₂ O-Ba	aa81	Not sensitive	5685.7*	Not sensitive
K ₂ O-Ba	aa91	Not sensitive	-4564.8*	Not sensitive
Ca ₂ ⁺ -Ba	aa101	Not sensitive	15642.2*	Not sensitive
K ⁺ -Ba	a111	-44279.4- 6.6491e-04	-44279.4	- 44279.4+6.6491e-04
β-MnO2-Ba	aa121	-42954.3- 2.3863e-08	-42954.3	- 42954.3+2.3863e-08

Note: The values of interaction parameters are presented within their confidence interval CI. The value of the parameter is shown in bold. In some cases there is no confidence interval, meaning that the results are very good and have tight bounds. * The CI is not estimated since the objective function was insensitive to those parameters.

Appendix 5 presents the Confidence interval calculation for the interaction parameters.

Fig. 6.1. Isotherm for adsorption of barium onto Ca-Cln and Ca-Mnt. Comparison of the experimental adsorption capacity found in the literature and the calculated adsorption capacity for barium adsorption.

Fig. 6.2. Isotherm for adsorption of barium onto β -MnO₂. Comparison of the experimental adsorption capacity found in the literature and the calculated adsorption capacity for barium adsorption

6. CONCLUSION

This is a first paper in the series of two papers to find an optimal adsorbent following computer-aided molecular design formulation. In this paper, we developed group contribution methods for barium and radium adsorption. The UNIFAC interaction parameters for the groups are computed using the available experimental isotherms for various adsorbents for barium and radium and an NLP optimization technique. These parameters are used to estimate the adsorption capacity at different concentration and these parameter values are found to be in very good agreement with experimental results. In part 2 of

the paper, we discuss the detail of the CAMD formulation and the optimization algorithms to find optimal adsorbents for the removal of barium and radium from produced waters from fracking.

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8. APPENDIX

Appendix 1. Calculation of van der Waals volume and surface

The constants representing the group sizes and surfaces areas R_g and Q_g are obtained from atomic and molecular structural data, the van der Waals group volume V_g , and surface areas A_g , as it is shown in Eq. A1 and Eq.A2. (Fredenslund et al., 1977).

$$R_g = V_g / 15.17 \quad \text{Eq.A1}$$

$$Q_g = A_g / 2.5e9 \quad \text{Eq.A2}$$

Where V_g and A_g are calculated from experimental data, namely, the so-called van der Waals radius (r_w) of each atom in the molecule representation

Radium (Ra): In the case of radium, a single spherical atom, the van der Waals volume is given by:

$$V_g = \frac{4}{3} \pi r_w^3 * N_A \quad \text{Eq.A3}$$

Where $r_w = 2.3 \text{ \AA}$ equivalent to $2.3e-8 \text{ cm}$, and N_A is the Avogadro number equals $6.023e23 \text{ moles/molecule}$, then $V_g = 30.696 \text{ cm}^3/\text{mole}$. For the surface area value, Eq.A4 is used:

$$A_g = \pi r_w^2 * N_A \quad \text{Eq. A4}$$

499 Then, $A_g = 1e9\text{cm}^2/\text{moles}$.

500 Finally, replacing the values of V_g and A_g into Eq. A1 and Eq.A2, respectively, we obtain $R_g = 2.023$ and

501 $Q_g = 0.4$

502 Table A1 presents the van der Waals volume and surface values of radium and other components in the
503 adsorption of radium.

504 Table A1
505 Van der Waals volume and surface values

Groups (g)	Amount of Groups	R_g	Q_g
Ra	1	2.023	0.4
$\text{Na}^{+ (a)}$	1	3.0	3.0
$\text{Cl}^{- (a)}$	1	0.9861	0.9917
$\text{H}_2\text{O}^{(a)}$	1	0.92	1.40

506 (a) Values of R_g and Q_g can be found at Kikic and Fermeglia, 1991

507

508 Appendix 2. Functional groups of the adsorbents

509 For these two molecules, the geometrical method presented by Bondi is used to define the van der
510 Waals volume and surface area (Bondi, 1968). Apart from the van der Waals radii for both atoms (r_1, r_2),
511 additional information related to the structure of the molecule is required, namely, the bond distances
512 (l), an auxiliary parameter (ma), and the height of sphere segments (h_1, h_2). Eq.A5 shows the van der
513 Waals volume of diatomic molecule.

$$514 \quad V_g = N_A(V_1^1 + V_2 - \Delta V_{2-1}) * 10^{-24} \text{ cm}^3/\text{mole} \quad \text{Eq.A5}$$

515 where V_1^1 , V_2 and ΔV_{2-1} are computed by Eqs.A6, A7, A8 and r is given in Angstrom units, then:

$$516 \quad V_1^1 = \pi h_1^2 \left(r_1 - \frac{h_1}{3} \right) \quad \text{Eq.A6}$$

$$517 \quad V_2 = \frac{4}{3} \pi r_2^3 \quad \text{Eq.A7}$$

$$518 \quad \Delta V_{2-1} = \pi h_2^2 \left(r_2 - \frac{h_2}{3} \right) \quad \text{Eq.A8}$$

519 To compute the height of sphere segments, Eqs.A9, A10 are used:

520 $h_1 = r_1 + 1 - ma$ Eq.A9

521 $h_2 = r_2 - ma$ Eq.A10

522 Finally, Eq.A11 is used to calculate the auxiliary parameter ma:

523 $ma = \frac{r_2^2 - r_1^2 + l^2}{2l}$ Eq.A11

524 On the other hand, the van der Waals surface area is computed using Eq.A12:

525 $A_g = 2\pi N_A(r_1 h_1 + 2r_2^2 - r_2 h_2)$ Eq.A12

526

527 Once again, after V_g and A_g are calculated from the previous equations, these values are replaced into

528 Eq. A1 and Eq.A2, respectively. Table A2 summaries the result of these values for the groups of

529 adsorbent used here.

530 Table A2

531 Information of functional groups of absorbents for calculation of R_g and Q_g

Groups (g)	l (Å)	r ₂ (Å)	r ₁ (Å)	V _g (cm ³ /mol)	A _g (cm ² /mol)	R _g	Q _g
SiO ₂	1.61	2.1	1.52	21.067	3.167e9	1.388	1.268
Al ₂ O ₃	1.935	1.84	1.52	16.829	2.759e9	1.109	1.104
MgO	2.11	1.73	1.52	15.368	2.602e9	1.013	1.041
Fe ₂ O ₃	2.098	1.94	1.52	18.528	2.918e9	1.221	1.167
K ₂ O	2.86	2.75	1.52	41.198	4.609e9	2.716	1.844
Na ₂ O	2.41	2.27	1.52	25.600	3.517e9	1.688	1.407
β-MnO ₂	1.922	1.26	1.52	10.731	2.036e9	0.707	0.815
(AlO ₂) ⁻	1.641	1.84	1.52	16.673	2.753e9	1.099	1.101
CaO	2.4	2.31	1.52	26.576	3.594e9	1.752	1.438
FeO	2.17	1.94	1.52	18.580	2.920e9	1.225	1.168

532

533 Appendix 3. Structure and properties of the adsorbents for radium and barium removal

534 Table A3 presents the minerals used by Ames et al., 1983b with their chemical composition and molecular

535 weight in the adsorption of radium. From this table, we can see the number of functional groups that are

536 contained in each adsorbent. The first four adsorbents belong to the clay mineral group also known as

537 hydrous aluminum phyllosilicates. The word “clays” was assigned early to fine grained material in

geological formations or soils with size less than 2 μ m (Velve and Meunier, 2008). The Clinoptilolite is one of the most abundant natural zeolite. It has been used for radioactive waste disposal and ammonia recovery from sewage effluents (Yang, 2003). The last adsorbent is silica gel which is most-used as a desiccant or adsorbent for moisture (Yang, 2003). For the chemical analysis of these minerals see Ames et al., 1983b. The calculation of the molecular weight for all clays was based on the chemical structure general formula (Deer et al., 1992).

Table A3

List of secondary mineral used in adsorption of radium and their molecular weight and pore volume values

Absorbent	Structure	Pore volume vp (cm ³ /g)	M ₀ (g/mol)	Type of mineral	Reference
Kaolinite	(Al ₂ O ₃)(SiO ₂) ₂ (H ₂ O)	0.278	222.127	Clay-mica group/phyll silicate	Diamond, 1970 Benco et al., 2001
Montmorillonite	(Na ₂ O) (MgO) ₂ (Fe ₃ O ₂) (Al ₂ O ₃) ₂ (SiO ₂) ₄ 2H ₂ O	0.172	786.374	Clay-mica group/phyll silicate	Diamond, 1970
Nontronite	(Na ₂ O)(Fe ₂ O ₃)(Al ₂ O ₃) ₂ (SiO ₂) ₄ ·2H ₂ O	0.255	665.920	Clay-mica group/phyll silicate	Diamond, 1970
Glauconite	(K ₂ O)(MgO) ₂ (Fe ₂ O ₃)(Al ₂ O ₃) ₂ (SiO ₂) ₄	0.164	778.736	Iron potassium phyllosilicate	Hassan and Shall, 2004
Clinoptilolite	(CaO)(Na ₂ O)(K ₂ O)(Al ₂ O ₃) ₃ (SiO ₂) ₃₀₋₂ 4H ₂ O	0.186	2320.62	Natural Zeolite	Yang, 2003
Silica gel	(SiO ₂)	0.43	60.083	Silica	Yang, 2003 Ruthven, 1984

On the other hand, Table A4, presents the chemical structure and molecular weight of the adsorbents used for adsorption of barium. Clinoptinolite tuff (Ca-Cln) is constituted by clinoptinolite-heulandite and mordenite with minor plagioclase, feldspar, cristobalite, quartz, and glass. The montmorillonite clay (Ca-Mnt), on the other hand, contains ~85% of montmorillonite associated with plagioclase, feldspar, glass, opal, and calcite. Beta-manganese oxide was also studied for the adsorption of barium. For more information about the adsorbent's composition please refer to Chavez et al., 2010 and Arafa et al., 1974. The molecular weight is calculated based on the chemical composition presented by the authors.

Table A4
Information about the adsorbents used in adsorption of barium

Absorbent	Structure	M ₀ (g/gmol)	Type of mineral	Reference
Clinoptilolite tuff (Ca-Cln)	$(K^+)(Ca^{+2})(K_2O)(Na_2O)(CaO)(AlO_2)^-_2$ $(Al_2O_3)_{3.1}(SiO_2)_{37.9}(H_2O)_{24}$	187.207	Natural Zeolite	Chavez et al., 2010
Montmorillonite (Ca-Mnt)	$(Na_2O)(MgO)_2(FeO)(Al_2O_3)_2(SiO_2)_4$ $_2H_2O$	399.104	Clay	Chavez et al., 2010
Beta-Manganese oxide	$\beta\text{-Mn}_2\text{O}$	86.937	Oxides	Arafa et al., 1974

Appendix 4. Calculation steps to compute the adsorption capacity for Kaolinite

Table A5 summarizes the important calculations followed to compute the adsorption capacity (q^{cal}) for Kaolinite. The table presents the expression used, its value and the equation used to demonstrate one point of Figure 5 (i.e. when concentration (C) in the equilibrium is equal to 0.018 mol/L). We used the interaction parameters for kaolinite shown in Table A6, which are also presented in Table 5 for all the interaction parameters involved in the adsorption of radium.

Table A5 Calculation steps to compute the adsorption capacity for Kaolinite

Description	Expression	Value	Source
Temperature (K)	T	298.15	Ames et al (1983)
Volume of solution (L)	V_{sln}	1	Assume
Ideal constant (J/molK)	R	8.314	Literature
Pore volume (cm^3/g)	vp	0.278	Table A3
Surface-phase capacity of Ra in Kaolinite (mol/g)	Γ_{mi}^s	0.0068	Eq.4
Molecular weight of solid (g/mol)	M_0	222.127	Table A3
Amount of solid (g)	m_0	50	Ames et al (1983)
Activity coefficient for the pure component	γ_{01}^*	1.66213	Eq.11
Initial concentration of radium (mol/L)	C_1	2.95	Ames et al (1983)
Initial moles of radium (mol)	n_1^1	2.95	Eq.19
Moles of adsorbate solid solution phase for radium (mol) (using the q from Ames et al (1983))	n_1^*	1.516	Eq.17
Moles of adsorbent in the adsorbate solid solution (mol)	n_0^*	0.225096	Eq.16
Moles of Bulk phase (mol)	n_1^b	1.433	Eq.18
	n_2^b	0.01	$C_{\text{NaCl}} * V_{\text{sln}}$

	n_3^b	48.76	$(V_{H_2O} * \rho_{H_2O}) / MW_{H_2O}$
Mole fraction of Adsorbent solid solution	x_0^*	0.1292	Eq.21
	x_1^*	0.8708	
Mole fraction of Bulk phase	x_1^b	0.0285	Eq.20
	x_2^b	0.0002	
	x_3^b	0.9713	
Mole fraction of surface phase	x_1^s	1	Eq.10
Activity coefficient from bulk phase	$\ln \gamma_1^b$	10.1494	Eq.22
	$\ln \gamma_2^b$	-8.8833	
	$\ln \gamma_3^b$	0.0213	
Activity coefficient from Adsorbate solid solution	$\ln \gamma_1^*$	0.1768	Eq.12
	$\ln \gamma_0^*$	-8.5292	
Gibb excess free energy (J)	G^{E*}	-3765.57	Eq.35
	G^{Es}	0	Eq.36
	G_{oi}^{E*}	1757.235	Eq.37
Difference of the chemical potential (J/g)	$\varphi^* - \varphi_{oi}^*$	-110.456	Eq.39
Total moles in the adsorbate solid solution (using the interaction parameters)	n_T^*	1.6024	Eq.38
Adsorption capacity calculated	q^{cal}	0.0279	Eq.34
Adsorption capacity experimental	q^{exp}	0.0303	Ames et al (1983)

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568 Table A6 Unifac interaction parameters for Kaolinite

Parameter	Value
Ra-Na ⁺	8968.14
Ra-Cl ⁻	73.45
Ra-H ₂ O	94335.54
Na ⁺ - Ra	2020.83
Cl - Ra	1335.69
H ₂ O - Ra	6627.52
Ra - SiO ₂	-846.70
Ra - Al ₂ O ₃	-3298.09
SiO ₂ - Ra	-71.19
Al ₂ O ₃ - Ra	6045.72

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Appendix 5 Confidence interval calculation of the interaction parameters

Reliability of the parameters is obtained by finding the confidence interval (Rasmuson et al., 2014). The approximate confidence interval is obtained by linearization of the nonlinear function with a first order Taylor series expansion around the estimated parameter using Eq.A13:

$$f(x_n, \theta) = f(x_n, \hat{\theta}) + \left[\frac{\partial f(x_n, \hat{\theta})}{\partial \theta_p} \right]_{\theta = \hat{\theta}} (\theta - \hat{\theta}) \quad \text{Eq.A13}$$

where $\hat{\theta}$ is the estimated parameter.

The first order derivative of the nonlinear function is the Jacobian. It can be represented as shown in Eq.A14

$$J_{n,p} = \left[\frac{\partial f(x_n, \hat{\theta})}{\partial \theta_p} \right]_{\theta = \hat{\theta}} \quad \text{Eq.A14}$$

where n is the experimental point where the derivative is taken and p is the parameter.

Since it is difficult to find the Jacobian theoretically, a numerical estimation can be done. The approximation of the Jacobian is done as follows: the parameters $\hat{\theta}$ where sum of square error (SSE) has been identified from the optimization problem where SSE has been minimized. At the optimal point of the parameters, one parameter is changed at a time by 1%, (denoted by $\hat{\theta}_{p,1\%}$). All other parameters remain at the minima. The function is calculated at this point. Then, this parameter is changed back to original and the next parameter is changed by 1% and the function is calculated. The approximate numerical estimation of the Jacobian is given by Eq.A15:

$$J_{n,p} = \frac{f(x_n, \hat{\theta}) - f(x_n, \hat{\theta}_{p,1\%})}{\Delta \theta_p} \quad \text{Eq.A15}$$

The $1 - \alpha$ confidence interval for $\hat{\theta}_p$ is determined by Eq.A16

$$\hat{\theta}_p \pm se(\hat{\theta}_p) t(n - p, \alpha/2) \quad \text{Eq.A16}$$

where $t(n - p, \alpha/2)$ is the Student's t distribution with $n - p$ degrees of freedom and $se(\hat{\theta}_p)$ is the standard error for parameter calculated using Eq.A17

$$se(\hat{\theta}_p) = s \sqrt{((J^T J)^{-1})_{pp}} \quad \text{Eq.A17}$$

where s is the standard deviation obtained from the objective function SSE

$$s = \sqrt{\frac{SSE}{n-p}} \quad \text{Eq.A18}$$

For some cases the confidence interval is very tight due to very small hessian. For cases where the Hessian is very large, the confidence interval is very large and the objective function is insensitive to the parameter changes.

A_g : Van der Waals surface area (cm^2/mol)	Greek letters
a_{nm} : Interaction parameters	γ : Activity coefficient
b : Langmuir constant	$\gamma_{GE,i}^*$: Activity coefficient of a binary adsorbate-solid solution
C : Equilibrium concentration in solution (mol/L)	ϕ^* : Chemical potential of the wetted solid adsorption of the pure component i (J/g)
C_i : Initial concentration of radium in solution (mol/L)	ϕ_{oi}^* : Chemical potential of the wetted solid adsorption of the pure component i (J/g)
E_q : Total number of equation used to solve the problem	ϕ_i : Volume fraction for UNIFAC calculation
G^E : Gibb excess free energy (J)	θ_i : Surface area fraction for UNIFAC calculation
g^{ad} : Free energy of immersion of the adsorbed solution (J/kg)	Γ_{mi}^s : Surface phase capacity of component i (mol/g)
h_1, h_2 : Height of sphere segments ($\text{\AA}$)	ρ : density (g/ml)
K : Langmuir constant	Subscripts
k_f : Freundlich constant	i : Component i ,
l : Bond distances ($\text{\AA}$)	0 : Adsorbent
m_0 : Mass of adsorbent (g)	1 : Adsorbate (radium or barium)
M_0 : Molecular weight of Adsorbent (g/mol)	$2,3,4$: Component 2, 3 or 4
MW : Molecular weight (g/mol)	O_i : Pure component i or pure adsorbed component i
ma : Auxiliary parameter	g : Group index
N_{gt} : Total functional groups	j : Number of components
N_A : Avogadro number	T : Total
n_f : Freundlich constant	Sln : solution
J : jacobian	H_2O : water
n : Molar quantity (moles)	Superscripts
q : Amount adsorbed for unit mass of adsorbent (mol/g)	E^* : Excess adsorbate-solid solution
q_i : Parameter for Van der Waal surface calculation	Es : Excess of the surface phase
Q_g : Van der Waals group surfaces of group K (m^2)	1 : Initial feed
r_i : Parameter for Van der Waal volume calculation	b : Bulk phase
r_w : Van der Waals radius ($\text{\AA}$)	$*$: Adsorbate solid solution
r_1, r_2 : Van der Waals radii for both atoms ($\text{\AA}$)	s : Surface phase
R_g : Van der Waals group volumes of group K (m^3)	ad : Adsorption
R : Ideal gas constant (8.314 J/molK)	C : Combinatorial
T : Temperature of adsorption (K)	R : Residual in ASS
vp : Pore volume of the adsorbent (cm^3/g)	Cb : Combinatorial in bulk phase
v_{oi} : Molar volume of the respective fluid (cm^3/mol)	Rb : Residual in the bulk phase
V_g : Van der Waals volume (cm^3/mol)	C^* : Combinatorial in ASS phase
V : Volume (L)	R^* : Residual in the ASS phase
x : Molar fraction	cal : Calculated
	exp : Experimental

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