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Optimal design of adsorbents for NORM removal from produced water in natural gas fracking. Part 2: CAMD for adsorption of radium and barium



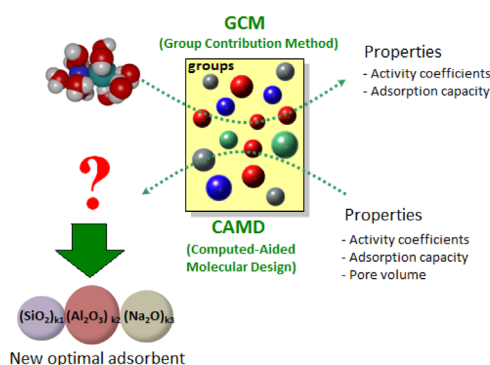
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HIGHLIGHTS

- First study of computer aided molecular design for Adsorption.
- Second paper in two part series.
- A novel approach to the problem of NORM removal from produced waters of fracking.
- New combinatorial optimization method to solve the problem.

GRAPHICAL ABSTRACT



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ABSTRACT

This is second paper in series in which we propose computer-aided molecular design (CAMD) methodology for the optimal design of adsorbents for adsorption of natural occurring radioactive material (NORM) of natural gas fracking waste. The adsorbent selection optimization problem is posed as a mixed integer nonlinear programming problem and a new algorithm called efficient ant colony optimization (EACO) is used to solve the problem. The algorithm maximizes the absorption capacity of the adsorbent subject to structural feasibility, thermodynamic property correlations, process conditions derived from produced water and mass balance on the adsorption process constraints. New adsorbents for removal of radium and barium together and individually are proposed. These adsorbents show far greater capacity to remove radium and barium from produced water than state of the art adsorbents found in literature.

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1. Introduction

Natural gas fracking is taking center stage in energy industries, hence it is imperative to look at environmental footprint of the technology. Fracking generates large amount of produced water

which contains significant amount of naturally occurring radioactive materials (NORM). Sylva et al. performed an analysis on the Marcellus shale gas produce water in four Pennsylvania counties (Silva et al., 2012). Table 1 presents their results on samples which were obtained from produced water tanks adjacent to the wells. It also presents results of produced water from the Barnett shale in Texas (Well-7) and a design case produced water whose composition is based on data from the literature.

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Nomenclature		∂p	Individual contribution for pore volume calculation
a_{nm}	Interaction parameters	<i>Greek letters</i>	
C	Equilibrium concentration in solution (mol/L)	γ	Activity coefficient
C_1	Initial concentration of radium in solution (mol/L)	φ^*	Chemical potential of the wetted solid adsorption of the pure component i (J/g)
C_2^b	Amount of barium allowed in the solution (mol/l)	φ_{oi}^*	Chemical potential of the wetted solid adsorption of the pure component i (J/g)
Cont	Accounts to a constant value for pore volume calculation	I_{mi}^s	Surface phase capacity of component i (mol/g)
F_1^*	Amount of radium allowed in the sludge stream (mol/g)	ρ	Pheromone evaporation factor
k_g	Decision variable that determines the group used to form the adsorbent	<i>Subscripts</i>	
ks	Size of the solution archive	i	Component i
m	Mass (g)	0	Adsorbent
M_0	Molecular weight of Adsorbent (g/mol)	1, 2	Adsorbate (radium and barium)
n	Molar quantity (moles)	3, 4, 5	Components (sodium, chloride and water)
nAnts	set of number of ants	0i	Pure component i or pure adsorbed component i
NC	Number of continuous variables	g	Group index g
ND	Number of discrete variables	T	Total
N_{gt}	Total groups used to form the molecule	<i>Superscripts</i>	
Nobs	Number of observations	1	Initial feed
q	Amount adsorbed for unit mass of adsorbent (mol/g)	*	Adsorbate solid solution
q_{EACO}	Algorithm parameter of EACO	ad	Adsorbent
R	Ideal gas constant (8.314 J/molK)	b	Bulk phase
SArc	Solution archive	cal	Calculated
T	Temperature of adsorption (K)	exp	Experimental
TDS	Total dissolved solids	opt	Optimal
TOC	Total organic carbon	s	Surface phase
v_p	Pore volume of the adsorbent (cm ³ /g)		
val	Valance of groups		
v_{oi}	Molar volume of the respective fluid (cm ³ /mol)		
V_{sln}	Volume of solution (L)		
x	Molar fraction		
%A	Percentage of adsorption		

As it can be observed from Table 1 that regardless of the well produced water contains significant salinity content, hardness species, metals and high levels of NORM in the form of radium isotopes (²²⁶Ra). In 2011, Gas Technology Institute (GTI) carried out a Techno-economic Assessment of Water Management Solutions project that was supported by a consortium of 23 companies (Hayes and Smith, 2011). This consortium identified several priority industrial challenges for the pre- and post-crossover stages of the water-based life cycle of a shale gas development area and identified NORM removal as one of the highest priority areas of research. They also ascertained that there is currently no commercial product on the market that is capable of selectively removing NORM from concentrated produced and flowback waters. In their final report to the Research Partnership to Secure Energy for America General Electric, they studied various adsorbents for the removal of radium from fracking waters and they found that the current state of the art technology is not economical to remove NORM from flowback and produced waters (Hayes and Smith, 2011). In this work, we propose and implement a novel computational tool for high-throughput screening and selection of new adsorbents for NORM removal. Computer aided molecular design (CAMD) methodology is proposed to obtain these new adsorbents.

CAMD systematically generates molecules from their fundamental building blocks. This approach is the reverse use of the group contribution method (GCM). In GCM, for a given molecular structure of a molecule, the properties such as physical, chemical, or biological can be estimated based on properties of its functional

groups. In CAMD, given the desired properties of a molecule, the molecule that satisfies these properties can be generated by combination of different building block groups (Kim and Diwekar, 2002a). GCM like UNIFAC form are the basis of CAMD methods (Fredenslund et al., 1977). In the first paper of this series, we obtained building blocks for clay base materials and GCM is used to generate adsorption isotherms to generated compounds, using these building blocks. CAMD methods have been applied to many areas, such as chlorofluorocarbon substitutes (Joback and Stephanopoulos 1989), extraction solvents (Li et al., 2002; Marcoulaki and Kokossis, 2002; Giovanoglou et al., 2003; Kim et al., 2004; Cheng and Wang, 2008), refrigerant, polymer and drug designs (Churi and Achenie, 1995; Duvedi and Achenie, 1996; Vaidyanathan and El-Halwagi, 1996; Maranas, 1996; Hostrup et al., 1999; Eden et al., 2004), absorption solvents (Macchietto et al., 1990; Pistikopoulos and Stefanis, 1998; Salazar et al., 2012), distillation solvents (Kim and Diwekar, 2002b; Kim et al., 2004; Xu and Diwekar, 2005, 2006), reaction and crystallization solvents (Lin et al., 2005; Karunanithi et al., 2006; Folic et al., 2008), value added products (Camarda and Sunderesan, 2005), and foaming agents (Yamamoto and Tochigi, 2008). Moreover, Samudra and Sahinidis (2013) has proposed a new approach for optimal design of CAMD problems by including the automate, augment and accelerate steps in CAMD. Recently, CAMD was used to generate new environmentally benign solvents using the EACO algorithm with better targeted properties in the acetic acid extraction from water. The model was formulated based on the infinite dilution activity coefficient that uses the UNIFAC method (Gebreslassie and

Table 1

Produced water composition from Pennsylvania Marcellus Shale Gas Wells and Texas Barnett shale (all quantities mg/L except where noted) (Silva et al., 2012).

County	Well-1 Bradford	Well-2 Bradford	Well-3 Bradford	Well-4 Butler	Well-5 Tioga	Well-6 Washington	Well-7 ^a	Design case
pH ^b	7.3	6.3	5.4	5.8	5.9	6.2	6.6	7.0
TDS	98294	155705	199242	68439	149188	122562	124421	132460
Na ⁺	26500	38200	51800	19200	39000	32300	33900	35000
Mg ⁺⁺	460	840	1290	570	1000	800	1170	800
Ca ⁺	5560	10280	13120	5360	13000	8700	10880	9500
Sr ⁺⁺	2030	3670	4580	1290	2600	2340	1750	2500
Ba ⁺⁺	6580	13200	11600	32	3500	5800	147	6200
Fe ⁺⁺	26	74	123	55	32	75	47	50
Mn ⁺⁺	1.5	2.5	3.4	1.7	2.7	4.3	1.2	3
Cl ^{-c}	57120	89429	116713	41845	90014	72525	76493	78407
SO ₄ ⁻	< 10	< 10	< 10	57	< 5	< 50	< 100	0
SiO ₂	16.7	11	13	29	39	18	33	0
Hardness as Ca ⁺⁺	9167	17196	20727	6899	16860	12782	13653	13772
²²⁶ Ra ^d	5400	7600	4200	4600	5600	820	2300	5000
TSS	202	282	500	62	520	210	898	0
Turbidity ^e	78	399	1160	17.4	192	45	164	0
TOC	< 10	11.8	11.8	72	151	160	88	0

^a Produced water from Barnett Shale (TX).^b Dimensionless.^c Adjusted to force ion balance (prior analyses found other anions were < 1% of the chloride on a molar basis).^d pCi/Liter.^e Turbidity units: NTU.

Diwekar, 2015). The results were compared to various optimization approaches presented in literature. It was found that EACO gave better solutions to CAMD. Therefore, we are using EACO in this work for solving this real world CAMD problem for adsorption. This is the first time CAMD is being proposed for the generation of adsorbents.

It is difficult to carry out numerous experiments related to removal of uranium and radium isotopes (Ames et al., 1983a, 1983b; Moon et al., 2003) and barium as they are hazardous materials (Arafa et al., 1974; Atun and Bascetin, 2003; Chavez et al., 2010). This work, circumvents those problems by using the CAMD framework to find molecules and adsorption capacity. Thus, through the functional groups, all possible molecules can be generated by exploring all combination. Once the molecules are generated, the properties of the molecules are predicted based on GCM like UNIFAC. In CAMD, the desired properties are enhanced by optimization, the resulting molecules are the optimal molecules which have desired properties.

2. Adsorption process description

As explained earlier and in the first part of this paper (Benavides and Diwekar, accepted for publication), the reason for pollution due to produced water from fracking is because of the high level of salinity content, hardness species and significant levels of NORM which cause health risks to people. According to Silva et al. (2012) pretreatment process is needed before removing radium and barium using adsorption. There are several pretreatment processes or softening processes. Silva et al. (2012) reported different processes to remove hardness species, metals, radium, and barium in order to recover water. Here, we proposed a separation scheme based on the results presented by Silva et al. (2012). According to these authors, at the initial stage of the pretreatment process, components such as Mg, Ca, Fe, etc. are separated through a precipitation process. Then, removal of radium and barium from the saline solution can take place. Fig. 1 illustrates the proposed adsorption scheme of radium and barium from produced water of shale gas production. We use the adsorbate solid solution theory (ASST) presented in the first part of this paper is that describes the adsorption behavior of radium

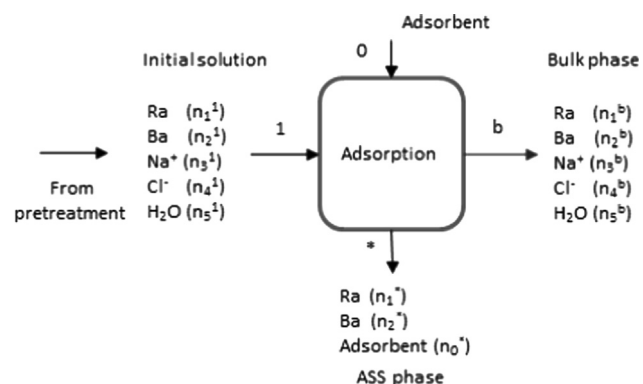


Fig. 1. Adsorption of radium and barium model. In this Fig. “1” represents the produced water that comes from the pretreatment stage, “0” represents the adsorbent added, “b” is the bulk phase and “*” is the adsorbate solid solution (ASS) phase.

and barium on the adsorbent by the use of G^E -models. For the purpose of this work, we use the initial feed information of the design case presented in Table 1 which contains high amounts of radium, barium, and salts. Note that the composition presented in Table 1 is expressed in milligrams per liter and picocuries per liter for the case of radium. These values were converted into mole per liter.

The mole balance equations presented next can be used to compute the moles and mole fractions of each component at each phase. As it can be seen, the moles per component i entering to the adsorption process (n_i^1) equals the moles in the ASS phase n_i^* and bulk phase n_i^b as shown in Eq. (1).

$$n_i^1 = n_i^* + n_i^b \quad \forall i \quad (1)$$

For the feed composition and bulk phase $i \in [1, \dots, 5]$, that is, radium (1), barium (2), sodium (3), chloride (4), and water (5). On the other hand, for the ASS $i \in [0, \dots, 2]$ which represents the adsorbent (0), radium (1) and barium (2).

The total feed and the mole fractions are calculated as shown in Eqs. (2) and (3):

$$n_T^1 = \sum_{i=1}^5 n_i^1 \quad (2)$$

$$x_i^1 = \frac{n_i^1}{n_T^1} \quad \forall i \quad (3)$$

Similarly, to compute the total moles and mole fractions for the bulk phase, the following equations are used.

$$n_T^b = \sum_{i=1}^5 n_i^b \quad (4)$$

$$x_i^b = \frac{n_i^b}{n_T^b} \quad \forall i \quad (5)$$

And for the adsorbate solid solution phase, we use

$$n_T^* = \sum_{i=0}^2 n_i^* \quad (6)$$

$$x_i^* = \frac{n_i^*}{n_T^*} \quad \forall i \quad (7)$$

3. Optimization problem CAMD for NORM removal

The primary requirement for an effective and economical adsorption process is an adsorbent with high selectivity and/or adsorption capacity. In this work, we emphasize on the adsorption capacity as the property for the selection of new adsorbents of NORM. Adsorption capacity “ q ” represents the amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent. This property depends on the adsorption temperature, the fluid phase, and the initial condition of the adsorbent. As presented in the first part of this paper series, the adsorption capacity is plotted as an isotherm and express in a Langmuir or Freundlich type equation (Suzuki, 1990.). However, Eq. (8) can also be used to express the adsorption capacity:

$$q = \frac{(C_1 - C)V_{\text{sln}}}{m_0} \quad (8)$$

where C_1 and C represent the initial produced water concentration and equilibrium concentration of the adsorbate while m_0 is mass of adsorbent and V_{sln} is volume of solution. Note: all the calculations presented here are performed for one liter of produced water. Since the numerator of Eq. (8) represents the molar quantity (n) of adsorbate (i.e. radium and barium) adsorbed, this equation can be rewritten in terms of moles of adsorbate removed, and thus, the objective function is presented in Eq. (9):

$$\max q = \left(\frac{n_{1,2}^1 - n_{1,2}^b}{m_0} \right) \quad (9)$$

where $n_{1,2}^1$ represents the initial moles of radium (n_1^1) and barium (n_2^1) in the solution,

$$n_{1,2}^1 = n_1^1 + n_2^1 \quad (10)$$

And $n_{1,2}^b$ represents the moles in the bulk phase for both radium (n_1^b) and barium (n_2^b),

$$n_{1,2}^b = n_1^b + n_2^b \quad (11)$$

The decision variable is represented by k_g , which denotes the number of times the group occurs in the molecule of the adsorbent, and g defines the index of functional group. The groups available for the adsorption of barium and radium are: SiO_2 , Al_2O_3 , Na_2O , MgO , K_2O , CaO and Na^+ . We are using these seven functional groups whose interaction parameters are obtained in the first part of this paper series (See Tables 5 and 6 for the interaction parameters).

On the other hand, the objective function presented in Eq. (9) is subject to a set of linear and nonlinear equality and inequality constraints that describe the operation conditions, the thermodynamic equilibrium of the adsorption process, the structural feasibility and boundaries of the decision variable:

$$0 \leq F_1^* \leq 1.106 \quad (12)$$

$$0 \leq C_2^b \leq 7.3E-4 \quad (13)$$

Eq. (12) represents the maximum amount of radium in mole per gram allowed in the sludge stream (i.e. ASS phase) so it can be treated through deep well injection (Silva et al., 2012), while Eq. (13) represents the amount of barium in mole per liter allowed in the solution (i.e. bulk phase). The following equation can be used to compute these two parameters:

$$F_1^* = \frac{n_1^*}{m_T^*} \quad (14)$$

$$C_2^b = \frac{n_2^b}{V_{\text{sln}}} \quad (15)$$

Based on Silva et al. (2012), if the salt recovered is used as road salt, this product must pass the TCLP (toxicity characteristic leaching protocol), which includes the requirements of barium content less than 100 mg/L (Rowan et al., 2011). In the case of the radium content, since there is no specification for radium in road salt limit (at least in Pennsylvania and New York), it can be assumed that must meet ^{226}Ra specification for disposal of solids as nonhazardous. In Pennsylvania, the permit limit is 25pCi/g (Silva et al., 2012).

Eq. (16) to Eq. (18) correspond to the mole fraction constraints for bulk, ASS, and surface phase, respectively.

$$0 \leq x_i^b \leq 1 \quad \forall i \in [1 \dots 5] \quad (16)$$

$$0 \leq x_i^* \leq 1 \quad \forall i \in [0 \dots 2] \quad (17)$$

$$0 \leq x_i^s \leq 1 \quad \forall i \in [1 \text{ and } 2] \quad (18)$$

Eqs. (19) and (20) represent the non-negativity constraints:

$$n \geq 0 \quad \forall n_i^b \text{ and } \forall n_i^* \quad (19)$$

$$m_0 \geq 0 \quad (20)$$

Eq. (21) makes sure that the thermodynamic equilibrium for both radium and barium adsorption process is satisfied where tol is a tolerance. The calculations of the terms for Eq. (21) are explained in the first part of the paper. However, it is important to mention that Γ_{mi}^s represents the surface capacity which involves the pore volume of each adsorbent and the molar volume of the respective fluid. In this case the pore volume is unknown since this value depends on the structure of the adsorbent that is also unknown. Therefore, we developed a group contribution method to determine the pore volume based on experimental data for known adsorbents (See Table A2 in Appendix A).

$$\left| x_i^b \gamma_i^b - x_i^* \gamma_i^* \exp \left(\frac{(\varphi_i^* - \varphi_{oi}^*)}{RT \Gamma_{mi}^s} \right) \right| \leq \text{tol} \quad (21)$$

$$0 \leq k_g \leq 20 \quad \forall g \in \text{integer } [1 \dots 7] \quad (22)$$

Eq. (22) represent the boundaries of the discrete variable k_g where $g \in [1 \dots 7]$. The maximum numbers of each groups allowed in the molecule are 20 and 7 functional groups are available for possible combination to generate a new adsorbent for radium and barium adsorption. Therefore, the general structure of the

molecule is determined according to the following equation:

$$(\text{SiO}_2)_{k_1}(\text{Al}_2\text{O}_3)_{k_2}(\text{Na}_2\text{O})_{k_3}(\text{MgO})_{k_4}\dots \quad (23)$$

$$\sum_{g=1}^{N_{gt}} \text{val}(k_g) * k_g = 0 \quad (24)$$

Finally, Eq. (24) represents the feasibility constraint regarding the structure of the molecule. $\text{val}(k_g)$ is the valance of each group and N_{gt} is the total groups used to form the molecule.

4. Solution strategy

The mixed integer nonlinear programming (MINLP) problem formulated seeks to maximize the adsorption capacity of the adsorbent subject to the constraints presented in Section 3. In this section, we present the solution strategy that solve the MINLP problem. This strategy combines the EACO algorithm (described in the next section) and CAMD (See Fig. 2). In the forward approach, the EACO algorithm generates molecules from the set of functional groups while CAMD predicts the properties of the adsorbents generated.

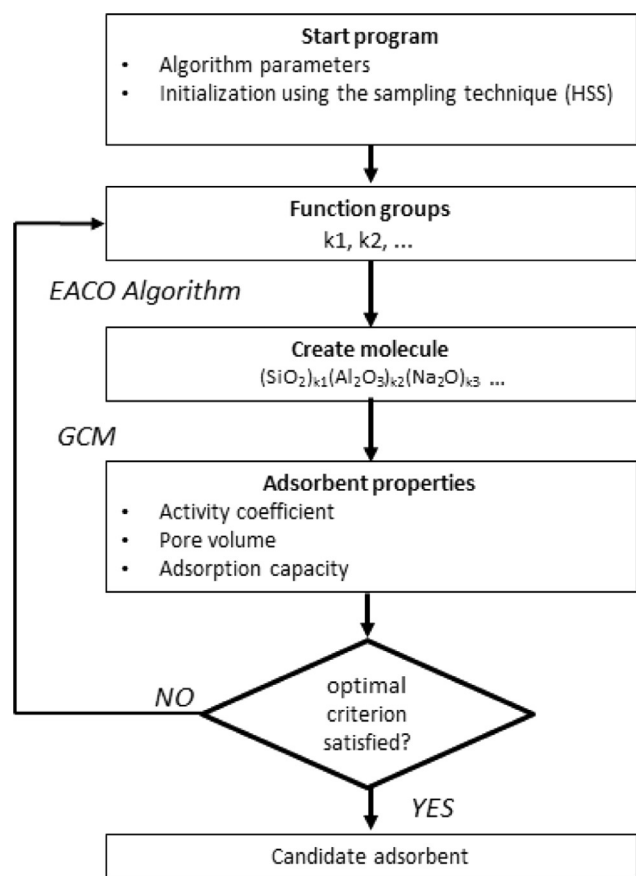


Fig. 2. Solution strategy for adsorbent selection problem. As shown in this figure, the algorithm parameters, the building block groups and their properties such as the volume and surface area parameters, and the interaction parameters between groups are first introduced. These the building block groups are uniquely designed to generate all possible molecules by exploring all possible combinations. Using the group combinations from this set of groups, adsorbent molecules are generated. Once the molecule is generated, its properties such as activity coefficient which is calculated through the UNIFAC models and pore volume which is used to calculate the surface capacity of the adsorbent (r_{mi}^s) are predicted. With these new properties, molar balance equation, constraints, and thermodynamic conditions are examined. If the stopping criterion is satisfied, then the molecule generated is a candidate adsorbent, otherwise, a new molecule is generated by grouping different functional groups using the EACO algorithm.

4.1. Efficient ant colony optimization (EACO)

The adsorbent selection MINLP model can be solved in many ways, but finding the optimal solution is not trivial. Usually, gradient based programming techniques can be used to solve this type of mathematical programming problems, however, the use of these techniques to find the optimal solution are limited by the need of convexity conditions, large combinatorial explosion, or discontinuous search domains (Diwekar and Xu, 2005). The problem at hand is a highly nonconvex problem due to the underlying thermodynamic models. Metaheuristic optimization strategies such as simulated annealing (SA), genetic algorithm (GA), and ant colony optimization (ACO) can provide a viable alternative to the gradient based programming techniques (Kirkpatrick et al., 1983; Holland, 1975; Dorigo, 1992). These methods are probabilistic methods based on ideas from the physical world. ACO methods have been receiving increased attention because of a series of successful applications in different disciplines such as routing, scheduling, machine learning, assignment, and design problems, and different branches of engineering (Dorigo and Stutzle, 2004). Even though, ACO algorithm was practiced with great success for combinatorial optimization problems, in recent years, the research focus has been extending on the combinatorial ACO algorithm to continuous and mixed variable nonlinear programming problems (Socha, 2004; Schluter and Gerdt, 2010; Gebreslassie and Diwekar, 2015). In this work, we use an efficient version of ACO algorithm study by Gebreslassie and Diwekar (2015) and Gebreslassie and Diwekar (under review). The ACO algorithm was first introduced by Dorigo (1992). This method is inspired by ants' foraging behavior where a population of simple, independent, asynchronous agents (i.e. ants) cooperate to find a good solution to the problem at hand. In the case of real ants, the problem is to find the food in a close vicinity of the nest, while in the case of artificial ants, it is to find a good solution to a given optimization problem (Dorigo and Stutzle, 2004). A single ant is able to find a solution to its problem, but only cooperation among many individual ants through stigmergy (i.e. indirect communication) enables them to find good or global optimal solutions. For instance, if an ant locates a food source, while returning back to the nest, the ant deposits pheromone on the ground in order to mark some favorable path that should be followed by other members of the colony. Over time, the pheromone will start to evaporate and therefore reduce the attraction of the path. The routes that are used frequently will have higher concentration of the pheromone trail and remain attractive. Thus, the shorter the route between the nest and food source imply short cycle time for the ants. Consequently, more ants are attracted by the shorter paths in the future. Hopefully, the shortest path will be discovered by the ant colony. ACO algorithm exploits a similar mechanism for solving optimization problems. In ACO algorithms, artificial ants are stochastic candidates for the solution construction procedures that exploit a pheromone model and possibly available heuristic information of the mathematical model. Artificial ants construct solutions by moving through each decision variable guided by the value of the artificial pheromone trails. This pheromone trails (i.e. numeric values) are the sole means of communication among the artificial ants. Pheromone decay, a mechanism analogous to the evaporation of the pheromone trail of the real ant colony, allows the artificial ants to forget the past history and focus on new promising search directions. Like the natural ants, by updating the pheromone values according to the information learned at each iteration, the algorithmic procedure leads to very a good and hopefully global optimal solution.

Table 2 describes the EACO algorithm. The EACO algorithm uses a better uniformity property of Hammersley Sequence Sampling (HSS) (Diwekar and Ulas, 2007). To start, the program requires an

Table 2
Summary of EACO algorithm.

```

1. Start program
1.1 Set initial parameters, and termination criterion
1.2 Initialize the solution archive (SArc (ks, NDIM)) using HSS and evaluate the objective function of the k solutions
1.3 Rank solutions based on the quality of the objective function (SArc=Rank (S1 . . . Sks)) and evaluate the weight of each solution.
2. While termination criterion is not satisfied
2.1 Generate solutions equivalent to the number of ants
  For all # nAnts
  2.1.1 Incremental solution construction
    For all # NDIM
    2.1.2 Probabilistically construct the combinatorial decision variables
    2.1.2 Probabilistically construct continuous decision variables
    End for # NDIM
  2.1.3 Store and evaluate the objective function value of the newly generated solutions
  End for # nAnts
2.2 Combine, rank and select the best k solutions, SArc= Best (rank (S1 . . . Sks+nAnt), ks)
2.3Update solution archives
End while

```

initial set of number of ants (nAnts), size of the solution archive (ks), number of continuous (NC), and discrete variables (ND), the pheromone evaporation factor (ρ), an algorithm parameter (q_{EACO}), and the termination criteria. Using a HSS technique the solution archive (SArc) of dimension ks by total number of decision variable (NDIM) is initialized. Once the solution archive is initialized, the objective function is evaluated with these values followed by ranking the solution archive based on the quality of the objective function. The weight of each solution is then determined according to the ranking of the solution in the solution archive using a Gaussian function. In the second part of the algorithm (point 2 of Table 2), each ant generates a solution according to the solution guide. First, an ant chooses probabilistically one of the solutions in the solution archive as a solution construction guide. This solution guide is decided by comparing the probability value of the solution and a random number. If this probability is greater than or equal to the random number then this solution is selected as solution guide to generate a new solution. Thus, all ants will construct a solution and this is accomplished in an incremental manner (i.e. variable by variable). At this point, the standard deviation is calculated based on the mean values of the selected solution guide. With this information, a new solution is generated by sampling the distribution. These new solutions are stored and the objective function of each new solution is evaluated. In the next step, the new sets of solutions are combined with the solution archive of the previous iteration 1.2. This new combined solution is then sorted according to the quality of the objective functions, and the first best ks solutions are selected and the worst nAnts size solutions are removed. This updating is analogous to the pheromone value update where the artificial ants are focusing on a best solution. Finally, the solution is updated by comparing so far best solution and the best solution from the updated solution archive. This second part continues until the stopping criterion, for example the maximum number of iterations.

As shown in the problem formulation, the optimization problem is subjected to equality and inequality constraints. The EACO algorithm handles these constraints by implementing an oracle penalty method proposed by Schluter et al. (2009). In general, constrained optimization problems are solved by transforming the problem into unconstrained optimization problem that is transforming the original objective function into a penalty function. In most cases, the penalty function is given as a weighted sum of the original objective function and the constraint violations (Schluter et al. 2009). Thus, the penalty function serves as an objective function. The main advantage of the penalty method is its simplicity. The oracle penalty method is a generalized method capable of handling simple and challenging constrained optimization problems and it is a simple method to

implement. In oracle penalty method, the objective function is first transformed into an additional equality constraint. The objective function becomes redundant in the transformed problem definition. Then minimizing the new constraint and minimizing the residual of the original equality and inequality constraints become directly comparable. Using a penalty function, the comparability property can be exploited. The penalty function balances its penalty weight each side of the transformed objective function and the violation of the original constraints. The implementation of the oracle penalty function can be found in Schluter and Gerdtts (2010).

5. Results and discussion

The solution strategy (Fig. 2) was run 50 times. From 1.80e9 possible combinations of adsorbents, 10 candidates of adsorbents were chosen according to the best adsorption capacity (i.e. q^{OPT}) in each optimization run. Among the parameter values used to solve the solution strategy, the best parameter values for this problem are the number of ants equal to 50, the size of solution archive as 500, tolerance value of 1e-8, evaporation factor as 0.75 and the algorithm parameter q equal to 1e-4. The computational studies were performed on a *ASUS Desktop PC M11AD Series with Intel (R) Core(TM) i5-4440 S CPU 2.80 GHz and 6 GB RAM*. The average CPU time over the 50 runs is 47 s. Table 3 presents a list of the candidate adsorbents found by the EACO algorithm that can be used to adsorb both radium and barium from produced water. We do not show the functional groups that are contained in the candidate adsorbents due to confidentiality. This table also presents the percentage of radium and barium adsorbed (%A), the molecule weight (M_0) and the amount of adsorbent needed since they are important parameters that affect the adsorption capacity. To compute the percentage of adsorption, we use the following equation:

$$\%A = \frac{n_i^1 - n_i^b}{n_i^1} \quad (25)$$

where i represents radium or barium, n_i^1 is the initial amount and n_i^b the amount in the bulk phase.

As observed in Table 3 the adsorbents are ranked based on the maximum adsorption capacity (q^{OPT}), from adsorbent AdNORM-RaBa01 with the highest capacity (1.45E-03 mol/g) to adsorbent AdNORMRaBa10 with the lowest capacity (7.16E-04 mol/g). It was found that to achieve higher adsorption more adsorbent is required affecting the adsorption capacity. For example, although, the first adsorbent has the highest capacity, 90.12% of radium and only 0.01% of barium is adsorbed using 13.77 g of adsorbent

Table 3

List of possible candidates for radium and barium adsorption.

Rank	q^{OPT} (mol/g)	Molecule	Molecular weight (g/mol)	% Adsorbed Ra	% Adsorbed Ba	m_0 (g)
1	1.45E-03	AdNORMRaBa01	2686.00	90.12	0.01	13.77
2	9.68E-04	AdNORMRaBa02	2328.40	99.13	0.64	22.93
3	8.96E-04	AdNORMRaBa03	2726.80	98.55	3.55	26.10
4	8.86E-04	AdNORMRaBa04	2219.90	96.86	0.09	24.20
5	8.80E-04	AdNORMRaBa05	2327.00	97.84	4.45	26.85
6	8.71E-04	AdNORMRaBa06	548.87	99.98	16.53	33.94
7	8.19E-04	AdNORMRaBa07	1276.40	99.96	4.24	29.30
8	8.15E-04	AdNORMRaBa08	2014.30	81.62	4.93	24.88
9	7.38E-04	AdNORMRaBa09	1985.70	99.51	2.73	31.49
10	7.16E-04	AdNORMRaBa10	2766.90	99.35	0.02	30.67

Table 4

Available groups per scenario.

Scenario	SiO ₂	Al ₂ O ₃	Na ₂ O	MgO	Fe ₃ O ₂	K ₂ O	(AlO ₂) ⁻	FeO	CaO	Ca ²⁺	K ⁺	β -Mn ₂ O	Na ⁺	Total available groups
1	A	A	A	A		A			A				A	7
2	A	A	A	A	A	A			A				A	8
3	A	A	A	A		A	A	A	A	A	A	A	A	12

AdNORMRaBa01. In contrast, adsorbent AdNORMRaBa06, which has a lower capacity (8.71E-4 mol/g) than the first adsorbent, is able to remove more radium and barium, that is, 99.98% of radium and 16.53% of barium using 33.94 g of this adsorbent. It can be inferred through the molecular weight that the adsorbents generated cover different sizes. These sizes vary from 8 to 50 total functional groups per molecule. In addition, the maximum amount of types of functional groups in each adsorbent were 4. Among the 10 candidates, 9 of them contained the group SiO₂, and 2 of them contained the group Al₂O₃. These are typical characteristics commonly found in adsorbents reported in the literature for radium or barium removal (Arafa et al., 1974; Ames et al., 1983a, 1983b; Moon et al., 2003; Atun and Bascetin, 2003; Chavez et al., 2010).

Moreover, it can be seen that all adsorbents from Table 3 favored significantly radium than barium adsorption. Due to this favorability, we decided to use the CAMD framework to study two more scenarios so these components can be removed separately. For instance, one scenario describes the adsorption of only radium which assumes that before adsorbing radium, barium is removed in a previous stage (e.g. by precipitation). In the case of barium, it is assumed that radium is removed first. For these new case studies, we had additional group interaction parameters available. Table 4 summarizes the group availability per scenario study: 1) radium and barium adsorption, 2) only radium adsorption, and 3) only barium adsorption. "A" means available information of interaction parameters for each group with respect of radium or barium. These information is obtained from the first paper in this series.

The results of the first scenario is presented in Table 3 and discussed previously. The adsorption of radium (scenario 2) and Barium (scenario 3) are solved and 50 runs for each scenario were performed. The average CPU time of scenario 2 is 25 s and for scenario 3 is about 58 s. The results are presented in Tables 5 and 6, respectively. When the results of Tables 3 and 5 are compared, it can be observed that the new candidates achieve higher adsorption capacities using less mass of adsorbent. In this problem, the problem proposes 3.7822e10 possible combinations of adsorbents, however using the EACO algorithm, it is reduced to the best 10 candidates. Among the 10 candidates, AdNORMRa07 is the adsorbent that allows the maximum adsorption of radium (99.44%). The molecular weights infer that the molecules contain several functional groups, in fact, it was found that the size of the molecules ranges from 35 to 72 total functional group and up to 5 different

Table 5

List of possible candidates for only radium adsorption.

Rank	q^{OPT} (mol/g)	Molecule	Molecular weight (g/mol)	% Adsorbed Ra	m_0 (g)
1	1.02E-02	AdNORMRa01	5738.11	98.06	2.12
2	4.01E-03	AdNORMRa02	6244.57	96.84	5.34
3	1.64E-03	AdNORMRa03	2344.16	97.30	13.11
4	1.64E-03	AdNORMRa04	3890.90	96.45	12.97
5	1.19E-03	AdNORMRa05	4444.20	90.72	16.81
6	1.19E-03	AdNORMRa06	5458.12	86.42	16.09
7	1.04E-03	AdNORMRa07	2227.96	99.44	21.22
8	8.89E-04	AdNORMRa08	4798.44	97.19	24.16
9	8.64E-04	AdNORMRa09	4574.85	95.69	24.47
10	8.46E-04	AdNORMRa10	3824.37	97.23	25.40

types of groups are combined in some of the molecules which makes these molecules bigger and more complex than the molecules of scenario 1. All the adsorbents for this scenario contain significant amount of the group SiO₂ and Na₂O which are commonly found in radium adsorbents.

Finally, the last scenario is compared with the candidate adsorbents of Table 3. Here, the number of possible combinations to create adsorbents significantly increases (from 1.80e9 to 7.36e15) due to the addition of more groups. With this addition, however, it can be observed that the new candidate adsorbents are able to achieve higher adsorption capacities (from 2.59E-01 mol/g to 4.88E-03 mol/g) and higher amounts of barium are adsorbed. It can also be seen that the amount of adsorbent is significantly reduced (around 85% less mass when taking average values). Therefore, the adsorption process can be improved by removing barium separately. Among the 10 adsorbents shown in Table 6, adsorbent AdNORMBa05 can removed the highest amount of barium (99.40%). In this scenario, the sizes of the molecules vary from 1 to 51 functional groups and up to 3 different groups were combined in some of the molecules. Similarly, the group SiO₂ is the most common group found in each molecule followed by group MgO.

6. Conclusion

This paper proposed a novel CAMD framework for optimal design of new adsorbents for the removal of radium and barium in

Table 6

List of possible candidates for only barium adsorption.

Rank	q^{OPT} (mol/g)	Molecule	Molecular weight (mol/g)	% Adsorbed Ba	$m_0(\text{g})$
1	2.59E-01	AdNORMBa01	3684.20	82.24	0.14
2	2.46E-01	AdNORMBa02	3010.80	89.00	0.16
3	2.13E-01	AdNORMBa03	2007.70	86.33	0.18
4	2.23E-01	AdNORMBa04	1645.00	95.05	0.19
5	7.22E-03	AdNORMBa05	86.94	99.40	6.21
6	6.63E-03	AdNORMBa06	194.23	66.25	4.51
7	6.06E-03	AdNORMBa07	388.45	86.20	6.42
8	5.19E-03	AdNORMBa08	1831.60	64.55	5.62
9	5.14E-03	AdNORMBa09	776.90	63.90	5.61
10	4.88E-03	AdNORMBa10	874.02	96.44	8.93

produced water of natural gas fracking. This framework depends on the properties of the set of functional groups that build the adsorbents of radium and barium. The MINLP model formulated was successfully solved using a novel algorithm called efficient ant colony optimization (EACO) algorithm. Based on the adsorption capacity of the adsorbents, 10 adsorbent molecules were selected as best candidate adsorbents. These molecules displayed the best potential of adsorption capacity and satisfied the operating conditions established in the adsorption process. We also presented results for individual adsorption of radium and barium by generating new possible candidate adsorbents with higher adsorption capacities. It was observed that by individual adsorption, more radium and barium can be removed from produced water. The optimal adsorbents generated were a mixture of ion exchange resins, clays and zeolites.

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Appendix A

Group contribution for pore volume values

To compute the surface phase capacity ($\Gamma_{\text{mi}}^{\text{s}}$) two models of adsorption for liquid mixtures can be used: the pore filling and the monolayer model. The pore filling model is the process in which molecules are adsorbed in the adsorption space while in monolayer all the adsorbed molecules are in contact with the surface layer of the adsorbent. Pore filling models use micro porous adsorbents which has a pore diameter of less than 2 nm, on the other hand, monolayer models use macro-porous and nonporous adsorbents which pore diameter is greater than 50 nm. In this work, we use pore filling models since it has been found that in practical separations, the requirement for adequate adsorptive capacity restricts the choice of adsorbents to micro porous adsorbents (Ruthven, 1984). This include both the traditional micro-porous adsorbents such as silica gel, activated carbon, and activated alumina as well as the recently developed crystalline aluminosilicates. Therefore, we use Eq. (A1) to compute the surface phase capacity when the pore filling model is used:

$$\Gamma_{\text{mi}}^{\text{s}} = \frac{v_{\text{p}}}{v_{\text{oi}}} \quad (\text{A1})$$

where v_{p} is the pore volume of the adsorbent and v_{oi} is the molar volume of the respective adsorbate. Table A1 presents the values of the molar volume for radium and barium.

Table A1

Molar volume for radium and barium.

Adsorbate	v_{oi} (cm ³ /mol)
Radium	41.091
Barium	39.125

Table A2Individual values of ∂p_{g} for each functional group.

Group index	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₃ O ₂	MgO	K ₂ O	CaO
∂p_{g}	0.03	0.181	0.004	0.08	0.848	0.483	0.093

On the other hand, pore volume v_{p} (cm³/g) can be obtained from the literature when the adsorbent is known (Suzuki, 1990). A list of adsorbents used in the work and their pore volume values is presented in Table A3 in the first paper series (Benavides and Diwekar, accepted for publication). However, as shown in the second part of this work, our objective is to generate new adsorbents that remove radium and barium from produced water. Therefore, using the structure of the adsorbents and pore volume information, we develop here a new group contribution method for pore volume calculations for adsorbents. The proposed GCM equation is presented below (Eq. A2):

$$\frac{1}{v_{\text{p}}^{\text{ad}}} = \sum_{g=1}^{N_{\text{gt}}} (k_{\text{g}} \partial p_{\text{g}}) + \text{Cont} \quad (\text{A2})$$

where N_{gt} is the total functional groups in the adsorbent, ∂p_{g} is the value of pore volume for each group g , k_{g} is the amount of groups g in the adsorbent ad, and Cont accounts to a constant value (equals 3.36 that results from the fitting).

To calculate the individual contribution (∂p_{g}), we formulate a parameter estimation problem where the objective function is to minimize the error values between the pore volume calculated ($v_{\text{p}}^{\text{cal}}$) using Eq. (A2) and the pore volume experimental values ($v_{\text{p}}^{\text{exp}}$) [37] as it is shown in Eq. (A3):

$$\min \text{Error} = \frac{1}{\text{Nobs}} \left| \frac{v_{\text{p}}^{\text{cal}} - v_{\text{p}}^{\text{exp}}}{v_{\text{p}}^{\text{exp}}} \right| \quad (\text{A3})$$

Subject to the non-negativity constraints for the pore volume of each functional group:

$$\partial p_{\text{g}} < 0 \quad \forall g \quad (\text{A4})$$

We use Matlab optimization tool package to solve this problem. Table A2 presents the individual contribution values of ∂p_{g} the group that can be part of the adsorbent molecule.

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