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Design of novel polymeric adsorbents for metal ion removal from water using computer-aided molecular design

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Abstract Heavy metals in drinking water act as contaminants that can cause serious health problems. These metal ions in drinking water are generally removed using cation exchange resins that are used as adsorbents. Generally, chelating resins with limited adsorption capacity are commercially available. Manufacturing novel resin polymers with enhanced adsorption capacity of metal ion requires ample experimental efforts that are expensive as well as time consuming. To overcome these difficulties, application of computer-aided molecular design (CAMD) will be an efficient way to develop novel chelating resin polymers. In this paper, CAMD based on group contribution method (GCM) has been used to design novel resins with enhanced adsorption capability of removing heavy metal ions from water. A polymer consists of multiple monomer units that repeat in a polymer chain. Each repeat unit of the polymer can be subdivided into different structural and *functional* groups. The adsorption mechanism of heavy metals on resin depends on the difference between activities in adsorbents and the bulk fluid phase. The contribution of the *functional* groups in the adsorption process is found by estimating the activity coefficient of heavy metal in the solid phase and bulk phase using a modified version of the UNIFAC GCM. The interaction parameters of the *functional* groups are first determined and then they are used in a combinatorial optimization method for CAMD of novel resin polymers. In this work, designs of novel resin polymers for the removal of Cu ions from drinking water are used as a case study. The proposed new polymer resin has an order of magnitude higher adsorption capacity compared to conventional resin used for the same purpose.

Keywords Chelating resin · Heavy metal ions · Group contribution method (GCM) · Adsorbate–solid solution theory (ASST) · Computer-aided molecular design (CAMD) · Efficient ant colony optimization (EACO)

Introduction

Heavy metals in drinking water act as contaminants because of the toxicity associated with them. It is thus necessary to remove heavy metal ions from drinking water. Some of these metals also have carcinogenic effects. Thus, wastewaters also need to be treated for the removal of heavy metals. The well-known toxic heavy metals include lead, copper, nickel, zinc, and cadmium. The primary reason for treatment is that the heavy metals are not biodegradable but accumulate in living organisms. They can cause diseases and disorders even at relatively low concentration. Possible sources of contamination of heavy metals in wastewater streams include industrial sources such as chemical, mining, metal plating, tanneries, painting, plumbing, as well as agricultural sources where fertilizer and fungicidal spray are used (Duran et al. 2008). The presence of heavy metals in earth is limited. Mining of the heavy metals is not environmentally benign. Heavy metal recovery is essential not only for health-related reasons but also for resources reuse and environment protection.

Many traditional treatment methods can be used for heavy metal (Pb^{++}, Cu^{++}, Ni^{++}, Cd^{++}, etc.) removal

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such as precipitation (Bhagat et al. 2004), membrane separation (Ritchie et al. 2001), reduction (Chen and Ray 2001), ion exchange (Shek et al. 2009), solvent extraction (Jung et al. 2008), and adsorption (Zhu et al. 2012) from different aqueous solutions with a broad range of concentrations. Among these conventional techniques, adsorption is the most common. Adsorption has been proven to be one of the most feasible, simple, easy to implement, and highly efficient method for the removal of heavy metal ions from polluted water.

Up to now, a number of novel adsorbents have been prepared and used to remove heavy metal ions. They are prepared from materials including tree materials (Ucun et al. 2009), agricultural wastes (Agouborde and Navia 2009), fly ash (Remenárová et al. 2014), modified clay materials (Gupta and Bhattacharyya 2005), nanoparticles (Mahdavi et al. 2015), natural rock (Sahan and Öztürk 2014), chelating resins (Atia et al. 2008), and biological materials including nanocellulose fibers (Kardam et al. 2014), matured leaves of neem (Ang et al. 2013), olive solid waste (Chouchene et al. 2014), and eucalyptus wood-based activated carbon (Venkatesan et al. 2014). In recent times, biochars were used for effective removal of heavy metals from aqueous solutions (Uchimiya et al. 2010). Biochar is produced from pyrolysis of biomass in a closed system with little or no oxygen at all (Inyang et al. 2012). The biomass could be agricultural byproducts, animal waste, and woody materials. In case of a cheap source of biomaterial, the cost of biochar production is mainly associated with the machinery and heating. Other than heavy metal removal from water, the process of anaerobic digestion for biochar production may also provide other benefits, such as producing renewable bioenergy and help in waste management (Maroušek et al. 2014a). Maroušek (2014c) has developed novel apertures for waste management with biochar as the product. Maroušek et al. 2015 have made a techno-economic assessment of the use of biochar formed from cellulose casings in heavy metal removal. Maroušek 2014b showed cost reduction in the use of biochar production. However, the removal ratio (mass of heavy metal removed/mass of adsorbents used) from conventional adsorbents is far from satisfactory. Moreover, commercial adsorbents are expensive that their use has been limited to an obvious extent. Therefore, cost-effective and more efficient alternative technologies or adsorbents are needed for the treatment of these wastewaters as well as drinking waters. In this work, we propose the design of novel chelating resins for the adsorption of heavy metals from drinking water using computer-aided molecular design (CAMD).

Selective adsorption technology with chelating resins has increased applications due to the simple and low-cost manufacturing. Commercial ion exchange resins for metal

ion removal were purchased from DOW chemicals and Rohm and Hass. Most of these resins are made of polystyrene crosslinked with divinyl benzene (DVB). Researchers have also obtained some series of chelating resins through the polymerization of conventional chelating monomers such as acrylic acid, methacrylic acid, and vinylpyridine (Dakova et al. 2007). Chelating resins with varied matrix structures and *functional* groups are also prepared with synthetic polymers and the ligands are then grafted by functionalization reactions (Donia et al. 2006).

Computer-aided molecular design (CAMD) for polymer design is a fast emerging systematic tool for efficient and reliable design of candidate polymers from their fundamental building blocks (Camarda and Maranas 1999; Sundaram and Venkatasubramanian 1998). Beyond the polymer design, the CAMD technique is practiced with great success in different disciplines such as solvent selection (Marrero and Gani 2001), solvent selection under uncertainty (Kim and Diwekar 2002a, b), and that with the use of heuristic optimization (Xu and Diwekar 2005), pharmaceutical process designs (Gernaey and Gani 2010), adsorbent design (Benavides et al. 2015), and bioethanol production (Alvarado-Morales et al. 2009). CAMD generates a large number of structural molecules with desired properties from a small set of structural groups. CAMD is the reverse use of the group contribution method. Different solution strategies are implemented to solve CAMD techniques: heuristic numeration (Hostrup et al. 1999; Li et al. 2002), knowledge-based technique (Yamamoto and Tochigi 2008) with multilevel approach (Harper and Gani 2000), molecular property clusters with algebraic equations (Chemmangattuvalappil et al. 2009; Eljack and Eden 2008), simultaneous inclusion of process and molecular design (Kazantzi et al. 2007), and optimization-based methods (Diwekar and Shastri 2011; Samudra and Sahinidis 2013).

Different approaches have been used for polymer design using CAMD. In some cases, the design was performed to generate individual polymer repeat units based on target property optimization. In some other cases, the contribution of monomer units is identified and different order connectivity indices between the monomer have been used to determine the configurational effect of polymer morphology. Satyanarayana et al. (2007) used group contribution method to predict the thermodynamic properties of polymer structure if the polymer structure is fully represented by well-defined contribution of the individual polymer repeat units. For the missing property contribution of the polymer repeat units, they use zero- and first-order connectivity indices. Satyanarayana et al. (2010) proposed a multiscale model-based approach that combines a CAMD technique for predicting polymer repeat unit properties with atomistic simulations for providing first-principle

arrangements of the repeat units. The approach follows the application of GC property models in the CAMD technique for the identification of polymer repeat unit structure. Then it incorporates a micro-scale analysis because the macro-scale CAMD algorithm was not able to give complete information on how the basic polymer repeat units should be arranged for the candidate polymeric structure that satisfies the desired polymer target properties. The simulations for the micro-scale model provide reliable estimates of the desired target properties based on the principles of quantum and statistical mechanics and statistical thermodynamics. Maranas (1996) addresses the optimal design of polymer products based on group contribution method. He has presented a systematic analysis framework for transforming a class of optimal computer-aided molecular design problems with nonlinear structure–property functionalities into equivalent mixed integer linear programming (MILP) problems. He considers two alternative design objectives; minimization of scaled error of design properties from some target values called *property matching*, and minimization/maximization of a single thermodynamic property subject to lower and upper bounds on the rest of the properties called *property optimization*. The framework is applied to the design of polymers where thermophysical and mechanical properties are estimated using group contribution methods. In this work, we propose the design of polymer resins based on computer-aided molecular design that follows the Maranas' (1996) approach. They are similar in the sense that minimization of scaled error of the interaction parameters of the missing thermodynamic properties of the building blocks, which are estimated from the experimental values, is used as an objective function. Secondly, maximization of the adsorption capacity of the candidate polymer resin subject to lower and upper bounds on the rest of the properties called *property optimization* is used. To the best of our knowledge, this is the first work that proposes the optimal design of a polymer resin based on computer-aided molecular design and group contribution method to estimate the thermodynamic properties of the candidate polymer resins.

In CAMD, the chelating resin polymers are subdivided into structural and *functional* groups. The interaction parameters of the heavy metal with structural and *functional* groups obtained from different chelating resins are then used in a combinatorial optimization methodology for computer-aided molecular design of novel resin polymers with enhanced adsorption property. The activity coefficient in the adsorbent resin polymers is obtained using UNIFAC group contribution method that uses the interaction parameter of each *functional* group. For example, polystyrene sulfonate is a cation exchange resin. It contains a sulfonic acid *functional* group as a cation exchanger. Other functional groups can also act as cation exchangers including carboxylic acid, phosphonic acid, phenolic, arsonic acid, and selenonic acid. that can act as strong or weak acid cation exchangers. With the same polymer backbone, different *functional* groups for cation exchange show different adsorption capacities of the resin polymer. For the backbone polymer, other than polystyrene, different poly-vinyl aryl compounds can also be used. It is the repeat units of the polymer that is divided into structural and *functional* groups. These structural and *functional* groups have varying interaction parameters with heavy metals. The activity coefficients in the complex adsorbent are obtained using group contribution method.

In this work, we have designed resin polymers for the adsorption of copper ion from drinking water. Copper is a widely used heavy metal and is considered as an essential element for human life. Like any other heavy metals, it may be potentially toxic above certain concentrations. Among various diseases associated to the presence of copper in the human body, kidney failure (Cox 1999) and lung cancer (Mahabir et al. 2007) are some of the most common. Copper can be removed from drinking water using cation exchange resins by the process of adsorption. Few commercial resins are generally used for this purpose. Researchers have synthesized various chelating resin polymers for the adsorption of heavy metal ions from aqueous media with Cu in particular. Jing et al. (2009) have synthesized N,N-di(carboxymethyl) dithiocarbamate chelating resin for the adsorption of divalent heavy metal ions including Cu. Baraka et al. (2007) have synthesized melamine–formaldehyde–DTPA chelating resin for the adsorption of heavy metal ions from water. Roy et al. (2004) have synthesized polydithiocarbamate resins supported on polystyrene for the removal of heavy metal ions. Dinu and Dragan (2008) have studied the adsorption of heavy metals on iminodiacetate chelating resins. They have also studied the adsorption of Cu. Hu et al. (2010) have synthesized thiacalix[4]arene-loaded resin and studied the adsorption of heavy metals including Cu. The synthesized novel polymers are studied for the adsorption kinetics, thermodynamics, and adsorption isotherm of heavy metals. In all the above experimental work on the synthesis of resin polymers, the researchers have prepared only one type of resin polymer for analysis. Furthermore, subsequent characterization of the polymers followed by studying the adsorption kinetics, thermodynamics, and adsorption isotherm to find their adsorption properties is laborious and time consuming. This is where CAMD for chelating resin polymer can be a useful alternative for fast and efficient design of adsorbent polymers.

In our CAMD of polymers for adsorption, chelating resin polymers are treated as solid phase in the bulk liquid. The UNIFAC group contribution method is used for estimating the activities of adsorbents in different phases. The

group interaction potentials are obtained by solving an optimization problem where the goal is to minimize the error between the theoretical estimation of adsorption with the experimental results obtained from adsorption isotherm. The optimal design of novel polymer resin is formulated as a mixed integer nonlinear programming problem. A new algorithm called efficient ant colony optimization (EACO; Gebreslassie and Diwekar 2015) is used to solve the problem. The optimization algorithm for the CAMD of adsorption resin polymer design model maximizes the adsorption capacity of the adsorbent subject to structural feasibility, thermodynamic property correlations, and process conditions and constraints.

Problem formulation is given in the next section showing the constraints under which CAMD of optimal polymer resins has been found. "Solution method for novel polymer resin design using CAMD" section describes the methodology used in this work including adsorbate–solid solution theory and UNIFAC group contribution method for activity coefficient in the balk and solid phases. "Case study" section gives the solution methodology. "Estimation of interaction parameters with GCM by minimizing the error" section describes a case study on the design of novel resin polymers for the adsorption of Cu ions from drinking water. "Results from the design of chelating resin for Cu ion adsorption" section describes the estimation of the interaction parameters. "Conclusions" section provides the results from the design of chelating resin for copper ion adsorption and Sect. 8 draws the conclusions from the present work.

CAMD for polymer resin design

The main goal of this work is to design a new or identify an existing set of candidate polymer resins with better adsorption capacity, q_{abs}, of copper ions from municipal water. This can be achieved by generating polymer resin structures that match or exceed the target thermodynamic property acquired using a CAMD technique. In order to find a set of candidate polymer resins that have the desired thermodynamic properties, an optimization problem based on the CAMD is formulated and the adsorption capacity of the polymer resin is maximized subject to structural constraints and thermodynamic property constraints.

Structural constraints These constraints are related to the number of building blocks involved in constructing the polymer repeat unit, the number of times each building block can be involved to build the polymer resin, and the chemical feasibility of the generated polymer repeat unit structures. For example, the structure of the polymer repeat unit must have two free attachments. That is, the structural integrity of the resin is confirmed by controlling the total

number of free attachments available for bonding in the molecule or repeat unit as shown below (Maranas 1996).

$$f = \sum_{i=1}^{N} (v_i - 2)n_i + 2, \tag{1}$$

where f is the number of free attachment; in designing a molecule, f should be zero, while for polymer repeat unit $f = 2$. v_i is the valence of the *functional* group and n_i is the number of times the *functional* group appears in the polymer repeat unit.

Thermodynamic property constraints These constraints are related to the target thermodynamic properties of the polymer resin. The thermodynamic properties of the polymer resin are formulated in terms of the thermodynamic relations and they are estimated following the CAMD technique for polymer design as explained in the following subsection.

Thermodynamic model of adsorption using adsorbate–solid solution theory

Adsorption process

Adsorption is a separation process in which molecules of a dissolved substance (adsorbate) moves from one phase to another phase due to the difference in activity between the two phases. In case of adsorption in a solid, the adsorbate from fluid phase, i.e., liquid or gas, adheres to the surface of solid adsorbent. The equilibrium concentration of the adsorbate in the fluid and the solid phase is the adsorption equilibrium which can be described by adsorption isotherms (Suzuki, 1990). The isotherms are illustrated in different mathematical forms including the Langmuir isotherm:

$$\frac{1}{q_{abs}} = \frac{1}{b} + \frac{1}{(bK)C}, \tag{2}$$

Where q_{abs} is the amount of adsorbate adsorbed per unit mass of adsorbent, C is the concentration of adsorbate in the bulk solution at equilibrium, and b and K are constants determined from the adsorption data. Adsorption equation used to describe the adsorption isotherm can also be represented by the Freundlich equation shown in Eq. 3. In this case, k_f and n_f are the Freundlich parameters.

$$q_{abs} = k_f C^{n_f} \tag{3}$$

Although adsorption can be useful for different separations that are difficult by other techniques including distillation, absorption, and membrane-based processes, it is not commonly employed due to the lack of both experimental data and suitable models that can be used to predict the equilibrium behavior of multicomponent mixtures (Berti et al. 2000). Recently, group contribution method has been applied with success for the design of adsorbents (Benavides

and Diwekar 2015; Benavides et al. 2015) using adsorbate–solid solution theory (ASST) for the removal of naturally occurring radioactive material (NORM) from natural gas fracking-produced water. In this work, a similar approach has been used for the design of resin polymers for the adsorption of heavy metals from drinking water.

Adsorbate–solid solution theory (ASST)

Adsorbate–solid solution theory (ASST) has been introduced by Berti et al. (1999) and Berti et al. (2000). They have considered the adsorbed phase to be a mixture containing the adsorbed species and the adsorbent as the additional component. Figure 1a shows the adsorption in solid surface, while Fig. 1b shows the adsorption as assumed in the ASST theory. The adsorption behavior of liquid mixtures on solid surfaces in ASST is described using the excess Gibbs energy G^E. The relation of the phase equilibrium for component is given as

$$x_i^b \gamma_i^b = x_i^s \gamma_i^s \exp\left(\frac{g^{ad} - g_{oi}^{ad}}{RT\Gamma_{mi}^s}\right) \tag{4}$$

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 of component i in the bulk phase and surface phase, respectively. 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 the temperature, ideal gas constant, and the surface phase capacity of component i, respectively (Berti et al. 1999; Berti et al. 2000).

In ASST, a new thermodynamic framework has been adopted that assumes the adsorption systems as a solution of the solid adsorbent and liquid adsorbate as shown in
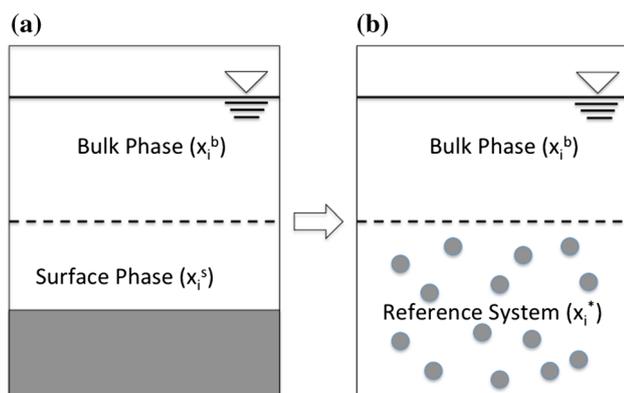
(a) **(b)**

Fig. 1 Classical description of the adsorption systems **a** the total amount of fluid molecules is divided in two independent phases that are assumed to be homogeneous: the adsorbed or surface phase and the bulk phase. The adsorbate solid solution **b** is defined as the reference system and the bulk phase is considered to be uninfluenced by the solid (Berti et al. 1999)

Fig. 1b. In this process, the influence of different structural groups of the adsorbent on the adsorption behavior is taken into account. The adsorption behavior of liquid on the solid mixture is expressed based on the chemical potential in both phases. Similar to Eq. 4, the equilibrium relation between the two phases for component i in terms of chemical potential is shown in Eq. 5:

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

where x_i^* is the fraction of component i in the adsorbate–solid solution, γ_i^* is the activity coefficient, and Γ_{mi}^s is the surface phase capacity. The surface phase capacity is the ratio of the pore volume vp of the adsorbent and the molar volume of the adsorbed fluid v_{oi}.

$$\Gamma_{mi}^s = \frac{vp}{v_{oi}} \tag{6}$$

$(\varphi^* - \varphi_{oi}^*)$ is the difference between the chemical potential of the wetted solid and that of the same wetted solid plus adsorption of the pure component i. The difference between the chemical potential of the wetted solid and that of the wetted solid at adsorption can be computed in terms of the excess Gibbs energy as follows:

$$\phi^* - \phi_{oi}^* = \frac{1}{m_0}\left(G^{E*} - G^{Es} - G_{0i}^{E*}\right). \tag{7}$$

Here, m_0 is the mass of the adsorbent and G^{E*}, G^{Es}, and G_{0i}^{E*}, are the excess Gibbs free energies of the adsorbate–solid solution, the surface phase, and the pure component adsorption, respectively. The Gibbs free energy in terms of activity coefficients for the adsorbate–solid solution is given as

$$\frac{G^{E*}}{RT} = \sum_{i=0}^{k} n_i^* \ln \gamma_i^* \tag{8}$$

where the index 0 refers to the adsorbent. For the pure component adsorption, the excess Gibbs free energy G_{0i}^{E*} is calculated using the activity coefficient γ_{oi}^* which is given by

$$\gamma_{oi}^* = 1 + \frac{1}{\Gamma_{mi}^s M_o} \tag{9}$$

The activity coefficients for the surface phase in the solid solution are represented by $\gamma_i(x_i^s)$. The excess Gibbs free energy of the surface phase G^{Es} is related to $\gamma_i(x_i^s)$ as

$$\frac{G^{Es}}{RT} = \sum_{i=1}^{k} n_i^s \ln \gamma_i(x_i^s), \tag{10}$$

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

$$n_i^s = x_i^s n_T^* (1 - x_0^*) \tag{11}$$

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

$$x_i^s = \frac{x_i^*}{(1 - x_0^*)} \tag{12}$$

Activity coefficient for bulk phase and adsorbate–solid solution using UNIFAC group contribution model

The activity coefficient in the bulk phase and in adsorbate–solid solution is estimated using UNIFAC method. UNIFAC stands for *functional*-groups activity coefficients and it resulted from UNIQUAC method (Universal Quasi-Chemical) that derives activity coefficient from interacting molecules. In the UNIFAC model, the activity coefficient is divided into two parts: combinatorial and residual. In case of bulk phase, the activity coefficient can be written as

$$\ln \gamma_i^b = \ln \gamma_i^{Cb} + \ln \gamma_i^{Rb} \tag{13}$$

For combinatorial part of component i

$$\ln(\gamma_i^{Cb}) = \ln\left(\frac{\varphi_i}{x_i^b}\right) + 5q_i \ln\left(\frac{\theta_i}{\varphi_i}\right) + l_i - \frac{\varphi_i}{x_i^b}\sum_1^j x_j^b l_j, \tag{14}$$

where

$$l_i = 5(r_i - q_i) - (r_i - 1) \tag{15}$$

$$\theta_i = \frac{q_i x_i^b}{\sum_j^M q_j x_j^b} \tag{16}$$

$$\varphi_i = \frac{r_i x_i^b}{\sum_j^M r_j x_j^b}. \tag{17}$$

Here θ_i and φ_i represent the molecular surface area and molar volume fraction of component i, respectively, and $j : 1, 2 \ldots M$ represents the number of components. The van der Waals volume and the van der Waals surface area of the component i are calculated from that of the *functional* groups of the component:

$$r_i = \sum_g^{N_{gt}} \vartheta_g^{(i)} R_g \tag{18}$$

$$q_i = \sum_g^{N_{gt}} \vartheta_g^{(i)} Q_g. \tag{19}$$

Here $g : 1, 2 \ldots N_{gt}$ is the *functional* group index and N_{gt} is the total *functional* groups in component i. R_g and Q_g are, respectively, the constants of group sizes and surface areas that are obtained from atomic and molecular structure data.

For residual part

$$\ln \gamma_i^R = \sum_g^{N_{gt}} \upsilon_g^{(i)} \ln \Gamma_g \tag{20}$$

where

$$\ln \Gamma_g = Q_g \left[1 - \ln\left(\sum_1^m \theta_m \psi_{mg}\right) - \sum_1^m \left(\frac{\theta_m \psi_{gm}}{\sum_1^n \theta_n \psi_{nm}}\right) \right] \tag{21}$$

Here m and n represent all the *functional* groups.

The group fraction and group surface area fraction for a *functional* group m are calculated using Eqs. 22 and 23, respectively:

$$X_m = \frac{\sum_1^j \vartheta_m^{(i)} x_j^b}{\sum_1^j \sum_1^n \vartheta_m^{(i)} x_j^b} \tag{22}$$

$$\theta_m = \frac{Q_m X_m}{\sum_1^n Q_n X_m} \tag{23}$$

The parameter ψ_{nm} is given by

$$\psi_{nm} = \exp(-a_{nm}/T) \tag{24}$$

where a_{nm} is the group interaction parameter for the UNIFAC model and T is the absolute temperature. It is to be noted that

$$a_{mn} \neq a_{nm}$$

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 from the same group (between m and m and between n and n).

In case of polymer phase, the adsorbate–solid solution theory is used. Here, a modified UNIFAC model is used to compute the activity coefficient. In the modified model, the pure component adsorption (γ_{oi}^*) has been incorporated:

$$\ln \gamma_i^* = \ln \gamma_{oi}^* + \ln \gamma_{GE,i}^* \tag{25}$$

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 a residual part (γ_i^{R*}):

$$\ln \gamma_{GE,i}^* = \ln \gamma_i^{C*} + \ln \gamma_i^{R*}. \tag{26}$$

Amount of adsorption using activity coefficient

The total amount of adsorption in the adsorbent (n_T^*) is obtained using the equations of the adsorption equilibrium given in Eq. 5 and the difference in chemical potential given in Eq. 7. The excess Gibbs free energy of the adsorbate–solid solution G^{E*}, excess Gibbs free energy of the surface phase G^{Es}, and the excess Gibbs free energy of the pure component adsorption G_{0i}^{E*} in terms of the activity coefficient are given as

$$G^{E*} = RT\left(x_0^* n_T^* \ln \gamma_0^* + x_1^* n_T^* \ln \gamma_0^*\right) \qquad (27)$$

$$G^{Es} = RT\left(x_1^s n^s \ln \gamma_1\left(x_1^s\right)\right) \qquad (28)$$

$$G_{0i}^{E*} = RT x_{0i}^* n_T^* \ln\left(1 + \frac{1}{\Gamma_{mi}^s M_0}\right) \qquad (29)$$

In case of only one adsorbate in ASS then $x_{0i}^* = x_1^*$. Also x_1^s is 1 since the surface phase consists of the activity coefficient of the pure component. Thus G^{Es} is zero. Using Eqs. 27–29 in Eq. 7 gives

$$n_T^* = \frac{\left(\phi^* - \phi_{01}^*\right)m_0}{RT\left(\left(x_0^* \ln \gamma_0^* + x_1^* \ln \gamma_0^*\right) - x_1^* \ln\left(1 + \frac{1}{\Gamma_{m1}^s M_0}\right)\right)} \qquad (30)$$

where $(\phi^* - \phi_{oi}^*)$ is obtained using Eq. 5. Γ_{mi}^s is the surface phase capacity determined as in Eq. 6.

Solution method for novel polymer resin design using CAMD

The polymer resin design problem can be solved using different approaches from the literature but finding the optimal design is not trivial. The polymer resin design is formulated as a mixed integer nonlinear programming (MINLP) problem that seeks to maximize the adsorption capacity of the polymer resin subject to structural feasibility, thermodynamic isotherm correlations, and material balance constraints. The equality constraints representing the property models described above are nonlinear and nonconvex. The gradient-based solution methods such as Branch and Bound (BB), Generalized Bender's Decomposition (GBD), and Outer Approximation (OA) are generally used for solving similar MINLP problems. However, these methods have limitations when there is large combinatorial explosion and the necessary condition of satisfying the convexity, or if the search domain involves a discontinuity (Diwekar and Xu 2005). Metaheuristic optimization strategies such as simulated annealing (SA) (Kirkpatrick et al. 1983), genetic algorithm (GA) (Holland 1975), and ant colony optimization (ACO) (Dorigo 1992) provide a viable alternative to the gradient-based mathematical programming techniques. Recently, there has been the application of the CAMD problem formulation that uses the efficient ant colony optimization (EACO) algorithm to solve new solvent selection (Gebreslassie and Diwekar 2015) and adsorption design problems (Benavides and Diwekar 2015, Benavides et al. 2015). To the best of our knowledge, this is the first work that formulates a CAMD model for the design of polymer resin. The CAMD optimization problem is solved using the EACO algorithm explained in the next section. In the forward approach, the EACO algorithm generates polymer resins from the set of

functional groups while CAMD predicts the properties of the new formulated polymer resin.

Efficient ant colony optimization (EACO) algorithm

ACO is a metaheuristic class of optimization algorithm inspired by the foraging behavior of real ants (Dorigo and Stutzle 2004). Natural ants randomly search food by exploring the area around their nest. If an ant locates a food source, while returning back to the nest, it lays down a chemical pheromone trail that marks its path. This pheromone trail helps indirectly communicate with other members of the ant colony. Eventually, over time the pheromone will start to evaporate and therefore reduce the attraction of the path. The shortest routes that are used frequently will have higher concentration of the pheromone trial and remain attractive. This is because the shorter route between the nest and food source implies short cycle time for the ants and these routes will have higher concentration of the pheromone trial. Consequently, more ants are attracted by the shorter paths in the future. Finally, the shortest path will be discovered by the ant colony (Dorigo and Stutzle 2004; Zecchin et al. 2006). In a similar fashion, artificial ants of the ACO algorithm are stochastic candidate solution construction procedures that exploit a pheromone model and possibly available heuristic information of the mathematical model. The artificial pheromone trails are used as a communication channel among the artificial ants. The pheromone evaporation allows the artificial ants to forget the past history (old solutions) and focus on the new promising search directions. Like the natural ants, the artificial ants update the pheromone values according to the information learned in the solution construction step. Finally, the algorithmic procedure leads to very good and, hopefully, a global optimal solution. In the conventional ACO algorithm, the random numbers needed for the probabilistic test and to fill the initial solution archive are based on the Monte Carlo sampling method.

Monte Carlo method is a numerical method that provides approximate solution to a variety of physical and mathematical problems by random sampling. In this case, the pseudorandom number generator produces samples that may be clustered in certain regions of the population and does not produce uniform samples. Therefore, in order to reach high accuracy, larger sample sizes are needed, which adversely affects the computational efficiency (Diwekar and Kalagnanam 1997; Diwekar and Ulas 2007). Gebreslassie and Diwekar (2015) proposed EACO algorithm that improves the performance of the conventional ACO algorithm for combinatorial, continuous, and mixed variable optimization problems by introducing the Hammersley sequence sampling technique (HSS). The initial solution archive diversity for continuous and mixed variable

optimization problems plays an important role in the performance of ACO algorithm. The uniformity property of the HSS technique is exploited to avoid clustering of the initial solution archive in a small region of the potential solution space. Moreover, the distribution of the random numbers generated for the acceptance probability of a solution component affects the performance of the ACO algorithm. Hence, in EACO algorithm, the multidimensional uniformity property of HSS is introduced to improve the computational efficiency of the ACO algorithm. The detailed presentation of the EACO algorithms can be found in Gebreslassie and Diwekar (2015). The major steps in EACO algorithm are shown in Table 1 and the algorithm proposed in this work that combines CAMD and EACO algorithm is shown in Fig. 2.

As shown in Fig. 2, the algorithm parameters, the building block groups and their corresponding properties such as volume and surface area, and the interaction parameters between the groups are first introduced. These building block groups are uniquely designed to generate all possible *polymer resins* by exploring all possible combinations. In the forward step, the EACO algorithm generates polymer resin adsorbents using the group combinations from the set of *functional* groups. In the backward step, the CAMD predicts the thermodynamic properties such as activity coefficient which is determined through the UNIFAC models. With these new properties, molar balance equation, constraints, and thermodynamic conditions are examined. If the stopping criterion is satisfied, then the polymer resin adsorbent is a candidate adsorbent; otherwise, in a new iteration a new polymer resin is generated by combination of the different building blocks using the EACO algorithm.

The EACO solver used to optimize the polymer resin design problem is shown in Table 1. Initially, it needs an initial set of parameters such as the number of ants (nAnts), the size of the solution archive (K), the number of continuous (NC) and discrete (ND) decision variables, the pheromone evaporation factor (ρ), an ACO algorithm parameter (q), and the termination criteria (maximum iteration (MAXITER), maximum number of consecutive iterations with no improvement of the objective function (CONITER), and tolerance (EPS)). Using an HSS technique, the solution archive (T) is initialized. Once the solution archive is initialized, the objective function is evaluated and the resulting solutions are ranked 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 kernel function. Moving forward, the termination criterion is tested in the second part of the algorithm. If the test of the termination criteria fails to satisfy, first an ant chooses probabilistically one of the solutions in the solution archive

as a solution construction guide. This solution guide is selected 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 the solution guide to generate a new solution. Thus, all ants will use this solution guide to construct new solutions. The solution construction 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 Gaussian Kernel is constructed for each decision variable and new solutions are 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 set of solutions is combined with the solution archive from the previous step. This new combined solution is then sorted according to the quality of the objective functions, and the first best K 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 the best solution and the best solution from the updated solution archive. This second part continues until the stopping criterion is satisfied.

Finally, as shown in the problem formulation, the polymer resin design problem includes equality and inequality constraints. The EACO algorithm handles these constraints by implementing an oracle penalty method proposed by Schluter et al. (2012). The oracle penalty method is a generalized method capable of handling simple and challenging constrained optimization problems. In oracle penalty method, the objective function is first transformed into an additional equality constraint and the objective function becomes redundant in the transformed optimization 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 is exploited. The penalty function balances its penalty weight in each side of the transformed objective function and the constraint violation. The implementation of the oracle penalty function can be found in Schluter and Gerdts (2010).

Case study

Choice of chelating resins for adsorption

Most ion exchange resins are polystyrene crosslinked with divinyl benzene. A schematic diagram of resin is shown in Fig. 3. The property of resin depends on chemical

Table 1 EACO algorithm for mixed integer nonlinear optimization problems

---

a. **Start program**

Set *K, nAnts, NC, ND, ρ, q, ξ* and termination criteria

Initialize solution archive *T(K, NC)* using HSS

Evaluate the objective function of the K solutions *T(K, NDIM)*

Rank solutions based on the quality of the objective function (T=rank(S_1 …S_K))

Evaluate the weight of each solution based on its rank *T(K, NDIM)*.

---

b. **While Termination criterion is not satisfied**

Construct solutions equivalent to the number of ants

  For all # nAnts

    Incremental solution construction

    For all # NDIM

        o   Probabilistically construct continuous decision variables

        o   Probabilistically construct discrete decision variables

    End for # NDIM

    Store and evaluate the objective function of the newly constructed solutions

  End for # nAnts

  Combine, rank and select the best K solutions, $T = Best(rank(S_1,...,S_K,...,S_{K+nAnt}),K)$

  Update solution

  End while

  End program

T is the solution archive and *K* is the size of *T*. nAnts is the number of ants. NC, ND, and NDIM are the number of continuous, discrete, and the total number of decision variables, respectively

composition, structure and formation, porosity, and *functional* group. In our search for novel resin polymers, the *functional* groups used are obtained from existing resin used for similar purpose. Two different chelating resins have been chosen and their *functional* groups have been identified to find the group contributors for novel polymer design. They are the thiacalix[4]arenes supported on anion exchange resin and dithiocarbamate (DTC) on polymeric support.

Metal ions like Cu++, Pb++, and Ni++ act as soft acids in water. According to the principle of hard and soft acids and bases (HSAB), sulfur-containing groups are mainly soft bases. It is therefore useful to use sulfur-containing *functional* group materials for the removal of metal ions from water (Kantipuly et al. 1990). Different types of dithiocarbamate (DTC) are widely used as sulfur-bearing complexing agents. They are immobilized onto diverse polymeric supports to remove heavy metals from water (Roy et al. 2003). Chelating resins with DTC have disadvantages including low adsorption selectivity and capacity toward divalent metals. Polymers with iminodiacetic acid (IDA) as the *functional* group have also been used to treat metal loading wastewater for eliminating heavy metal ions (Juang and Wang 2003). Polymers with ethylene-
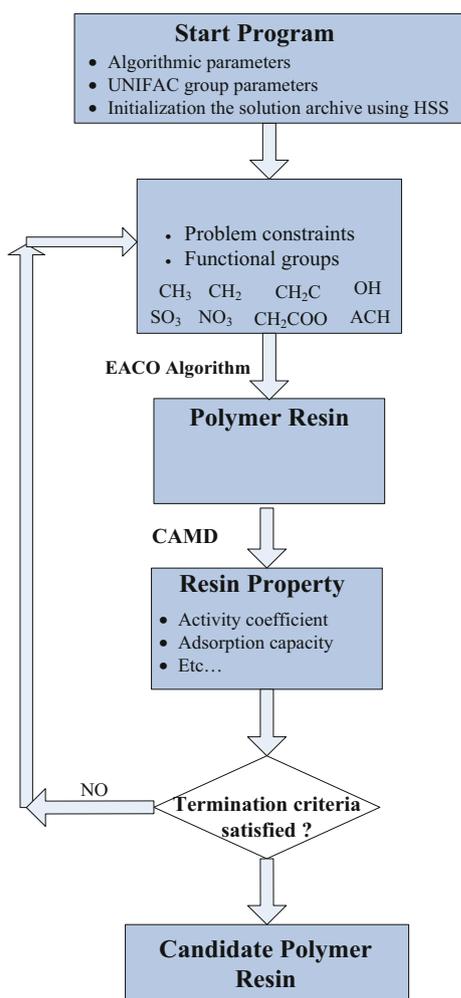
Fig. 2 A basic algorithm that integrates the EACO algorithm and CAMD for design of polymer resin
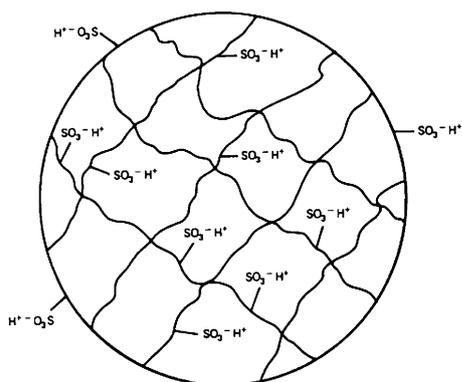

Fig. 3 Schematic diagram of resin. (http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0041/0901b80380041d4e.pdf?filepath=liquidseps/pdfs/noreg/177-01395.pdf&fromPage=GetDoc)

diaminetetraacetic acid (EDTA) type of group structure offer extremely high affinity and selectivity toward commonly encountered metal cations (Atzei et al. 2001). In the present work, Cu++ adsorption on polymer-supported N,N-di (carboxymethyl) dithiocarbamate (PSDC) is one of the two resins that have been used for the analysis.

The thiacalix[4]arene is an important receptor compound (Hu et al. 2010). The usefulness of thiacalix[4]arenes is due to their selective complexing abilities to heavy metal ions by the coordination of the bridging sulfur atom and two adjacent phenoxide O⁻ groups, and simultaneously they have no interaction with alkali metal ions and alkaline earth metal ions, such as Na+ , K+ , Ca++, and Mg++ (Morohashi et al. 2001). The immobilization of thiacalix[4]arenes onto a commercial anion exchange resin gives an excellent selective adsorbent of heavy metals. Thiacalix[4]arenes immobilized in a polymer matrix can also act as sensors for heavy metal ions. Thiacalix[4]arenes or their derivatives also have been deposited onto gold to prepare transducers for the detection of Hg+ (Dridi et al. 2008) and Cu++ (Ali et al. 2006) ions in water. In the present work, Cu++ adsorption onto thiacalix[4]arene immobilized onto a strongly basic 717 anion exchange resin has been used for the analysis.

Identification of functional groups

The structural and *functional* groups used in our analysis to find novel resin polymer are obtained from two different chelating resins that have been used for the adsorption of Cu and other heavy metal ions from water. They are the polystyrene-supported N,N-di (carboxymethyl) dithiocarbamate (PSDC) and styrene-supported resin containing quaternary ammonium groups (–N(CH₃)OH) onto which thiacalix[4]arenetetrasulfonate (TCAS) is immobilized.

The different structural and *functional* groups identified from PSDC are shown in Table 2. Table 2 gives the *functional* groups along with their van der Waals surface Rk and volume Qk. (–A–) represents the cyclic group in styrene and ACH is the CH *functional* group attached to (–A–). The *functional* groups as identified from PSDC are shown in Fig. 4.

The different structural and *functional* groups from TCAS resin supported on polystyrene with quaternary ammonium groups (–N(CH3)OH) have been identified. Table 3 gives the *functional* groups and their van der Waals surface (Rk) and volume (Qk) properties. (–A–) represents the cyclic group present in thiacalix[4]arenetrasulfonate, (–A–) represents the cyclic group in styrene, and ACH is the CH *functional* group attached to (–A–). The *functional* groups as identified from TCAS are shown in Fig. 5.

Table 2 *Functional* groups along with their van der Waals surface Rk and volume from (PSDC)

Functional group	Rk	Qk
(–A–)	2.71	1.944
CH$_2$	0.6744	0.54
S	0.791	0.856
ACH	0.5313	0.4
C	0.312	0.084
N	0.2854	0.092
CH$_2$COO	1.6764	1.42
H$^+$	0.287	0.435

Fig. 5 Thiacalix[4]arenetetrasulfonate with identified functional groups [Hu et al. 2010]
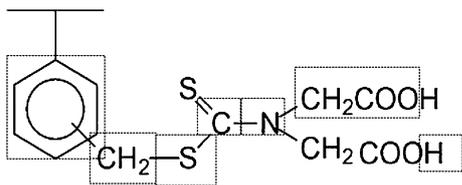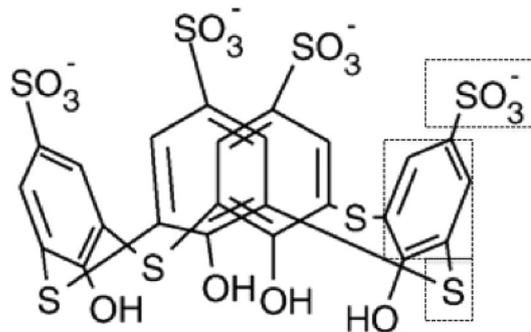

Fig. 4 Styrene-supported *N*,*N*-di (carboxymethyl) dithiocarbamate (PSDC) on which *functional* groups are identified [Jing et al. 2009]

Table 3 *Functional* groups along with their van der Waals surface Rk and volume from (TCAS)

Functional group	Rk	Qk
(–A–)	2.55	1.856
SO$_3$	1.582	1.28
S	0.791	0.856
O$^-$	0.418	0.559
(–A–)	2.71	1.944
ACH	0.5313	0.4
CH$_2$	0.6744	0.54
N	0.2854	0.092
CH$_3$	0.9011	0.848
OH	1	1.2
H$^+$	0.287	0.435

Estimation of interaction parameters with GCM by minimizing the error

To find the unknown values of the interaction parameters (i.e., ab_{nm} and ap_{nm}), we have compared the adsorption found in the literature and that obtained from the thermodynamic model of the adsorption systems as given above in Sect. 3. We have used optimization techniques to solve the parameter estimation problem. The goal is to minimize the normalized error function (Err) as an objective function for this problem. This objective function is shown in Eq. 31. The interaction parameters are the decision variables. This

function represents the normalized value of the difference between the adsorption capacity from the experimental values (q^{exp}) given by the adsorption equilibrium and the calculated q^{cal} using the modified UNIFAC model for the activity coefficient. This adsorption capacity difference is applied for both the adsorbents (PSDC and TCAS) used in our analysis.

$$\min \text{Err} = \sum_1^{AD} \sum_1^{Eq} \left| \frac{q_{Eq,AD}^{cal} - q_{Eq,AD}^{exp}}{q_{Eq,AD}^{exp}} \right|,$$
$$\text{s.t} \qquad \text{Eq. 2} \tag{31}$$

Where AD is the adsorbent used and Eq is the total number of equations used to solve the problem. We have used 20 experimental data points, i.e., 20 equations. The calculated adsorption q^{cal} is obtained using Eq. 32:

$$q^{cal} = \frac{x_1^* n_T^*}{m_0}, \tag{32}$$

where $\{x_1^*\}$ is the mole fraction of adsorbate in adsorbate–solid solution, n_T^* is the total number of moles in adsorbate–solid solution as obtained using Eq. 30, and $\dot{m}_0$ is the mass of adsorbent. The nonlinear programming (NLP) optimization solution methods are used to determine the UNIFAC interaction parameters used to determine n_T^* for q^{cal}.

The interaction parameter optimization problem is solved using the efficient ant colony optimization algorithm (Gebreslassie and Diwekar 2015). The algorithm terminates if it reaches the maximum number of iterations (*MAXITER* = 3000), or if the tolerance (*EPS* = 1E−6) that is the relative difference between the solutions found in two consecutive iterations is lower than or equal to the parameter *EPS* for a set of consecutive number of iterations (*CONITER* = 200). The parameters used in the EACO algorithm are the solution archive size $K = 300$, number of ants *nAnts* = 40, *q* = 1E−3, and pheromone evaporation parameter $\rho = 0.7$. The main results are discussed below.

Table 4 Interaction parameters (ab_{nm}) for bulk phase in TCAS

	Cu	SO$_4$	H$_2$O
Cu	0	ab12	7218.5
SO$_4$	ab21	0	ab23
H$_2$O	4.361	ab32	0

Table 5 Interaction parameters (ab_{nm}) for bulk phase in PSDC

	Cu	NO$_3$	H$_2$O
Cu	0	ab12	7218.5
NO$_3$	ab21	0	466.6
H$_2$O	4.361	97.5	0

The experiments for adsorption of Cu in PSDC and anion exchange resin-supported TCAS are conducted in the aqueous solution of copper nitrate and copper sulfate, respectively (Jing et al. 2009). Tables 4 and 5 present the known and unknown values of the interaction parameter (ab_{nm}) for the groups present in the bulk phase in the aqueous solution of copper nitrate and copper sulfate, respectively. As it can be seen, there are 6 unknown interaction parameters. The known interaction parameters are obtained from Kikic et al. (1991).

There are thirteen unique *functional* groups identified from the two selected resins, PSDC and anion exchange resin-supported TCAS. Table 6 shows the interaction parameters involved in the adsorbate–solid solution where there are 26 unknown interaction parameters. All of them are related to copper group. According to ASST, there is no interaction between the groups in the solid phase (polymer phase) (Berti et al. 1999, 2000). The interaction parameters between the groups on the polymer phase are taken as zero.

The experimental adsorption isotherms as obtained from the literature are compared with those from the calculated values. The adsorption isotherms for the PSDC and TCAS are shown in Figs. 6 and 7, respectively. In these figures, we compared the adsorption capacity as obtained from experiment (q^{exp}) and the calculated adsorption capacity (q^{cal}) as obtained using the interaction parameter shown in

Table 6 Interaction parameters (ap_{nm}) for ASS

	Cu	(–A–)	CH$_2$	S	ACH	C	N	CH$_2$COO	H$^+$	(–A–)	SO3	O$^-$	CH^3	OH
Cu	0	ap12	ap13	ap14	ap15	ap16	ap17	ap18	ap19	ap110	ap111	ap112	ap113	ap114
(–A–)	ap21	0	0	0	0	0	0	0	0	0	0	0	0	0
CH$_2$	ap31	0	0	0	0	0	0	0	0	0	0	0	0	0
S	ap41	0	0	0	0	0	0	0	0	0	0	0	0	0
ACH	ap51	0	0	0	0	0	0	0	0	0	0	0	0	0
C	ap61	0	0	0	0	0	0	0	0	0	0	0	0	0
N	ap71	0	0	0	0	0	0	0	0	0	0	0	0	0
CH$_2$COO	ap81	0	0	0	0	0	0	0	0	0	0	0	0	0
H$^+$	ap91	0	0	0	0	0	0	0	0	0	0	0	0	0
(–A–)	ap101	0	0	0	0	0	0	0	0	0	0	0	0	0
SO$_3$	ap111	0	0	0	0	0	0	0	0	0	0	0	0	0
O$^-$	ap121	0	0	0	0	0	0	0	0	0	0	0	0	0
CH$_3$	ap131	0	0	0	0	0	0	0	0	0	0	0	0	0
OH	ap141	0	0	0	0	0	0	0	0	0	0	0	0	0

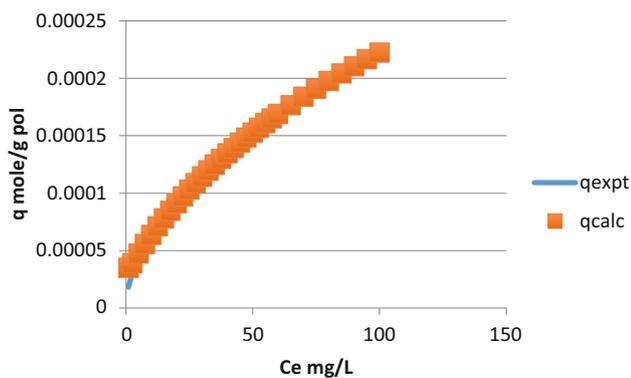**Fig. 6** Adsorption isotherm of Cu on PSDC. Comparison of the experimental capacity with the theoretical capacity
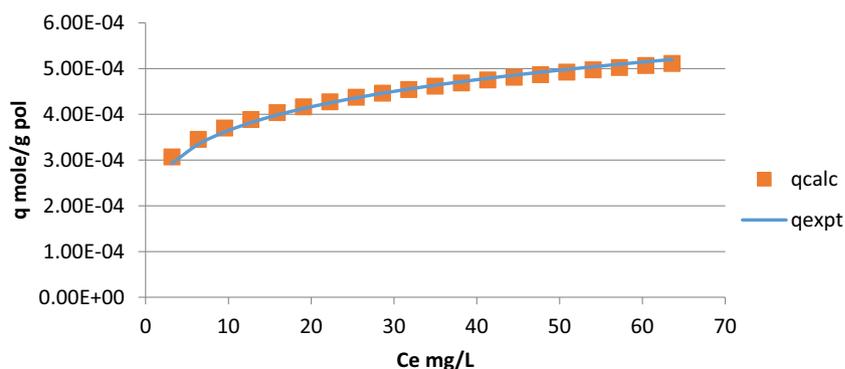
Fig. 7 Adsorption isotherm of Cu on TCAS. Comparison of the experimental capacity with the theoretical capacity

Table 7 Interaction parameters in nitrate solution

	Cu	NO₃	H₂O
Cu	0	−3439.13771	7218.5
NO₃	12,232.69353	0	466.6
H₂O	4.361	97.5	0

Table 8 Interaction parameters in sulfate solution

	Cu	SO₄	H₂O
Cu	0	−9074.30020	7218.5
SO₄	−2540.25716	0	−185,624.642
H₂O	4.361	17,869.84153	0

Tables 7, 8, and 9. The calculated adsorption capacity (q^{cal}) for PSDC and basic anion exchange resin-supported TCAS uses the interaction parameters for the bulk phase from Tables 7 and 8, respectively. It can be seen that the experimental and estimated adsorption capacity values of q are in good agreement.

Tables 7 and 8 show the values of the interaction parameters determined among all possible functional groups as found in the bulk phase. Table 9 presents the values of the interaction parameters determined among all possible functional groups as found in the polymer phase.

Results from the degn of chelating resin for Cu ion adsorption

In this work, the optimal configuration of a monomer unit under structural and thermodynamic conditions is proposed. The objective function maximizing the adsorption capacity subject to equality and inequality constraints related to the structure and UNIFAC model of the polymer as shown in Eq. 33 is

$$\max_{kg} q_{abs} = \frac{n_1^1 - n_1^b}{m_0},\tag{33}$$
$$\text{s.t}$$

where n_1^1 are the initial moles of Cu ++ in the solution, n_1^b are the moles of Cu ++ in the bulk phase, m_0 is the mass of the adsorbent, and k_g is the decision variable that gives the number of times group g occurs in the polymer repeat unit. All calculations are performed in one liter of the solution. At each iteration, we started with a given number of initial moles n_1^1. Then we estimate the moles in the bulk phase at equilibrium n_1^b,. select a subset of functional groups, and ensure that the thermodynamic equilibrium for adsorption process (Eq. 5) is satisfied within a tolerance. The total number of functional groups used to find optimal

chelating resin is 13 and a maximum of 10 groups per molecule are allowed. Therefore, the search space is composed of $13^{10}(1.38 \times 10^{11})$ combinations. The interaction parameter between the building blocks and the three UNIFAC parameters: surface area, volume, and interaction parameters and the group free attachments are described in the previous section.

The algorithm terminates if it reaches the maximum number of iterations (*MAXITER = 2000)*, or if the tolerance (*EPS = 1E−6*) that is the relative difference between solutions found in two consecutive iterations is lower than or equal to the parameter *EPS* for a set of consecutive number of iterations (*CONITER = 100*). The algorithm parameters used for the EACO algorithm are the solution archive size $K = 300$, number of ants $nAnts = 50$, $q = 1E-4$, pheromone evaporation parameter $\rho = 0.75$, and Oracle (Ω) $= 5$. The main results are discussed below.

Through our CAMD, the algorithm uses the *functional* groups that will give the building blocks required to create one monomer unit (repeat unit) of the chelating resin polymer. The interaction parameters of Cu++ with different *functional* groups as obtained using group contribution-based ASST are used for the design of novel resin polymers using the CAMD and combinatorial optimization method. The structural integrity of the resin is confirmed by controlling the total number of free attachments available for bonding in the molecule or repeat unit as given in Eq. 1. The only parameter used for simulation is the maximum number of times each *functional* group can be present in the optimally designed monomer unit. This is given in Table 10. The range of the *functional* groups is selected based on the number of times they appeared in TCAS resin supported on polystyrene with quaternary ammonium groups (–N(CH₃)OH) and polystyrene-supported *N,N*-di (carboxymethyl) dithiocarbamate.

The solution strategy was run ten different times, and the adsorption capacity and number of times each *functional* group appear in the designed resin polymer are

Table 9 Interaction parameters with the *functional* groups in polymer phase

	Cu	(–A–)	CH$_2$	S	ACH	C	N	CH2COO	H$^+$	(–A–)	SO$_3$	O$^-$	CH$_3$	OH
Cu	0	15,126.2855	3932.6307	33,258.8849	4154.7920	4148.4096	–95,017.6165	1336.2879	428.5148	13,799.3403	–326.6874	2624.7174	215,723.4941	6193.656
(–A–)	–1739.1174	0	0	0	0	0	0	0	0	0	0	0	0	0
CH$_2$	458.10404	0	0	0	0	0	0	0	0	0	0	0	0	0
S	2120.8477	0	0	0	0	0	0	0	0	0	0	0	0	0
ACH	13,576.3722	0	0	0	0	0	0	0	0	0	0	0	0	0
C	98,408.7822	0	0	0	0	0	0	0	0	0	0	0	0	0
N	8988.6951	0	0	0	0	0	0	0	0	0	0	0	0	0
CH$_2$COO	–8668.5911	0	0	0	0	0	0	0	0	0	0	0	0	0
H$^+$	198.5400	0	0	0	0	0	0	0	0	0	0	0	0	0
(–A–)	10,642.5086	0	0	0	0	0	0	0	0	0	0	0	0	0
SO$_3$	54.5977	0	0	0	0	0	0	0	0	0	0	0	0	0
O$^-$	1641.5827	0	0	0	0	0	0	0	0	0	0	0	0	0
CH$_3$	1341.0931	0	0	0	0	0	0	0	0	0	0	0	0	0
OH	3937.8473	0	0	0	0	0	0	0	0	0	0	0	0	0

Groups in the polymer phase do not interact with each other

Table 10 Functional groups and the minimum and maximum number of times they can be present in the repeat unit of the resin polymer

Group	Valency	Mini	Max
(–A–)	2	1	2
CH$_2$	2	0	6
S	2	0	4
ACH	2	0	3
C	4	0	1
N	3	0	1
CH$_2$COO	1	0	2
(–A–)	4	0	4
SO$_3^-$	1	0	4
O$^-$	1	0	4
H$^+$	1	1	4
CH$_3$	1	0	12
OH	1	0	4

shown in Table 11. Table 11 also shows the number of iterations required to satisfy the termination criteria, maximum amount adsorbed (mole/gm pol), and gram of polymer used. The results show resins (3, 4, 8, 9, 10) with enhanced adsorption capacity of the candidate polymer resins that is approximately an order of magnitude higher than the commercially used resin. Commercial resin polymers of polystyrene crosslinked with divinylbenzene (DVB) as in Amberlite IRC-718 show an adsorption capacity of 0.0011 mol/g pol (Lin et al. 2000), whereas resin polymers designed with CAMD shows an adsorption capacity as high as 0.0073 mol/g pol as found in 3, 4, 9, and 10. This adsorption capacity of the designed resin polymer is also much higher than that of the conventional adsorbents including biochar produced by pyrolysis of corn straw, which shows an adsorption capacity of almost 0.0002 mol/g (Chen et al. 2011). Four out of five suggested groups have shown high adsorption capacity. Since styrene is the building block onto which the adsorbing *functional* group has to be immobilized, the minimum number of times group (–A–) should be present is taken as one. Candidate 9 contains –CH$_2$COO– as well as ACH which is a CH group attached to group (–A–). The optimization is performed on the basis of 1 l of water containing Cu++. The amount of polymer required for adsorption is 0.16 g for candidate polymer resin 4 and 0.21 g in all three other candidate polymer resins (3, 9, 10).

Conclusions

In this work, we have developed a technology for the design of novel resin polymers useful for the removal of heavy metals from drinking water. A polymer repeat unit is

Table 11 Adsorption capacity of Cu on novel designed resin polymers. The number of times each functional group appears in the monomer unit is shown

Resin no.	No. Iter	Adsorption (mole/g pol)	Gram polymer	–A–	CH2	S	ACH	C	N	CH2COO	H$^+$	–A–	SO$_3$	O$^-$	CH$_3$	OH
1	326	6.67E−05	4.8596	2	2	1	0	0	0	0	2	1	1	2	0	0
2	260	6.47E−05	8.6499	1	0	0	1	0	0	0	2	0	1	2	1	0
3	323	0.007327	0.21405	1	2	0	0	1	0	0	4	0	1	1	8	0
4	637	0.0072512	0.16881	1	2	1	0	1	1	1	0	0	1	1	0	0
5	155	3.80E−05	17.599	1	0	0	2	0	0	0	4	0	2	2	4	0
6	303	5.08E−05	10.799	1	2	0	0	0	0	0	1	0	0	1	0	1
7	380	4.64E−05	22.562	1	0	0	3	0	0	0	2	0	3	1	0	0
8	471	0.005807	0.078825	1	0	0	1	0	0	2	2	0	0	1	0	1
9	370	0.007328	0.21451	1	2	4	2	0	0	2	4	1	1	3	0	1
10	313	0.0073273	0.21432	1	2	0	1	1	0	0	2	3	0	2	0	1

divided into structural and *functional* groups. The structural and *functional* properties of a polymer depend on these groups. We have used the adsorption theory and develop new group contribution method (GCM) to predict the interaction properties of each group present in the adsorbents based on their thermodynamics. We have also used a novel CAMD framework to design adsorbent polymers with improved properties using the properties of the structural and *functional* groups that have been developed by the group contribution methods. Optimal design of novel polymer is achieved using a mixed integer nonlinear programming problem. The algorithm for CAMD of adsorption resin polymer design maximizes the adsorption capacity of the adsorbent subject to structural feasibility, thermodynamic property correlations, and process conditions and constraints. We have tested the proposed methodology on the adsorption of Cu from drinking water. The designed resin showed an improvement of approximately one order of magnitude. Although a cost analysis is beyond the scope of this paper, a comparison of adsorption by the designed resin with any known adsorbents including biochar shows much higher performance. This method can also be applied for the design of resin polymers for the removal of any other heavy metals.

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