



Study on the Adsorption of Samarium and Gadolinium Ions by a Biopolymer Microcapsules Containing DEHPA/ TOPO Extract

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Received 26 Oct. 2013; Final version received 18 Dec. 2013

Abstract

In this study, the adsorption behavior of an alginate biopolymer microspheres containing D₂EHPA/TOPO (DTMCs) toward samarium (III) and gadolinium (III) ions was examined under various conditions. Scanning electron microscope (SEM) and thermogravimetric analysis (TGA) techniques were used to characterize the structure of microspheres. The average size of the microspheres was estimated around 500µm by SEM and also TGA technique showed that the microcapsules was stable until 150 °C. It was found that Sm (III) and Gd (III) ions can be adsorbed onto DTMCs in the concentration range 5-50 ppm while the uptake of these ions completed just 30 minutes. The results of adsorption suggested that the Freundlich isotherm was in good agreement with the experimental data. Furthermore, the study on the reaction mechanism showed that chemical reaction was controlling step compared to film and intraparticle diffusions.

Keywords: Alginate microcapsules, DEHPA–TOPO mixture, D₂EHPA extract, Biopolymers, Kinetics mechanism.

Introduction

The separation of the rare earth elements (REEs) is difficult because of the similarity of chemical properties derived from their equal valence and similar ion radii. Among the REEs, gadolinium and samarium have found a variety of applications in nuclear and non-nuclear industries. For instance, these elements are widely used in the nuclear reactors as controlling materials of neutron fluxes [1-3]. From the economical standpoint, the existence of a large number of steps in the separation of REEs can account for the high prices of them at present. Accordingly, there is a growing interest in the development of new separation methods for the separation of REEs as a group or from one another.

Biopolymers are selective, nontoxic, and cost efficient, and thus highly competitive with ion exchange resins. Among biopolymers, alginate is more important due to its remarkable ion exchange properties, acid stability, and ease of sol-gel transformation [4,6]. In addition, sodium alginate has some other advantages such as 1) non irritant; 2) good surface areas; 3) Ease of use and mixing; 4) cheap and having good shelf life; 5) suitable setting time that can be controlled with temperature; 6) minimal use of organic solvents. In fact, the water-soluble sodium alginate with high viscosity is able to disperse and stabilize both liquid droplets and solid particles by which the formed emulsion or suspension can be easily

gelified and granulated through dripping in Ca^{2+} solutions. On the other hand, calcium crosslinks two adjacent alginate chains and thus results in the formation of multinuclear microcapsules (MCs) [7]. It has been suggested that microencapsulation can solve some disadvantages of solvent extraction methods such as phase separation, phase mixing and leakage of extractant as well as eliminate the need for complicated equipments in the extraction process [8, 9].

Previous studies have shown that the microencapsulation of organic extractants such as Cyanex 302, Aliquat 336, Trioctylamine and Di-(2-ethylhexyl) phosphoric acid (DEHPA) in polymeric matrix was achievable and can be successfully used for the separation of transition heavy metal ions [8-13]. Although increased attention has been paid to the separation of REEs using organic extractants, little effort has been made to the use of binary extractants in alginate microcapsules for the separation of REEs ions [14, 15]. Since it has been proved that the synergic effect between certain binary extractants such as DEHPA and Trioctyl phosphine oxide (TOPO) enhances the adsorption of metal ions, research in the field of microencapsulation using binary extractants would be a valuable effort [16,19]. In continuation of our previous research work that was conducted to address the synthesis and applications of the alginate microcapsules (DTMCs) consisting DEHPA and TOPO

extractants for the adsorption of uranyl ions in aqueous solutions, the current study is attempted to investigate the adsorption behavior of DTMCs for Gd (III) and Sm (III) ions under the same conditions [20].

Experimental

Material

Di-(2-ethylhexyl) phosphoric acid (DEHPA) pure assay 85% was purchased from Fluka, Switzerland. Sodium alginate was obtained from BDH (England). Trioctyl phosphine oxide (TOPO) of 99% purity, phosphoric acid A.R. assay 80% and all other reagents were supplied by Merck AG. (Germany).

Preparation of Microcapsules

First, in order to liquefy the part of the extractant of MCs, an appropriate amount of TOPO (powder form) was added to DEHPA so that in which the weight ratio of TOPO to DEHPA was 1:2 [20]. After gentle heating of the mixture up to 60°C along with simultaneous stirring of it, the transparent solution was obtained.

For preparation of sodium alginate (NaALG) solution, 14.4 g from its powder was added to the 400 ml boiling water while it was vigorously mixed by a high shearing agitator. Heating was ceased immediately after introducing NaALG, but agitation continued for further 30 min. Afterward, the resulted viscous solution underwent 14 min centrifugation for separating

the solid residues, and the obtained clear solution with a NaALG content of about 3.6 % w/w was considered for MCs preparation.

The fabrication of DTMCs was accomplished by adding 3.6 g DEHPA-TOPO liquid to 100 ml of the above-mentioned NaALG solution, kneading of the mixture for about 2 hrs by a high speed agitator. Then the resulting viscous solution (sol) was injected dropwise into 0.1 mol.dm⁻³ Ca(NO₃)₂ solution. For adjusting the size of the sol droplets, a pneumatic cutting system was utilized to set a controllable air flow around the injecting 0.3-mm medical needle. The formed DTMCs was gently stirred in the Ca (NO₃)₂ solutions for about 3 hrs in order to be hardened. Then, MCs was washed with pure water threefold and after separation, it was dried at 40°C for about 10 hrs [12]. Under these conditions, the amount of DEHPA-TOPO mixture became 50% in the dried DTMCs.

Physical Characterization of Microcapsules

The particle size, morphology, and surface structure of the prepared MCs were studied by scanning electron microscopy (SEM, 1455-VP, LEO). The degree of dispersity for the extractant in the alginate matrix was assessed by SEM image.

The thermal stability of MCs was evaluated by Thermogravimetric analysis (TG, SATA 1500 Scientific Rheometric) at temperature range 25-700°C and heating rate of 5°C /min.

Equilibrium Uptake Experiments

The investigation of equilibrium uptake for the MCs granules was performed by the batch method. A solution (10 ml) of 5-200 ppm Samarium and Gadolinium in water was contacted with 0.1 g of the abovementioned adsorbents in the propylene bottle at 25°C, and shaken for about 4 hr. Supernatant was then separated by decanting and analyzed by ICP technique.

The uptake percentage, R (%), and the distribution coefficient, K_d (ml/gr), are defined as

$$R = [(C_i - C_t) / C_i] \times 100 \quad (1)$$

$$K_d = [(C_i - C_f) / C_f] \times V / m \quad (2)$$

Where C_i, C_t and C_f (ppm) are the concentration of ions at the initial state, at time t, and at equilibrium respectively. m (g) the weight of MCs; V (ml) the volume of aqueous phase.

Results and discussion

Morphology

The average size of microcapsules was estimated by scanning electron microscopy SEM (Figure 1a). Average size of DTMCs was estimated 5 μm (Figure 1b).

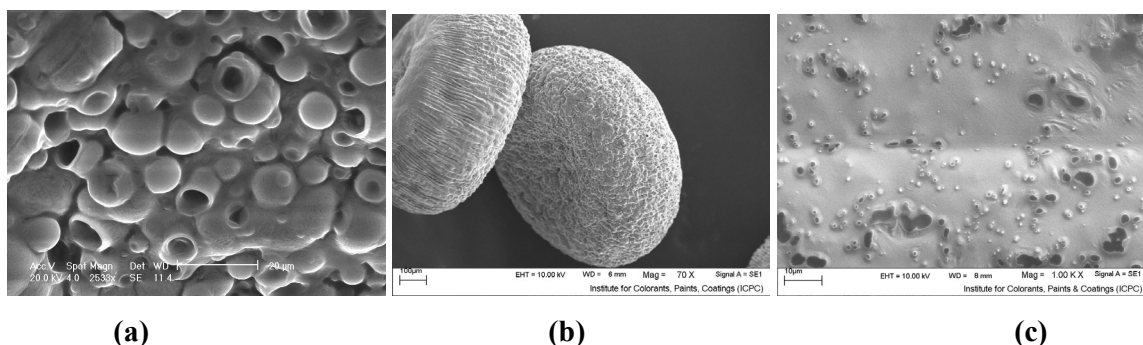


Figure 1. SEM image of; (a) DTMCs (b) Surface Morphology of DTMCs (c) and cross section of MCs.

Thermal Stability

Thermogravimetric analyses (TGA) is a useful means of the study of polymeric materials. In the case of the MCs, the results of TGA revealed that there were two considerable structure variation; First, between 100-150°C, and second was about 200°C (Figure 2). For the first variation, two main reactions are possibly involved in the polymeric degradation. (1) Acid-based mechanism. (2) Redox reaction of alginate [12, 16]. Weight losses emerge around

200°C and this is the point that MCs exchange due to degradation of alginate matrix. The lower weight loss of MCs below 200°C is more likely due to its lower alginate content (80% comparing to 100% of pure alginate), and higher thermal stability is related to both DEHPA and TOPO. Above 200°C, decomposition of both DTMCs and calcium alginate is initiated excessively, but there are some differences between their degradation behaviors. Whilst the MCs loss about 80%

of their weight until 400 °C; the weight loss of pure alginate hardly reaches 45%. Since only 20% of the DTMCs consist of mixed extractant, the foregoing difference can not be only attributed to evaporation and losses of extractants, but quite likely oxygenated acidic extractant causes depolymerization of alginate

(a polysaccharide) and its oxidation to gaseous products. Apparently, the matrix-extractant interaction is appreciable only at higher temperatures (i.e. above 200°C). If it was not so, the rate of decomposition of MCs under 200°C must be greater than that of alginate.

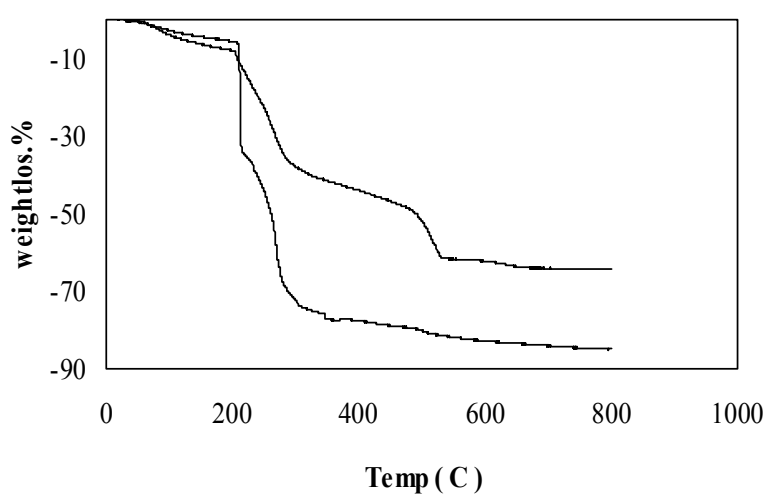
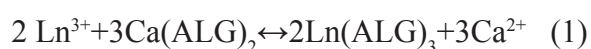


Figure 2. Thermogravimetric analysis (TGA) of (a) DTMCs; 20% D₂EHPA/TOPO (b) and Ca(ALG).

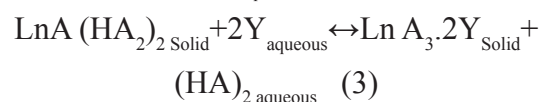
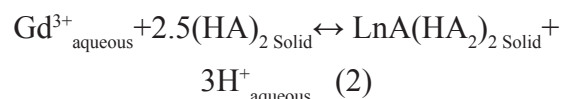
Uptake Equilibrium

Both alginate and extractant constituents of DTMCs have uptake ability for samarium and gadolinium ions. It has been suggested that the uptake of metal ions by alginate proceeds through an ion exchange reaction (1) in which the carboxylic groups of calcium alginate acts as active sites [11, 12].



The extractant component of the DTMCs is

a mixture of DEHPA and TOPO compounds. Eq(2) and eq(3) show mechanism of reaction between DEHPA/TOPO with Lanthanides (3).



In the above formulae HA and Y denote DEHPA and TOPO, and (a) and (o) subscripts designate aqueous and organic phases, respectively.

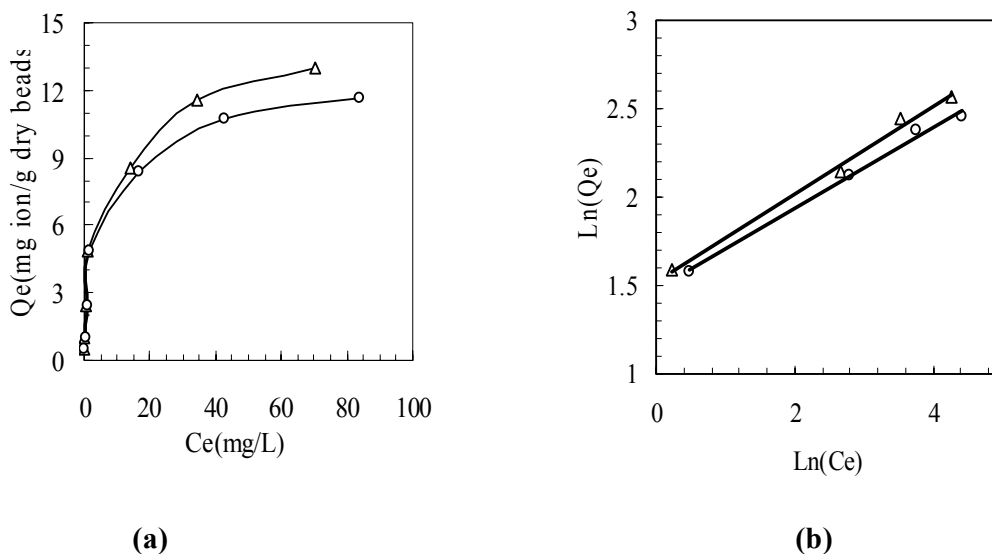


Figure 3. (a) Adsorption isotherms and (b) Freundlich plot for the Uptake of Sm (III) and Gd (III). Δ : *Gd*, \circ : *Sm*.

Figure 3-a shows the experimental adsorption isotherm of Gadolinium and Samarium for DTMCs. Equilibrium experiment showed that under a definite initial concentration (from 5 to 50 ppm), DTMCs is able to fully adsorb Samarium and Gadolinium ions from solution. This feature arises from a much higher affinity of DEHPA/TOPO toward these ions compared with that of alginate matrix.

The linear form of the Freundlich isotherm model is given by the following equation:

$$\ln(q_e) = \ln K + \frac{1}{n} \ln(C_e)$$

K and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity of the sorbent, respectively. The Freundlich constants were determined after fitting the data to the respective equations through linear

regression analysis. Adsorption isotherms of DTMCs were fitted with the Freundlich's equation (Figure 3-b). With the Samarium and Gadolinium concentration less than 200 ppm, a remarkable fitting was observed from which the following equations were deduced:

$$q_e = 4.58 C_e^{0.248} \text{ for } \mathbf{Gd} \quad (4)$$

$$q_e = 4.38 C_e^{0.228} \text{ for } \mathbf{Sm} \quad (5)$$

Where q (mgU/g) and C_e (ppm) denote the equilibrium adsorption, and concentration, respectively

Uptake Kinetics

Kinetics studies show that there is a relatively fast uptake rate for DTMCs so that it attains 90% equilibrium level within 20 min (Figure 4-a). As shown, the uptake of gadolinium is faster than samarium.

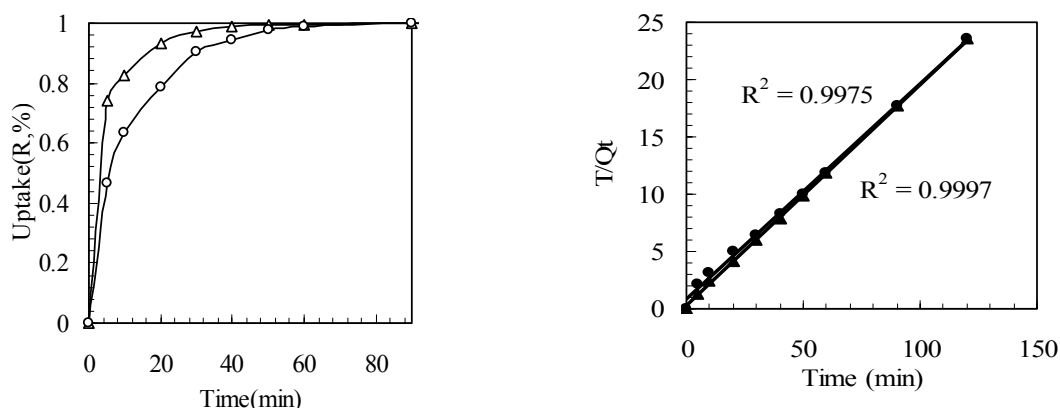


Figure 4. (a) Kinetics of Sm and Gd in terms of uptake percentage (R, %) and (b) Modeling of uptake kinetics by pseudo second order chemical reaction model, in both Δ : Gd, \circ : Sm.

For modeling of the kinetics, two different approaches were considered, a newer shrinking core model (SCM), and an older pseudo-second order chemical reaction (PSCR).

The advantages of SCM are: providing a better physical picture of the uptake process, and possibility of obtaining diffusion coefficients

or the reaction rate constant from kinetics data.

There are three different types of shrinking core models which are liquid film resistance SCM, intraparticle resistance SCM, and reaction control SCM. Mathematically, these are represented by the following formulae:

$$X = \frac{3D}{C^0 R \delta} \int_0^t C dt \quad \text{Liquid film resistance} \quad (7)$$

$$1 - 3(1 - X)^{2/3} + (1 - X) = \frac{6D_e}{C^0 R^2} \int_0^t C dt \quad \text{Intraparticle resistance} \quad (8)$$

$$1 - (1 - X)^{1/3} = \frac{k''}{\rho R} \int_0^t C dt \quad \text{Reaction-controlled kinetics} \quad (9)$$

where “X” is fractional attainment to the equilibrium defined by eq. (3) and C (mmol/dm³) is concentration at any given time of t, D (cm².s⁻¹) and D_e (cm².s⁻¹) denote diffusion rates of liquid film and matrix of MCs, respectively. Also, R (cm) stand for the radius of particle, and δ (cm) shows the thickness of liquid film.

Other parameters include C⁰ the concentration of active sites of the adsorbent (mmol/dm³), ρ (g/ml) as its density and finally k'' the rate constant of adsorption reaction.

The best fitting of the kinetics data for both Samarium and Gadolinium was provided by chemical reaction in SCM (Figure 5-a, b).

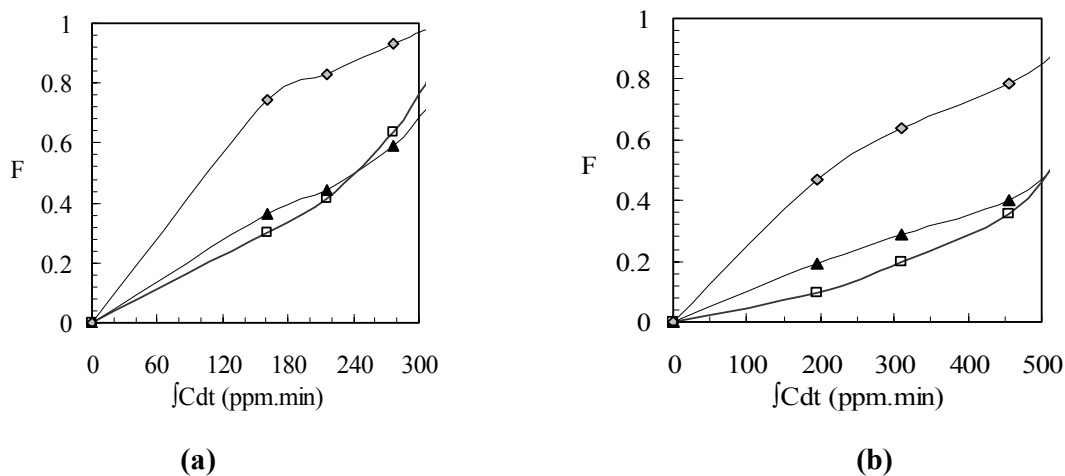


Figure 5. Modeling of uptake kinetics by shrinking core model, at 50 ppm (a) for Gd and (b) for Sm.

The second kinetics model (*i.e.* PSCR) assumes that the sorption rate is proportional to the square of the number of unoccupied sites of the adsorbent:

$$\frac{dq}{dt} = k(q_{eq} - q)^2 \quad (10)$$

q and q_{eq} denote the adsorption values (mmol (lanthanide) /g (adsorbent)) at time t and in the equilibrium, respectively. The result of application of this model is represented in Figure (4-b). A nearly perfect fitting of the experimental data demonstrates the ability of the model in prediction of the uptake rate and an implicit emphasis on dominating the chemical reaction in controlling sorption kinetics.

Conclusion

1- Microencapsulation of the TOPO/DEHPA with the calcium alginate matrix presents a simple, but effective method for synthesis

of the selective adsorbents. The prepared microcapsules are inexpensive, and useful for different uptake services such as separation of lanthanides from extreme aqueous solution.

2-Equilibrium experiment showed that, under a definite initial concentration (from 5 to 50 ppm), MCs are able to fully adsorb Samarium and Gadolinium ions from solutions. This feature arises from a much higher affinity of DEHPA/TOPO toward these ions compared with that of alginate matrix.

3-It was shown that uptake kinetics can be modeled by using both shrinking core model (SCM) and pseudo-second order chemical reaction model (PSCR). The application of the former revealed that the rate controlling step of adsorption was primarily slow chemical reaction of lanthanides ions with the MCs.

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