Application of emulsion nanofluids membrane for the extraction of gadolinium using response surface methodology

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ABSTRACT

In this work, an emulsion nanofluid membrane (ENM) was applied to effectively extract gadolinium. Simultaneous emulsification of nanoparticles and surfactant was performed to stabilize the ENM. Multi-walled carbon nanotubes (MWCNTs) nanofluid was employed as liquid membrane. The ENM composed of diisooctylphosphinic acid (CYANEX 272) as carrier, MWCNTs as nanoparticles, Span-85 (sorbitan trioleate) as surfactant, kerosene as organic diluent and nitric acid as internal phase. The effects of important operating variables i.e., carrier concentration, MWCNTs concentration, surfactant concentration, mixing speed, internal phase concentration and feed phase pH were investigated. Response surface methodology (RSM), according to central composite design (CCD), is used to optimize the process variables and a regression model for extraction percentage was developed. The 3D response surfaces of gadolinium (III) extraction efficiency were achieved and significance of six important variables and their interactions on extraction efficiency were found out. The desirability function was performed to simultaneously evaluate all the factors and determine the best possible goals for each response. The optimum condition for gadolinium extraction were: The optimum condition for gadolinium extraction were: 0.84 M of CYANEX 272, MWCNTs concentration of 318.05 ppm, 2.91% (v/v) of Span-85, mixing speed of 188.15 rpm, 1.27 M of HNO$_3$ as internal phase reagent, feed phase pH of 3 and desirability value of 0.904. Under the optimized condition, the extraction of Gadolinium (III) reached the maximum of 92.05%.

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1. Introduction

The rare earth elements (REEs) consist of 15 lanthanides, plus yttrium and scandium. They are divided conventionally into two main groups: the light REEs (Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd) and the heavy REEs (Y, Tb, Dy, Ho, Er, Tm, Yb, Lu) [1]. In the last few decades, REEs have gained great attention and vastly used for additives to steel or alloys [2], magneto-optic storage discs, metallurgy, hydrogen storage materials, ceramic industry [3], permanent magnets, nuclear fuel control, electro or cathode rays, and household batteries [4,5] owing to their unique properties. Gadolinium is used for both its high magnetic moment and its phosphors or scintillated property [6]. Gadolinium has found a variety of applications in nuclear and non-nuclear industries [7]. Gadolinium oxide is widely used in the nuclear power industry as a radiation shielding and thermal neutron absorber [8]. The resistance of iron, chromium and related alloys to high temperatures and oxidation would be improved by addition about 1% of gadolinium to them [9]. In medical field, the mixture of gadolinium (III) and ethylenediaminetetraacetic acid (EDTA) dopants is used as an injectable contrasting agent in magnetic resonance imaging (MRI) [10]. As the applications of gadolinium increased in the production and life, it is essential to separate and enrich such element in high purity and large amount [11].

Liquid membranes used an alternative separation technology, in order to extract REEs [12–14]. One of the promising methods of liquid membrane processes is Emulsion Liquid Membrane (ELM). ELM offers some advantages over solvent extraction such as simplicity, requirement of small quantities of extractant, simultaneous extraction and stripping in a single stage and low energy consumption [15–17]. ELMs are usually made by creating a water-in-oil emulsion which is stabilized by a surfactant. This emulsion contains the extractant (carrier) in the oil phase and the stripping agent in the internal aqueous phase. The emulsion is then dispersed by a relatively low agitation into an aqueous feed phase containing the solutes to be separated [18].

The major obstacle to the application of ELM either in laboratory or industrial scale is the lack of the stability of the emulsion globules which resulted in the loss of extraction efficiencies. The resistance of the individual globules against coalescence and rupture of globules at high shear stress are defined as the stability of emulsions [19,20]. The

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globule rupture and osmotic swelling are the two main phenomena that had negative effect on emulsion stability [21].

Besides surfactants, nanoparticles have been also used widely in emulsification since the arrival of Pickering emulsions in 1907 [22]. They can absorb at the liquid–liquid interface and stabilize the dispersed phase drops against coalescence by providing a steric hindrance around them [23–25].

Due to specific properties and potential technological applications of particle-stabilized emulsions, they have attracted considerable research interest. The most interesting properties are: (1) long period stabilization of emulsion with or without minimum amount of surfactant [26, 27] and (2) using particle stabilized emulsion droplets as initial templates for invention of advanced materials with complex hierarchical structure [28]. Although the emulsion resistance to creaming mainly increased due to an increase in viscosity by addition of surfactant to a particle-stabilized emulsion, it surprisingly led to increasing the coalescence. Simultaneous emulsification of particles and surfactant caused to synergistic stabilization at intermediate concentrations of surfactant. In this case, emulsions are completely stable to both creaming and coalescence [29]. One of the advantages of this way is that the consumption of both surfactant and nanoparticles is lower compared with in emulsions stabilized only with surfactants and nanoparticles. In this method, the wettability of nanoparticles is tailored by electro-static and hydrophobic interaction between the surfactants and nanoparticles [30].

Binks and his colleagues found that there is a synergism between surfactants and nanoparticles in preparing stable emulsions against creaming and coalescing [31]. Furthermore, similar results were reported for oil in water emulsions comprising hydrophilic Silica nanoparticles and non-ionic surfactants [29]. In our previous work [32], it was found that simultaneous presence of nanoparticles and surfactant caused to 52% reduction in D_{32} compared to the system containing nanoparticles alone (without surfactant). Lan et al. [22] found that using appropriate amounts of cationic surfactant can make the hydrophilic nanoparticles partially hydrophobic, decrease the interfacial tension, and improve the adsorption of nanoparticles at the interface.

The objective of the present work is employing nanofluid as liquid membrane to investigate the extraction of Gd(III) through ELM. The emulsion nanofluid membrane (ENM) was stabilized by simultaneous emulsification of MWCNTs and Span-85. The MWCNTs nanofluid was employed as liquid membrane. Statistical experiment design was used to optimize the process parameters such as carrier concentration, MWCNTs concentration, surfactant concentration, mixing speed, internal phase concentration and feed phase pH. An attempt was made to study the linear, square and interactive effects of process parameters on extraction efficiency of Gd(III). A regression model for extraction percentage of Gd(III) was developed.

2. Materials and methods

2.1. Chemical materials

All chemicals were of analytical grade and were used as received without further purification. Diisooctylphosphinic acid (CYANEX 272) was purchased from Fluka (Buchs, Switzerland) and used as mobile carrier. Gadolinium (III) nitrate hexahydrate (Gd(NO$_3$)$_3$.6H$_2$O, 99.9% purity) was purchased from Sigma-Aldrich Chemie GmbH (Schnelldorf, Germany). MWCNTs (diameter < 8 nm, length = 30 μm, purity > 98%) were obtained from the Research Institute of the Petroleum Industry (RIPI, Tehran, Iran). Sorbitan trioleate (Span-85) as a surfactant and kerosene (reagent grade) as a diluent were procured from Sigma-Aldrich (Schnelldorf, Germany). Nitric acid (HNO$_3$ (65%)) and Sodium hydroxide (NaOH) were purchased from Merck, Co. (Darmstadt, Germany). The stock standard solution of 1000 mg·l^{-1} of Gd(III) was prepared by dissolving Gd(NO$_3$)$_3$.6H$_2$O in deionized water. Feed phase solutions were made by diluting the stock solution. The pH value of the feed

phase was measured by a Metrohom 780 pH meter with a combined electrode.

2.2. Experimental design

A design of experiment statistical software (Design-Expert 10.0.4 software, Stat-Ease Inc., Minneapolis, MN, USA) was employed to design statistically the minimum number of experiments using "Minimum Run Resolution V Design (MinRes V)" design [33]. A total of 40 experiments were carried out to optimize the chosen key variables for the extraction of Gd(III). The experiments with different carrier concentration, MWCNTs concentration, surfactant concentration, mixing speed, internal phase concentration and feed phase pH were employed simultaneously covering the spectrum of variables for the percentage extraction of Gd(III) in the CCD. The range and different levels of individual variables in coded and uncoded form were given in Table 1. The coded values of variables along with the experimental data and predicted responses are given in Table S1 in the Supporting information.

The regression analysis was performed to estimate the response function as a second order polynomial [34,35]. Then, response surfaces and 3D plots were drawn to visualize the individual and interactive effects of the variables for the extraction of Gd(III). The optimum conditions were first achieved in coded values and then converted to the uncoded.

2.3. Experimental procedure

Emulsion nanofluid membrane was prepared by dispersing required amounts of MWCNTs for each concentration into the surfactant solution by Ultra-Turrax T18 Basic homogenizer (IKA-WERK, Germany) at 15000 rpm for 5 min. The surfactant solution consisted of different portions of Span 85 as the surfactant, carrier reagent (CYANEX 272) and kerosene as an organic diluent. Then, the dispersion was followed by sonication in an ultrasonic bath (DSA100-SK2, DESEN, China, 40 KHz, 100 W) for 30 min.

To make a primary W/O emulsion, 30 ml of internal stripping phase was added drop wise to an equal volume of the prepared MWCNTs dispersion. The mixture was stirred continuously at 6000 rpm for 10 min to obtain a milky-white stable emulsion. The fresh emulsion nanofluid was prepared each time before experiments.

The experiments were carried out in a 2 l glass reactor. The reactor was equipped with two PTFE crescent-shaped paddles, rotating motor, digital agitation speed controller, circulator, thermal jacket, thermometer, temperature controller and sampling valve. The prepared emulsion was smoothly dispersed into mixing chamber with feed phase solution and stirred for about 10 min. At the end of the mixing, the stirred solution was allowed to separate by gravity. Samples of about 5 ml were taken from solution. The experimental set-up and procedure is schematically shown in Fig. 1.

To avoid any probable mass transfer and remove remained emulsion droplets, samples were filtered through a filter paper (Whatman, No.1, USA). Then, the samples were analyzed by ICP-AES (Thermo Jarrell Ash, Model Trace Scan, Canada) Gd(III) ions' concentration after extraction. All experiments were performed at 25 °C ± 0.5 °C.

Table 1
The levels of different process variables in coded and uncoded form for the extraction of Gd(III).

Independent variable	Range and levels				
	$-\alpha$	-1	0	$+1$	$+\alpha$
Carrier concentration (X_1, M)	0.25	0.5	1	1.5	1.75
Surfactant concentration (X_2, %v/v)	0.5	1	2	3	3.5
MWCNTs concentration (X_3, ppm)	0	100	320	540	640
Mixing speed (X_4, rpm)	135	150	180	210	225
Internal phase concentration (X_5, M)	0.25	0.5	1	1.5	1.75
Feed phase pH (X_6)	0.5	1	2	3	3.5